NOVA SCHOOL OF SCIENCE & TECHNOLOGY

DEPARTAMENT OF

CONSERVATION AND RESTORATION

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BSc in Architectural Engineering

LOOK AT THE WORLD BEHIND THE GREEN DOOR

REPRODUCTION OF GREEN ENAMEL BASED ON HISTORICAL RECIPES

MASTER IN GLASS AND CERAMIC ART AND SCIENCE

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Reproduction and Characterization of green Enamel Recipes

This document was created with Microsoft Word text processor and the NOVAthesis Word template.

ACKNOWLEDGEMENT

I am deeply grateful to:

- Professor Andreia Ruivo, for her patience, assistance, and advice throughout this project,
- Professor Fernando Quintas, for his helpful suggestions, kind words and positive energy during my study,
- Dear Carla Machado for her support and collaboration within my research,
- Professor Marcia Vilarigues and all the VICARTE team,
- My family, specially my husband Elias for their help, encouragement and motivation,

Without their help, I would not have been able to complete this journey.

I would also like to extend my sincere gratitude to everyone who helped me during my study. Thank you for your help, time and contribution.

Abstract

Stained-glass windows in Portugal have a high historical value. Acquiring a vast knowledge of colored/painted glass and glass-making techniques is essential in maintaining and repairing historic windows. Green color is a very common color used in stained-glass windows, however, green historical recipes haves not been highly researched yet. Focusing on this lack of Information, this study will explore: 1) the reproduction and characterization of historical green enamel recipes, 2) creating glass artworks and using them in architectural design.

With the aim of reproducing green enamels based on historical recipes, the first part of this thesis includes the study and interpretation of green enamel recipes from the book "L'Arte Vetraria" by Antonio Lodovico Neri (1576-1614). In the second part, in order to show how the obtained enamel looks, some glassy artworks are made and painted with these obtained enamels. Additionally, these painted artworks are used to make three-dimensional architectural models.

To compare the effect of various parameters, the procedure of enamel production was done by different approaches. By using three different recipes (No. 97, 98 and 99) of Neri's book, three different production strategies, and 2 to 5 different kiln temperatures, a total of 27 different samples were produced. As a visual outcome, recipes No. 97 and 99 (which contain three-time burned copper) resulted in blue paint (dark blue and shiny blue color), while recipe No. 98 (which contains three-time burned copper) presented a green color. This result was in accordance with the performed color analysis results (Colorimetry and Reflectance Spectroscopy).

The colors obtained prove that grinding, mixing and kiln temperature strongly affect color and quality of the paint. Ingredients need to be ground and mixed properly to result in uniform and very fine powder. More ever, the kiln temperature should be high enough (around 700 ºC) to melt the components, give green color to paint, and make a glassy surface over painted object. It is observed that changing the kiln temperature from 650 ºC to 700 ºC has a strong effect on the obtained paint. All samples present a gray color when heated at 650 ºC, while they present different colors at 700 ºC.

Based on obtained results, the paint which was made by 3rd producing strategy (by using well- ground mixture and an uninterrupted firing process at 700 ºC) in accordance with recipe No. 98 has an acceptable green color, and it could be used to paint stained-glass windows in the preservation or restoration of historic buildings.

In the artistic part of this study, three specific artworks (Star-Cross tiles, Beehive tiles, and the Glass Wall) were created by glass casting, were painted with the produced green enamels, and were covered by using the epoxy-resin (to shape as solid tiles). Additionally, these artworks were used to create 3D models of architecturally designed spaces and decorative objects by using a computer simulation software.

Keywords: Stained glass, glass painting, green enamel, historical recipes, three-dimensional modeling, architectural design,

RESUMO

Os vitrais em Portugal, têm um elevado valor histórico. Adquirir um vasto conhecimento de vidro colorido/pintado e técnicas de fabricação de vidro é essencial na manutenção e reparação de janelas históricas. Embora o verde seja uma cor usualmente usada em vitrais, as receitas históricas desta cor ainda não foram muito estudadas. Este estudo enfoca: 1) a reprodução e caracterização de receitas históricas de esmalte verde, 2) criando obras de arte em vidro e usando-as no projeto arquitetônico.

Com o objetivo de reproduzir esmaltes verdes a partir de receitas históricas, a primeira parte desta tese compreende o estudo e interpretação de receitas de esmaltes verdes do livro "L'Arte Vetraria" de Antonio Lodovico Neri. Na segunda parte, para expor os resultados do esmalte produzido, serão feitas e pintadas algumas obras de arte vítrea com o esmalte produzido. Além disso, essas mesmas obras de arte serão usadas para fazer modelos arquitectónicos tridimensionais.

Para comparar o efeito de vários parâmetros, o procedimento de produção do esmalte foi feito por diferentes abordagens. Usando três receitas diferentes (nº 97, 98 e 99) do livro de Neri, três estratégias de produção diferentes e 2 a 5 temperaturas de forno diferentes, foi produzido um total 27 amostras. Como resultado visual, as receitas de nº 97 e 99 (que contém cobre queimado três vezes) resultaram uma tinta azul (cor azul escura e azul brilhante), enquanto a receita nº 98 (que contém cobre queimado três vezes) apresentou uma cor verde. Este resultado esta de acordo com os resultados da análise de cor realizada. (Colorimetria e Espectroscopia de Reflectância).

As cores obtidas provam que a moagem, mistura e temperatura do forno afetam fortemente a cor e a qualidade dos esmaltes. Estes precisam ser moídas e misturadas adequadamente para resultar num pó uniforme e extremamente fino. Mais ainda, a temperatura do forno deve ser alta o suficiente (em torno de 700 ºC) para fundir componentes, dar cor verde à tinta e fazer uma superfície vítrea sobre o objeto pintado. Observa-se que a mudança da temperatura do forno de 650 ºC para 700 ºC tem um forte efeito no esmalte obtido. Todas as amostras apresentam coloração cinza quando aquecidas a 650 ºC, enquanto apresentam cores diferentes a 700 ºC.

Com base nos resultados obtidos, a tinta que foi feita pela 3ª estratégia de produção (usando mistura bem moída e processo de queima ininterrupta a 700 ºC) de acordo com a receita nº 98 tem uma cor verde aceitável e pode ser usada para pintar vitrais na conservação ou restauro de edifícios históricos.

Na parte artística, três obras de arte específicas (intituladas azulejos Star-Cross, azulejos Beehive e Glass Wall) foram criadas por fundição de vidro, pintadas com os esmaltes verdes produzidos e cobertas com resina Epoxida (para forma como ladrilhos sólidos). Além disso, as obras de arte foram usadas para criar modelos 3D de espaços arquitetonicamente projetados usando um software de simulação de computador.

Palavras-chave: Vitrais, pintura em vidro, esmalte verde, receitas históricas, modelagem tridimensional, projeto arquitetônico,

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INTRODUCTION

"The windows of the church are the Sacred Scriptures which keep away the wind and rain, but allow passage of the true sun (which is God) into the hearts of the faithful"

(Roman Catholic Bishop of Mende 1220-96) [1]

1 Introduction

1.1 Historical recipes of glass painting

Generally speaking, the term "Stained-glass"[1] is used for colored/painted glass (as a material) and also for decorative windows, which were created from a set of colored/painted glass [1]. "From a structural point of view, stained glass is a set of several colored or colorless glasses which may or may not be painted, joined by lead cames[2] and mounted on a structure of iron or wood and placed in building windows" [2]. Throughout its thousand-year history, stained-glass has been applied usually to the windows of churches and other significant buildings [3]. To make these decorative windows, the set of colored or painted pieces of glass are arranged to form patterns or pictures, held together (traditionally) by strips of lead and supported by a rigid frame [3-6]. From an architectural view-point, it can be said that stained glass windows were an essential component of Medieval and Renaissance buildings by providing light to brighten the interior and displaying permanent imagery that proclaims the importance of place. In that era, many public buildings conveyed grand narrative themes through sculptural elements on the exterior as well as stained-glass and wall painting in the interior [7-8]. Complex pictorial ensembles carried messages of salvation and commentaries on medieval society, especially its powerful leaders [8].

Historical stained-glass windows often deserve preservation and restoration. Acquiring vast theoretical knowledge and practical skills about original methods of enameled/painted/colored glass production is vital for the preservation/restoration process. The critical importance of acquiring related skills to reproduce historic stained-glass is the main motivation for re-reading, translating, annotating and explaining historic glassmaking treatises and re-creating stained-glass paint.

The historic glass recipe books often provide information on glassmaking processes and the materials and equipment used. These documents offer a precious source of information on the evolution of chemical and material sciences and their relationship to glassmaking [9].

One of the first manuscripts referring to the production of stained glass is the one by the monk Theophilus, dated from the 12th century, which explains the main steps of the process. The procedures described by the author have not suffered significant changes over time [10]. The oldest "systematic publications" known about glass, glass paints and stained glass are the ones by Antonio Lodovico Neri (1576-1614) in his book "L'Arte Vetraria" which was published in 1612 [11].

Concerning the production of glass-based paints based on historical treatises, quite a few publications were published recently [9]. Some of these works were devoted to translations and interpretations of historical

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[1] Refer to Chap. 6.1 for more details

[2] Lead Came is a slender grooved lead bar used to hold together the panes in stained glass.

texts, but some others focused on the reproduction of recipes [9, 12, 13]. These recent researches aimed to study the evolution of the chemical composition (raw materials) and production technology of some specific historical paint during several centuries, and the effects of this development on important features of obtained stained glass. Tracing the historical evolution of enamels [1] production will enhance the understanding of materials and production methods used in the creation of stained-glass windows, providing new tools to develop conservation strategies and promote public appreciation of the technical knowledge necessary to produce these artworks.

Over the last years, in VICARTE research unit several studies have already been made concerning the reproduction and characterization of glass-based paints which were produced based on historical stained-glass recipes. These studies aimed to reproduce grisaille, silver-stain, blue, yellow and red paints. In the continuation of this series, the current study has been proposed to reproduce green enamel based on historical recipe books. Green is a common color used in stained-glass windows which was used with different intensities to produce images on windows. Therefore, reproducing the historic green enamel is an important milestone in preserving and restoring of historical stained-glass windows (Figure 1-1).

(a) (b) (c)

Figure 1-1: Examples of historical stained-glass windows with different hues of green colored glass:
a) Flight into Egypt, 17th century, National Palace of Pena, Portugal [14]
b) Last Supper, 17th century, National Palace of Pena, Portugal [15]
c) Stained glass panel, 19th century, National Palace of Pena, Portugal [16]

This project aims to reproduce and characterize green enamels of stained-glass based on historical recipes. This study has focused on *"L'art vetraria"* (Neri's recipes) to reproduce green enamels. In this source, there are three recipes for green paint with different coloring components that need to be prepared based on the original recipes which are in Italian language.

[1] Refer to Chap. 6.1 for more details

Even though there are several historic treatises for enamel production, the lack of needed information is still critical for green enamel. Three brief recipes can be found in Neri's book with historical guidelines for producing this paint. However, without detailed instructions, following the main recipe step by step as described in the original recipe is a real concern. The main factor for the success of the production of the green enamel is to obtain an intense green color as a final result. This problem is explored here by asking about how to produce the material in terms of quantity and production process or the role of different furnace temperature on the final results.

By studying and interpreting several historical treatises, the production techniques (from the preparation of the pigment to the paint preparation) are discovered. In the first step of this study, selected raw materials used in the production of green enamels are chemically characterized. After providing and processing the raw material, green enamels are produced based on selected historical recipes. Finally, some important parameters such as firing temperature, grinding level, and binding agents are studied to observe the color differences.

Because of the historical value of stained-glass windows in Portugal, it is extremely important to acquire vast knowledge of colored/painted-glass making techniques. Even though green color is highly used in stained-glass windows, green historical recipes have not been researched sufficiently. This study will contribute to a deeper understanding of the reproduction methods of green enamels and more detailed insight into the technology behind the stained-glass painting techniques, which could improve awareness of this incredible heritage present in Portugal and pave the way to restore priceless historical windows.

The key steps done in this study are:

1) Study of the production of glass paints, from the preparation of the pigment to the preparation of the paint; Deep study and interpretation of historical recipes with the aim of knowing enamel reproduction techniques;

2) Identification and characterization of raw materials which have been used in the production of enamel paint in selected recipes;

3) Chemical characterization of raw materials used for reproduced paints;

4) Practicing to acquire abilities to follow the historical recipes; Identification of shortcomings and critical points of production processes which could be effective in final results, and planning a proper route to overcome them;

5) Color testing of obtained results, and results analysis;

6) Applying the obtained green enamels in architectural design by making glass artworks, and painting them with the obtained enamels. Using these produced artworks to create 3D models of architecturally designed spaces;

The last item (No. 6) of the steps mentioned above was done to find a way to commercialize the green enamel production technology. To do so, three specific glass artworks were made and painted with the produced green enamel. Then these artworks were used to make 3D models of architecturally designed spaces and decorative objects by computer simulation software.

1.2 Green Glass in Art and Architecture

Because of having a positive psychological effect, green color has a historical bond with architecture and has been used for a long period in architectural design. In addition, glass is the most used material to provide transparency and light, and is one of the most commonly used facade materials in contemporary architecture. Therefore, green glass could be a magical element which can present significant properties and provide new possibilities to design. In order to use the obtained green enamels to design architectural spaces, three steps were taken: First of all, three specific glass artworks (Star-Cross tiles, Beehive tiles, the Glass Wall) were produced. At the next step, they were painted with the enamels which were produced in this study. Finally, these painted artworks were used to make 3D models of architecturally designed spaces and decorative objects by computer simulation software.

1.2.1 Green in Artworks

Green color is one of the main colors which artists have used to create artworks since a long time ago. Green pigments have been used since antiquity, both in the form of natural earth and malachite, used primarily by Egyptians. Greeks introduced veridigris (blue-green copper-based pigments), one of the first artificial pigments. By virtue of advances in chemistry, a new generation of green pigments were introduced in the late 18th century: cobalt, emerald and viridian green [17].

Green can stand for awakening, the color of planet life, new beginning and growth. Green is also considered as a superhuman powers such as Celtic green man who is an important vegetation and fertility god. In Islam green is the most important color, Mohamad's green cloak represented paradise, renewal and spiritual refreshment. [18].

In the words of psychology, the green color is commonly associated with nature, spring, growth, life, and youth. Getting inspired by this fact leads me to use green enamel which belongs to the environment. This color has been used for a long time, and has a historical bond with architecture and art. It is also the color of religion, especially in Islamic countries. From another viewpoint, based on color psychology, green color also represents a symbol of health, fertility, tranquility, peace, safety and luck. Green is often described as a refreshing and calming color. For this reason, green objects, whether in the real world or even in virtual space, are used to make a playful or childlike world for children [19, 20].

As an example, "The Japanese Bridge" (1899), an oil painting by Claude Monet, has shown in Figure 1-2. In this painting, Monet uses the color of hope together with the symbol of a bridge. The bridge stands for the uniting of people and revives hope for a peaceful future. Incidentally, Monet's use of Emerald Green pigment, which contained arsenic, may have contributed to his blindness in later life [17].

In architectural design, green color is widely used in hospitals and health centers. It signifies health, life and calmness. That is why health care facilities incorporate shades of green into their decoration. Moreover, based on expert opinions, the green color has a remarkable effect on security, rest and relaxation. Green also enhances positive cognitive outcomes, such as improved memory, problem-solving, positive thinking [21-23].

In current research, to show the appearance of obtained enamel on glassy objects, the green enamel which has been reproduced from Neri's recipes has been applied on some artworks which has been made from float and frit glass. Since these artworks are used to design architectural spaces, it has been tried to revive the historical bond (with architecture and art) by representing the above-mentioned characteristics of the green color.

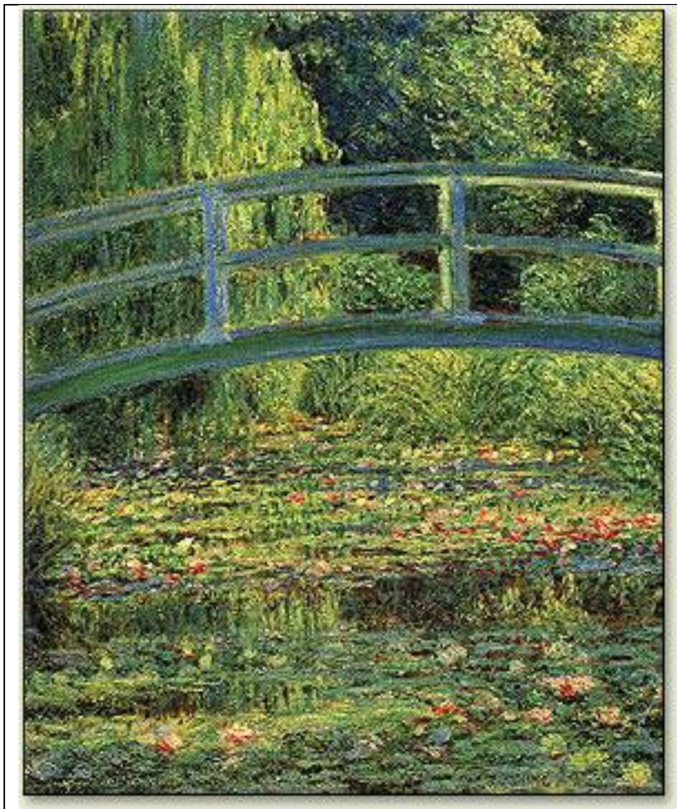


Figure 1-2: "The Japanese Bridge" painting [17]

1.2.2 Architectural Glass

Architects may be required to provide many information and details of materials related to the building. They must conceptualize and experiment with different materials in order to have the best result. Glass, a fascinating material, usually quite visible in most places, has become an extraordinarily useful in architecture. Glass and architecture have a long-lasting partnership since its invention in pre-Roman times. Glass could be subjected to diverse processes like coloring, painting, etching, grinding, cutting, fusing, bending, carving, and could be used in different clarity like colored, colorless, opaque, translucent, or transparent [24]. With this in mind, glass is the most used material to achieve transparency and light, and one of the most commonly used facade materials in contemporary architecture. Architectural glass is a magical material which can present so many different properties such as transparency to architects by providing new possibilities to design.

Glass was used in Gothic architecture to convey spiritual connotations. In window openings, colored glass changed light to provide an ethereal ambiance and evoke a spiritual response. [24]. Since the medieval periods, colored glass has been used extensively in ecclesiastical, public, and private buildings to "paint with light", and to show the beauty of color by light. Stained glass, as an architectural element, exists as both a facade element and an interior decorative member, making it a unique challenge in design and execution. A significant component of stained glass is the mixing of colored glass and painted elements, which are often intended to tell a story or convey a mood to the viewer [25].

As an outstanding remark, it is worth mentioning the importance of colored glass in traditional Iranian architecture. Contemporary architecture emphasizes on the sustainability and efficiency of natural lighting in structures. Traditional Iranian architecture commonly uses natural light to create a friendly environment with various emotional responses in the users. Colored glass plays a significant role in this heritage in the form of wooden framed windows (Orsi or Orosi) with Girih designs (a decorative Islamic geometric art form). Daylight passes through these Orsis, and it projects different colors into the interior, creating different psychological stimulations in the viewer. Colored glass is used in this manner to manipulate the user's moods, thus playing a significant role in the environmental psychological effect [26].

The contemporary view point tends to integrate the indoor and outdoor space. This idea appeared in nineteenth century and reflected a drastic shift in thinking about nature. It was as a consequence of evolutionist belief which recognize human as a part of nature (not master of it). The more modern architect tried to remove that barriers and division between inside and outside, to invite nature in [24].

In this research, because of my background in architecture, I tried to make a bridge between architectural design and green-glassy artworks. Computer modelling software is used to demonstrate how architectural spaces would look with green artworks. Using green-glassy artworks which were painted by obtained green enamels in architectural spaces could be an interesting and challenging work. Additionally, I have done some investigations in related areas such as historical Islamic recipes of colored glass, history of glass making techniques, and application of colored glass in Iranian architecture, was enthusiastic to work on reproducing the green enamel. Additionally, some similar researches for reproducing other enamels such as red and blue had been done in VICARTE research group which could shed some light on this way in order to understand the old recipes and find the closest batch to the original one.

2

Historical Recipes for Stained Glass Paints

2 Historical Recipes for Stained Glass Paints

2.1 A Short History of Historical Recipes

Stained glass is colored/painted glass (as a material) or works created from it (decorative windows). Stained-glass painting techniques are usually divided into grisailles (brown and black), silver stain (yellow to orange), sanguine (yellowish to brownish-reds), and enamels (with different colors) [28]. The art of stained glass flourished with the construction of cathedrals in the Medieval time, especially in the 13th century during the Gothic architecture. Enameled/painted glass started to use in stained glass windows from the second half of the 15th century, and reached its peak between the 16th and 17th centuries [11, 29].

During the Medieval period knowledge was restricted to workshops, either in a religious or urban context. From the 14th century and mainly during the 16th century, the number of manuscripts increased, achieving the highest point during the 17th and 18th centuries [10]. The oldest systematic publications presented to glass, glass painting and stained glass are the ones by Antonio Neri (1612) and André Felibien (1676) which opened the way to several translations, annotations and experiments all around Europe, in order to maintain the knowledge of ancient glass painters and combining them with the technologies available [10]. We can mention the publications which were written by Johann Kunckel, (1679), Robert Dossie (1758), Pierre Le Vieil (1774), Reboulleau and Magnier (1825), Georges Bontemps (1868), as a few of significant historical treatises during last centuries [10, 11].

In recent decades, because of increasing interest in the investigation of written historical sources about stained-glass production and glass painting materials, several studies have been accomplished. These studies present mainly on translations and interpretations and rarely explore the recipes reproduction. However, some significant studies have been made concerning historical stained-glass production techniques [11, 12, 14].

The characterization of stained glass in Portugal has been studied as a subject of interest for many years. The research on Portuguese stained-glass has also been developed at VICARTE and the Department of Conservation and Restoration. Some significant studies which were done recently in Portugal are listed hereunder:

In 2018, Andreia Machado did her study on the study of historical stained-glass painting techniques, namely blue enamels, sanguine red, and grisaille. This study [11] concluded that the choice of the raw materials for the production of the paint, the binder used to apply the paint, and parameters such as firing temperature and heating rate, have a strong impact on the outcome.

The study of Márcia Vilarigue [12] shows that variation in the composition of the two main components of the grisaille —colorants and lead based glass— has an impact on the thermal behavior of the grisailles and compatibility with glass substrates. Their results show how the composition of the grisaille is directly related to a good or poor adhesion of the paint to the substrate.

In [30] and [31], the author present in-depth studies of some historical publications, which were written by Johann Kunckel (1679), Simon Eikelenberg (around 1700), and Willem van Laer (1721). He also provides a short overview of the key ingredients in the preparation of Rosichiero glass (a transparent red glass).

Santos et all. In [14] made a study on the relationship between historical sources on the preparation and use of sanguine from the fifteenth to the nineteenth centuries. To do this, she selected 40 representative recipes and reproduced them. She concluded that the grinding and decantation processes are central steps for obtaining fine powder, and the adhesion of sanguine paint is strongly influenced by the binder, composition and morphology.

The study of [12] done in 2020, has focused on the reproduction of three historical recipes of Neri for red enamel glass. By using electric and wood-fire furnaces, the authors wanted to investigate the role of the melting conditions and furnaces used to the obtained final colors. The results indicate that temperature control is more important than having control of the furnace atmosphere, and the melting at the right temperature is fundamental for the quality of the final product.

Based on a recent study, the different raw materials used in the grisailles production as well as firing temperature, and the pigments-base glasses proportion can significantly impact on the final appearance, and the chemical and mechanical stability of the grisailles [29].

2.2 Green Enamels Recipes of Neri

The book "L'art vetraria" (the art of glass) by Antonio Neri (1576-1614) is the main reference of this research. The treatise is divided into seven books. The first chapters of his treatise deal with the preparation of raw materials, followed by the preparation of various types of glass. On the sixth book, Neri presents the recipes for enamels of colors. The original version of this book has written in Italian, and at least two different English translated books were accessible (Table 2-1). Because of some differences in the context of these translated books, especially about the quantity of materials used in recipes, it needed to refer to the original version to figure out what the original recipes say. By comparing these translated books with the original one, and replacing some wrong or imprecise translated words with accurate equivalents, a revised version of this book in English language was obtained by the author of this current thesis. The original text and this new translated text are represented in the following subdivisions.

Table 2-1: Two accessible English translated books of Neri book

Book 1	The Art of Glass: The World's Most Famous Book on Glassmaking (Progress in understanding glass making) written by Antonio Neri, Translated & Annotated by Christopher Merrett [32]
Book2	The Art of Glass by Antonio Neri, Translated & Annotated by Paul Engle [33]

2.2.1 L'art Vetraria (The Art of Glass in Original Language)

The original version of the green recipes (Pages 83-88) of Neri's book is presented hereunder:

LIBRO SESTO DELL' ARTE VETRARIA, DI PRETE ANTONIO NERl

Nel quale si mostra il modo di fare tutti li Smalti da Orefici per smaltare sopra oro in diversi colori con le regole, & ma-terie che tingono, & I modi de' suo chi per fare tali smalti con ogni squisita diligenza, & chiare demostrationi (dimostrazioni) possibili in simili materia.

In questo Sesto libro si mostra il modo di fare gli Smalti di più colori per vfo delli Orefici da Smaltare sopra Oro, & altri 12urnace12, cosa gustosa, & vaga, & anco in se non solo lauorosa ma necessaria assai, poiché si vede che I 12urnace12 12urnac di Smalti di più colori, fanno una vaga, & nobili vista allettando oltre a modo li occhi de I riguardanti, & perché è una delle parti prin-cipali del vetro, & necessaria, & parendomi sia per essere grata, & gustosa al' 12urnace12h mi sono messo a descrivere molti modi di fare più forte di smalti, che come materia spettante a l' arte vetra-ria, & una delle sue appartenenze nobili, & non volgare, ma par-ticolare in pochi, & asciò questa opera non fosse priva di mate-ria cosi vaga utile, & necessaria ne ho fatto il presente Sesto libro per gusto, & benefitio (benefizio) 12urnace12h.

Materia con la quale si fanno tutti li Smalti Cap. XCIII

PIGLISI piombo fine per esempio libre trenta stagno fine, libre trentatré, questi 12urnace12 insieme si *calcinino nel fornello, come si è detto del piombo a sua luogo, 13urnace13h si 13urnace per setaccio. Questa calcina si 13urna bollire in acqua chiara, & vaso di terra pulito, cioè pignatto, com ha bollito un poco si levi dal fuoco, & si voti l' acqua per inclination (inclinazione), che portera secco della calce metallica più sottile, si rimetta nuova acqua sopra la residentia della calce, & si 13urna bollire, & si decanti come sopra, & questo si refteri tante volte, che l' acqua non porti con secco più calcina, & la refudentia 13urnace13he rimarrà nel fondo, si può tornare a calcinare per cavarne le paste più sottile per ebullition (ebullizione) di acqua 13urnace, come sopra allora si ifuapori tutta l'acqua che ha portato secco la parte sotille della calce, & questo à lento fuoco, & massime nell'ultimo acciò non si guastasse la calce, la quale in fondo rimarrà sottilissima, molto più che la calce ordinaria. Pigliasi a dunque di questa calcina sottile libre cinquanta, fritta di cristallo fatta con tarso bianco benissimo macinato, & passato per setaccio fitto libre cinquanta, sale di tartaro bianco, come si è insegnato oncie otto, ogni cosa benissimo polverizzata, & mescolati si 13urna passare per setaccio, & si rimetta questa materia in pignatte di terracotta nuove, dandoli fuoco per dieci hore (ore), poi caua questa materia, e polverizzata bene, & serbala in luogo asciutto, & coperto che non vi vadi polvere che questa e la materia con la quale si fanno tutti li smalti di tutti I colori.*

Smalto verde. Cap. XCVII.

In padellotto (padellatto) invetriato con vetro bianco all'ordinario in la 13urnace, metterai libre quattro di materia sopraddetta da fare tutti li Smalti, che in dieci hore (ore), o dodici farà fuso, & pulita benissimo, questa allora si tragietti in acqua, & si rinforni nel suo padellotto, & si laffi pulire benissimo, come è ben pulita se li dia ramina di tre cotte fatta con piastre di rame nelli vasi della 13urnace, come si è detto al suo luogo, & di questa oncie due, con la quale mescolerai denari due di scaglia di ferro, che cade dalla incudine ben macinata, queste due polvere darale a questa materia in tre volte sempre mescolando bene la materia acciò incorpori il colore, & guardando di quando in quando se il colore piace, & come sta a segno, si laffi pulire bene, & incorporare bene il colore poi si cavi di 13urnace al solito, che questo farà smalto verde per Orefici bello.

Altro Smalto verde. Cap. XCVIII.

Habbi (abbi) materia con la quale si fanno tutti li Smalti, & per esempio libre sei, con essa mescolerai benissimo Ferretto di Spagna benissimo macinato oncie tre, & con questo mescola di due di Croco di Marte, questa materia cosi unità mescolate bene mettile in padellotto invetriato benissimo con vetro bianco lassa pulire, come è pulita tragitta in acqua, & ritorna la in padellotto 13urnace esso pulirà, guardà allora se il colore ti piace; acciò possa caricare, o scaricare, & come il colore sta a segno lassa pulire, & incorporare il colore, poi caualo di 13urnace al solito, che questo farà uno smalto verde per Orefici bello.

Queste 13urnace si fanno di quattro in sei oncie in circa in tutti li Smalti.

Altro Smalto verde. Cap. XCIX.

In padellotto invetriato al solito come si fa nella 14urnace di vetri, metterai libre quattro della sopraddetta materia, che fa tutti li smalti & in poche hore (ore) pulirà, come è pulita all'ora si tragietti in acqua, & di nuovo si ritorni nel suo padellotto, & si lasci pulire, & allora se li dia queste due polvere mescolate in tre volte, cioè oncie due di ramina di tre cotte fatta di scaglie di battitura di calderai, come si è detto al suo luogo, & denari due di Croco di Marte, fatto con l'aceto, queste polvere ben mescolate si diano alla materia di sopra quando è fusa, & pulita bene mescolando, & incorporando le polvere, hauendo (avendo) sempre avvertenza di ben guardare, & considerare quando I colori stanno a segno, come questo farà tale si cavi a l'ordinario in focacce, laffando prima pulire, & incorporare bene il colore, questo farà uno smalto per Orefici bello, & vago.

2.2.2 The Art of Glass of Neri (L'art vetraria)

To be assured of the instructions and quantity of ingredients, the English translated version of the book "L'art Vetraria" [32, 33] was revised by the author of this study. The translated version is presented hereunder:

SIXTH BOOK OF GLASS ART, OF A PRIEST ANTONIO NERI

Wherein is shown the way to make all the gold-smith's enamels, to enamel upon gold in diverse colors, with rules, and the materials which color, and what fires make those enamels, with exact diligence and clearest demonstration possible.

Enameling on gold and other metals is a fair and pleasing thing, and in its self not only laborious, but necessary, since we see metals adorned with enamels of many colors make a fair and noble shew, enticing beyond measure the eyes of the beholders. And because it is one of the most principal, and a most necessary part of glass, and it appearing to me to be a thing grateful and pleasing to all, I set myself to describe many ways to make several sorts of enamels, as a thing not vulgar, and belonging to this Art, and one of its most noble appurtenances. And that this work might not be deprived of a matter so pleasant, profitable and necessary, I have made this sixth Book for the delight and benefit of all.

CHAP. XCIII: The Material wherewith all enamels are made.

Take of fine Lead 30 pounds, of fine Tin 33 pounds, Calcine them together in a Kiln, and sieve them, Boil this Calx a little in clean water in clean earthen vessels, Take it from the fire and decant off the water by inclination, which will carry with it the finer part of the Calx, put fresh water on the remainder, then boil and decant as before, repeat this as long as the water carries off any Calx.

Recalcine the gross remaining Calx, and then draw off again the more subtle parts, as before. Then evaporate the waters which carried off the finer Calx at a gentle fire, especially at the last, that the Calx may not be wasted, which will remain at the bottom much finer than the Ordinary. Take then of this fine Calx, of Crystal Frit made with Tarso, ground and sieved fine, of each 50 pounds, of white salt of Tartar eight ounces, powder, sieve and mix them well: Then put this stuff into a new earthen pot baked, giving it a fire for ten hours, then powder it and keep it in a dry covered place. Of this stuff are made all the enamels of whatsoever colors. This shall be called the stuff for enamels [*The Base Component of all Enamels*].

To avoid our Authors repetitions observe

1. The pots wherein enamels are made must be glassed with white glass and bear the fire.

2. Mix and incorporate well the colors and stuff for enamels.

3. When the enamel is refined, and the color good, and well incorporated, Take it from the fire with a pair of tongs for the goldsmith's use.

4. The way to make enamels is this:

> Powder, grind, and sieve well the colors, and mix them first well one with another, and then with the stuff for enamels, then set them in pots in the furnace, when they are all melted and incorporated cast them into water, and when dry set them in the furnace again to melt (which they soon do) make a proof, and if the color be too high, Take out some of it and add more of the stuff for enamels, and if too light add more of the color at pleasure to your content, then take it out of the furnace.

CHAP. XCVII: A Green Enamel.

Take of the stuff for enamels four pounds, put it in the furnace, and in ten or twelve hours it will be melted and refined, cast it into water, and put it again into the furnace in its own pot, when it is refined, give it of Brass thrice calcined two ounces, wherewith mix of scales of Iron well ground two ounces, put them in at three times, mixing and incorporating them every time, and ever and anon see whether the color please, when it is well Take it from the fire.

CHAP. XCVIII: Another Green Enamel

Take of the stuff for enamels six pounds, wherewith mix well “Ferretto of Spain” well ground three ounces, and mix with it 48 grains of “Crocus Martis”, put them into the furnace, &c. These furnaces are made from about four to six inches for all enamels.

CHAP. XCIX: Another Green Enamel

Take of the stuff for enamels four pounds, which in few hours will be refined, then cast it into water, and put it again into the furnace, and let it refine, then add these two powders well mixed at three times, to wit, of Brass thrice calcined two ounces, of “Crocus Martis” made with Vinegar 48 grains, put them in the furnace, and when they are well incorporated, Take them from the fire: This is a fair and good enamel.

2.2.3 Comparison of different translations with Original book

As mentioned above, comparison between the original version of Neri's book (in Italian language) and translated books resulted in revised translated version. The brief results of this comparison are shown in Table 2-2. To find a reliable equivalent for used quantities and units, one needed to know the meaning of these units in the time and location in which the book was written. To do so, by referring to pages 87-88 of "Encyclopedia of Scientific Units" [34], old Italian measure used before adopting the metric measures in Italy were extracted. Based on this book in Florence 1 Libbra = 12 Oncia = 288 Denaro = 6912 Grain = 339.5 gr.

Additionally, some expression in Neri's recipes are vague or un-common in contemporary literature, and they need to be clarified. Table 2-3 give an explanation and definition for these old words.

Table 2-2: Comparison of different translations with Original book

	Book 1	Book 2	Original Book	metric equivalence
Chap 97 (XCVII) *The Base Component of all Enamels** Thrice cooked copper Iron Flake	 Four pounds Two ounces Two ounces	 L lbs L oz 2 pwt	 libre quattro oncie due Denari due	 1358 gr 56.58 gr 2.36 gr
Chap 98 (XCVIII) *The Base Component of all Enamels* Spanish Ferretto Crocus Martis	 Six pounds Three ounces 48 grains	 6 lbs L oz 2 oz	 libre sei oncie tre [oncie] due	 2037 gr 84.87 gr 56.58 gr
Chap 99 (XCIX) *The Base Component of all Enamels* Thrice cooked copper Crocus Martis	 Four pounds Two ounces 48 grains	 L lbs L oz 2 pwt	 Libre quattro Oncie due Denari due	 1358 gr 56.58 gr 2.36 gr

* "*The Stuff for Enamels*" was used in English translated version of Neri's recipes for the base component which is used for all enamels. In this thesis we use "*The Base Component of all Enamels*" or "*The Base Component*"

Table 2-3: Explanations of some un-common expressions of Neri's recipes

Word	Explanation
To calcine	1) to convert into Calx by heating or burning, 2) to heat (a substance such as inorganic materials) to a high temperature but below the melting or fusing point, causing loss of moisture, reduction or oxidation, and the decomposition of carbonates and other compounds,
Calx	1) a powdery metallic oxide formed when an ore or mineral has been heated, 2) the crumbly residue left when a metal or mineral has been subjected to calcination,
Lead and Tin Calx	It is produced from Calcined Lead (PbO) (47.67 % wt) and Calcined Tin (SnO_2) (52.33 % wt)
Cristal Frit	A sodium-rich glass, that appeared in Murano in the 15th century. It is considered a glass of high quality, known for its transparency. It was made from Polverino-salt and Tarso,
Tarso	1) SiO_2 (Silicon dioxide) 2) a specie of very white marble, Sand, white quartz 3) Quartz pebbles from Ticino river in in Switzerland which are very rich in silica,
Polverino-salt	1) Na_2CO_3 (Sodium Carbonate) 2) Salt of Levantine coastal plant ashes, 3) the coastal plant ashes for the production of polverino-salt came from the Levant region in Syria,
Tartar-salt	Sal di Tártaro or Pearl-ashes: Potassium carbonate (K_2CO_3), [35]
Tartaro	Tartaro or Grumma Tartaro or Grumma is obtained from wine lees, extracted from the bottom of the wine barrels. These ashes, rich in potassium, would also be treated to obtain a salt rich in potassium carbonate (K_2CO_3) [11].
Cristallo frit	Tarso (SiO_2) + Polverino-salt (Na_2CO_3)
Spanish Ferrecto (ferretto di Spagna)	1) Copper sulphide [36], 2)One-time burned copper [37],
Crocus Martis	Fe_2O_3
Calcined copper	$CuO + Cu_2O$

3

METHODS (EXPERIMENTAL PART)

3 Methods (Experimental Part)

"I couldn't make stained glass without the nourishment of painting. The idea of bringing that kind of liquid, fluid, transparent color into our daily experience. Once you've tasted it, you really want another lick at that lolly."

Brian Clarke (an Architectural Artist) [27]

This chapter is devoted to explaining the methodology of producing the green enamels and the characterization of painted samples.

3.1 Enamel Producing

The sixth book of the treatise "L'Arte Vetraria" presents raw materials and recipes for the production of enamels in two steps: first, the production of *The Base Component of all Enamels* (as defined as "*the Stuff for all Enamels*" in English translated version of Neri's book [32, 33]) which is used to produce all the enamels of whatsoever colors (Chapter 93 The Material to Make all Enamels), and secondly the production of each enamel. Neri proposes three recipes for the green enamels: Chapter 97-"A Green Enamels", Chapter 98-"Another Green Enamel", and Chapter 99-"Another Green Enamel".

3.1.1 Producing of *The Base Component of all Enamels*

The Base Component was produced in three steps:

The first step is the production of Lead-Tin Calx: Based on the Neri's recipes, in order to make Calx it was supposed to calcine the mixture of fine Lead and fine Tin with 1:1.1 ratio. In this project metal cubic forms of Lead-Tin (Figure 3-1) were used.

The second step is the production of Cristallo frit by Tarso and Polverino-salt. In this project, Sodium carbonate (Sodium Carbonate anhydrous (Reag. Ph. Eur.) PA-ACS, produced by PANREAC Co.) was used for Polverino-salt and white quartz (Sand, White Quartz, produced by Honeywell Fluka) for Tarso.

Last step is mixing of Calx with Cristal frit, and Tartar-salt. In this project Potassium sodium tartrate tetrahydrate (Potassium Sodium Tartrate 4-hydrate (Reag. USP, Ph. Eur.) for analysis, ACS, ISO, produced by PANREAC Co.) was used instead of Tartar-salt.

Raw materials and respective weight ratio percentage (%wt) used for the production of green enamels has shown in Table 3-1.

Calx: Appropriate number of Lead-Tin cubes were placed into the crucible (a ceramic container), and the crucible was put into the kiln. The kiln was set for 5.5 ºC/min heating rate, and maximum temperature 650 ºC for 14 hours to get calcined. Then, calcined powder (Figure 3-2) was ground and sieved finely.

Table 3-1: Raw materials and respective chemical compounds used for the production of green enamels

The Base Component	1- Calx (Calcined Lead-Tin cubes) (49.76 % wt) 2- Cristallo frit (49.76 % wt) (Cristallo frit: white quartz (60.60 % wt) + Sodium carbonate (39.40 % wt)) 3- Potassium sodium tartrate tetrahydrate (0.48 % wt)
Recipe Chapter 97	1- *The Base Component* (95.84 % wt) 2- Three-times burned Copper (3.99 % wt) 3- Burned Iron (0.17 % wt)
Recipe Chapter 98	1- *The Base Component* (93.50 % wt) 2- Spanish Ferrecto (one-time burned copper) (3.90 % wt) 3- Crocus Martis (Fe_2O_3) (2.6 % wt)
Recipe Chapter 99	1- *The Base Component* (95.84 % wt) 2- Three-times burned Copper (3.99 % wt) 3- Crocus Martis (Fe_2O_3) (0.17 % wt)

Figure 3-1: Lead-Tin Cubes

Figure 3-2: Calx: Calcined Lead-Tin

Cristal frit: Cristal frit is made of white quartz and sodium carbonate. To make Cristal Frit, 182 gr of finely sifted white quartz and 118 gr of sodium carbonate were mixed together. The resulting mixture was put in the kiln. The kiln was set for 6.5 ºC/min heating rate, and maximum temperature 1100 ºC for one hour. Then the molten glass was poured into cold water in order to break the glass into several pieces. The obtained glass was then dried and ground on a mechanical grinder. The process for producing Crystal frit is shown in Figure 3-3.

(a)	(b)	I

Figure 3-3: Producing Cristal Frit: a) mixture before firing, b) after firing, c) final product

Then, to provide *The Base Component*, at first, 29.85 gr of fine Calx, and 29.85 gr of Crystal Frit, and 0.29 gr of potassium sodium tartrate tetrahydrate were appropriately mixed. The resulting powder was put into a ceramic crucible, and it was placed into the kiln. The kiln was set for 6.5 ºC/min heating rate, and a maximum temperature of 1200 ºC for one hour. The melt was then dropped into water. The resulting material for *The Base Component* is shown in Figure 3-4.

Figure 3-4: A crucible and obtained "The Base Component" inside a steel bowl

3.1.2 Producing of The Green Enamels

To produce three green enamels, the coloring ingredients of each three recipes were prepared based on Neri's recipes (Table 3-1):

Recipe 97) These materials are required for "A Green Enamel": *The Base Component* 16.81 gr, three-times burned Copper 0.70 gr, Burned Iron 0.03 gr.

Recipe 98) To make "Another Green Enamel" these materials are required: *The Base Component* 16.81gr, Spanish Ferrecto 0.70 gr, Crocus Martis 0.47 gr. Instead of Spanish Frrecto, One-time burned copper has been used (Figure 3-5). In this project one-time burned copper was used instead of Spanish Ferrecto.

Recipe 99) To make "Another Green Enamel" these materials are required: *The Base Component* 16.81 gr, three-times burned Copper 0.70 gr, Crocus Martis 0.03 gr.

(a)	(b)

Figure 3-5: a) Burned Copper (Spanish Frrecto), b) burned iron

Iron and copper have been burned at 650 ºC for 60 minutes, and sieved to make fine powder. To make three-times burned copper, the firing and sieving process were repeated for three times.

Obtained coloring ingredients of three recipes were shown in Figure 3-6.

Before proceeding further, the coloring ingredients of each recipe (all ingredients of a recipe with the exception of the base component) were added together and mixed. Let's call it *The Coloring Component*. So, each recipe has just two components: *The Base Component* and *The Coloring Component*.

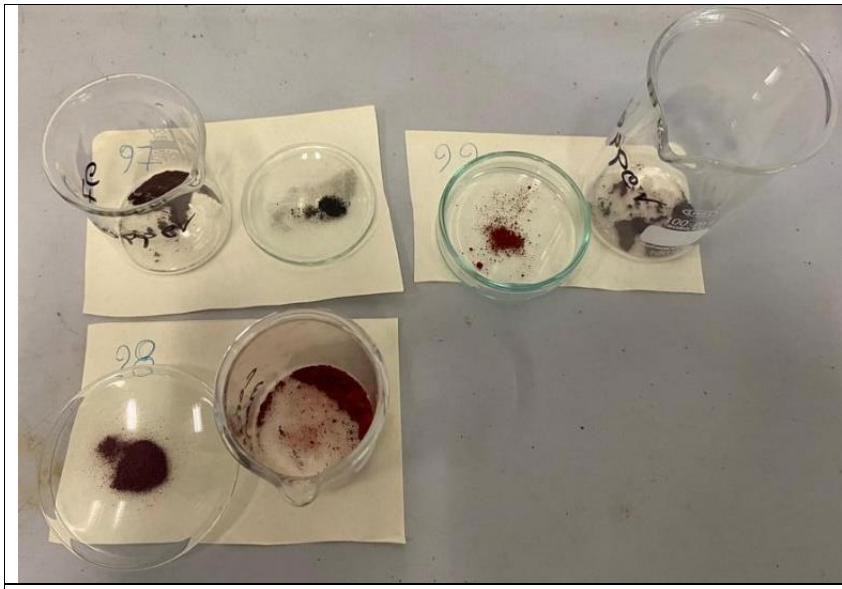


Figure 3-6: Coloring ingredients of three recipes

Now, specified amount of *The Base Component* was put inside three alumina crucibles[1], and the crucibles were put in the kiln (the kiln was set for 6.5 ºC/min heating rate, and a maximum temperature of 1200 ºC). After around 90 minutes (at 1200 ºC), the crucibles were taken out of the kiln (just for some seconds to avoid thermal shock), and *The Coloring Component* of each recipe was added to the related crucible, and mixed with a metal stick, then the crucibles were put back in the kiln. After around 60 minutes (at 1200 ºC), the mixing process (taking out of the kiln for some seconds, stirring by a metal stick, and putting back into the kiln) was repeated, one more time. Again, after around 60 minutes, the crucibles were taken out of the kiln, and were thrown inside the water (Figure 3-7).

As it was mentioned above, the ingredients were mixed with a metal stick during the firing process. To avoid thermal shock the mixing process should be done just in some seconds. However, because of the high viscosity of the glass material, the mixing process could not be done properly. Also, some quantity of the ingredients was stuck to the stick, influencing the homogeneity of the mixture.

After ending the firing process, throwing crucibles in water, and breaking crucibles, the enamel was achieved. Resulted enamel for recipe 98 is shown in Figure 3-8. Then, the crucibles content was ground for 10 min by a grinding equipment (electric mortar) (Figure 3-9). The resulted powder of each enamel is shown in Figure 3-10 for three different recipes.

[1] Refer to Chap. 6.2 for more details

Figure 3-7: Different Steps of Enamel producing process

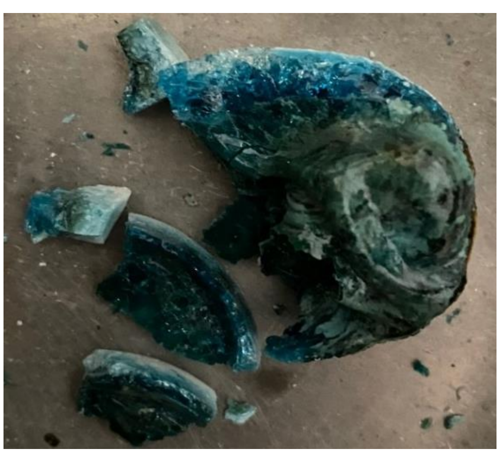
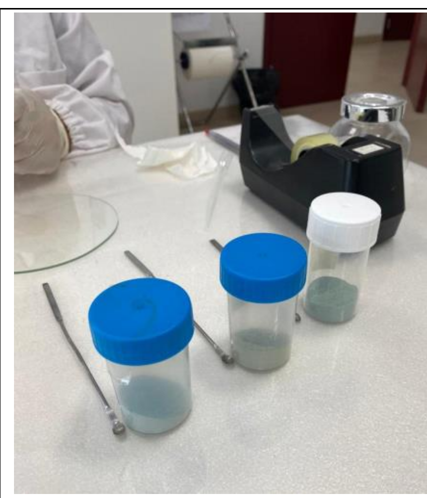
		

Figure 3-8: Resulted enamel after firing process	*Figure 3-9: Electric motor (Grinding equipment)*	*Figure 3-10: Resulted color powder based on three different recipes*

In the final step, in order to apply the coloring enamels, lavender oil was used as a binder. By mixing the produced enamel pigment with lavender oil a paint was formed to apply with a palette-knife on a glass slide (a thin flat piece of glass). Produced paint contains coarse particles and appears as non-uniform substance. Therefore, a homogeneous layer could be challenging to obtain by the palette-knife (Figure 3-11). The painted samples were then put into the kiln (at 650 ºC, for 30 min).

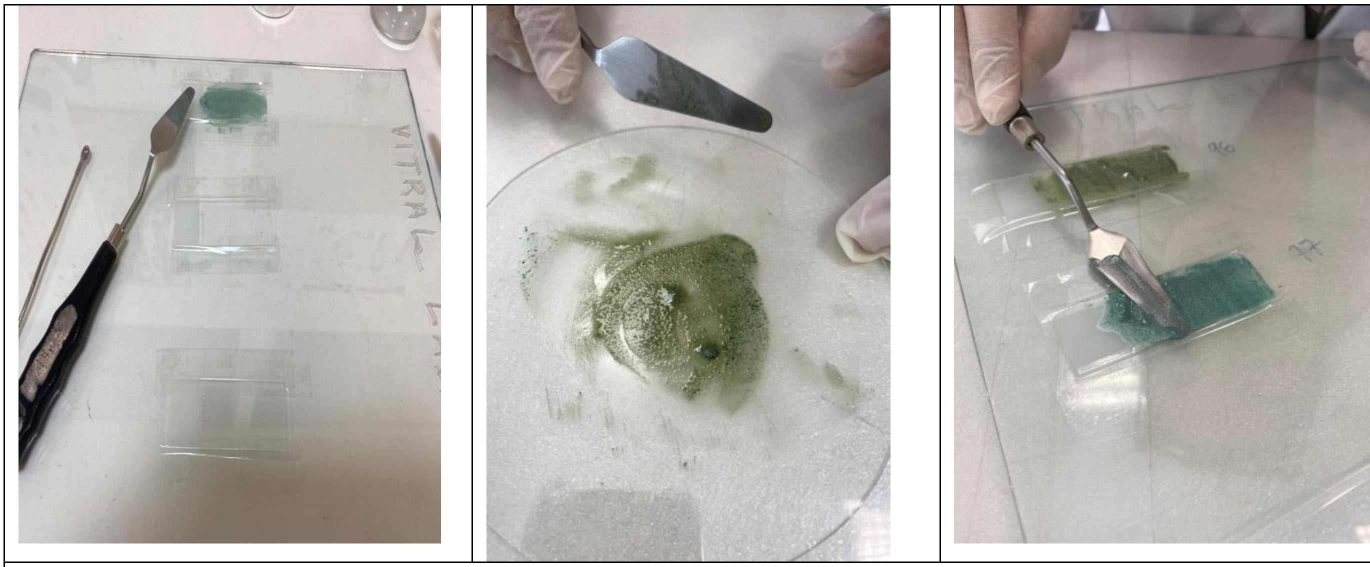


Figure 3-11: Painting process

3.1.3 Developed Strategies

The enamel producing method which was explained above, was exactly based on Neri's recipes. To try to produce better results, this method was slightly modified. These developed procedures were named as the second and third strategies.

In the second strategy, instead of using *The Base Component* (as a ready-prepared material), the ingredients of *The Base Component* were used. This strategy was applied to avoid the loss of some material by adding the ingredients of the base component to the same crucible where the green enamel is produced. At first step, 10 gr of crystal frit was put in each of the three crucibles, then they were put in the kiln (with 6.5 ºC/min heating rate, and a maximum temperature of 1200 ºC). At the second step, Calx and Tartar salt (Potassium sodium tartrate tetrahydrate), and at the third step *The Coloring Component* were added (with an around 60 min time interval in each step). It is worth to mention that after adding each material to the content of crucibles, to make mixture more homogenous, they were mixed by a metal stick in a similar way with the first strategy. Then, the crucibles were thrown inside the water. To obtain finer powder (which results in more homogenized paint), the resulted enamels (after firing and cooling processes) were ground for 20 minutes (while it was 10 minutes in the first strategy) in the electric mortar. The next steps (mixing with lavender oil, painting on glass slides, and baking the paint) are performed like the first strategy. However, to ensure that enamel particles would melt properly, the kiln temperature chosen was higher (in 700 and 750 ºC).

In the third strategy, all ingredients of *The Base Component* and also *The Colorings Component* were mixed together (outside the furnace), and the mixture of all the ingredients was put in the furnace (with 6.5 ºC/min heating rate, and a maximum temperature of 1200 ºC) (Figure 3-12). It means, in contrast with the first and second strategies, the mixture went through an uninterrupted firing process. In this way, there was no need to mix the molten mixture with a metal stick at high temperatures. After firing, the next process (throwing in cold water, grinding, mixing with lavender oil, painting, and baking) are performed like the second strategy. However, to investigate the effect of temperature and the fluidity of enamel on the final resulting color, this experiment was done for a wide range of kiln temperatures (in 650, 675, 700, 725, and 750 ºC).

(a) (b) I

Figure 3-12: Enamel producing process with third strategy: a) after mixing before firing, b) inside the kiln, c) after firing

3.2 Characterization of Enamels

The color, composition, and crystallography of raw material and the obtained enamels need to be characterized through colorimetry, reflectance spectroscopy, and X-ray diffraction (XRD).

Colorimetry[1], the science of color measurement, is widely employed to express color in numerical terms and to measure color differences. To do this, LAB and LCH color coordinates are used [38]. In this study, the reflectance spectra were obtained by using the AvaSpec-2048 Fiber Optic Spectrometer based on the AvaBench-75 symmetrical Czerny-Turner design with a 2048-pixel CCD Detector Array. The spectrometer has a fiber optic entrance connector, collimating and focusing mirror and diffraction grating. A choice of 15 different gratings with different dispersion and blaze angles enables application in the 200–1100 nm range. The light source was AvaLight-HAL Tungsten Halogen. To perform these analyses, an integrating sphere was used.

X-ray diffraction (XRD) was performed using an MPD X'Pert PRO powder diffractometer from PANalytical with a Cu Kα radiation source (λ = 1.540598 Å) and equipped with an 1D X'Celerator detector. Powder samples were mounted on a Si 0-background holder and the XRD scans were performed in the range of 15 to 90 ° (2θ) in the Bragg-Brentano configuration, with a scanning step size of 0.033 ° in 2θ.

The XRD diagram can be used to distinguish between the amorphous and the crystalline materials. The produced XRD curve of amorphous materials has a broad hump and no any sharp diffraction peaks, the presence of sharp diffraction peaks is an indication of crystalline material [39].

[1] Refer to Chap. 6.3 for more details

4

RESULTS AND DISCUSSION

4 Results and discussion

"Far more than religion, or war, or academic treatises,
skill shaped civilization."

Paul Greenhalgh (an Art and Design Professional) [40]

Green enamels were produced based on Recipes No. 97, 98 and 99 by using different strategies and different firing temperatures (3 recipes, 3 producing strategies, and 2 to 5 different kiln temperatures), which gave a total of 27 produced samples.

As defined hereunder, specific coding instructions are used to name them (similar with [14]). The first part of this code (E1-E3) point to the enamel-producing strategy, and the second part (R97, R98, R99) reference to the number of the recipe in Neri's book, and the last part (T: 650, 675, 700, 725, 750 ºC) represent the kiln temperature. The results after firing the painted samples are listed below (from Table 4-1 to Table 4-5).

Table 4-1: Enamels produced by the 1st synthesis method based on recipes 97, 98 and 99, fired at 650, 700 ºC

Sample	Experiment Result	Sample	Experiment Result
E1 R97 T650		E1 R97 T700	
E1 R98 T650		E1 R98 T700	
E1 R99 T650		E1 R99 T700	

Table 4-2: Enamels produced by the 2nd synthesis method based on recipes 97, 98 and 99, fired at 700, 750 ºC

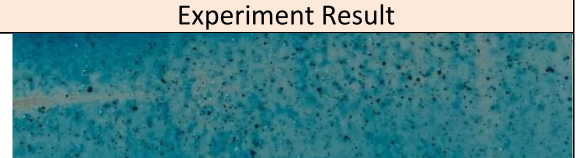
Sample	Experiment Result	Sample	Experiment Result
E2 R97 T700		E2 R97 T750	
E2 R98 T700		E2 R98 T750	
E2 R99 T700		E2 R99 T750	

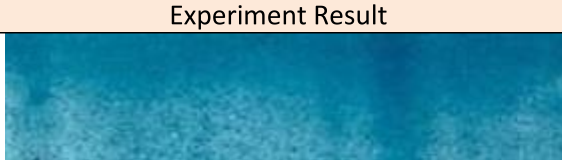
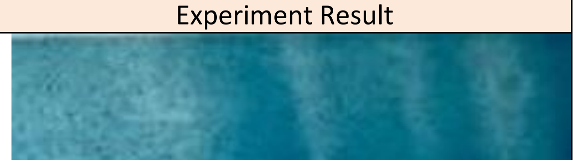
Table 4-3: Enamels produced by the 3rd synthesis method based on recipes 97, 98 and 99, fired at 650, 675 ºC

Sample	Experiment Result	Sample	Experiment Result
E3 R97 T650		E3 R97 T675	
E3 R98 T650		E3 R98 T675	
E3 R99 T650		E3 R99 T675	

Table 4-4: Enamels produced by the 3rd synthesis method based on recipes 97, 98 and 99, fired at 700 ºC

Sample	Experiment Result
E3 R97 T700	
E3 R98 T700	
E3 R99 T700	

Table 4-5: Enamels produced by the 3rd synthesis method based on recipes 97, 98 and 99, fired at 725, 750 ºC

Sample	Experiment Result	Sample	Experiment Result
E3 R97 T725		E3 R97 T750	
E3 R98 T725		E3 R98 T750	
E3 R99 T725		E3 R99 T750	

4.1 Evolution of enamel producing method

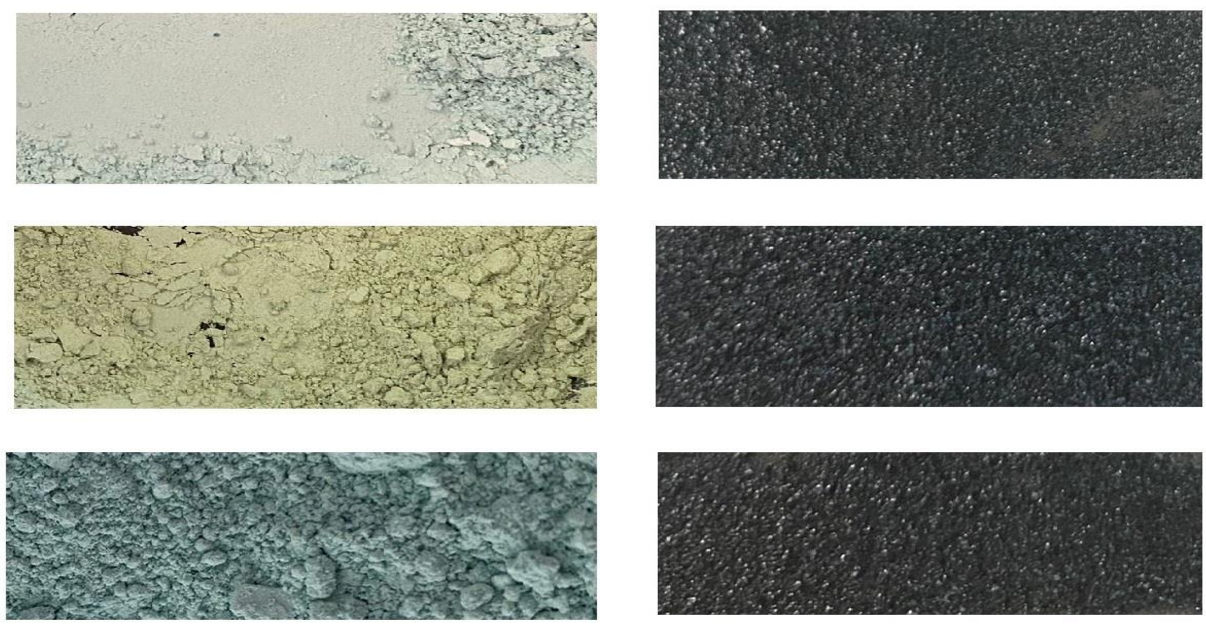
Through this research, the procedure of enamel production evolved to a technique which provides satisfying paint with appropriate homogeneity and acceptable green color. Obtained results from the first, second and third producing strategies were shown above (Table 4-1, Table 4-2, Table 4-3, Table 4-4 and Table 4-5). Comparison of these results shows that grinding, mixing and firing processes could significantly affect color of final results, as was already seen in previous studies [11, 41].

Results of the first and second strategies of production (Figure 4-1 and Figure 4-2) show that the surface of painted samples are so rough and uneven, and colors of some samples are almost grey (instead of green). Therefore, in order to obtain finer powder (more homogenized powder), at the second strategy, resulted enamels (after firing process) were ground for 20 minutes (while it was 10 minutes in the first strategy) by an electric mortar. Additionally, a low kiln temperature (650 ºC) might be too weak to melt the pigments, and it could not give the desired green color to the resulted paint.

R97

R98

R99



(a) (b)

Figure 4-1: Results from first strategy (E1T650): a) After grinding, b) after firing (at 650 ºC)

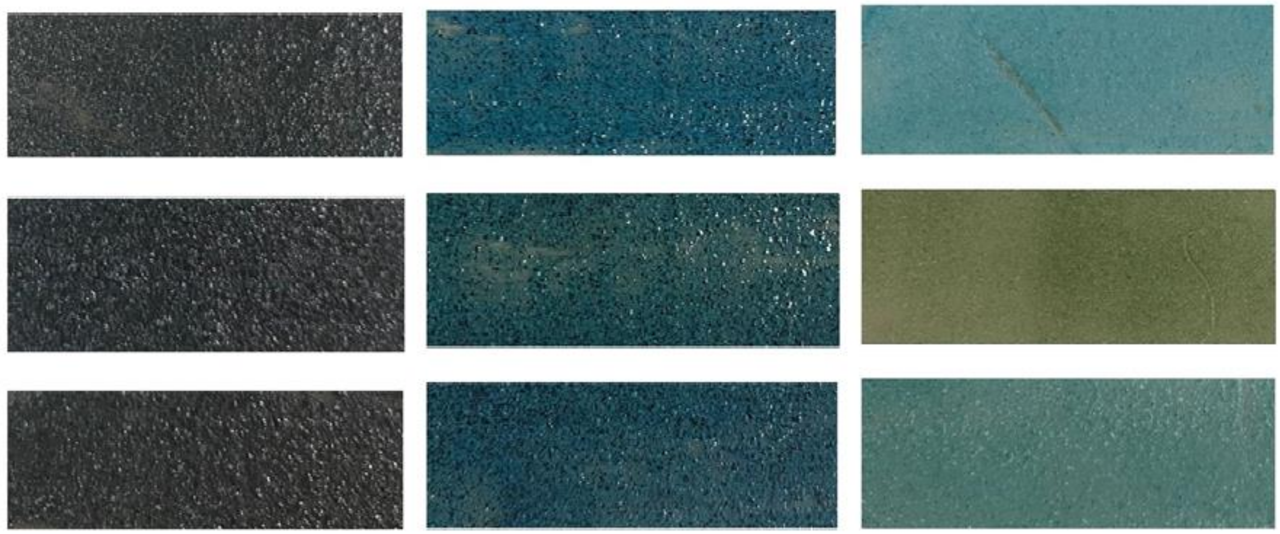
R97 R98 R99			
	(a)	(b)	I

Figure 4-2: Results from three different strategies: a) E1T650, b) E1T700 and c) E2T700

4.2 Raw Materials Analysis

All raw materials (Crystal frit, Calx, Iron, three-times burned copper and one time burned copper) have been analyzed by XRD in order to check which initial compounds were used in the different recipes (four recipes for "*The Base Component"* and also coloring ingredients). By doing so, some important details were obtained such as the type of oxides used, the lack of crystallinity present on the crystal frit and chemical compounds.

Diffractogram of the Crystal Frit is shown in Figure 4-3 which presents that amorphous structure without any pick of crystallinity.

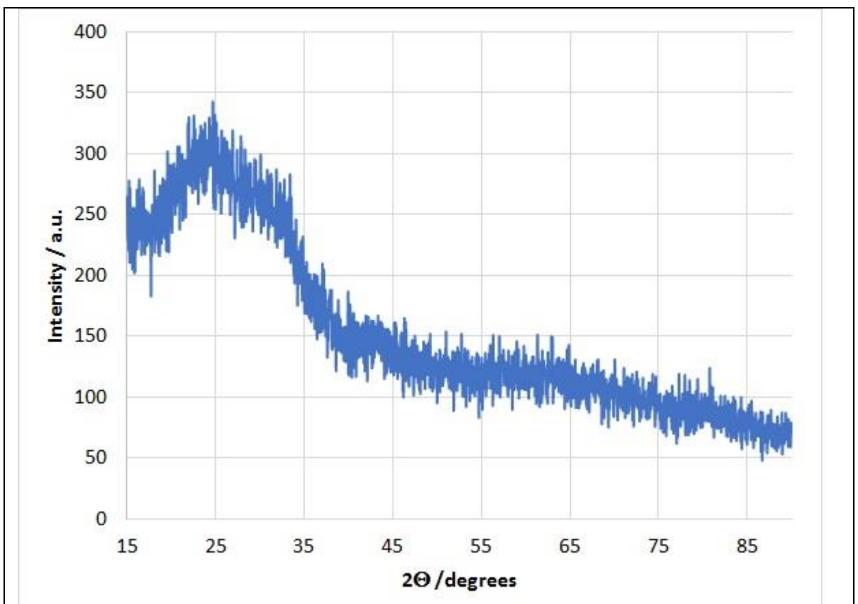


Figure 4-3: Diffractogram for Crystal Frit

X-ray diffraction (XRD) of iron oxide presents the existence of hematite in our result. Diffractogram of Iron (Iron heated at 650ºC) and the Hematite (Fe_2O_3) Rruff [42] is shown in Figure 4-4. As it shows, the resulting diffractogram for iron is in accord with the hematite diffractogram.

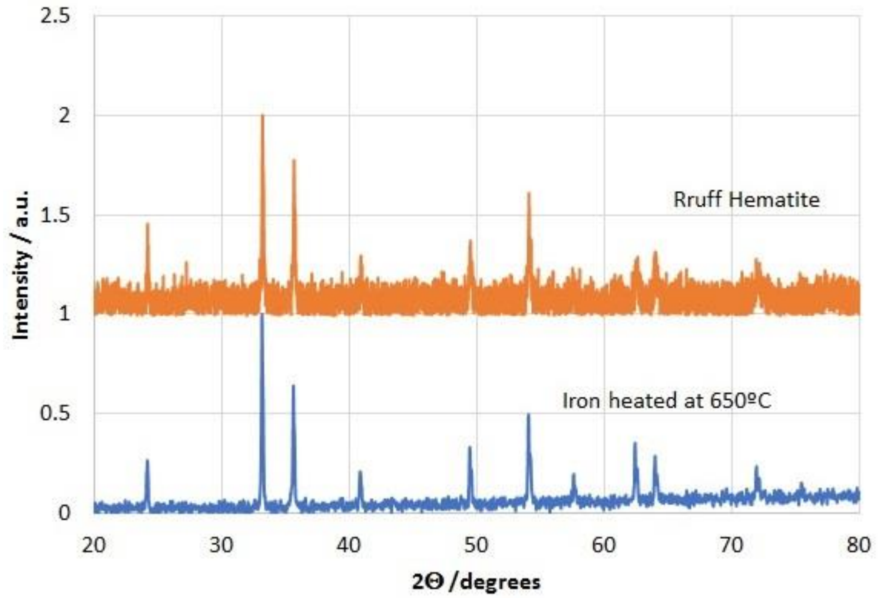


Figure 4-4: Diffractogram of iron heated at 650ºC and Hematite diffractogram RRUFF ID: R040024

The diffractogram of Calx is shown in Figure 4-5. Comparing this diffractogram with the XRD pattern (Figure 4-6) of some Pb and Sn compounds (SnO_2, PbO_2, $PbSnO_4$ and $Pb_2Sn_2O_6$) reveals the presence of a mixture of lead and tin components which is in accordance with previous studies such as [43]. It is important to refer that from the lead-tin metal calcination it was obtained a mixture of different lead and tin compounds which can interfere with the final results.

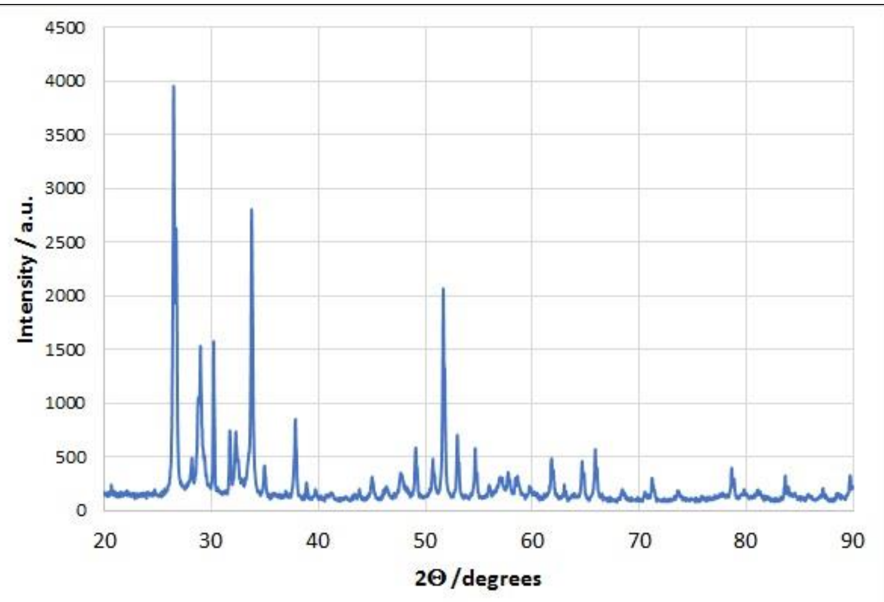
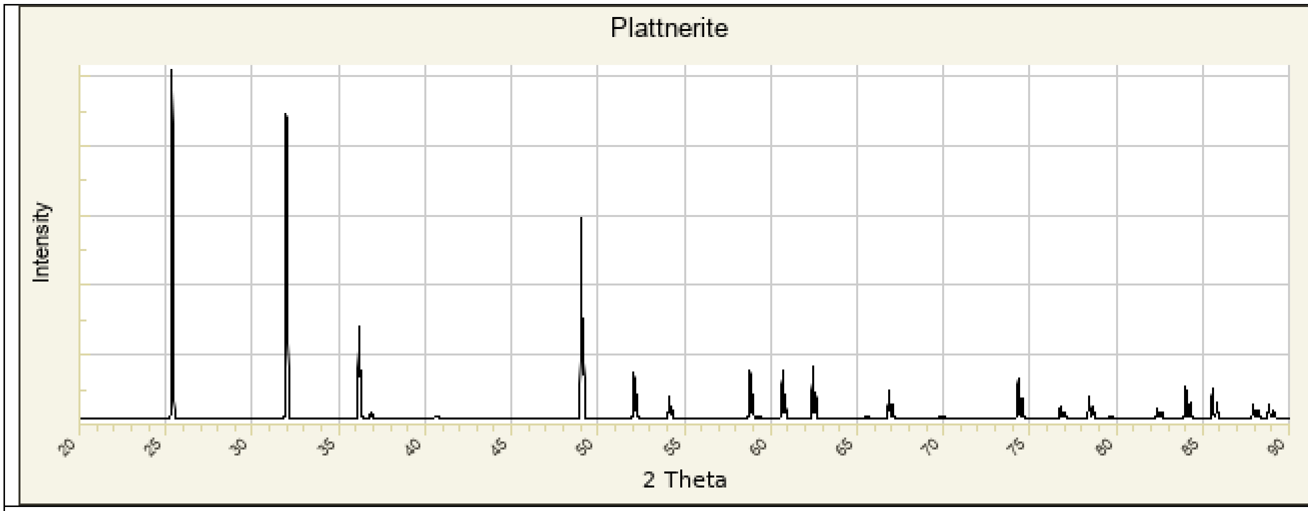
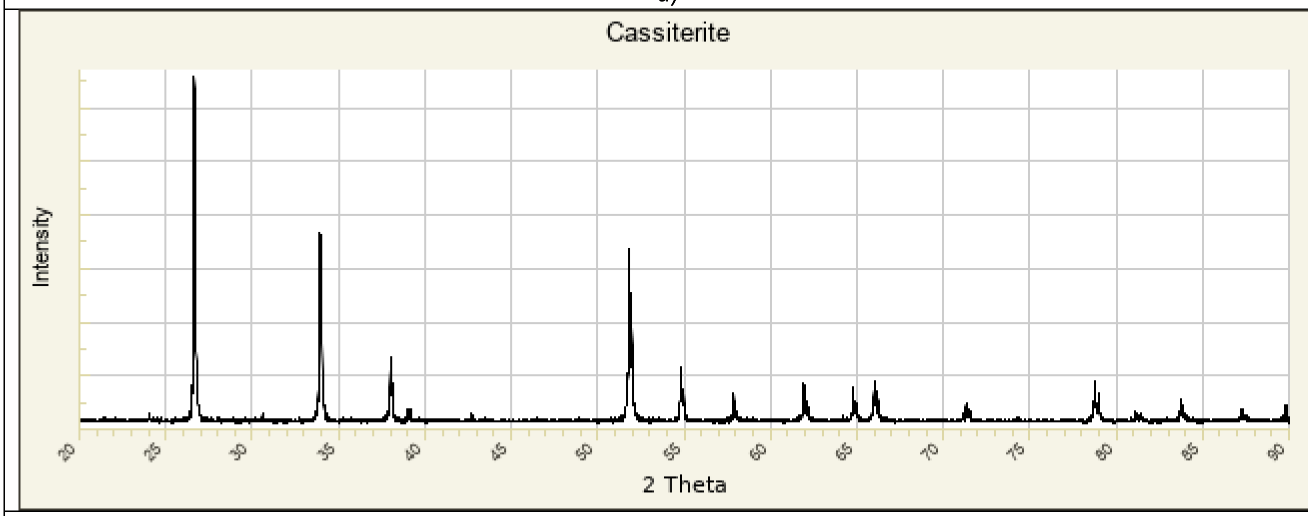


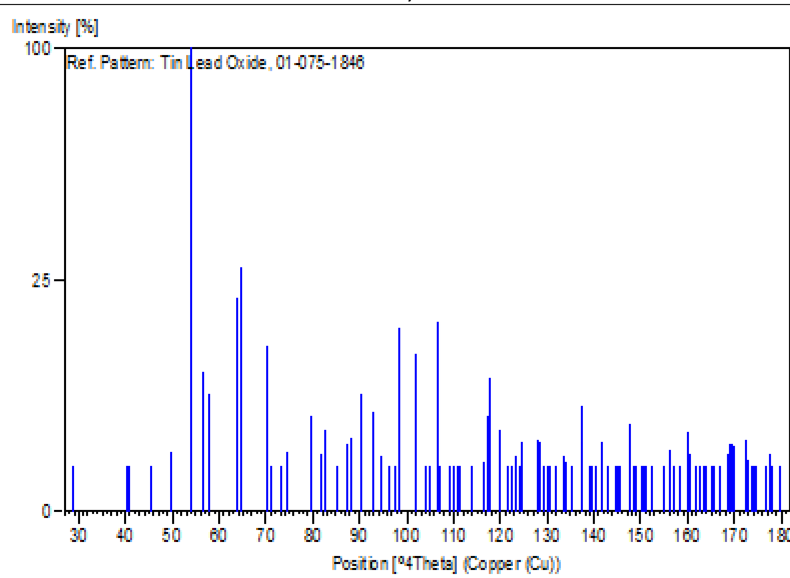
Figure 4-5: Diffractogram for Calx



a)



b)



c)

Figure 4-6: Diffractogram of a) Plattnerite (PbO_2) b) Cassiterite (SnO_2) [44, 45] and c) ($SnPb_2O_4$)

The pattern diffractogram for copper oxide (Cuo, Cu_2O) is shown in Figure 4-7 and Table 4-6 (These results were obtained by Joana Vaz Pinto, a member of CENIMAT|i3N research center and CEMOP/UNINOVA Technological Center, FCT NOVA). Three-times burned copper and one-time burned copper were characterized by XRD, and related diffractograms were shown in Figure 4-8. Both diffractograms present the existence of CuO and Cu_2O. However, the higher intensity of the CuO-related peaks can indicate that this compound is higher in the three-times burned copper than one-time burned copper. To justify the higher amount of CuO in three-times burned copper, we can say that in this process, there is more time for the copper to be in contact with oxygen at high temperatures in the furnace. Therefore, more copper in a more oxidative state was obtained, Cu^{+2}.

Table 4-6: Identified Patterns List

Ref.Code	Score	Compound Name	Chem. Formula	Scale Fac.	Displ. [°2θ]	RIR	SemiQuant [%]	Cryst. Syst.
00-048-1548	81	Copper Oxide	Cu O	0.412	-0.061	0	-	Monoclinic
00-005-0667	68	Copper Oxide	Cu_2 + O	1.006	-0.074	0	-	Cubic

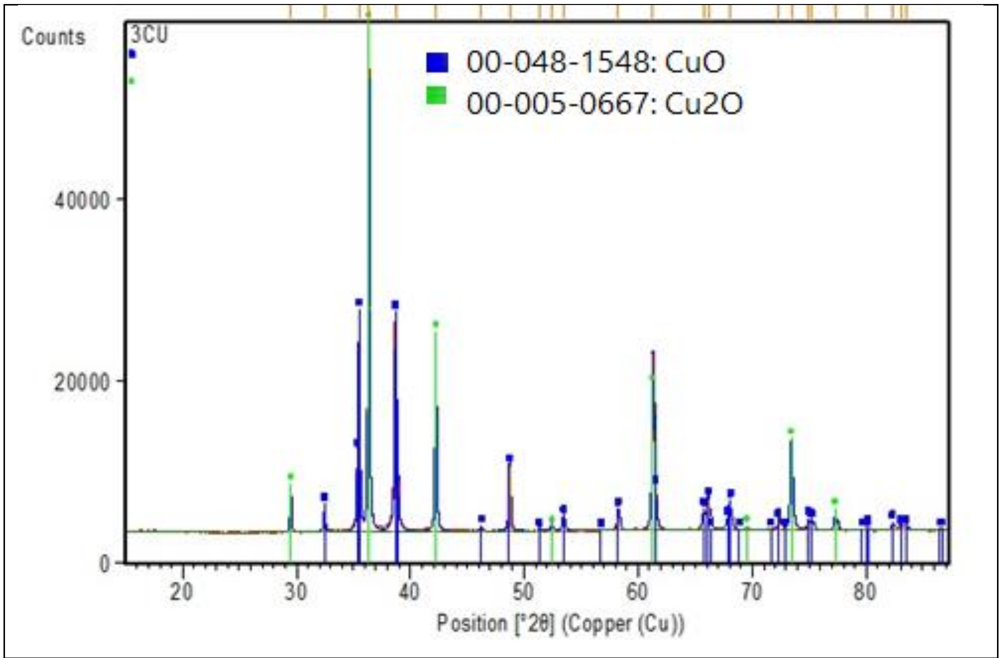


Figure 4-7: XRD pattern for Copper Oxide

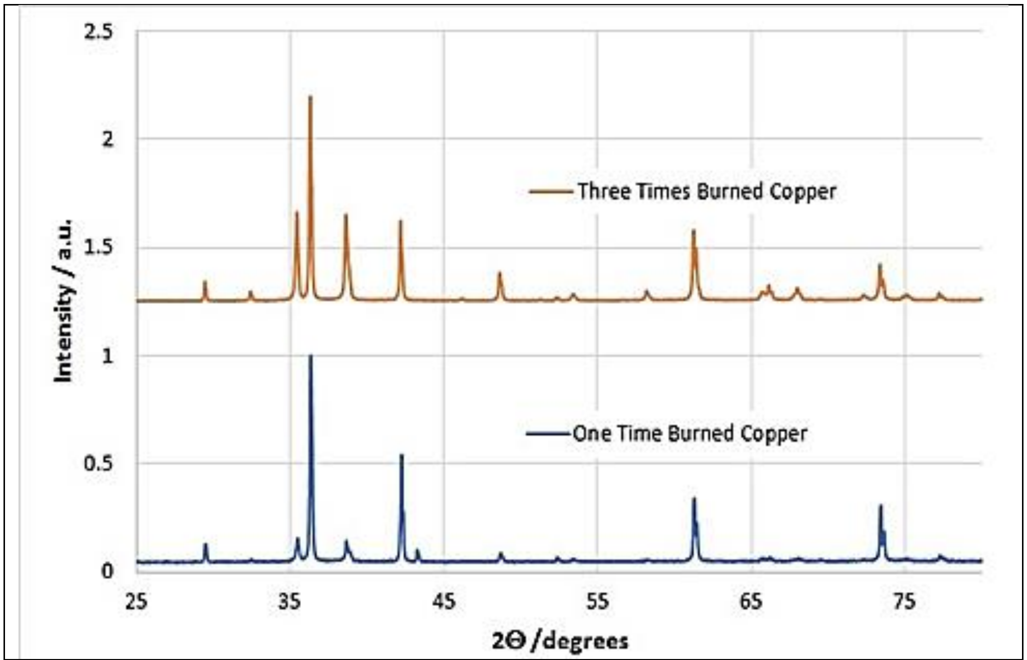


Figure 4-8: Diffractogram for one time and three-times burned copper

4.3 Optical Characterization

4.3.1 Colorimetry

Colorimetric results which were calculated from the mean average of three measurements, and their value of standard-deviation (σ) are presented in Table 4-7.

*Table 4-7:Mean average of L*a*b* coordinates and their standard-deviation values (σ) for painted samples*

Sample Name	L*	a*	b*
E1R97T650	39.39 ± 0.45	-3.32 ± 0.29	-2.27 ± 0.43
E1R98T650	39.05 ± 0.89	-4.05 ± 0.31	-0.94 ± 0.36
E1R99T650	43.38 ± 1.68	-2.75 ± 0.66	-1.50 ± 0.81
E1R97T700	52.25 ± 1.12	-15.16 ± 0.39	-10.49 ± 0.44
E1R98T700	51.58 ± 0.88	-13.86 ± 0.45	-3.55 ± 0.18
E1R99T700	49.56 ± 0.36	-11.76 ± 0.30	-7.54 ± 0.45
E2R97T700	60.56 ± 0.77	-20.25 ± 0.49	-15.85 ± 0.76
E2R98T700	61.84 ± 0.44	-19.74 ± 0.73	-6.30 ± 0.15
E2R99T700	62.95 ± 0.88	-20.60 ± 0.41	-18.93 ± 0.44
E2R97T750	63.31 ± 0.04	-22.12 ± 0.14	-18.90 ± 0.13
E2R98T750	58.49 ± 1.04	-23.17 ± 1.03	-7.99 ± 0.71
E2R99T750	65.44 ± 0.37	-17.85 ± 0.92	-14.94 ± 0.27
E3R97T650	55.56 ± 0.64	-3.25 ± 0.39	0.87 ± 0.40
E3R98T650	47.97 ± 0.22	-8.11 ± 0.42	-1.59 ± 0.52
E3R99T650	53.45 ± 5.35	-3.10 ± 0.79	-2.16 ± 0.27
E3R97T675	60.18 ± 5.30	-8.40 ± 2.33	-6.24 ± 2.33
E3R98T675	52.59 ± 0.41	-11.01 ± 0.13	-1.36 ± 0.69
E3R99T675	47.78 ± 1.20	-8.01 ± 0.18	-6.31 ± 0.06
E3R97T700	65.50 ± 0.71	-10.70 ± 0.26	-8.39 ± 0.63
E3R98T700	57.47 ± 1.18	-18.50 ± 1.13	-4.30 ± 0.01
E3R99T700	59.85 ± 2.51	-10.56 ± 1.99	-7.01 ± 0.73
E3R97T725	63.37 ± 3.36	-14.56 ± 2.83	-11.15 ± 2.55
E3R98T725	60.56 ± 1.36	-20.11 ± 1.69	-4.82 ± 0.52
E3R99T725	54.70 ± 0.83	-16.98 ± 0.43	-13.53 ± 0.55
E3R97T750	64.73 ± 1.10	-17.99 ± 1.41	-15.55 ± 0.78
E3R98T750	61.67 ± 0.51	-20.36 ± 0.13	-5.47 ± 0.03
E3R99T750	62.85 ± 2.50	-14.54 ± 2.75	-11.37 ± 1.61

To show the effect of enamel-producing strategies, kiln temperature, and different recipes on obtained colors, these results were plotted by MATLAB software and are shown in Figure 4-9, Figure 4-10, Figure 4-11 and Figure 4-12. Additionally, to have a clear understanding of resulted colors, these trends have been shown in Figure 4-13 and Figure 4-14. Based on these figures, resulted colors are in Blue-Green part of L*a*b* space.

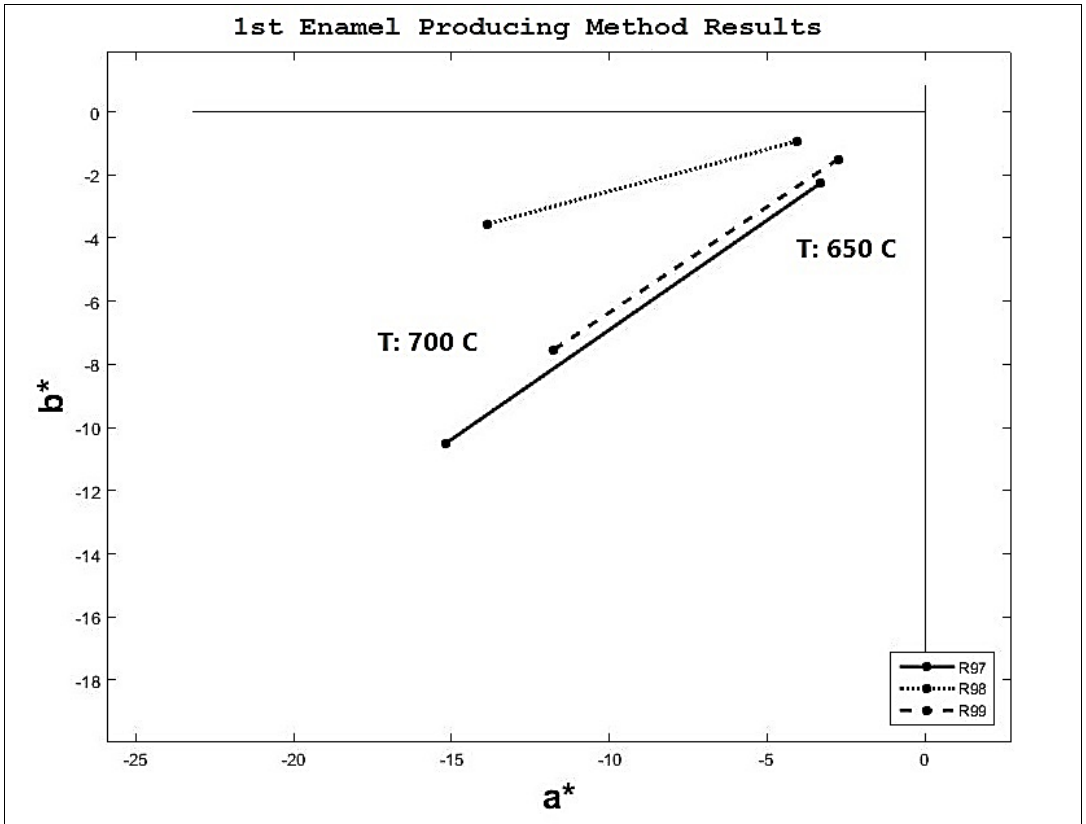


Figure 4-9: Results of 1st Enamel Producing Strategy

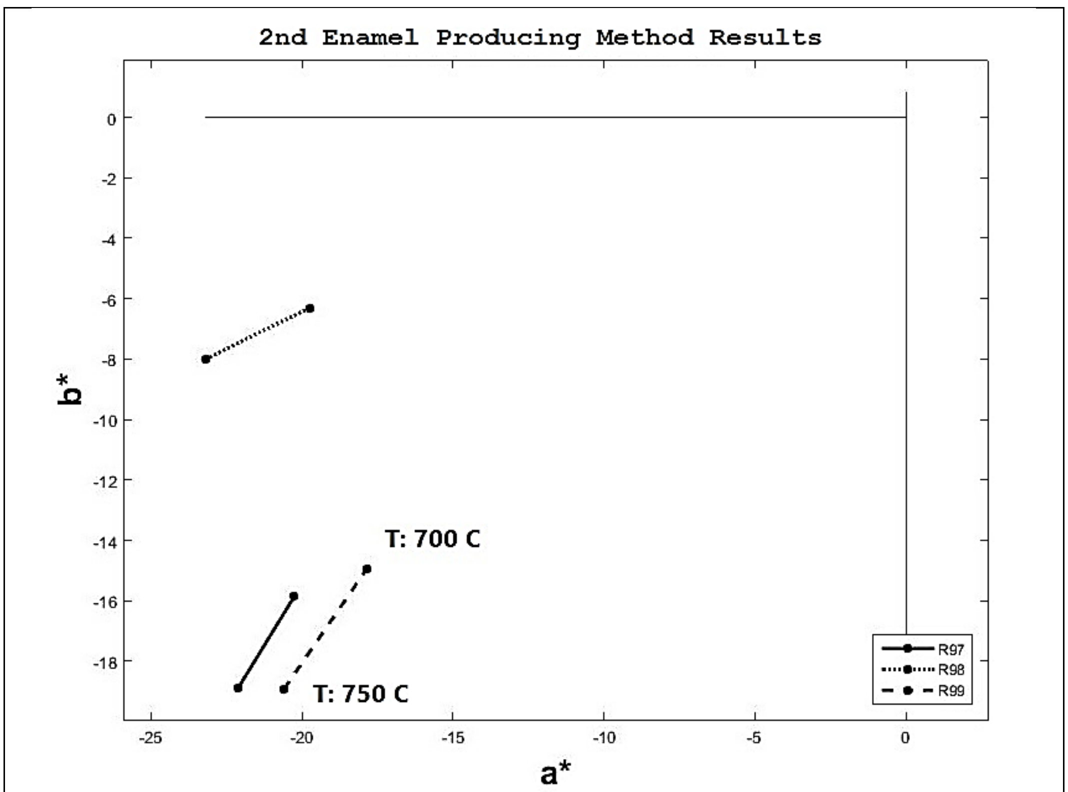


Figure 4-10: Results of 2nd Enamel Producing Strategy

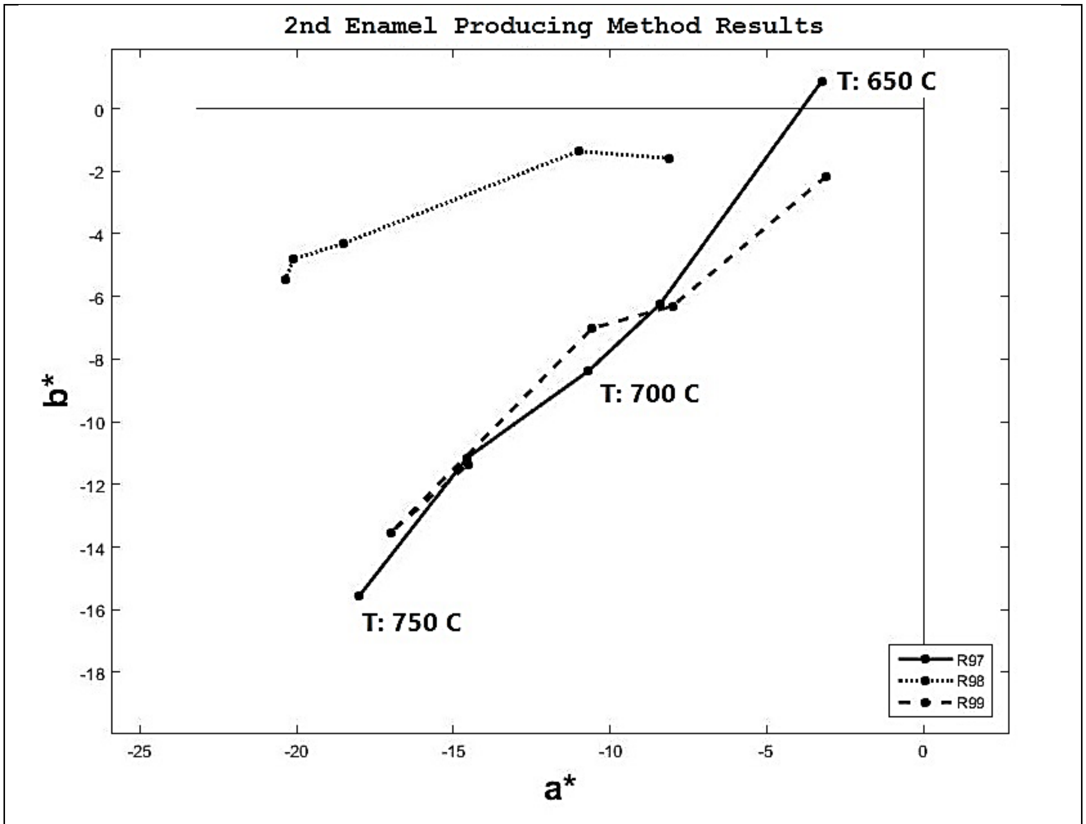


Figure 4-11: Results of 3rd Enamel Producing Strategy

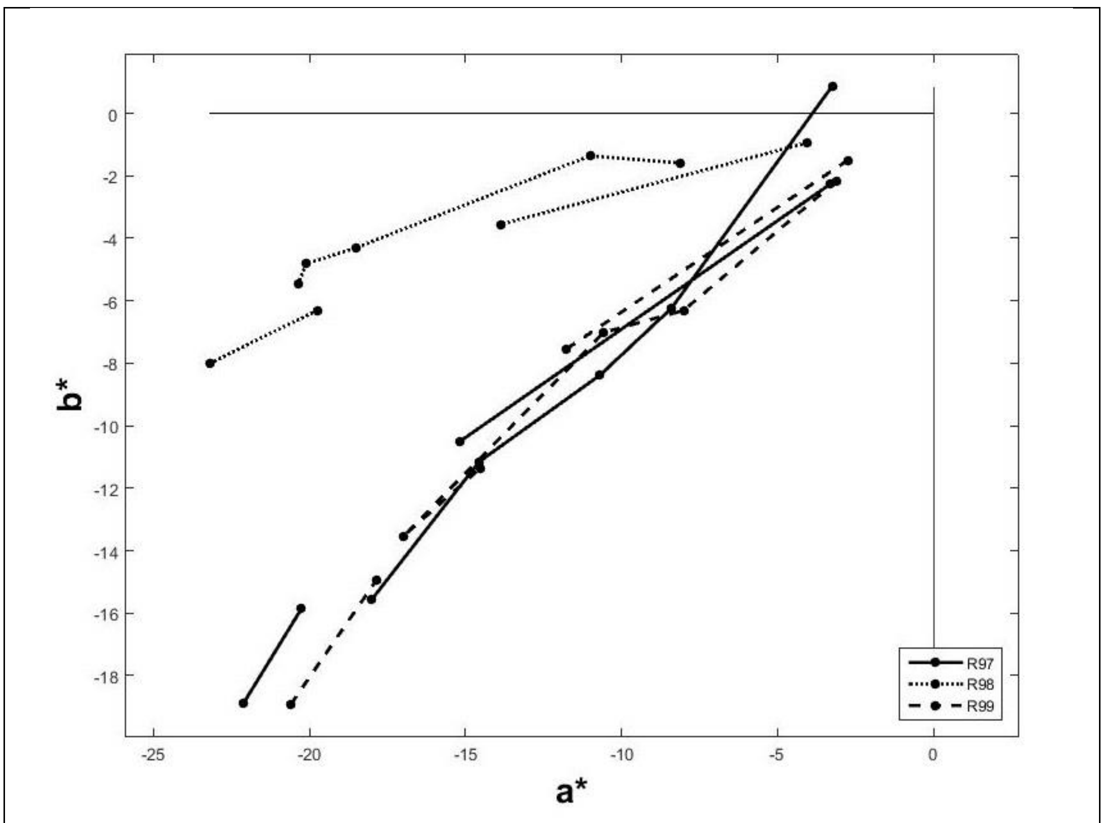


Figure 4-12: All Results of Enamel Producing Strategy

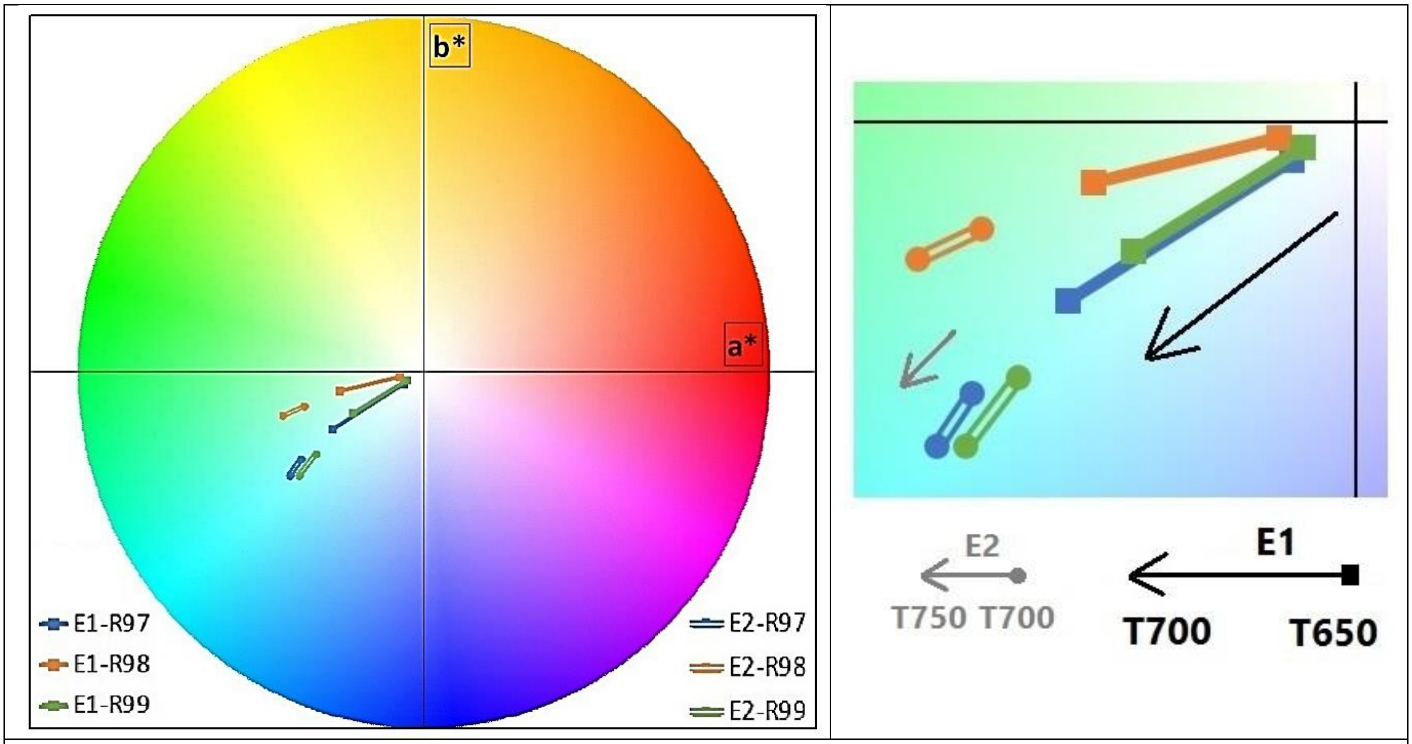


*Figure 4-13: L*a*b* Colorimetric Results of 1st and 2nd Enamel Producing Strategy Samples*

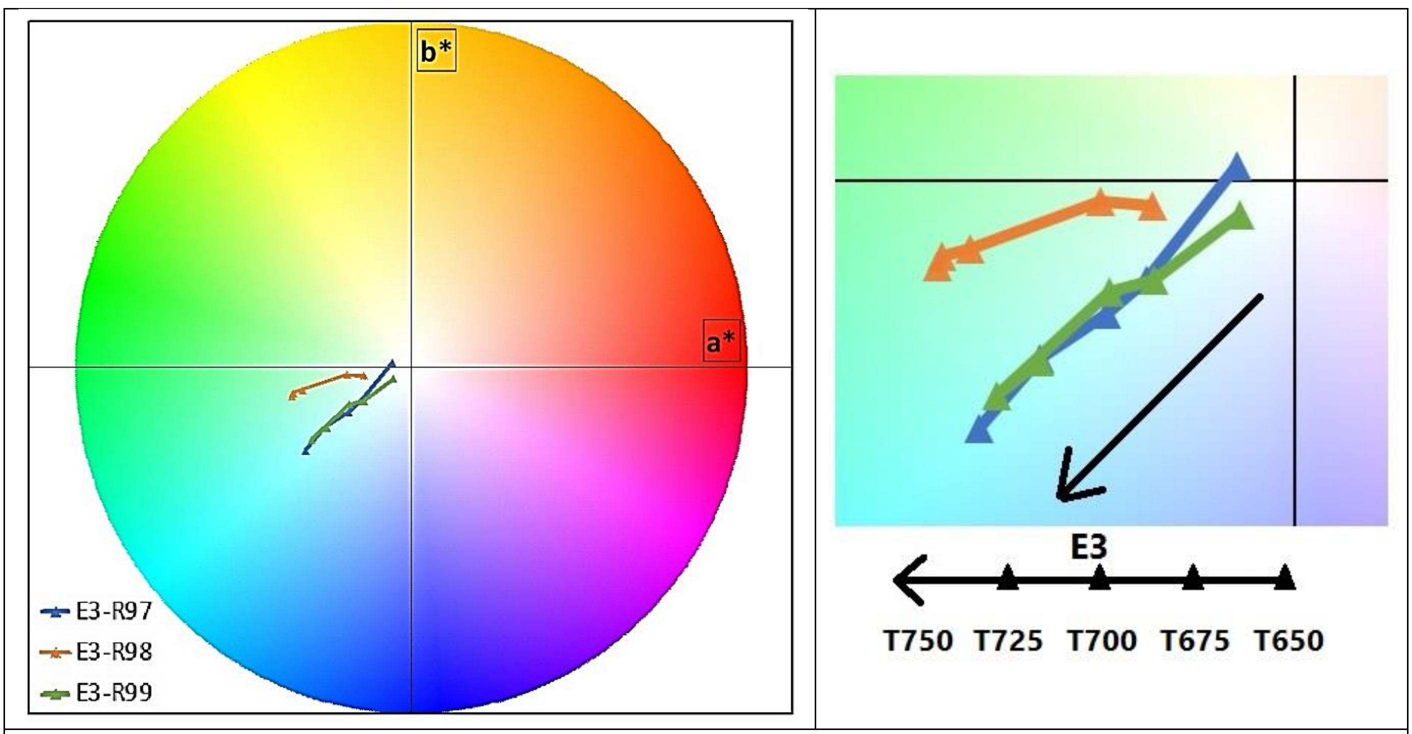


*Figure 4-14: L*a*b* Colorimetric Results of 3rd Enamel Producing Strategy Samples*

By Analyzing the colorimetry test results (Figure 4-9 to Figure 4-14), these results can be drawn:

L- In any case (Figure 4-12), obtained points for recipe 97 (solid line) and recipe 99 (broken line) are so close to each other, but points of recipe 98 (dotted line) are pretty far. This result says that recipe 97 and 99 are very similar and the resulted paint have almost the same blue color, but recipe 98 is a different method and it leads to distinguishable results (green color).

2- Based on colorimetric results (Figure 4-13, Figure 4-14), results of recipe 98 are always greener than two other recipes results.

3- By increasing the kiln temperature (from 650-750 ºC), absolute value of a* and b* goes up which means intensity of the color increases by temperature.

As soda lime silicate glasses, glass samples with only copper oxide appear intense blue, while glasses containing low percentages of copper oxide and a concentration of lead oxide are emerald-green instead of common turquoise-blue [46]. A modification of the copper local environment probably leads to less absorbing in the green wavelength range. In our case, all obtained enamels have lead oxide (because of Calx) and copper oxide (because of burned copper), but the enamels of R97 and R99 (which have three times burned copper) probably contain high amount of copper oxide and appear blue, while the enamel R98 (which have three times burned copper and less amount of copper oxide) appear green.

Based on Neri's recipes, all obtained enamels were expected to be green, but this was not observed in the results of recipes no. 97 and 99, probably because of the lack of homogeneity of the produced enamels, due to the fact that it was just produced in a very small quantity, or the quantity of lead was not enough to obtain the expected results.

Concerning enamel R97 and R99 (which have three times burned copper), having a bigger amount of CuO (instead of Cu_2O), and accordingly the high content of Cu^{2+} can originate a more intense blue color. One also needs to pay attention to iron and copper ratios. Based on some studies [47], when the iron content is smaller than the copper content, the redox interactions (oxidation-reduction reaction) between iron and copper could change the glass color from green to blue-green color. This may occur due to the existence of Fe^{3+}, which may oxidize the remaining Cu^{+} (that does not present any color), and results in a bluer color (by increasing the concentration of Cu^{2+}). Recipe 98, which presents a greener color, probably has a higher amount of iron and a lower quantity of Cu^{2+}. In this case, the absorption of Fe^{3+} around 420 nm and 440 nm [48] can also influence the obtained color. After all, future experiences by changing the copper and iron ratios in this type of materials should be performed to better understand the iron and copper oxidation states influence in the obtained color.

4.3.2 Reflectance Spectroscopy

At this part of the study, the color of the enamels reproduced was characterized by reflectance spectroscopy, in order to assess the differences between the obtained results. The reflectance spectra were obtained for the 27 painted samples, by using the AvaSpec-2048 Fiber Optic Spectrometer. All results from spectroscopy for 27 samples (3 recipes, 3 producing strategies, and 2-5 different kiln temperature) are presented hereunder.

To investigate the effect of the kiln temperature, the recipe, and enamel producing strategy different groups of curves are shown in Figure 4-15, Figure 4-16 and Figure 4-17. Having 15 curves in Figure 4-17 makes it a little hard to investigate similarities or dissimilarities. So, this diagram divides to three diagrams which correspond to three recipes (Figure 4-18, Figure 4-19, and Figure 4-20).

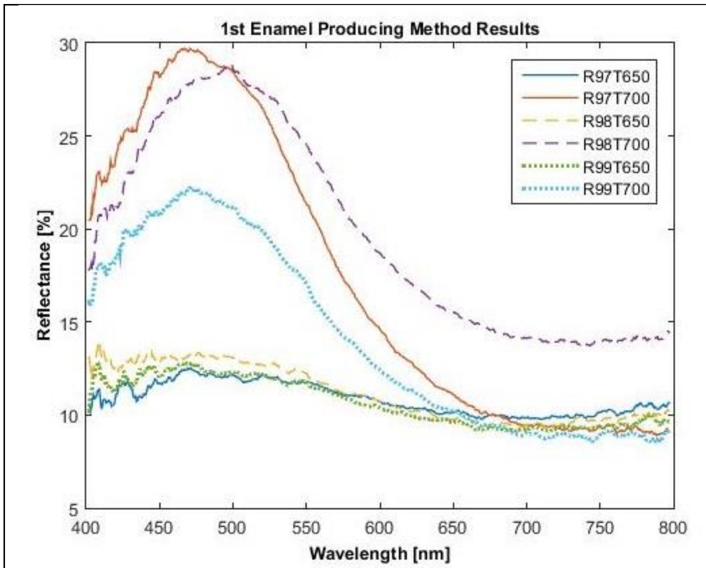


Figure 4-15: Spectroscopy Results: 1st enamel producing strategy (6 samples: 3 different recipes and 2 different kiln temp.)

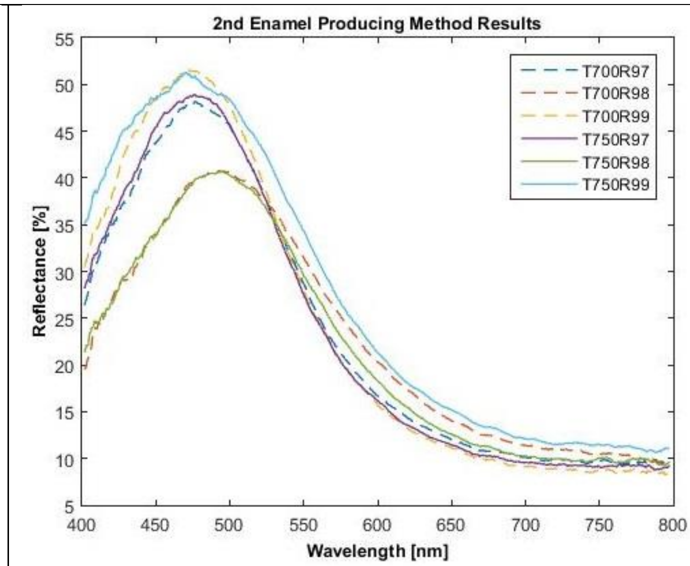


Figure 4-16: Spectroscopy Results: 2nd enamel producing strategy (6 samples: 3 different recipes and 2 different kiln temp.)

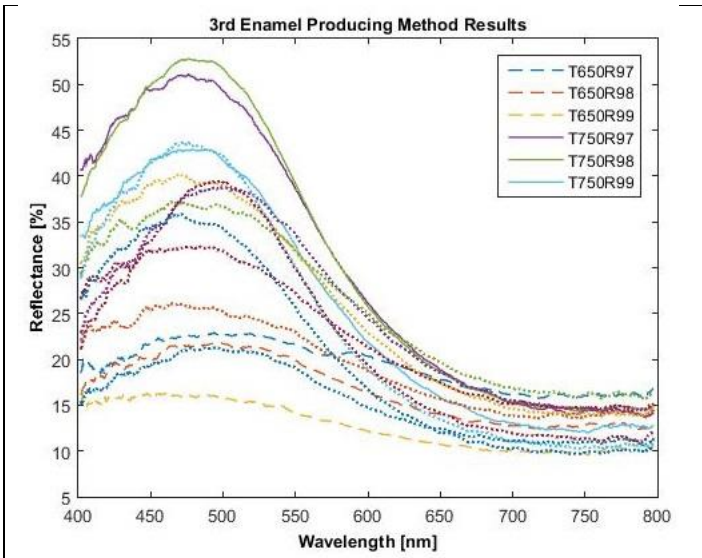


Figure 4-17: Spectroscopy Results: 3rd enamel producing strategy (15 samples: 3 different recipes and 5 different kiln temp.)

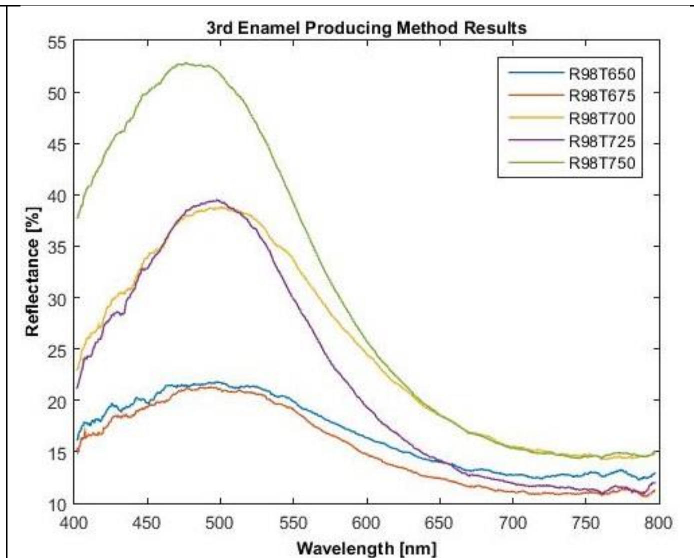


Figure 4-18: Spectroscopy Results: E3R98 samples in 5 different kiln temp.

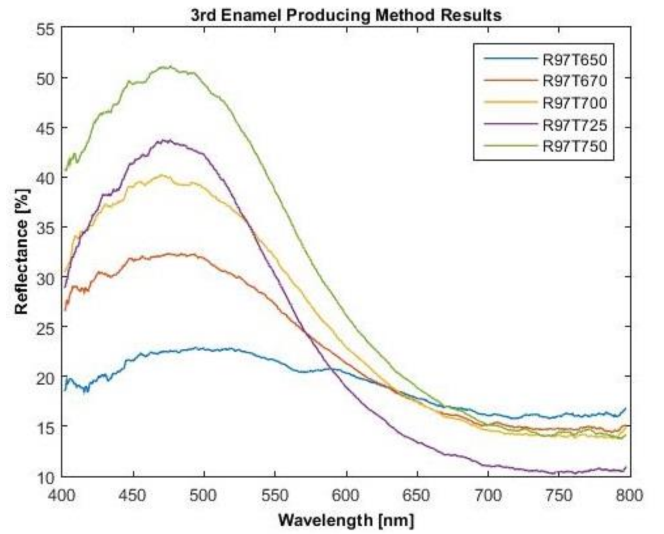


Figure 4-19: Spectroscopy Results for R97 of 3rd enamel producing strategy (5 different kiln temp.)

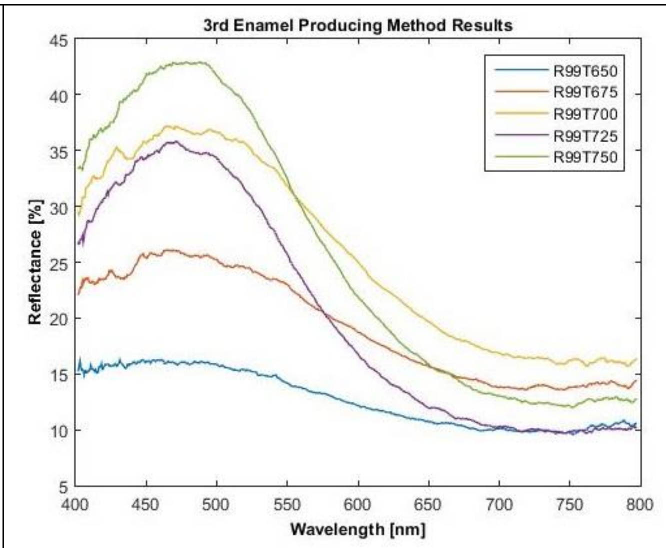


Figure 4-20: Spectroscopy Results for R99 of 3rd enamel producing strategy (5 different kiln temp.)

In the reflectance diagram, high value of reflectance indicates more intense reflected light which could interpret more intensive color.

Based on the above diagrams (Figure 4-15 to Figure 4-20), these results can be drawn:

L- All the spectra present the characteristic band of Cu^{2+} at around 800 nm (which represents the existence of CuO in the samples), however some deviations can be observed.

2- Diagrams of E1T650 for all three recipes are almost the same, because pigments may not melt at the lower temperature (650 ºC).

3- Changing the kiln temperature could be very effective (e.g. E1T650-E1T700), or almost ineffective (e.g. E2T700-E2T750).

4- Similar to the colorimetric results, spectroscopy diagrams for E3R97 and E3R99 have similar behavior, but peak-altitude for R97 is higher than R99.

5- The general trend of E3 diagrams shows that the value of 700-750 ºC for kiln temperature leads to high reflectance value. Probably, at this higher temperature range, pigments could melt and give color to the mixture which leads to more intensive reflected color.

4.4 Green enamel in Artworks

What are the criteria to choose the artworks to be made in this research?

The main goal of this study is producing green enamels. There is no doubt that green color mostly represents nature in our mind. Having connection with nature or environment is one of the principles to choose an artwork to make. Being related to architecture and history could be the second criteria. Finally, having charm, attraction and visual beauty could be others. Based on these principles, three specific glassy artworks (Star-Cross tiles, Beehive tiles, the Glass Wall) has been chosen to produce in this study. At the second step, they were painted by the produced enamels. And finally, these artworks were used to make 3D models of architecturally designed spaces and decorative objects by computer simulation software (Autodesk 3ds Max).

As a way to show the modeling ability and painting proficiency of this software, some intangible and geometrically-complex objects were made and were painted with a variety of intensity and tones of green color (Figure 4-21).

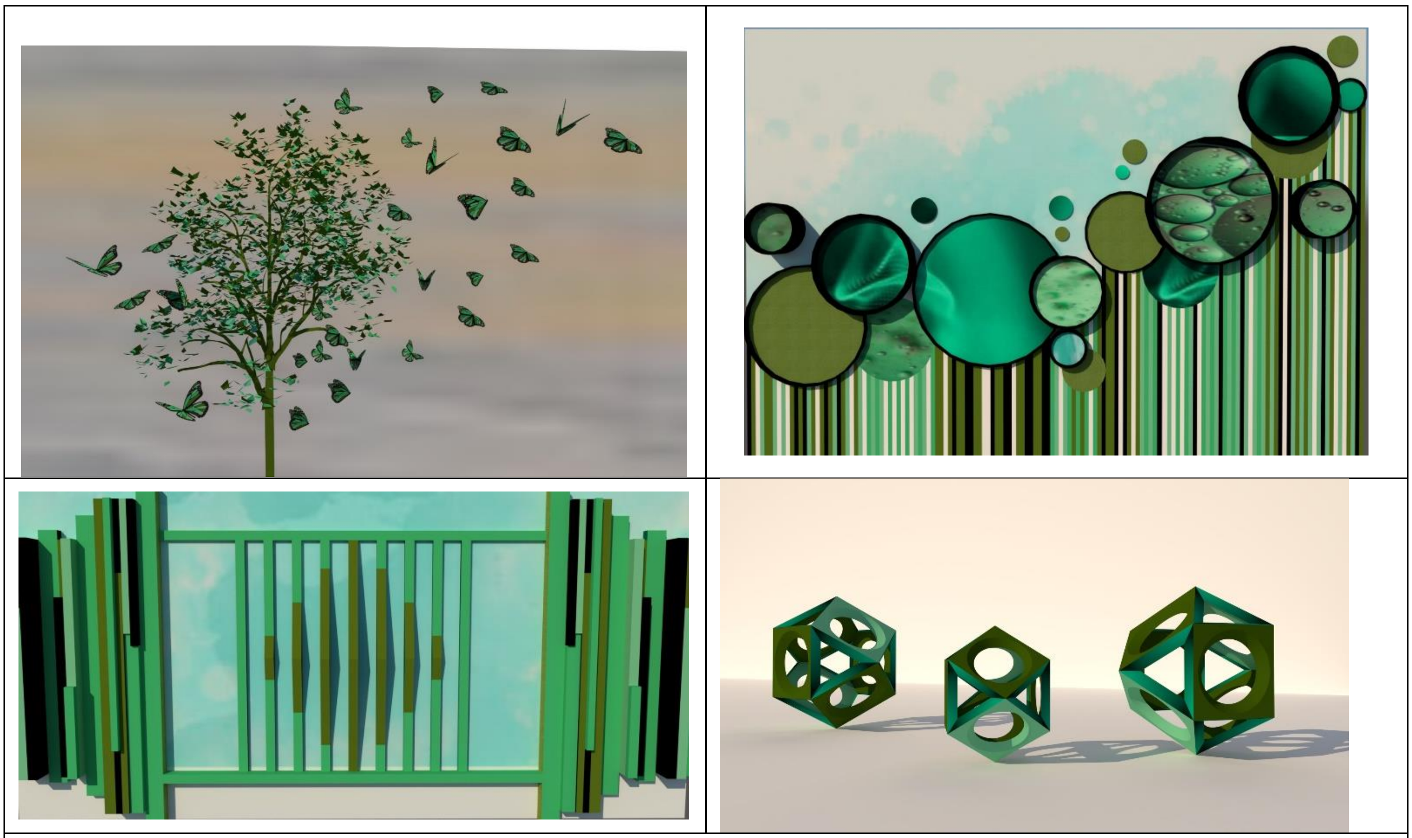


Figure 4-21: Example of green painted 3D objects with diverse intensity and tones

4.4.1 Star-Cross Tile

The Star-Cross (Chalipa) pattern is composed of two different many-sided geometric shapes (eight-edge star and cross) which get matched with each other like a puzzle. This pattern has been made in Iran, Azerbaijan, and some other Islamic countries. Based on one of the previous researches of the current author [49], these tiles generally have a single-colored form with a little gold veins for decorative drawings. Most of them are in green, blue and turquoise glaze. Artists have created interesting puzzle structures by combining stars and cross tiles (Figure 4-22).

Having theoretical background (because of the previous research about Takht-e Suleyman), and the sense of belonging to this area (Takht-e Suleyman was located near the author's hometown), and fascination of this pattern motivated the author of this research to choose this Star-Cross pattern to reproduce them in this study. In current research, a copy of this puzzle tiles was made by glass casting method. To reproduce the glassy Star-Cross tiles, frit glass (Atlantic soda lime glass) put in kiln, and heated up (maximum 830 ºC). Mold casting process of melted glass was done by using one-part plaster molds (Figure 4-23).

In this step, these glassy tiles were painted by three different types of glass paints which had been made in current research based on Neri's recipes by third strategy of enamel producing. Before firing process, these painted tiles were laid out on an open surface for ten days to get completely dried by air drying. These enamels need a high temperature to elaborate the proper result. With this in mind, in order to maintain the shape of tiles in high temperatures, each piece had to be put in the related mold. Each piece of Star-Cross fired in the kiln with a maximum of 700 ºC only for 10 minutes. The resulted color for each recipe is quite close to the color of samples. The paint had been stuck on tiles surface, and the shapes of tiles remained the same. However, in some parts, the surface of the painting had become rough with some small holes and bubbles inside the color which could be the result of using much oil during the painting processes. Based on obtained results (Figure 4-24), three different recipes led to clearly distinguishable colors (shiny blue, green, dark blue) on these tiles.

Nowadays, architectural design with considering this puzzle tiles could be a great incorporation into traditional architecture. In other words, architects are given the opportunity to create an extension of traditional design on contemporary architecture. Three-dimensional model of a room which was decorated by this pattern was made by computer simulation software and is shown in Figure 4-25.

Figure 4-22: Star and cross tiles (Fritware, overglaze painted with colors and gold (lajvardina)) [50]

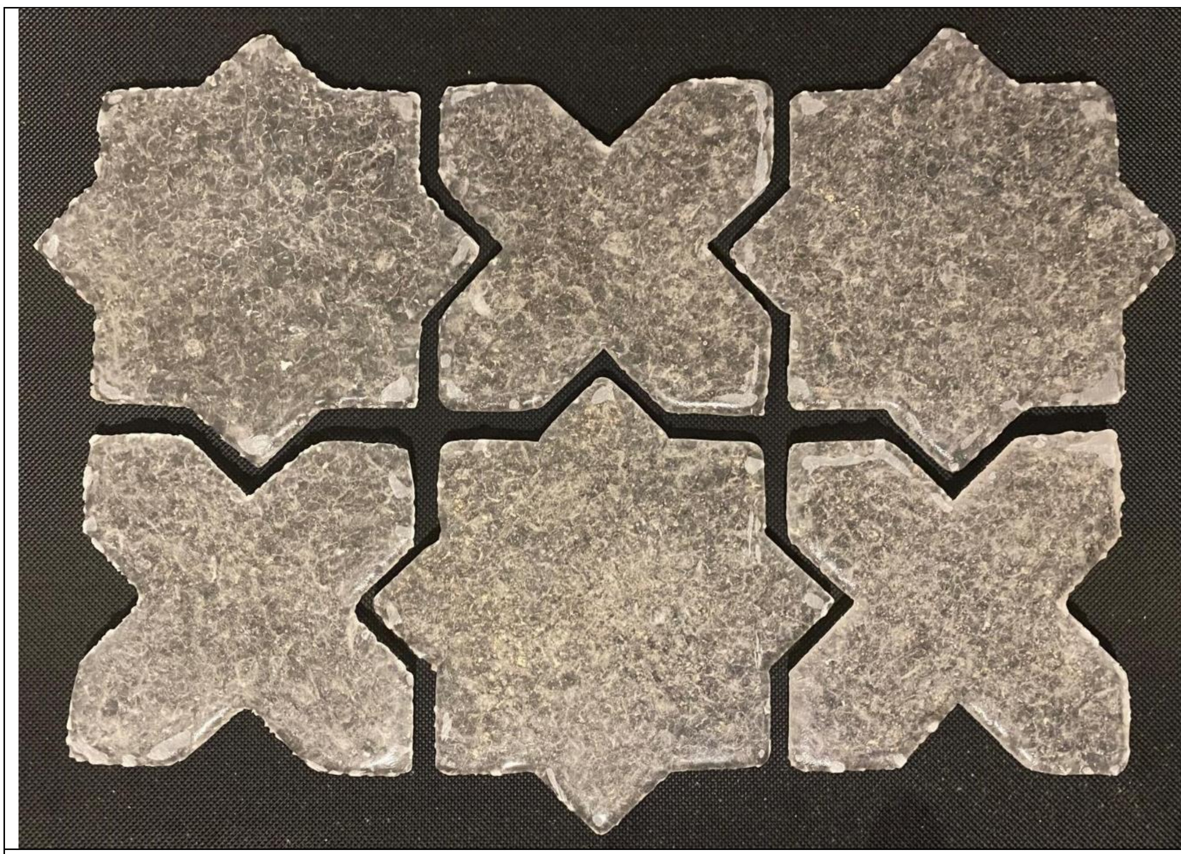


Figure 4-23: Star-Cross tiles of glass

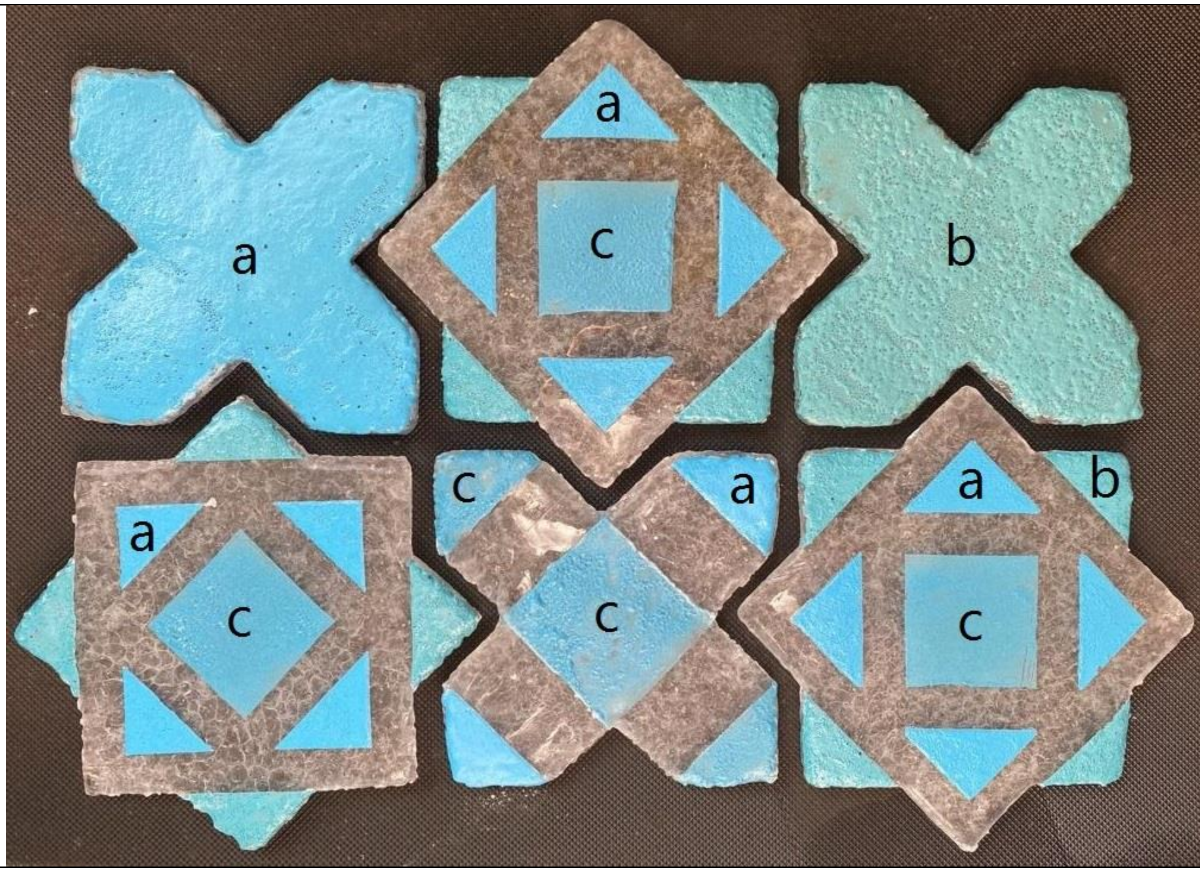


Figure 4-24: Star-Cross tiles painted by different types of produced paint (a: R99 shiny blue, b: R98 green, c: R97 dark blue)


Figure 4-25: Application of glassy Star-Cross tiles in architecture

4.4.2 Beehive tiles

A beehive is an enclosed structure in which some honey bee species live in. Hive is used to describe an artificial/man-made structure to house a honey bee nest. The nest's internal structure is a densely packed group of hexagonal prismatic cells made of beeswax.

A group of glassy beehives were made, and arranged closely to make a cluster of grapes. The component of this design, has been produced from frit glass with green enamel (recipe R97 in the kiln with maximum for 830 ºC) (Figure 4-26). To keep this cluster inside a transparent frame, they were put inside a mold and was cast in resin-epoxy[1] (Figure 4-27). The containers of epoxy resin and its hardener which was used in this study has shown in Figure 4-28. In Figure 4-29 the mold which was made for resin casting is shown. Also This pattern could also be used in architecture, whether inside the building or outside in the I (Figure 4-30 and Figure 4-31).

Figure 4-26: Glassy beehive

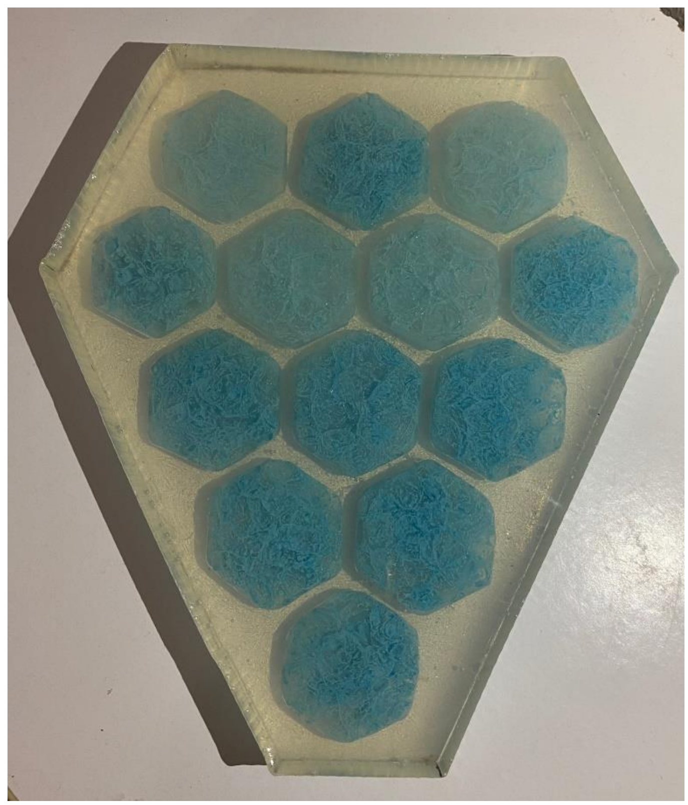


Figure 4-27: Glassy beehive with resin epoxy cover

[1] Refer to Chap. 6.4 for more details

Figure 4-28: Containers of Epoxy Resin and hardener

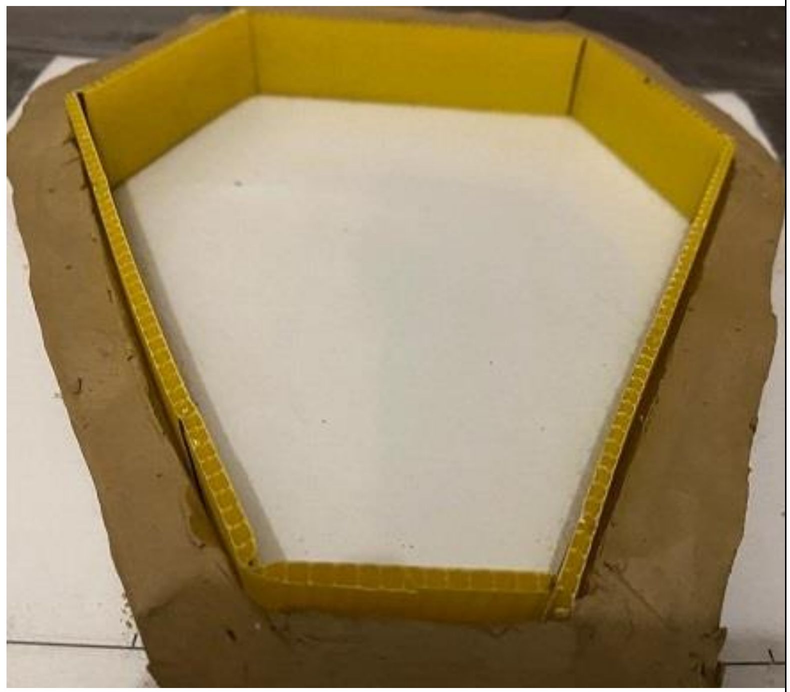


Figure 4-29: The mold for epoxy-resin casting


Figure 4-30: Application of glassy beehive in architecture

Figure 4-31: Application of glassy beehive in architecture

4.4.3 Glass Wall

Making a strong connection between inside and outside of the buildings can allow any individual to feel outside while living inside. It makes us able to live without barriers. With careful planning and spatial arrangement, such a connection can create an environment where you can enjoy an outdoor area inside the building.

There is no doubt that glass is considered as a main material to connect inside and outside the building. With this in mind, it was tried to use small fused glass pieces in order to design the glass walls. Based on this work, we will be able to create a new design on the glass surface as well as we could reduce the transparency in order to provide more privacy inside the house.

Some small glassy objects were used to design a picture which calls flying birds or swimming fishes in mind (Figure 4-32). By using resin-epoxy, this design has turned to be a solid transparent tile (Figure 4-33) which can be used to make a glass wall. The tile was named as “Flying Birds”. The small fused glass was made with Atlantis soda lime glass. By using the computer simulation techniques, different three-dimensional models was created to show the application of this glassy tile to make a glass wall (Figure 4-34, Figure 4-35, and Figure 4-36).

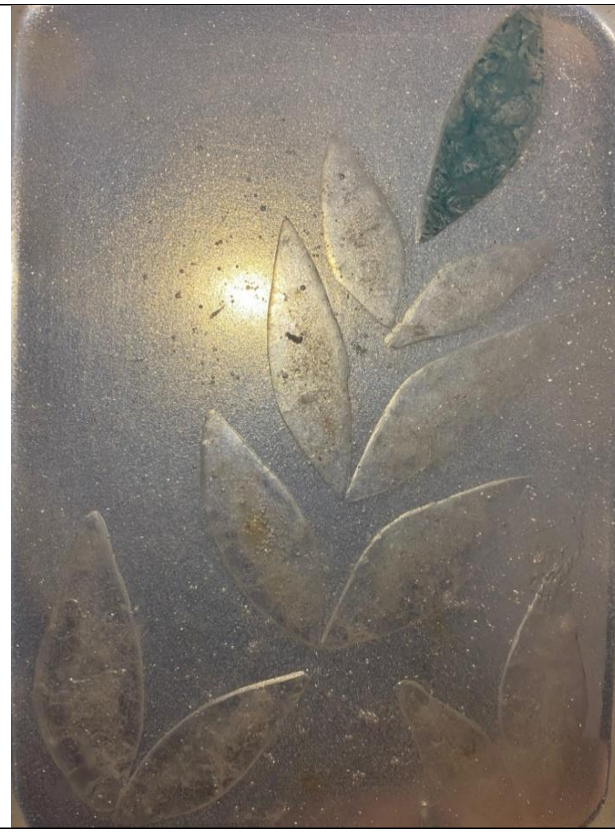


Figure 4-32: "Flying Birds" inside a plastic container	Figure 4-33: "Flying Birds" with resin epoxy cover

Figure 4-34: Application of glass walls in Architecture

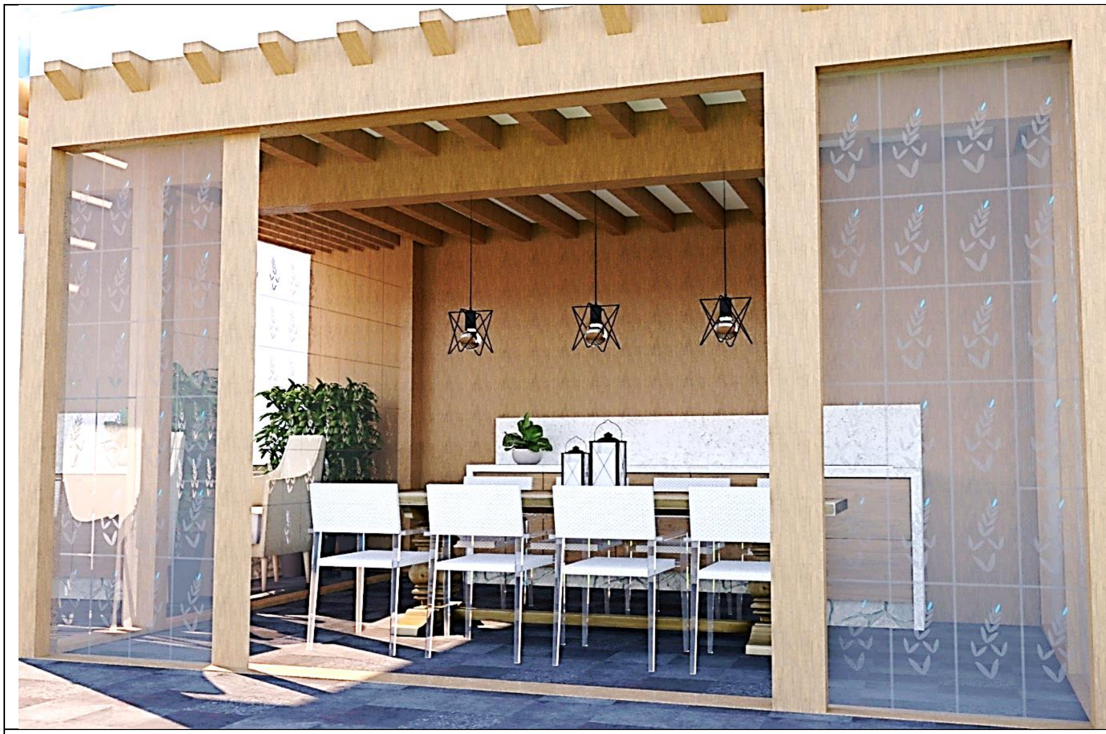


Figure 4-35: Application of glass walls in Architecture

Figure 4-36: Application of glass walls in Architecture

5

CONCLUSION

5 Conclusion

The present study has been focused on the study of historical painting techniques applied to stained glass, especially on the reproduction of green enamels based on Neri's book. This research started with the study and interpretation of "*L'art vetraria*" written by Antonio Lodovico Neri in 1612 in which three recipes of green enamel had been chosen to study in order to reproduce them. By comparing different English translation of this book with the original book (which was in Italian language), and referring to some other contemporary resources, it was tried to find equivalent name for old words. It needs to know what and how much modern chemical materials should be used for a specific recipe.

Based on the research goal, it was tried to keep both scientific and artistic viewpoints. Therefore, the current research could be divided into two parts: scientific (producing the enamels in the laboratory) and artistic (making glassy artworks, painting with produced enamels, and making 3D architectural models). These two parts are in combination as the enamels which have been produced in the first part, are used in artistic part. In the first part, the characterization of selected raw materials, used for the production of three different green enamels (based on 97, 98 and 99 recipes), was performed according to the instructions provided by the works of Antonio Neri. Because these historical recipes did not mention about the process by details, as well as just present us insufficient tools to analyze the process which has been done in the past, it positions us to see patterns that might be invisible or impossible to repeat in the present. Because of this problem, enamel producing route was developed in three steps to obtain acceptable results. In Chapter three, these steps have been mentioned as first, second and third enamel producing strategies. The third strategy led to proper results for all three recipes which are close to the green color. Each recipe was applied on glass-slides (Lâminas), and they went through with four different firing process in order to investigate the effect of kiln temperature. Overall, depends on different recipes, producing strategies, and kiln temperatures totally 27 different samples were produced.

To find a suitable way to name the resulted samples, a specific coding instruction was used. This method resulted in convenient and proper route to compare samples and find similarities or contrasts between 27 samples (3 recipes, 3 producing strategies, and 2-5 different kiln temperature).

Based on obtained painted samples, grinding, mixing and kiln temperature have strong effects on color and quality of the paint. To have a uniform mixture, the produced enamels need to be ground for a sufficient period of time to become very fine powder. Additionally, the mixing process should be done properly to obtain a homogenous mixture. More ever, the kiln temperature should be high enough to fuse pigments. Based on the first strategy results, which were all gray, 650 ºC is insufficient to fuse pigments. Additionally, inappropriate techniques to mix the semi-molten sticky mixture (i.e. by metal stick) could change the weight percentage of mixture ingredients (in comparison with Neri's recipe). Because unknown amount of sticky mixture could adhere to the metal bar.

As a visual outcome, recipes no. 97 and 99 result in dark blue and shiny blue color respectively, while recipe number 98 presents a green color. By referring to Table 3-1, It might be concluded that the use of three-times burned copper as a coloring agent in recipe 99 and 97 leads to blue color rather than green.

The color analysis tests of resulted samples (Colorimetry and Spectrometry) prove that the increasing of kiln temperature (650 to 750 ºC) results in the increasing of color intensity (absolute value of a* and b*), but the influence of this parameter varies in different recipes, production strategies, and kiln temperature value,

The obtained enamels (which contain copper oxide and lead oxide) were presumed to result in green color, however, this was not observed in the results of recipes 97 and 99. It might be because of the lack of homogeneity of the produced samples (due to a very small quantity of production). To find another reason, it needs to pay attention to iron and copper ratios. The redox interactions between iron and copper could change the glass color from green to blue-green color. Having a bigger amount of CuO (instead of Cu_2O), and Fe_2O_3 (the existence of Fe^{3+} and Cu^{2+}) could also change the color to blue, because the existence of Fe^{3+} and Cu^{2+} can influence the obtained color in this way.

Based on spectroscopy test results, all the spectra present the characteristic band of Cu^{2+}. This feature of diagrams represents the existence of CuO in the samples. Additionally, similar to the colorimetric results, changing the kiln temperature (650-750 ºC) has a strong effect on intensity of reflected light, but it depends on related recipe, production strategies, and the kiln temperature value. As an example, diagrams of E3R98 show that in some temperature ranges (650-675 ºC and 700-725 ºC), the kiln temperature has almost no effect, but in some other temperature ranges (675-700 ºC and 725-750 ºC) the kiln temperature has a remarkable effect. It could be mentioned that the value of 700-750 ºC for kiln temperature leads to high reflectance value. Probably, at the higher temperature, pigments get fused and give color to the mixture which leads to more intensive reflected color.

In the artistic part of this study, green glass enamels were used to paint three different artworks (Star-Cross tiles, Beehive tiles, the Glass Wall) which had been made by glass casting and using epoxy-resin to cover them. Additionally, these artworks were used to make 3D models of architecturally designed spaces and decorative objects by computer simulation software.

6

Appendix

6 Appendix

6.1 Stained Glass and Enamel

Stained glass is colored glass as a material or works created from it. Throughout its thousand-year history, the term has been applied almost exclusively to the windows of churches and other significant religious buildings. As a material, stained glass is glass that has been colored by adding metallic salts during its manufacture, and usually then further decorating it in various ways. The colored glass is crafted into stained glass windows in which small pieces of glass are arranged to form patterns or pictures, held together (traditionally) by strips of lead and supported by a rigid frame. Painted details and yellow stain are often used to enhance the design. The term stained glass is also applied to windows in enameled glass in which the colors have been painted onto the glass and then fused to the glass in a kiln; very often this technique is only applied to parts of a window [3].

Stained-glass painting techniques are usually divided into grisailles (brown and black), silver stain (yellow to orange), sanguine (yellowish to brownish-reds), and enamels (with different colors) [28].

“Enamel” has three different meaning: the outer surface of a tooth, a type of shiny paint and a glassy substance which is applied on metal or glass. Enamel (vitreous enamel) is a material made by fusing powdered glass to a substrate by firing, usually between 650 and 850 °C. The powder melts, flows, and then hardens to a smooth, durable vitreous coating. Enamel can be used on metal, glass, ceramic, stone, or any material that withstand the fusing temperature [51]. In this research, the term “enamel” is most often restricted to work on glass. In this case, an enamel can be defined as a glass that melts at a lower temperature than the glass to which it is applied. It is usually applied on the front side of the stained-glass panel. It is composed of a base glass (lead-silica glasses), a coloring agent (burned metals or pigments (e.g., hematite and umber)) and a binder. Both base glass and coloring agent are mixed together and melted at high temperatures. While fused, the glass is poured into cold water creating a thermal shock, which breaks the glass into several chunks. These pieces of glass are ground into a fine powder to mix with a binding agent, such as Arabic gum or an essential oil. By doing this, the paint is produced, and it is used to paint the substrate glass. After firing the paint, the result is a homogeneous layer of enamel over the substrate glass that can be opaque or more translucent [11].

The base glass is responsible for the adhesion of the paint to the glass substrate after firing. The main differences between the different base glasses are the proportion of lead oxide to silica. The Vehicle (Medium/Binder/Flux) is a binding agent which provides the plasticity necessary for the application of the glass-based paint to the glass substrate. Urine, wine, vinegar, gum Arabic, and water are the most common vehicles used in painting. All of these vehicles are organic materials that would have been carbonized during the firing process and thus absent in the final product [28].

Stained-glass paint, whether is referred to grisaille, sanguine or enamels, can present many conservation issues. They can be related to external factors such as relative humidity and temperature variations, to the way of applying the paint by using the incorrect proportion of ingredients (pigment-binder ratio), to adhesion problems between the paint layer and the base glass, to the heating conditions, such as low firing temperature and a high annealing rate, or inherent to the composition of the paint layer [11].

Studies have been conducted in order to access the mechanisms of degradation, among which the formation of micro-cracks dividing the surface of the paint layer, due to different thermal expansion coefficients between the enamel and the base glass, or a degradation of the latter leading to a detachment of the paint layer. Studies also indicate the relation between the micro-cracks and the thickness of the enamel layer. In some cases, the enamel layer can be intact, but cross-sections of the samples show cracking of the base glass underneath [10].

What is the Importance of The Revival of Stained Glass?

Historic preservation or restoration is generally regarded as the practice of protecting or preserving sites, buildings, structures, objects or districts which reflect elements of cultural, social, economic, political, archaeological or architectural history. This history is important because it connects us to specific times, places and events that were significant milestones in our collective past. The ability to revisit these preserved elements from time to time provides us with a sense of place, and maintains continuity between our past and our present by preserving a trail of how we arrived at where, and who we are today [52].

Historical building restoration not only preserves high-value buildings for the future, it also preserves our country's past. As a country, we have such a long, rich and detailed history and these buildings reflect that. They are the visual representation of our history; a testament to the architectural prowess of our ancestors. Saving heritage buildings from demolition is also important to the growth of the economy in the local area in the long term. Not only do historical building restoration projects bring in a whole host of builders, decorators, tradesmen, craftsmen, and contractors, but they will actually also boost the local economy through the tourism and leisure industries further down the line once the renovations are complete. Restoring larger historical buildings can be an extremely effective way of boosting the local economy [53].

Therefore, Historic buildings are worth preserving and restoring for a number of reasons from cultural, social, educational, economic and environmental aspects like retaining the city Identity, promotion of cultural tourism, and economic sustainability.

6.2 Alumina Crucible

Alumina crucibles (Figure 3-12 b) which were used in this research as a container to melt them in kiln. These crucibles which tolerate high temperature were produced by the Slip-casting method.

Slip means the mixture of clay and water that is used for decorating pots. Slip casting is a ceramic forming technique for pottery and other ceramics, especially for shapes not easily made on a wheel. In this method, a slurry of clay and water is poured into a porous mold, usually made of plaster. The slurry coats the mold wall, and water is absorbed into the plaster, thereby drying the slurry closest to the wall. After some time, the mold is emptied of the excess slurry. The process usually takes at least 24 hours per piece. It gives very precise and consistent shapes, and is now the most common technique used for commercial mass-produced pottery. It is also commonly used for sanitaryware, such as toilets and basins, and smaller pieces like figurines and teapots [54, 55].

These are some needed information to make alumina crucibles:

1) REAGENTS OR RAW-MATERIALS: Distilled water, Carboxymethyl cellulose (CMC), Dolapix CE64 (Polyelectrolyte Dispersant), Magnesia (Magnesium oxide, MgO), Alumina (Almatis CT 3000 SG), Hydrochloric acid, HCl (37%),

2) LABORATORY MATERIAL: Graduated cylinders, Pipette, Rubber Pumpette, Spatula, Vessel (2 dm^3),

3) LABORATORY EQUIPMENT: Universal indicator paper, Laboratory stirrer, Balance,

4) PREPARATION OF FRESH SLIP

4-1. Add by the indicated order below, while stirring the following components:

Distilled water: 1000 ± 5 cm^3

Carboxymethyl cellulose (CMC): 3,00 ± 0,01 g

Dolapix CE64 (Polyelectrolyte Dispersant): 6,00 ± 0,05 cm^3

Magnesia (MgO): 0,50 ± 0,01 g

Alumina (Almatis CT 3000 SG): 1250 ± 2 g

*) Alumina, CMC and Magnesia should be added slowly.

4-2. Measure the pH, and check if the value is pH = 9,0 ± 0,2. If not, add HCl to a maximum volume of 3 cm^3. If the pH cannot be checked add 2 cm^3 of HCl (37%) per 1 dm^3 water.

4-3. Stir vigorously the fresh prepared slip, not less than 1h.

5) SLIP CASTING

5-1. Plaster molds must be well dried before casting.

5-2. Put the well stirred slip into plaster molds to cast the crucibles, which normally take between 1h up to 6h.

5-3. As water absorption proceeds, more slip is added until crucible wall thickness is reached (about 0,5 cm)

5-4. In the end, the inner slip is recovered for further use.

5-5. The crucibles should be kept inside the plaster molds while contracting and drying, for at least 1 day.

5-6. Drying, takes at least 1 more day, by putting outsider plaster molds in a relatively dry room environment.

6) FIRING

Firing the alumina crucible in high temperature at an electric furnace according the firing schedule (Figure 6-1):

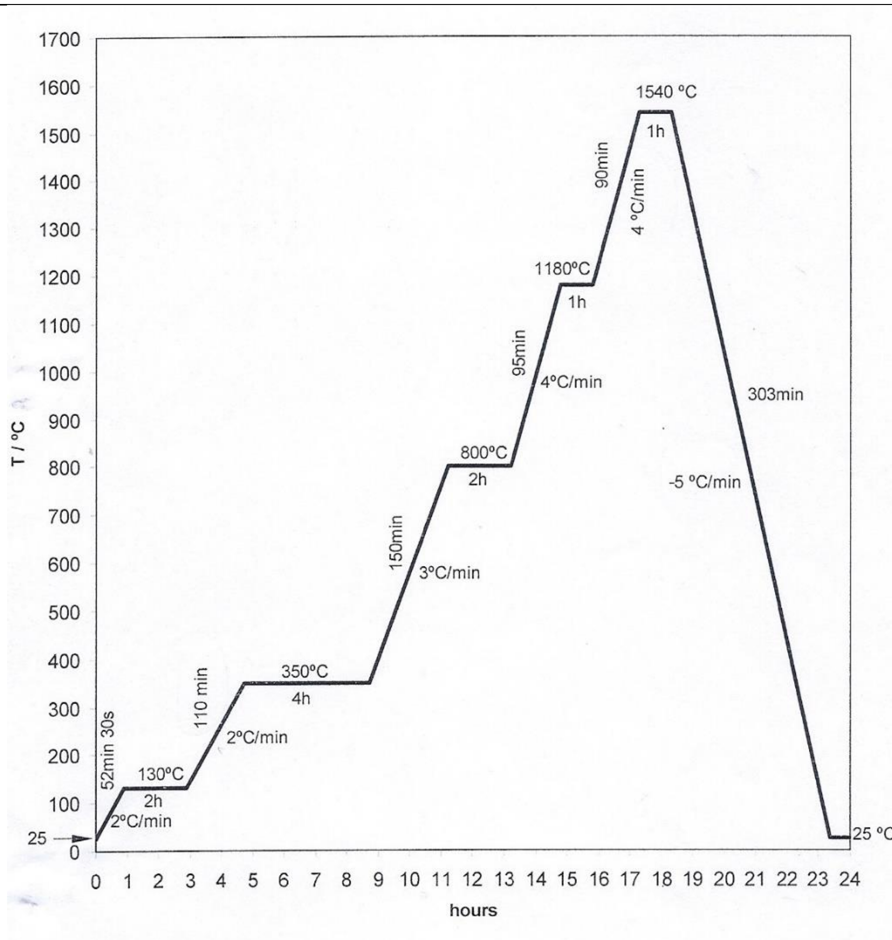


Figure 6-1: Firing schedule

6.3 Colorimetry and Color space

Colorimetry, the science of color measurement, is widely employed in commerce, industry and the laboratory to express color in numerical terms and to measure color differences between specimens. To do this, LAB and LCH color coordinates are used (Figure 6-2, Figure 6-3, Figure 6-4, Figure 6-5).

The CIELAB color space (or CIE L*a*b* coordinates), defined by the International Commission on Illumination (CIE: Commission Internationale de l'Eclairage) to identify color differences. The L*a*b* color space was modeled after a color-opponent theory stating that two colors cannot be Red and Green at the same time or Yellow and Blue at the same time. As shown below, L* indicates lightness, a* is the red/green coordinate, and b* is the yellow/blue coordinate. Deltas for L* (ΔL*), a* (Δa*) and b* (Δb*) may be positive (+) or negative (-). The total Color Difference, Delta E (ΔE*), however, is always positive [38].

ΔL* (L* sample minus L* standard) = difference in lightness and darkness (+ = lighter, – = darker)

Δa* (a* sample minus a* standard) = difference in red and green (+ = redder, – = greener)

Δb* (b* sample minus b* standard) = difference in yellow and blue (+ = yellower, – = bluer)

$$\Delta E_{ab}^{*} = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$ *Equation 6-1*

L*a*b* color is a device-independent color model that is used for reference, as it approximates human vision containing the following variables: L* for Luminosity or Lightness (measured on a scale of 0 [Black] to 100 [White]), a* for Red (+/Positive) to Green (-/Negative), and b* for Yellow (+/Positive) to Blue (-/Negative). It is often compared to a GPS, as all colors are described in terms of coordinates [56].

The L*C*h* color space is similar to L*a*b*, but it describes color differently using cylindrical coordinates instead of rectangular coordinates. In this color space, L* indicates lightness, C* represents chroma, and h is the hue angle. Chroma and hue are calculated from the a* and b* coordinates in L*a*b*.

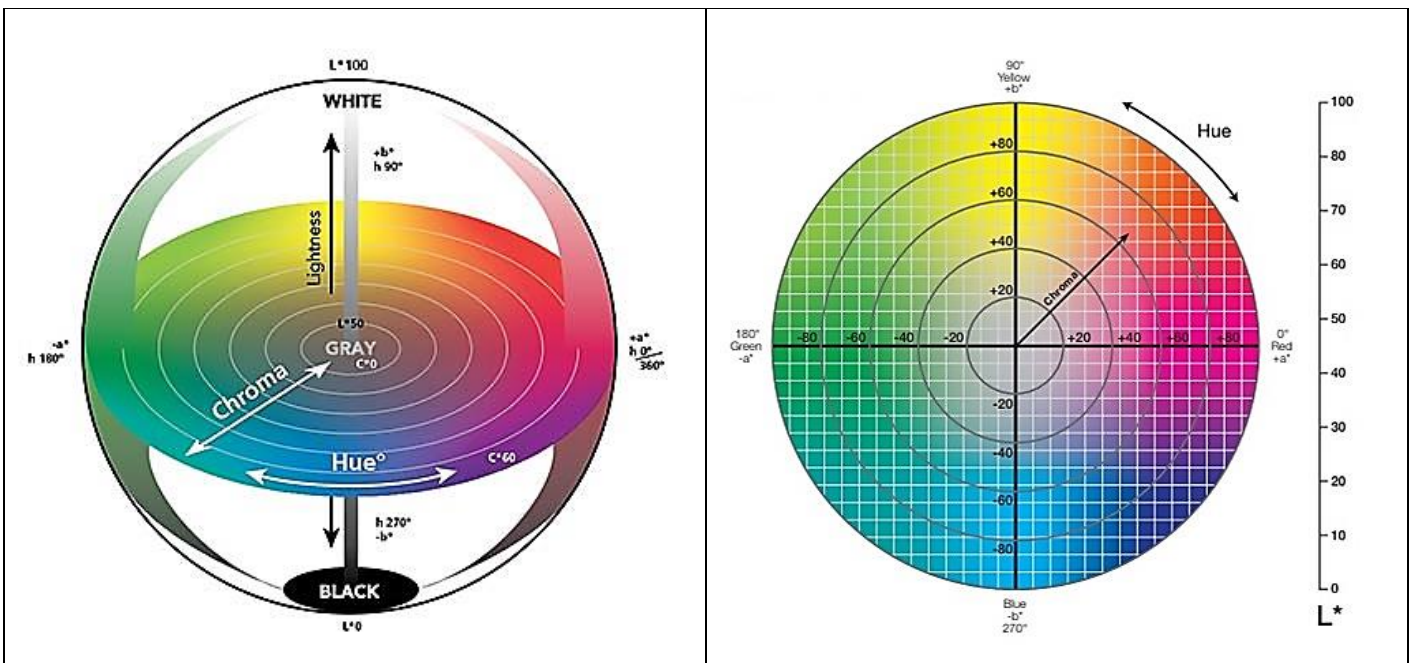


*Figure 6-2: L*a*b and L*C*h* color space [57].*

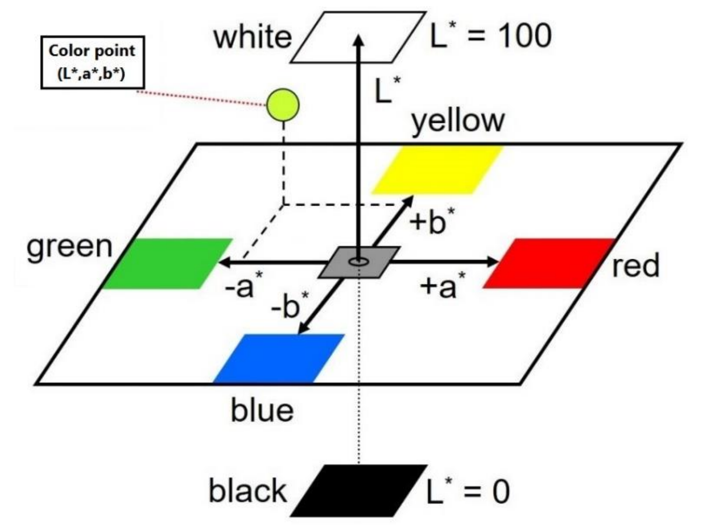


Figure 6-3: L*a*b* color space [58]

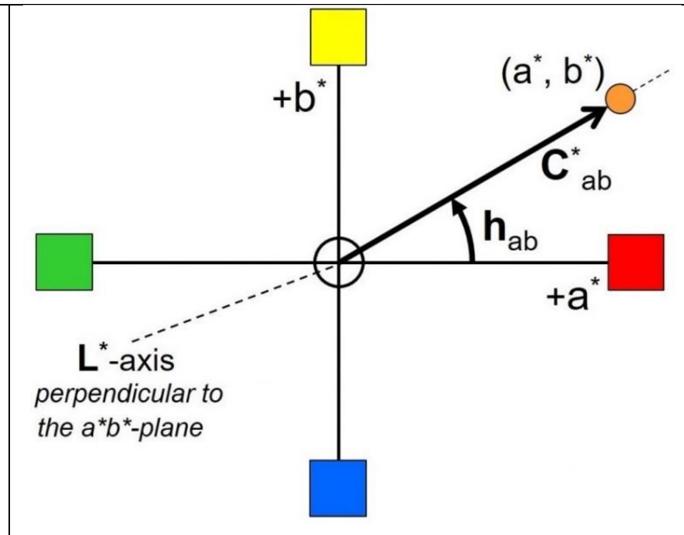


Figure 6-4: L*C*h* color space [58]

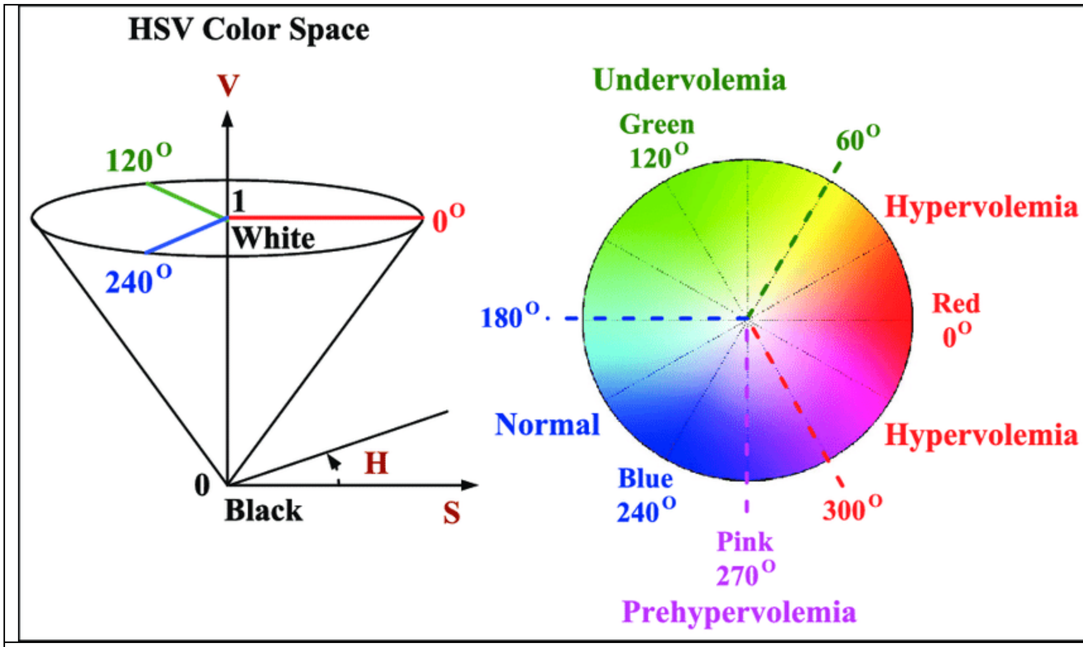


Figure 6-5: HSV color space [59]

6.4 Epoxy Resin

Epoxy resins are a class of reactive pre-polymers and polymers which contain epoxide groups (The epoxide group involves two carbons and one oxygen forming a three-membered ring structure.). Epoxy resins may be reacted (cross-linked) either with themselves (in the presence of catalysts), or with a wide range of co-reactants including polyfunctional amines, acids, phenols, alcohols and thiols (usually called mercaptans). These co-reactants are often referred to as hardeners or curatives, and the cross-linking reaction is commonly referred to as curing [60, 61].

Reaction of poly-epoxides with themselves or with polyfunctional hardeners forms a thermosetting polymer, often with favorable mechanical properties and high thermal and chemical resistance. Epoxy resin has a wide range of applications for a variety of purposes [62].

Epoxy resin possesses tough mechanical properties, good chemical resistance, and high adhesive strength, which makes it highly useful for various applications. Epoxy resin is superior to other types of resins because it has low shrink during cure, and excellent moisture and chemical resistance. (Curing is a chemical process employed in polymer chemistry and process engineering that produces the toughening or hardening of a polymer material by cross-linking of polymer chains) [63].

The class of pre-polymers and polymers which Epoxy-resin belong to them, when reacted with hardeners or curing agents, form a strong, durable substance used in a variety of commercial and industrial applications. Epoxy resins used in building and construction applications can help increase the lifespan of buildings by improving the durability of the structural parts, engineering adhesives and paints. Epoxy resins provide a protective layer that separates food and drinks from the metal used to make their cans. The epoxy resin coatings also help to minimize the corrosion of the metal, which could compromise the safety of the food or drink. “Uncured” epoxy resins refer to the polymer containing multiple epoxy groups produced from a reactive process. “Cured” epoxy resins (also known as epoxy) have undergone a chemical reaction which “cross-linked” polymer chains. This process uses a variety curing agents, also known as hardeners. The term “epoxy resins” can refer to both the cured end product and the uncured resin [64].

7

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