ENAMELING APPLICATIONS ON METAL FROM PAST TO FUTURE

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JUNE 2011

ENAMELING APPLICATIONS ON METAL
FROM PAST TO FUTURE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF SOCIAL SCIENCES
OF
IZMIR UNIVERSITY OF ECONOMICS

BY

AYTÜL DAVRAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF ART
IN GRADUATE SCHOOL OF SOCIAL SCIENCES

JUNE 2011

Approval of the Graduate School of Social Sciences

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ABSTRACT

ENAMELING APPLICATIONS ON METAL FROM PAST TO FUTURE

DAVRAN, AYTÜL

MA, Department of Design Studies

Supervisor: Prof. Dr. Murat Bengisu

June, 2011, 80 pages

This study examines the accounts of enameling and related processes by the way of decorative and functional applications. It sets out to show that enameling inhabits the past, present and future. For the future studies, this thesis suggests that nanostructured glass like coatings could be alternative for enameling and the designers could benefit from these coatings.

Keywords: Enamel, Glass like coatings, Corrosion protection, Nanostructured enamel coating.

ÖZET

GEÇMİŞTEN GELECEĞE METAL ÜZERİNE MİNE UYGULAMALARI

DAVRAN, AYTÜL

TEZ DANIŞMANI: PROF. DR. MURAT BENGİSU

TASARIM ÇALIŞMALARI YÜKSEK LİSANS PROGRAMI

Haziran, 2011, 80 sayfa

Bu calisma, mine ve benzer diğer fonksiyonel ve dekoratif yüzey kaplama uygulamalarını analiz etmektedir. Bu kapsamda mine kaplamasını geçmiş, günümüz ve gelecek uygulamalarına dikkat çekmektedir. Gelecekteki uygulamalar için, nanoyapıdaki camsı kaplamaların mineye altenatif olacağı ve tasarımcıların bu uygulamalardan yararlanmaları gerektiği belirtilmiştir.

Anahtar Kelimeler: Mine, Camsı kaplamalar, Korozyon önleme, Nano boyutlu mine kaplamalar

ACKNOWLEDGMENTS

I express sincere appreciation to Prof. Dr. Murat Bengisu for his guidance and insight throughout the research. I also want to thank Yrd. Doç. Dr. Mine Ovacık for her suggestions and comments, motivated me throughout my thesis. To my family, espeially my children, Şan and Demir, I thank them for understanding my frequent absences.

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

It is significant that, to create an article, which survives against the damaging environment, and has high structural strength together with aesthetically appealing brilliant colors and reflectivity, but does not create any hazardous waste, is very difficult.

Developments in the fields of chemistry and materials science will help finding new materials, which would last for millennia, engineering studies will develop optimal processes for products and the environment; and finally with the imagination of designers, aesthetic, function and environmental aspects will come together in innovative ways to create a desired article.

1.2 Aim of the Study

The aim of this thesis is to supply a framework to the visualization of sustainable metallic design objects through the development of materials and methods. This thesis does not intend to evaluate the objects from the standpoint of artistic design, but rather investigate the materials, methods and applied media for architectural and industrial design purposes. This study focuses on the relationships and intersections between function, aesthetic and environment. It argues the necessity of metal usage in design and architecture, in a manner of creating aesthetic for long usage. With the emphasis on contemporary methods, this study shows the diversity of enamel techniques and opportunities for creative product development. This study aims to understand the parameters of sustainable, decorative and functional metal objects in the medieval and contemporary time line, and propose new materials for protection of metals, while focusing on various implementations in decorative arts, architecture and industrial design.

1.3 Structure of the Study

This study examines the accounts of enameling and related processes by way of a detailed analysis. It sets out to show that enameling inhabits the past, present and future. The following chapters are organized as follows:

Chapter 2 describes enamel, enameling and substrates of enameling.

Chapter 3 examines the information incorporated into historical context and reviews the methods about earliest experimenters and their milieus of enamel.

Chapter 4 examines the various contemporary applications and details of aspirations analyzed by the methods and their visual representation. Beautification of surroundings through enameled panels is explored. Particular attention is given to environmental factors.

Chapter 5 analyzes the consequences of the developments in approach, concluding with a brief estimation of future applications and methods.

Chapter 6 comprises the conclusion of the thesis to analyze the applications of enameling give decorative and functional properties to the surface. For the future studies, this thesis suggests to find an answer to the question of how nanostructured glass like coatings can be alternative for enameling.

CHAPTER 2

BASICS OF ENAMELING

Cohen (2002) describes the beauty of fine enameling, as artwork is created with colors and textures that bring joy to the heart. Unlike painting and fabric arts, enamels won't fade with time; they are one of the longest lasting mediums available. According to Ball;

> In social terms, enamel has infiltrated diverse spheres of life. Enameled jewelry and objects d'art, fashioned for the opulent pleasure of kings and nobility, are well organized. (Ball, 2006)

Meeting materials challenges has always required an interdisciplinary approach. Meeting sustainable materials challenges presents an exciting opportunity to push this further, while still maintaining profitability (Esty, 2009). Working with materials to enlighten the nature of commerce, to improve interactions with the environment and climate requires understanding the consequences of materials utilization throughout the product life cycle. Pushing materials technology forward in line with sustainable development is one of today's challenges. One of the many definitions of sustainable development is given as follows:

> The level of human activity that can meet the needs of the present without compromising the ability of future generations to meet their own needs (Apelian, 2008).

2.1 Enamel

Enamel, substance of the nature of glass is a compound traditonally composed of silica SiO_2, which is the most common mineral of earth, and borax $Na_2B_4O_7$, and potash K_2CO_3. As enamel is the mixture of various raw materials and elements, usually it is based on borosilicate glass mixed with oxides of titanium, zinc, tin, zirconium, aluminum, etc. to improve corrosion and wear resistance and aesthetic features (Rossetti, 2009). Enamel differs from glass principally in two points; first, it is more easily fusible, secondly, oxides produce opacity (Brewster, 1832). Color is obtained by adding mineral oxides (cobalt, copper, iron, etc.) to the batch before melting in a furnace between 1100°C and 1300°C. The mixture remains in the furnace about an hour and then a rapid quenching creates a structure of glass, which is called enamel frit (Hodges 1976, 63).

The enamel frit is broken into smaller pieces and is ground to fineness of 80 mesh (≤177µm), which is required for artistic use that is about equal in coarseness to table salt, and to fineness of about 200 mesh (≤74µm) for industrial use.

Figure 2.1: Enamels
(Source: http://www.escolproducts.co.uk/)

The origin of the word enamel is doubtful. In old French it was spelt "esmail", that is probably connected to the word "smelt", and the German "smeltzen", from which also the word "smalt" is derived (Cunynghame, 1906). In general the word "enamel" is used to describe glazed surfaces including teeth, paint, varnishes and resign finishes. In this study, the term enamel is used to describe a vitreous substance, which has been fused upon a metal surface.

Enamels are usually arranged into three classes, transparent, semi-transparent, and opaque. The basis of all kinds of enamel is a perfectly transparent and fusible glass, which is rendered either semi-transparent or opaque, by the admixture of metallic oxides (Martin, 1813). Transparent enamel provides a color effect, which permits the color of the enamel or metal underneath it to be seen as looking through colored window glass. The opaque enamels produce a solid color effect completely covering the surface underneath as a base coat with other enamels applied over it. Liquid form enamels are finely ground glass in distilled water; pre-mixed colors in oil are also available.

Ground-coat enamel contains metal oxides (Ni, Co, Cu oxides), which promote enamel to metal adhesion. Furthermore, depending on the metal to be enameled, other constituents are added. To obtain acid-resistance TiO_2 is used. For alkali resistance, ZrO_2 is added. ZrO_2 and Al_2O_3 additions are used to improve corrosion resistance. Cover-coat enamels increase the chemical resistance and aesthetic quality.

2.2 Enameling

Enameling is the art of laying enamel on metals, such as gold, silver, copper, and melting it (Martin, 1813). One or more layers of thin coat enamel is applied with the use of a spatula or a paint-brush, by sifting, spraying or dipping, to a pre-prepared metal surface. When heated to a high temperature of about 780°C - 830°C the enamel melts and fuses to the metal to create an enameled article.

Hrabovska explains that enamel coating is the final product of physico-chemical reactions in the process of the heat treatment of glass of complicated chemical composition together with other components of inorganic character combining the properties of glass and ceramics with the ability of adhesion to metal (Hrabovska, 2009).

The glassy coating formed on a metal substrate produces various color effects. The quality of enamel coating depends on the pre-treatment of the metal substrate surface and the quality of enamel slip. Enamels with lower melting and firing temperatures can lower costs substantially (Lazutkina, 2008). Thus, further studies directed toward improving the known compositions and developing new types of enamels will create new technologies oriented toward saving energy and material resources (Minko, 1999).

2.3 Enameling Substrates

Metals for enameling are the substrates entirely covered in multicoloured glass. Enamel deposited on a metal surface produces a vitreous coating, which protects the metal from the effect of different conditions such liquid and gaseous. The adhesion of enamel coating on metal is the combination result of mechanical adhesion forces and chemical bonds. When heating applied, metal and enamel expand, if the enamel's coefficient of expansion is not lower than the metal, enamel can crack or flake of the metal (Darty, 2004). Enamel increases the life of metal and improves the external appearance of the metal. Enamel can be applied to most metals as gold, silver, copper, bronze, steel, cast iron, stainless steel and aluminum. By applying identical enamels to various metals, it is possible to achieve different colors come out on different metals, because of the chemical contents and different melting points. Hartley has done many trials on different precious metals and the results are explained below by grouping the metals (Hartley, 2005).

Gold is generally used for the more exclusive artworks (Van der Linden, 2009). It has the advantage of not oxidizing and accumulating brown-red oxides known as firestains as well as creating brilliant colors under transparent layers. Gold is the best substance for enamelling because its richness of color exhibits a beautiful tinge through the enamel (Martin, 1813). 100% gold is called as pure 24K or fine gold and the melting point is 1063°C, as it is too soft, it can be used as a decorative addition to a lesser karat gold. 22K, 18K yellow gold contain silver and copper, 22K, 18K white gold contain silver and palladium. These metals are very suitable for enamelling.

Silver is categorized according to silver content as followings;
Pure silver has 99.9% silver and the melting point is 960°C, allows higher firing temperature than standard silver. It is preferred because of the white color of the metal is brilliant and reflective when seen through transparent enamels (Darty, 2004). Standard or Sterling Silver has 92.5% silver and 7.5% copper content, because of copper it will oxidize and create firestains, special attention is necessary to achieve clarity and brilliant colors. Hardenable silver alloy has 99.65% silver, 0.2% magnesium and 0.15% nickel, the melting point is more than 1000°C. Since there is no copper inside, it is more suitable than other silvers for enamelling without firestains.

Copper has been the most inexpensive and satisfactory metal for use in enameling generally used on smaller or medium sized pieces. It is easy to cut and shape and offers the fewest problems in fusing wide range of enamels to its surface. When copper is heated firestains can be generated on the surface and these areas cannot be enameled, these firestains must be regularly removed between firings. In spite of the difficulties in the enameling process, copper has additional advantages when aping colors on the surface. It is suitable when using opaque colors and also when clear enamel or transparent colors are fired directly onto the surface.

Silver-plated steel and **gilding metal** from enamel suppliers are more economical than pure silver or gold for use with transparent enamels. Steel is suited for large-scale pieces due to its strength.

Low carbon steel & iron plates can be enamelled with the same enamels for copper, silver and gold. Steel is appropriate for large panels, murals or architectural enamels.

Stainless steel does not require ground coat enameling. High expansion enamels are used on 304 stainless steel, low expansion enamels are applied on 410 stainless steel.

Bronze, brass & nickel contain zinc that makes difficult to enamel. Multiple firings cause bubbles in the enamel that is why firings must be minimized.

Platinum is not chemically suitable for enamelling; as the melting temperature is too high (1769°C), glass cannot be fused in the metal since the adhesion between the two substances is not sufficiently powerful to keep them together. However there are several techniques of treating surface to be enamelled.

Aluminum can be enamelled as well but special low temperature and high expansion enamels (these are not the same enamels used on copper, silver and gold) must be applied by sifting on hot aluminum since aluminum's melting point is 660°C (Darty, 2004).

Titanium has 1800°C melting point, because of the low expansion rate, many trials must be done to determine which types of enamels are suitable. Genarally opaque enamels are preferred since the transparent colors turn gray from the oxides in the metal (Darty, 2004).

CHAPTER 3

MEDIEVAL ENAMELING

> *"Enamel has survived, and at times thrived, since it's ancient beginning, despite the meager support it has received through the formal avenues of education, museums, and the marketplace. Enamellist's devotion to their craft has no doubt contributed to the endurance of the medium through history." (Goss, 2003)*

The shaping of early metal objects and production practices into metallurgical traditions reflects many visual possibilities (Roberts, 2008). One of the ancient decorating techniques applied on metallic objects is the 2500 years old enameling. It is believed that enamel work had its origins in with early civilizations around the Mediterranean from the sixth century B.C. or even earlier. Greek sculpture from the fifth century B.C. shows surfaces with areas of inlaid metal covered with enamel. The ancient Greek goldsmiths inlaid their jewelry with thin coatings of white and blue enamel between gold wires. The enamel process had spread to England and Ireland and than continued to move slowly from Europe to Asia Minor and the Middle East, to India and China, and then to Japan. Inspired by the works of Byzantine, German and French artists, various forms of enamel have been developed in Russia beginning from 11^{th} century (Wagenblass, 2008) .The remarkably well-preserved enameled pottery and jewelry found on sites of ancient Egyptian and Persian civilizations testify to the astonishing durability of this material. The golden age of enameling was between the 6^{th} and the 11^{th} century, during the Byzantine period. Works from this period heavily influenced the whole of western production throughout the

12^{th} century. Enameling is considered to be one of the finest and often most expensive methods of jewelry crafting. Since enamel colors are brilliant and they are very durable, through centuries enamel was used in various ways as a substitute for the costly process of inlaying gold with gems.

Medieval enamel articles can be distingushed according to the techniques they were created. In the following sections, these techniques are described by the figured examples. All these techniques rely on arts & crafts require expertise, take a lot of time, but their quality is good and the created objects are unique through the centruies.

3.1 Cloisonné

Cloisonné is the oldest form of enameling, dating from the 13^{th} century BC, when it was first developed probably in Egypt and from where it was transferred in the Mycenean period to Cyprus (Higgins, 1980). Coisonne´ is defined as enamel is set in areas on the surface bounded by strips of metal arranged in cells to form a pattern (Higgins, 1980). The name "Cloisonné" comes from the French word 'cloisson', which means room or closed cell.

In this technique, thin metal wires or strips framework an area by attaching to the metal surface in order to create patterns. Attachment of wires can be achieved by soldering them into the surface. This technique is used for enamels and for gemstone inlays. After creating the closed cells, liquid enamel is poured into the cell to fill it and the object is fired. Each color stays in its own cell defined by the wire and does not diffuse into the surrounding cells. Since the enamels shrink when melted, this application is repeated several times in order to fill the cells. After firing, grinding and polishing the surface of glass and metal, the enamel looks like inlayed gem. Cloisonné was developed by Byzantine artisans and between the ninth and the twelfth centuries, they used thin gold plaques. In the following centuries, gold usage was rare and instead silver filigree styles were developed.

Fig.3.1: Medallion with Christ from an Icon Frame, ca. 1100, Byzantine
(Source: http://www.metmuseum.org/toah/works-of-art/17.190.678 (October 2006)

The medallion shown in fig.3.1 was made in Byzantium, ca.1100 identified as the finest surviving example of cloisonné enamel. In this Byzantine technique, compartments, or cells, were outlined by thin sheets of gold or silver, filled with colored glass paste, and then fired at a high temperature, with the melting glass forming a solid surface.

Cloisonné was also used to create reliquaries beside the champleve technique (Figure 3.2). This reliquary was created in late 8th or 9th century in Byzantium with cloisonné enamel on gold and silver. This small, finely made cloisonné enamel box is one of the earliest examples of a reliquary made to contain a fragment of the True Cross (Evans, 2001).

Fig. 3.2: Reliquary of the True Cross (Staurotheke), late 8th–early 9th century Byzantine; Made in Constantinople .

(Source: http://www.metmuseum.org/toah/images/hb/hb_17.190.715ab_av1.jpg)

3.2 Champlevé

Champlevé is the first enameling technique for a decorative surface on metal, which gives the strongest combination of metal and enamel for flat and shaped areas. The name Champlevé comes from the French word 'champs', which means 'field', and 'levé', meaning 'lifted' or 'raised'. The technique describes the fields, cut out of the metal to receive the vitreous enamels. The fields are created by etching, carving or casting in order to remove or mold the materials. This technique is applied especially on less expensive material, since most of the material is removed from the object. The technique for champlevé differs from cloisonné, in which the fields are created with flat metal strips by soldering on the surface of the object. When the cells are properly filled with enamels, the object is fired until the enamel melts. After cooling, as the powdered glass shrinks in volume, it is necessary to refill the cells with enamel and repeat the firing process several times. Afterwards, the surface is carefully polished. Many champlevé enamels in France were created in the period of 1000-1400 A.D. for the honor of Christian monasteries and cathedrals. In medieval Christianity, relics, which are physical objects of a holy person or holy site, were stored in enameled containers called reliquaries (Boehm, 2000). In figure 3.3, a reliquary example of medieval church treasuries shows the technique of champlevé enamel on gilded copper.

Fig. 3.3: Chasse of Champagnat, ca.1150
(Source: http://www.metmuseum.org/toah/works-of-art/17.190.685 (October 2006)

3.3 Basse-taille

Basse-taille comes from the French name ‘email en basse taille’, meaning ‘low cutting’. Basse-taille enamel, is a method of working with translucent or transparent enamel on metal that may be combined with opaque enamel. The method was invented in the fourteenth century; prior to this, all enamel was opaque. The purpose of using transparent enamel is to create a very thin layer of glaze for reflecting the light falling on the enamel, back from the gold or silver. In this technique, the metal surface is carved, chased, etched, engraved or patterned from the front or hammered from the back to give the reliefs on gold and silver. This technique improves adherence of the enamel and creates a pattern that will be seen through the enamel. Enameling is applied over the surface by translucent or transparent colours magnifying brilliant patterns made as the base of design. The technique is very similar to ‘champleve’. Sometimes it is very difficult to make a distinction between them, as in ‘basse taille’, a transparent layer is used as a ground enamel, but in ‘champleve’, the opaque one is used.

Contrary to other techniques applied with metal barriers, in Basse-taille the various colors are not divided from each other as shown in fig. 3.4, that is why after each color applied it must be dried completely before another color is added (Benton, 2009).

Fig. 3.4: Basse-taille enamel in The British Museum, produced in 1340.
(Source: http://www.learn.columbia.edu/treasuresofheaven/relics/Reliquary-Pendant-for-the-Holy-Thorn.php)

3.4 Guilloche

Guilloche is a French word for "engine turning" and this is a kind of 'basse-taille' technique introduced in the nineteenth century. Engine turning is the mechanical cutting of lines on metal to create a reflection of light through the overcoating of transparent enamel on the pattern. The reflection of light can be seen as the piece is moved from side to side (Cohen, 2002). Geometric patterns, mostly wave designs, were created with engraving machine lathes, especially from the late 1890s into the early 20th century.

In the late 19^{th} century, the Russian house of Faberge used the Guilloche technique for luxury items and well known Imperial eggs, which were commissioned by the Czar Alexander III as gift to his wife each easter (Darty, 2004). Between 1842 and 1918, Art Nouveau jewelers were particularly fond of enamel (Hesse, 2007) and Carl Faberge, master enamel craftsman of his time, produced enameled jewelry, cases, boxes and ornament decorated with enamels of the highest quality in terms of their evenness and smoothness of texture (Davison, 2006).

In 1897 Carl Fabergé presented a special Easter "Coronation egg" (fig. 3,5), one of the most splendid items he had ever created. The egg had been covered with a thin layer of pure silver that had been hammered, engraved, polished, and finally enameled a deep gold color over the guilloche patterns (Swan, 1999).

Fig.3.5: Coronation egg
(Source: http://www.forbes.com/2004/01/08/cx_pm_0108fcphotoessay_print.html)

3.5 Peint

Peint, which is a form of painted enameling, relies more on drawing and colors than the other techniques. Peint articles are beautiful miniatures and plaques produced in France from the 16th to 18th centuries under the influence of the patronage of wealthy families (Linden, 2009). In this technique, gold, silver and copper base are cut into the required size and shape. After cleaning with acid and water, opaque or transparent ground enamel colors mixed with oil and are laid over the front surface evenly. When the first coat of enamel is fixed, the drawing is applied with a needle on the enameled surface.

One of the greatest enamel painters, Leonard Limosin worked in the style of the School of Fontainebleau. He is accepted to be the best portrait painter of Renaissance France. One of his plaques enameled on copper portraying Henri d'Albret, brother-in-law of the French king Francis I (1497–1547), has still an extraordinary appearance (Figure 3.6).

Fig.3.6: Henri d'Albret (1503–1555), King of Navarre, Plaque, mid-16th century (Source: http://www.metmuseum.org/toah/works-of-art/49.7.108 (October 2006)

3.6 Ronde Bosse

Ronde Bosse is the French art form developed in the fourteenth century, as a technique for enameling irregular round surfaces of small-scale sculptural objects. The metal was usually chosen as gold, although silver and copper have also been used. The main difficulty was to support and protect the objects during firing. In the Renaissance period, many splendid ronde bosse articles have been created, which are now in the galleries of British Museum and Victoria& Albert Museum.

Figure 3.7: The Holy Thorn Reliquary © The Trustees of the British Museum
(Source: http://www.britishmuseum.org)

The reliquary shown in fig.3.7 is an example of the art of ronde bosse enamel. The Holy Thorn was made of gold in 1397 and two panels on the base are enameled.

3.7 Grisaille

Grisaille comes from the French "gris", meaning gray. It is a method of surface painting enamel in white and greys on a dark blue or black background. The white enamel is scratched before the plate is fired, on a counter-enameled copper plaque. Traditional grisaille is painted in tones of white areas built up in layers to produce a complete shaded picture, sometimes outlined with gold. This technique originated in the early 15th century in Limoges, France. One of the finest surviving examples, “Monkey Cup”, shows the enamel was applied over the silver, without the grooves or the incised patterns for the guidelines of enamels as in Champlevé and Cloisonné (Figure 3.8).

Fig. 3.8: Beaker ("Monkey Cup"), ca. 1425–1450, Silver, silver-gilt, painted enamel (Source: http://www.metmuseum.org/toah/works-of-art/52.50)

3.8 Plique a Jour

Plique à Jour means ‘braid letting in daylight’. Objects made with this technique are like miniature stained-glass windows, the lead lines in the windows being represented by the metal cells in the enamel (Maryon, 1971). Plique-a-jour uses the same techniques as cloisonné, except that transparent enamel is fired in backless openings or cells so that light goes through and gives a stained glass window effect on a tiny scale. In this technique, metal strips are soldered to each other, instead of the base metal, and create the structure of the object. This technique was developed in the late 14th century in France. Due to the delicacy of this technique, only few examples exist today. The Mérode cup now housed in the Victoria and Albert Museum dates from the 15th Century (Figure 3.9).

Fig.3.9: The Merode Cup; silver-gilt with translucent enamels; lid separate
(Source: http://collections.vam.ac.uk/item/O93263/cup-and-cover-the-merode-cup/)

There are several techniques in plique-a-jour. In one of them, cells in the pattern of metal part are filled by very fine 60 mesh (≤250μm) even finer washed enamels. Another method uses cloisonné wires within the framework but in this technique, soldered contact points should be as less as possible since enameling solders flow at high temperatures. An alternative method for avoiding solders in the pattern is to embed the wires into a thin layer of enamel flux. After firing, the copper is etched away and the cells are filled by enamels and than the flux is removed very carefully (Hartley, 2005).

Fig.3.10: A Silver-Gilt, Plique-à-jour and Cloisonné Enamel Footed Cup - 1890
(Source: http://www.christies.com/LotFinder/lot_details.aspx?intObjectID=5424557)

Fig.3.11: A Silver Guilloché, Champlevé and Plique-à-jour Enamel Tazza (Source:http://www.christies.com/LotFinder/lot_details.aspx?pos=8&intObjectID=5424554&sid)

Figure 3.10 shows cloisonné and plique-à-jour enameled cup that was created in 1890 by Russian enamelers, and figure 3.11 shows another Russian imperial example from 1908-1917, in this example translucent red enamel is used over a wavy guilloché ground, and for the flower heads plique-à-jour technique is used, the exterior of the bowl is decorated with champlevé.

CHAPTER 4

CONTEMPORARY ENAMELING

Enameling has changed since the mid-twentieth century. The developments of manufacturing possibilities for cast iron and steel enabled these materials to be used as substrates for enameling. Enameled steel has become a sophisticated material that meets modern day requirements of aesthetic qualities, hygiene, and respect for the environment thanks to long time usage and waste minimization. There is evidence for renewed interest in enameling to transcend traditional conceptions of the medium, to abandon the purely decorative and technically proficient in pursuit of less exhausted possibilities (Backlin,1959).

The new generation of designers is playing with forms and mixing styles to create surprising objects and furniture, which combine aesthetic and functionality together. Enameling is a world so diverse, that no other medium can compare (Karen, 2002).

Enamel involves the design of lines, shapes, colors and textures and transforms them into imaginative surfaces or objects by means of the technique or craft of enameling. It is the reward of patience and merely glass fused to metal however it can make an object priceless with its unique characteristics and aesthetics. As a medium it can be used across a wide variety of formats from a tiny jewel to an architectural scale artwork that will cover an entire wall (Ball, 2006).

It is obvious that enameling resides in two intersecting arenas: decoration/fine arts and function/industrial applications. There are many new opportunities in both directions and an auspicious future for this ancient enduring medium, that is tenaciously tied to its traditional skills and interpretations (Browne, 2002).

Contemporary artists learned from historical craft techniques and applied established techniques to produce modern examples. Follett[1] explains the historical and contemporary craft practice and the importance of their research project called, "Past, Present and Future Craft Practice". This project reveals that craft based design to be considered as a concern for innovation, a fusion of art, science, engineering, and technology.

Contemporary enamelists investigate new applications to combine decoration, function and fine art with alternative materials by using ancient techniques together with present and future challenges.

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[1] *Prof. G. Follett is Dean of the Jordanstone College of Art and Design at the University of Dundee, Scotland. Her work investigates the development of plique-à-jour enamelling with precious metals and is held in the permanent collection of the Victoria and Albert Museum, the Roy Strong collection in the Victoria and Albert, and the National Museums of Scotland. She has attracted £1.2 million EU funding to bring design expertise and technology to the Small to Medium-sized Enterprise sector.*

4.1 Contemporary Examples of Fine Enameling

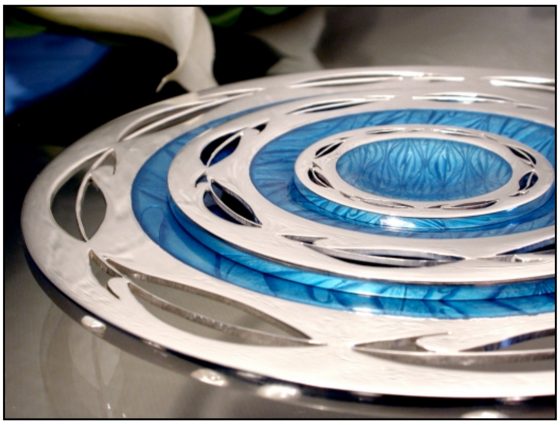

Fig.4.1: Enamel Bowl created by Rachel Gogerly
(Source: http://www.rachelgogerly.co.uk/gallery/silverwork/1)

In Fig.4.1, a transparent enamel bowl is presented. Tranparent enamels show clearly the patterns on the surface and allow the light to pass through for creating brilliant colors. Gogerly combines contemporary design with classic enamel techniques of champlevé, basse-taille and guilloche. She utilizes the clarity and vibrancy of the transparent enamel colors by hand engraving and lathe turning to create geometric and symmetrical engraved patterns beneath the enamel. Today enamelers do not make their own enamel colors; however, the grinding and washing of enamel colors is still done by hand so that the correct consistency of enamel powder can be achieved.

Cockrell describes enameling as follows;

> Enameling seems very close to magic, powdered glass is sifted onto a piece of copper, melted for a few minutes in a small kiln and cooled, and it then glows with permanent color. The color produced can be vivid or subtle, plain or shaded, light or dark, just you choose. Unlike paints they do not fade with time, so your work will last for a long time (Cockrell, 2007).

Fig.4.2: 'Summer Bowl', 1998, plique-a-jour, enamel and fine silver created by Merilyn Bailey.
(Source: Craft Arts International No. 62, 2004, p:51)

Bailey uses plique-a-jour enamel technique to create illusions of depth and play with light as it reflects off one surface through another (Fig.4.2). She has adopted stained-glass windows effect to vessels, bowls and dishes. When designing plique-a-jour, she incorporates cells in the design as squares and rectangles to cope with stress cracks in the corners or along an edge so the enamel remains perfectly stable (Lomny, 2004). Advances in technology and changes in fashion created elaborate frames with coloured enamels. In the contemporary era, decoration has changed to be modern, but the techniques employed throughout the centuries, remained very similar.

The Jeweller's Directory of Decorative Finishes describes enamels as following;

> Enamels give a vibrant finish to work, or are used great effect in a very subtle way to give just a hint of color. They can be used to create a "stained glass window" effect or to look like a painted picture. The brightness of the metal behind the enamel is used with transparent enamels to give a feeling of depth and quality to the color (McGrath, 2006).

Fig.4.3: Pebble Collection 2011 created by Ruth Ball
(Source: http://ruthballenameldesign.com)

Remarkable effects can be achieved in enamel. Enameling offers jewellery limitless color possibilities, many subtleties of surface and textures. It has the ability to enhance form with the power to mesmerise (Ball, 2006).

Figure 4.3 shows an example of inovative new form created with cloisonne technique. As Browne exemplifies that craft enamelling, combines traditional skills and personal interpretations, Ball's 2011 pebble collection, exhibits her inspiration for the design, as follows;

> This collection takes its inspiration from my small collection of river stones. I value them for their beauty and sheer simplicity of sublime color and form. Recapturing their essence in enamel seems to highlight their intrinsic quality, and provides the influence for a versatile collection of jewels and silverware pieces (Ball, 2011).

Fig.4.4: Celebration platter
(Source: http://equilibrium-design.co.uk/silverware.aspx)

Example given in fig.4.4 shows a teak wood platter inlayed with silver dots and a scoop spoon to compliment a fine enamel dish designed and made by Ball. On this design as Grath specifies opaque enamels are used to give a richness of color on metal that could be achieved in any other way (Grath, 2006).

The Jeweller's Directory of Decorative Finishes, broadens enameling opportunities as following;

> Of all the decorative techniques, enameling offers the widest choice in terms of color. It is truly wonderful medium for expressing ideas and design, and creates endless opportunities for creating patterns in both color and textures (Grath, 2006).

Fig.4.5: Enamel on copper by Jean Ames, 1950
(Source: www.enamelarts.org)

Figure 4.5 shows one of the Limoges-style enamel copper plates of Jean Ames, who is a follower of Karl Dreup's work (fig. 4.6).

Fig.4.6: Enamel on steel by Karl Dreup (1904-2000)
(Source: www.enamelarts.org)

Fig.4.7: Enamel on copper and silver by Sarah Perkins, 2003
(Source: www.enamelarts.org)

Perkins creates vessels, teapots, bowls, vases and containers with fine enameling. She gives a mat, non-glassy finish to the enamel surface (fig.4.7).

Fig.4.8: Enamel on silver by Harlan Butt, 2007-2008
(Source: www.harlanbutt.com)

Fig.4.9: Enamel on silver by Harlan Butt, 2006
(Source: www.harlanbutt.com/silver-enamel-2006)

Fig.4.10: Enamel on silver by Harlan Butt, 2007
(Source: www.harlanbutt.com/silver-enamel-2007)

a b

Fig. 4.11: Van Cleef & Arpels Timepieces
(Source: http://timepiecescatalogue.vancleef-arpels.com/)

In fig.4.11-a, Lady Arpels Centenaire timepiece is represented with a natural white mother-of-pearl disk that rotates around the dial every three months, with a second part, which is hand-painted enamel that shows a garden, which represents the four seasons as a unique aesthetic effect. In Fig.4.11-b, Van Cleef & Arpels presents a new and unique dial (produced in 2011), decorated with champlevé enamel resembling a hot air balloon rising into the air inspired by the Jules Vernes novel “The Extraordinary Voyages”. In the watch making history, designers used their technical innovation to transfer watches into jewelry pieces. They engraved, enameled the metal and applied their painting skills for creating specialty timepieces. Baron explains that the creation of each dial entails finding the most suitable enameling technique for each design and then developing this technique so that it allows to remain faithful to the initial creative idea. In order to have diverse aesthetic possibilities of enamel, the vitreous enamel technique evokes lightness and transparency and contrasts with other elements on the dial (Baron, 2011).

Fig.4.12: Frey Wille fine art jewelry
(Source: www.freywille.com)

Fig.4.12 shows an example of fine enameling, created by Frey Wille, fine art jewelry producer. Frey Wille uses enameling to create modern jewelery with the aim of producing timeless masterpieces of decorative art. The primary focus of Frey Wille's products is to use the combination of 24-karat gold and pure enamel to maximize aesthetic pleasure. As Cohen (2002) decribes, in fine enameling, where artwork is created with colors and textures that bring joy to the heart, Frey Wille links fashion and art together with the inspiration coming from nature and the feelings of joys that life creates. In the collections of Frey Wille, pure enamels are available in yellow gold plated or white palladium mountings. Strong colors such as yellows, reds, blues and greens are predominant in the yellow gold version and join as color pairs to shine bright surrounded by creams and blacks. In other collections, the white palladium version uses oranges, greens, lilacs and pinks.

4.2 Enamel Street Signs

Enamel signs emerged as jewel of British advertising in the late Victorian era for commanding public attention. The term "Street Jewelry" denotes the enameled-iron advertising signs in common use from the 1880's to the mid Twentieth Century. These signs reflected in their design, typography and textual content the social and economic atmosphere of the contemporary technological and industrial practice. At the start of the Twenty-first Century, advertising media has become a part of everyday life and appreciated more universally than any other (Baglee, Morley, 2005).

Early enamel signs, still surprisingly have unique and distinct color sharpness, which still can be admired. Fig.4.13-a shows enamel colors are unique in appearance; fade proof, resistant to light and the enamel sign perfection that was produced in 1900. Fig.4.13-b shows the “British Dominions Motor Insurance” sign.

a b

Fig.4.13: Enamel signs, produced c.1900
(Source: www.oldsydneysigns.com)

Enamel stays as vibrant as the day it was produced regardless of ultra violet radiation, industrial pollutants where the other surface finishes would fade or peel over. Enameled advertising signs reproduce any image with a gloss or matt finish. Since the colors of graphic design are created using mineral pigments fuse into the surface at at high temperature, the images last as long as the underneath enamel panel.

Highly durable materials such as steel enamel enable providing color and surface protection in high traffic areas. The specific characteristic of non-combustible feature makes the material ideal for underground usage in case of fire and wherever the fire considerations are important.

Fig. 4.14: Vitreous enamel line diagram panel
(source: http://www.specifile.co.za/Specifier/index.php?option=com_content&view)

Fig.4.14 shows fire protection test of Vitraclad enameled steel, performed by Vitrex, result showed that the material is heat and fire resistant up to 750 degrees Celsius, firelab concluded: "The product evaluated would be regarded as non-combustible." Additionally vitreous enamel does not promote flame spread or smoke and does not give off any toxic gasses.

In Gloucester Road Station which is one of the first London Underground stations, signages in the station reburnished in the early 1990s. The current condition of these signages is as good as when they were installed in 1992. This examples show the durability and longebility of enamel.

Fig.4.15 explains a demonstration against vandalism subjected in urban environment with spray paints and scratched with keys, on the three signs such as an enamel, a pre-coated aluminum and a powder coated aluminum signs. The enameled panel could not be scratched with key since the hardness of enamel allows the surface to resist mechanical abrasion and prevent scratching. Like glass, the surface of enameled steel is very hard, which means that it is extremely resistant to scratching, abrasion, and wear.

Fig.4.15: Vandalism demonstration on London underground signages
(Source: http://www.ajwells.com)

Fig.4.16 and fig.4.17 show pre-coated aluminum roundels. After drying of spray paint, the paint is being wiped with standard graffiti removing chemicals and the chemical agent removes the spray paint and also the graphics on the pre-coated and powder coated aluminum. After cleaning the scratches are clearly visible and the graphic is partly removed.

Fig.4.16: Pre-coated aluminum roundel.
(Source: http://www.ajwells.com)

Fig.4.17: Powder coated aluminum directional sign
(Source: http://www.ajwells.com)

Fig.4.18 shows graffiti could be easily removed from vitreous enameled panels using chemical solvent without affecting the graphics of enamel since enamel is resistant to most alkali, all acids (at room temperature) except hydrofluoric acid, all organic solvent and detergents.

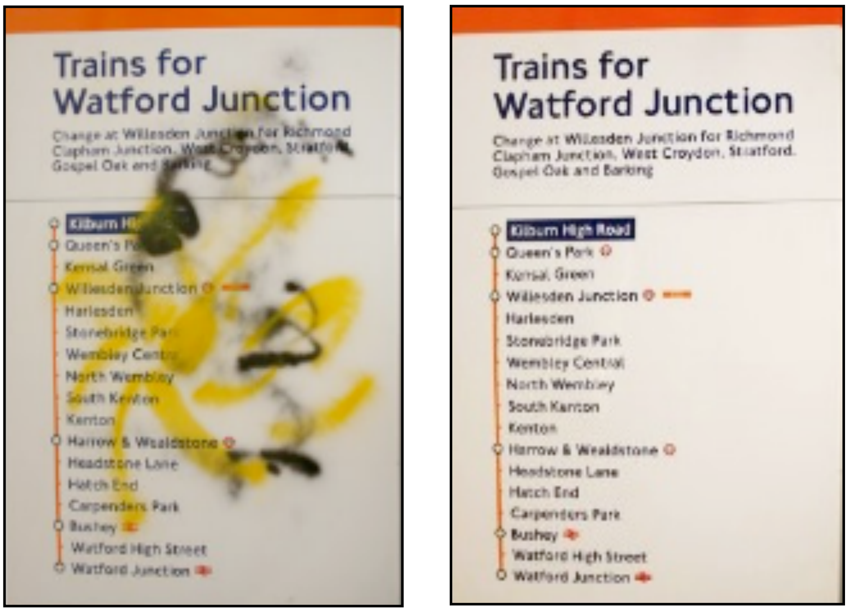

Fig.4.18: Vitreous enamel line diagram panel
(Source: http://www.ajwells.com)

As a result of this study; in the working environment the pre-coated and powder-coated aluminum signage would need re-plating as the graphics are damaged but the enamel panel is as good as new, there is no damage on the surface.

The result presents that, enameled steel is extremely resistant to environmental attacks, which is the contribution of mechanical strength and formability of steel, on the other hand durability and glossy appearance of enamel. In opposition to other outdoor materials, rain, atmospheric pollution, ultraviolet radiation and marine atmosphere will not cause any changes in the appearance of the enameled surface.

4.3 Enameled Outdoors Structures

The borders of outdoors furniture are changing; now sofas, terrace showers, umbrellas, lightings, kitchen equipment, chairs and tables are designed with the appropriate material withstand outdoors conditions. The outdoor objects all must be waterproof and the surface must be impervious to attack and damage by rodents and insects. In order to realize these entire material characteristics, and also have corrosion resistance, it is necessary to use enameled metal to guarantee minimum 30 years usage without any signs of corrosion on the metal. Placing of outdoor murals, public arts and outdoor furniture in the cityscape beautifies and makes urban environment more pleasant. Becker (2004) defines the characters of public art as "inspire awe, draw out deep emotions, and make us smile, engage young people and refresh our perspective". Fleming (2005) also defines that the public artworks are magnifying and providing enjoyment to public.

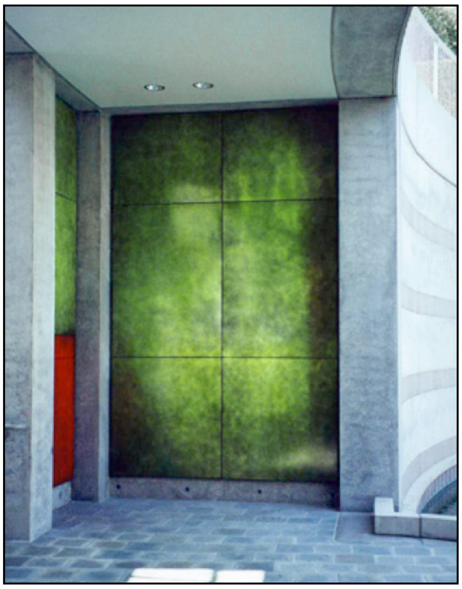

Fig.4.19: Vera Ronnen, The enamel niche by Vera Ronnen
(Source: http://www.ajwells.com)

Fig.4.19 and fig.4.20 show, enameled steel panels were created by enamel sculptor Vera Ronnen. Ronnen's work combines medieval and modern industrial enameling techniques to create unique large-scale architectural works. Enamel colors are applied by sieve to the pre-enameled surface in several layers, followed by multiple firings for the superimposed colors. Opaque and transparent colors fuse in the kiln over large, industrially enameled steel surfaces, resulting durable and graffiti resistant enameled structures to be used in public art.

Fig.4.20: Vera Ronnen, The enamel niche by Vera Ronnen
(Source: http://www.ajwells.com)

Fig.4.21: The Project of enamelled balls by Diarmuid Gavin at the 2004 Chelsea Flower Show
(Source: http://www.ajwells.com)

Fig. 4.21 shows brightly colored enameled balls integrated in the landscape created by Diarmuid Gavin at the 2004 Chelsea Flower show.

Gavin's interpretation creates permenant colored artefact in the nature, parallel to the expression of Jourdan in "Designing pleasurable products";

> "We have gained pleasure from the natural environment" such as colorful flowers, another source of pleasure has been the artefacts with which we have surrounded ourselves" (Jourdan, 2000).

4.4 Architectural Cladding

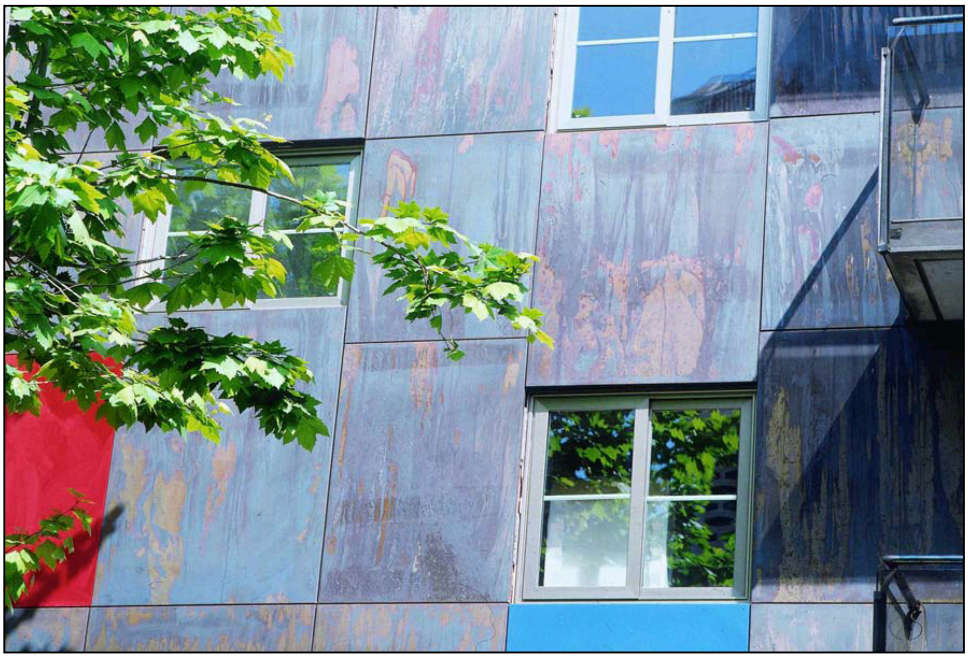

Fig.4.22: The Project of Casa de Veíns in Salou, Tarragona, Spain. Architect:Antoni Pinyol, enameled by URBART with INOXFOC®
(Source: www.urbart.net)

Brand explained the whole idea of architecture is permanence. In wider use, the term ‘architecture’ means ‘unchanging structure’. But in reality it is an illusion (Brand, 1994). Any external surface in an urban area allows visual changes due to the interactions of atmospheric pollutants, wind and rain (Simpson, 1970). The physical degradation or erosion of surfaces can cause changes in texture, as well as changes in shape or visual definition. The rate of this deterioration is dependent on the characteristics of the material (Simpson, 1970). Understanding materiality in respect to climate of surrounding makes it possible to design objects that become more beautiful as it ages. Weathering directly affects the surface as defined at The American Heritage Dictionary; “to expose the action of the elements, as for drying, seasoning, or coloring” and “to discolor, disintegrate, wear, or otherwise affect adversely by exposure”.

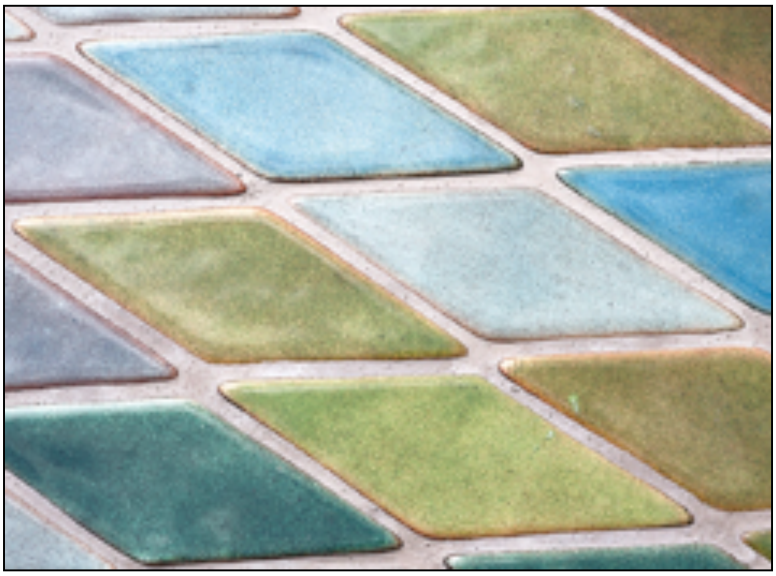

Fig.4.23: Enamel tiles
(Source: www.interiordesign.net/newproducts/8118-Kiln_Enamel_Architectural_Tiles.php?intref=sr)

Fig. 4.22 shows architectural enameled steel panels as façade of an apartment building. They are coloured and textured for the surface of buildings where a maintenance free color façade is required. These surfaces require minimum maintenance, and due to the durability, enameled panels can be replaced when a building is being renovated. The use of enameled steel for cladding buildings or for decoration, is aesthetically pleasing solution. On the other hand enameled panels are also used in laboratories and hospital environments where the hygiene properties are critical importance.

Enameled copper tiles shown in fig. 4.23 are used for exterior of the buildings. These examples show that enameled metal is an ideal solution for outdoor application that increases the durability of substrate material to direct UV exposure.

Fig.4.24: The unique art cladding. Architect:Lincoln Miles and artist Lisa Traxler, enamelled by A.J.Weels in 2010
(Source: http://www.ajwells.com)

A sample project in fig.4.24 is showing both functional and aesthetic enameled panels fabricated, fired and then installed using power magnets to seamlessly hold the cladding in place.

4.5 Enameled Kitchenware

Materials technology has been shaping the direction of modern kitchenware design, cast iron emerged in kitchens in the mid 19^{th} century and later aluminum had been developed in the late 19^{th} century but the most significant advance was the development of stainless steel in the 1930s. Production changed from crafts into industrial in all fields, metallic surfaces, special color effects, and reflective finishes have increasingly found their way and turned into a prestige object beside having functuality in kitchens (Baldwin, 2007).

For the purpose of abrasion resistance, impact resistance, room-temperature stain resistance, heat resistance, and cleanability, stainless steel and enameled steel have been used for the kitchen appliance market. Especially enameled steel is capable of withstanding the many stresses are subjected in cooking applications as explained by Clendinning;

> Technical innovations developed during the war, such as metal enameling, found new commercial applications. The widely used of enamel metal surfaces for stove construction were a design innovation of the early 1920s that replaced the old cast-iron models. Not only were enameled cooking stoves simpler to keep clean, their smooth surfaces appeared more sanitary (Clendinning, 2004).

A new design Smeg oven is shown in fig.4.25 that relates to the past as an example of enamel colored appliance coming from the history of Smeg.

Figure 4.25: New design enamel colored Smeg oven
(Source: www.smeguk.com)

Enamels used for self-cleaning oven cavities, stove grates, hot water tanks contain adherence-promoting oxides and they are extremely heat-resistant to operating temperatures of about 600°C.

Several tests performed in Ferro corporation, show how enamel compares to stainless steel. For the comparison tests, two porcelain enamels were run against 304 brushed stainless steel: A cover coat (Ferro PC168C on PL52 ground coat) that is typically used on cooktops; and an aluminum enamel (Ferro GL4317) that can be used on cookware (Baldwin, 2007). Foodstuff stain results (Table1) showed that enameled steel is used for cookware prevent any stain to the growth of bacteria and do not absorb odors by the absence of micro pores for any accumulation of dirt.

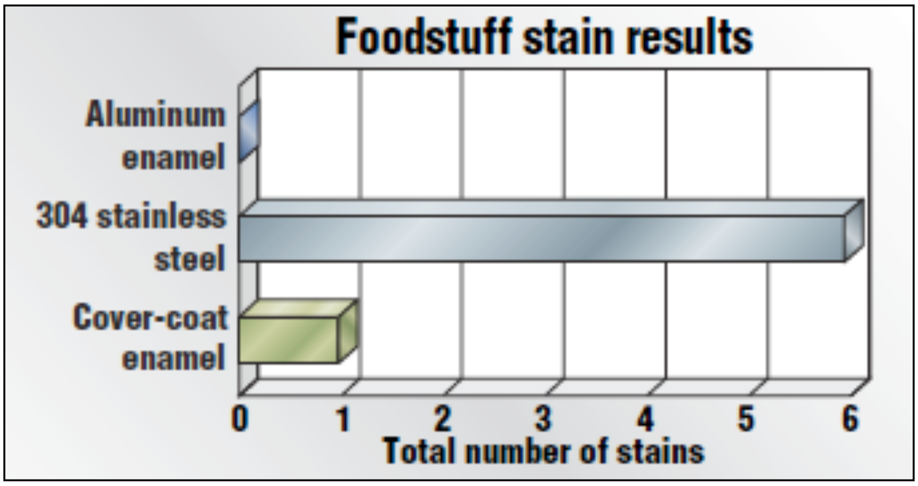

Table 1: Ferro comparison test of stain
(Source: www.machinedesign.com)

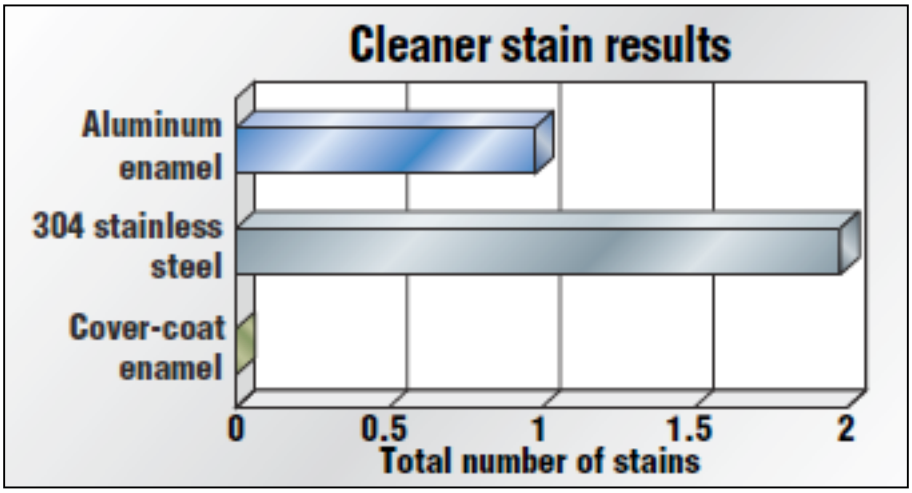

Table 2: Ferro comparison test of cleaner
(Source: www.machinedesign.com)

Highly resistant smooth surface to the abrasive and chemical cleaners is given in table 2. Surfaces stand up to acids, alkalis, water, solvents, oils and do not change physical or chemical properties or appearance.

The coating resists heat well enough to be used on exterior surfaces of cookware and as well on the surface of cooktops (fig.4.26), and do not discolor from heat (table 3).

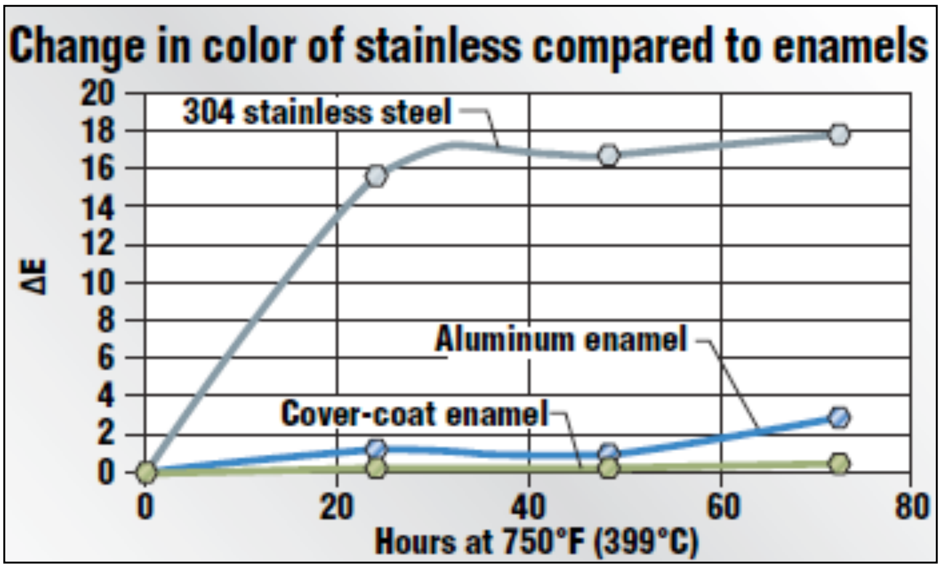

Table 3: Ferro comparison test of color resistance against heat
(Source: www.machinedesign.com)

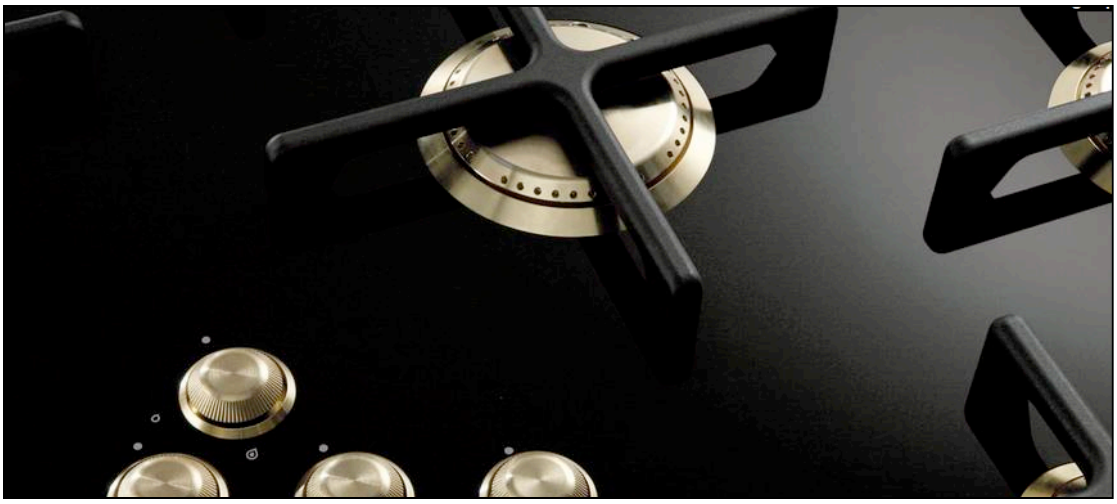

Figure 4.26: Heat resistant enamel coating on cooktops.
(Source: www.smeguk.com)

Fig.4.27: Enameled saucepan
(Source: www.fiveprime.com)

Performance benefits of enamels that are used in kitchen appliances and kitchen tools (an example is shown in fig. 4.27) are summarized in Table1.

Sanitary quality	Excellent barrier to odor & bacteria by hard & dense surface
Easy cleaning	Surface contamination easily removed by hardness & abrasion resistance
Scratch & abrasion resistance	More abrasion resistant than the hardest organic coatings
Chemical & corrosion resistance	Inorganic oxides provide impervious surface that is resistant to chemicals. Excellent corrosion resistance extend base metal life.
Fire resistance	Physical & chemical properties are not effected by heat.
Color stability	No change in color or gloss after 15 year exposure to weather.
Impact resistance	Enamel fractures due to the impact of base metal is permanently deformed.
Flexibility	Have good flexibility when applied to thin metal substrates.
Environment friendly	Application process requires no solvent.

Table 4: Summary of enamel properties

4.6 Enameled Sanitary Ware

Hygiene and sanitary properties of the enameled steel makes it possible to design wide range of bathtubs, wash-hand basins and sinks in a variety of shapes and sizes.

Fig.4.28: An enameled cast iron art bath by artist Mel Howse
(Source: http://www.ajwells.com)

In figure 4.28 an enameled cast iron created by glass artist Mel Howse, her work provides the diversify of new areas in surface construction and the development of design through its practical application.

In the world's biggest enamelling furnaces, Kaldewei uses glass-forming natural materials to produce special enamel for bathtubs (fig. 4.29) and shower trays (fig. 4.30) with a surface that is guaranteed to remain durable for at least 30 years (included in company's guarantee condition).

Fig.4.29: Steel enameled bath by Kaldewei
(Source:www.kaldewei.com)

According to the Environmental Product Declaration of Kaldewei GmbH & Co. KG (Declaration number[2] EPD-KAL-2009111-E):

> Kaldewei steel enamel baths and shower trays comply with DIN 4102, Part 1 “Fire behaviour of building materials and elements Class A”. The steel-glass composite is therefore neither combustible nor oxidising. The softening temperature of the enamel-steel composite is above 700°C.
>
> Kaldewei steel enamel baths and shower trays can be easily sorted out at the end of their service life. They are 100% recyclable without the need to separate the steel from the enamel. No environmental pollution is caused during the dismantling and separation.

[2] Steel enamel baths and shower trays, Institut Bauen und Umwelt, www.bau-umwelt.com

Fig.4.30: Steel enameled shower tray by Kaldewei
(Source: http://www.kaldewei.com/steel-enamel/material-competence)

4.7 Enameled Interior Surface

Vera Ronnen is an artist; her work combines medieval and modern industrial enameling techniques to create unique large-scale and site-specific architectural works. She applies the colours by sieve in several layers to a pre-enameled steel surface, which than undergoes multiple firings to create a vibrancy in blue-green. Color is the most alluring design element in her works while satisfiying the unique surface qualities.

Enameled interior elevator doors (fig. 4.31, fig.4.32) that Ronnen created enforce the possibility of collaborating art and architecture emerge as one pleasurable object. Jordan states the need of creating "pleasurable" objects have recently become very popular in the design via link between aesthetic and usability metrics (Jordan, 2002).

Fig.4.31: The unique art elevator doors / Lobby of Diener & Diener Architects
(Source: www.veraronnen.com)

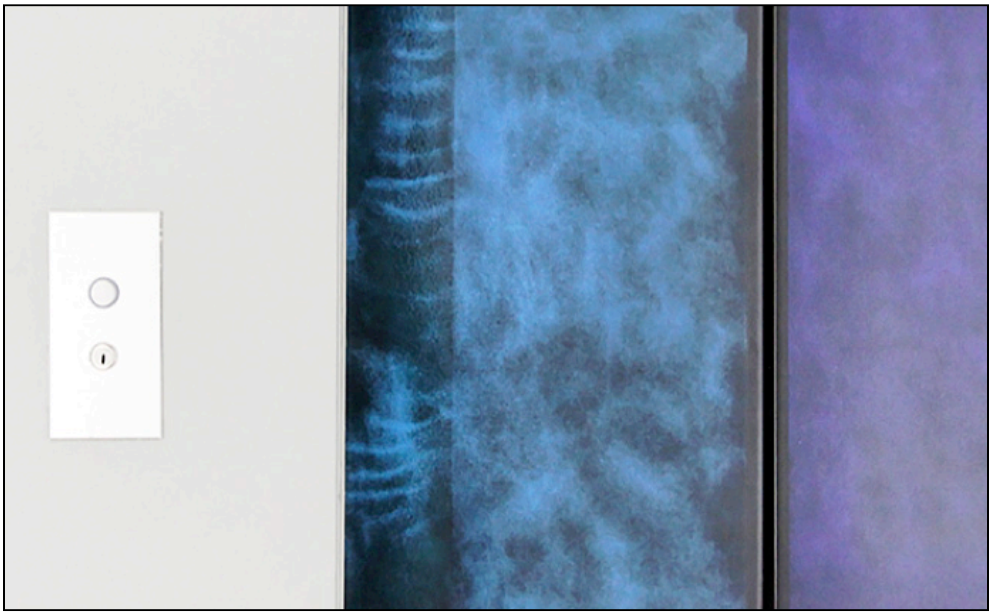

Fig.4.32: The unique art elevator doors / Lobby of Diener & Diener Architects
(Source: www.veraronnen.com)

Postrel express that there is a “rise of artistic consciousness” in product design; the art in designing products has become the expectations of the recent cultural and technological changes (Postrel, 2004).

Fig.4.33: 12 elevator doors in Boston / Architect: Hugh Stubbins
(Source: www.veraronnen.com)

As Dewey articulates, integration of emotions may be constructed by vibrancy of enamel colors in the ambience (fig. 4.33 and fig. 4.34) as aesthetic balance of the maker’s intent and the perceiver’s expectations that lives in experience (Dewey, 1980).

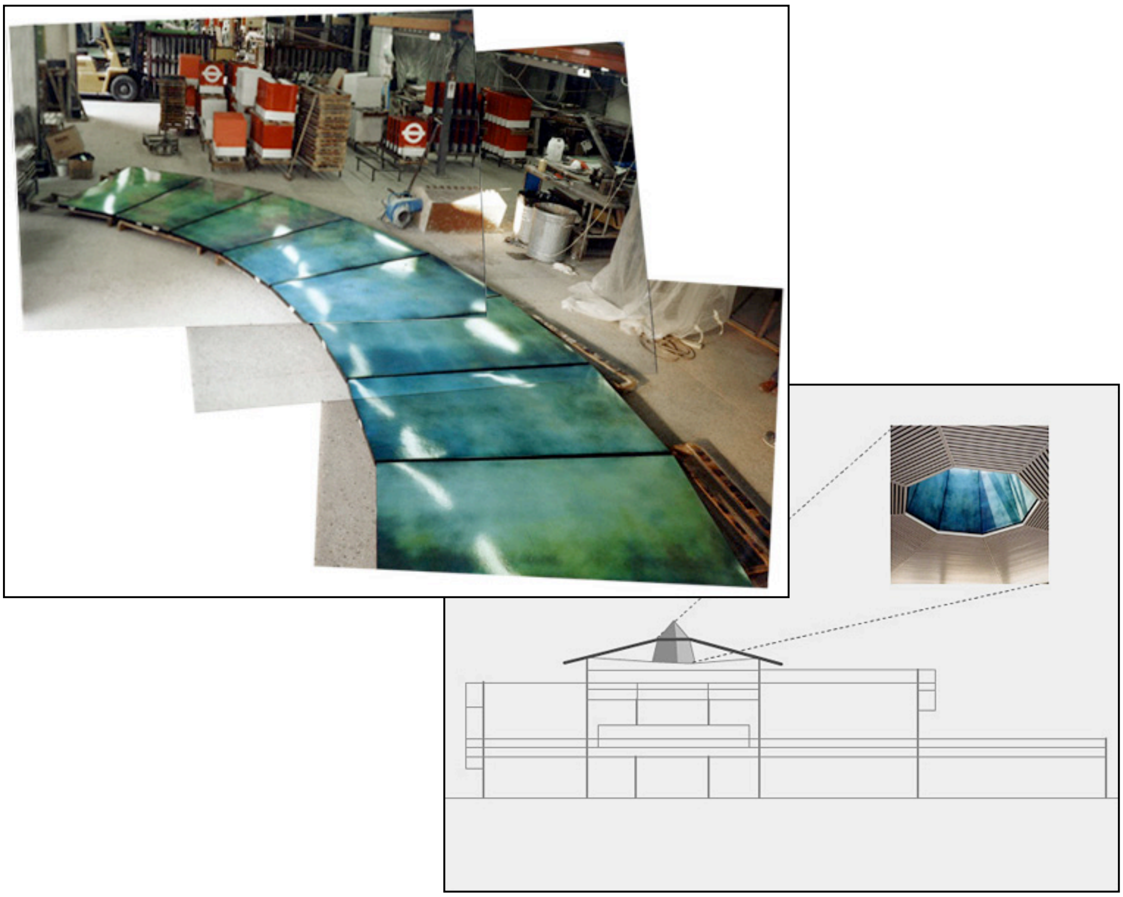

Fig.4.34: Skylight / Omer Hi-tech Industrial Park / Architect: Zarhy Architects
(Source: www.veraronnen.com)

4.8 Enameled Furniture

Jordan (2000) argues; 'Designing Pleasurable Products' looks both beyond usability, considering how products can be both ergonomic and a joy to own, the need for creating “pleasurable” human factors, suggesting a closer link between aesthetic and usability metrics. More than ever, designers and technologists are considering human factors in the product design process.

Consumers are now seen as key for the usability of products, figure 4.35 is an example of the products fits the desires of users.

Fig.4.35: Enameled table called "Jottable"
(Source: www.3rings,designerpages.com)

Writeable table uses one of the characteristics of enameled surface. Generally handwritten notes are forgotten on small papers, but the enameled table surface offers a place to write down the sudden ideas and diagram. The hygienic feature makes it ideal for daily usage and dirt is easly removed from the hard and abrasion resistant surface.

4.9 Enameled Surfaces in Industry

Enameled steel has important applications in industry, especially in the most corrosive atmospheres for chemical reactors, dryers, tanks and other plant storage systems in the chemical and food industries.

Fig.4.36: Enameled industrial lining at Pfaudler Balfour Plant.
(Source: http://www.iom3.org/content/vitreous-enamel-industrial)

Corrosion of glassy materials is a very complicated process influenced by several external and internal parameters. Chemical composition, internal stress and inhomogeneity of the glass are the main parameters determining behaviour of the material in corrosion environment (Siwulski, 2008).

The use of enameled steel makes them easier and cheaper to clean, improves resistance to fire and corrosion caused by combustion gases. Therefore enameled steel is an excellent material for the manufacture of flue linings (fig.4.36) and exhaust manifolds.

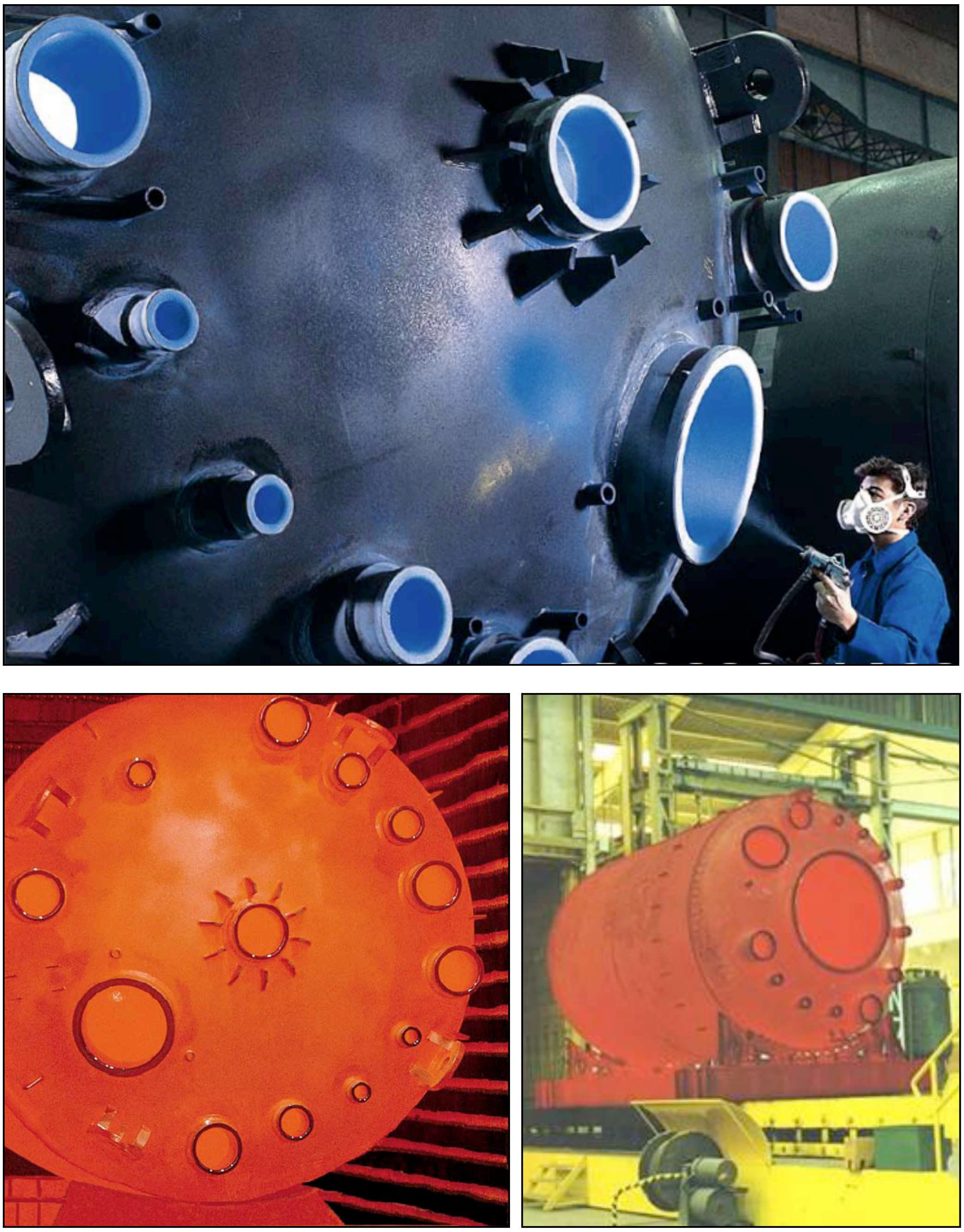

Fig.4.37: Enameled vessel at Dietrich Company.
(Source: www.ddpsinc.com/de-dietrich-expertise/3009-glass.html)

Enamel is sprayed like paint on the surfaces of vessel to be glass-lined, than fired several times at high temperatures in an electric furnace (fig.4.37).

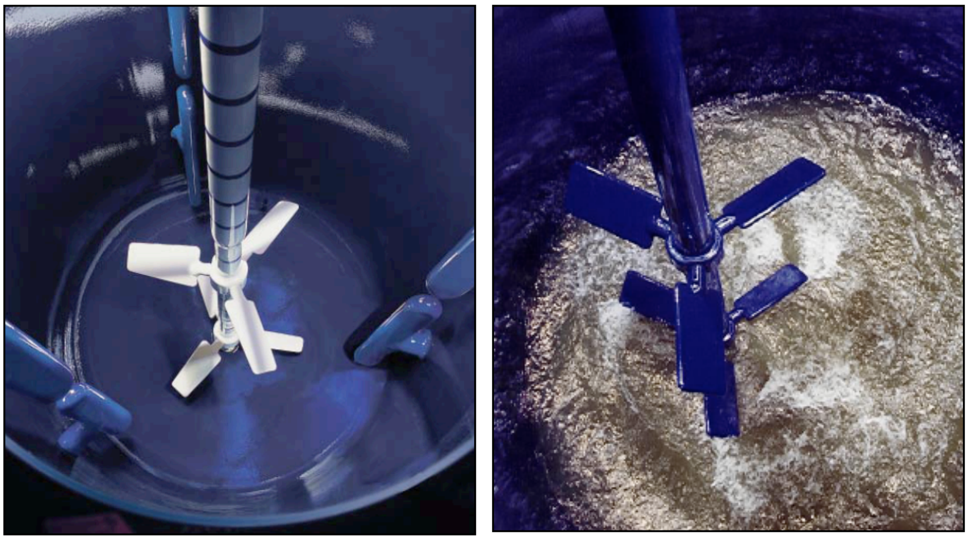

Fig.4.38: Enameled tank at Dietrich Company.
(Source: www.ddpsinc.com/de-dietrich-expertise/3009-glass.html)

Enamel coating is ideal solution for its hard glossy surface and resistance to corrosion and scratching in food containers (fig. 4.38).

Furthermore, because of its resistance to high temperatures and heat reflection properties, it is widely used in heat exchangers.

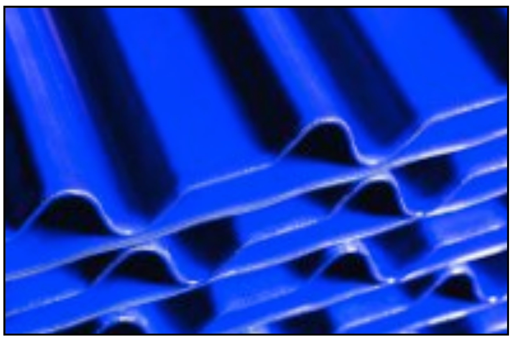

Fig.4.39: Enameled elements at Howden Company.
(Source: www.howden.com/en/Products/HeatExchangers/EnamelledElements)

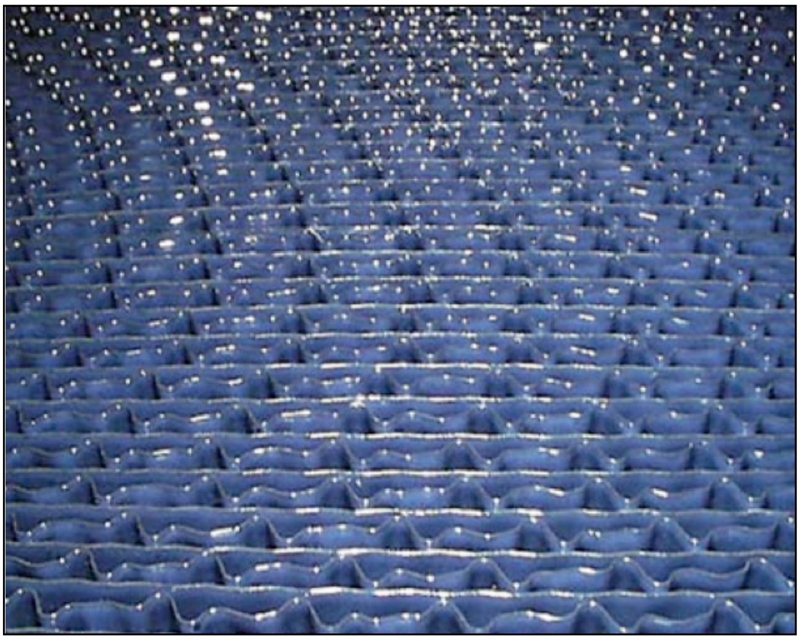

Fig.4.40: Enameled heat exchanger lamels.
(Source: www.ferrotechniek.com/downloads/Heatexchanger1.pdf)

During the operation of a heat exchanger there is an efficieny loss caused by erosion, corrosion and fouling on the lamels. Enameling processes produce the heat exchanger lamels with the optimum combination of corrosion protection and cleanability.

Since enameled elements are used in the lowest temperature of air preheaters, and in the even more aggressive environment found in gas-gas heaters, enamel coatings specifically developed to have low porosity, high acid resistance, good edge coverage with good compression and cleanability properties.

CHAPTER 5

FUTURE GLASS LIKE COATINGS

Today increasing metal production volume brings increasing energy and material consumption with it. New markets demand additional surface properties together with new quality aspects. To satisfy these demands, new materials and alternative production possibilities are under research.

The quality and properties of glass enamel coatings are predetermined to a large extent by the phase composition and structure of the coating itself, by the type of interaction between the metal substrate and the coating, and by the composition of the adhesive layer.

The technical and economic trends in conserving natural and energy resources are now beginning to be very important. Single coat enameling, which allows conserving raw materials and power by reducing the coats and number of firings, is one such promising trend. The use of single-layer coatings makes it possible to obtain a higher-quality surface on the articles, since the coating becomes more elastic and shock-resistant when the resulting coating thickness decreases (Yatsenko, 2007). One coat enamel combines the properties of the undercoat and surface layers, i.e., the protective and decorative properties (Yatsenko, 2002). One of the fundamental conditions for formation of a continuous, strong, defect-free enamel coating on metals, especially a single-coating, is the appropriate preparation of their surfaces before applying the enamel (Yatsenko, 2004).

Conventional corrosion protection coatings, based on hydrocarbon systems, form a thin layer between the substrates and the surroundings. **Organic** coatings contain epoxy and polyurethane resins as top and primer coatings; give protection and flexibility but on the other hand they are less resistance to abrasion and mechanical damage. The most important disadvantage they have is the degradation by aging under UV light, which is why they are not convenient for outdoor usage (Avcı, 2004).

Contrarily, **inorganic** coatings such as enamels have been preferred for chemical and mechanical durability for outdoor and extreme conditions. On the other hand, inorganic coatingsbased on silica are brittle and less resistant to mechanical impacts. Cracks in the coating can cause major damage for the coatings and the substrates. In the worst case the enamel can break and peel off from the substrate. Nanotechnology helps to eliminate the drawbacks of inorganic coatings by decreasing the grain size of additives in enamel to the nanometric level in order to increase the strength, fracture toughness, adhesion and stiffness of the composite structure.

Nanotechnology deals with understanding the behavior of materials at the nanometer scaleas well asthe manipulation and fabrication of materials to obtain nanostructured objects (Gates, 2005). Nanotechnology combines organic and silica based inorganic coatings, that are called hybrid coatings by using sol-gel preparation method.

Typically, sol-gel **hybrid** coatings are nanoscale to several milimeters thick transparent or pigmented layers reminding varnish or lacquer. By combining these two systems, the organic content provides good adhesion and sufficient flexibility, which enables crack free surfaces, and the inorganic silica nanoparticles give corrosion protection and hardness to the metals.

Fig. 5.1: The iridescent nacre inside a Nautilus shell
(Source: www.websters-online-dictionary.org/definitions/Nacre)

Fig. 5.1 shows an example of nanostructured inorganic material and organic "glue" bond together. This strong and resilient, biologically formed organic-inorganic composite material is called “nacre” or “mother of pearl”. Nacre combines the hardness of crystalline minerals like aragonite (calcium carbonate - $CaCO_3$) with the flexibility of organic substances such as elastic biopolymers, making them one of the most stable materials in nature.

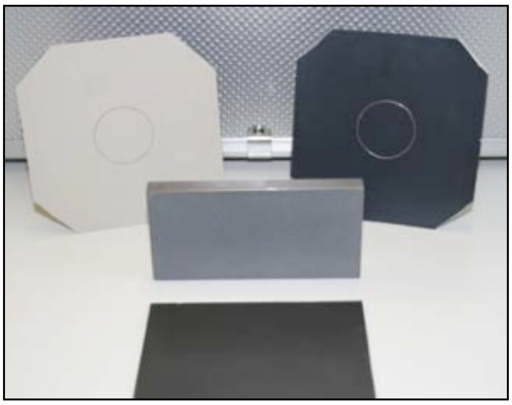

Fig. 5.2: Glass coated metal substrates
(Source: www.inm-gmbh.de /wp-content/uploads/2011/04/glassceramic_en.pdf)

Fig. 5.2 shows an example of 2–5 µm nanostructured inorganic glass-ceramic coating which combines wear protection and corrosion protection at high temperatures (up to 900 °C) on steel, metal and alloys. It was produced by nano composite sol-gel system in dip chambers and spray cabins. Scratch and wear protection of metal, as a result of inorganic coating, eliminates hardening and the need for chromium coating.

To parallel the definition of hybrid coating, Bakul (2004) has depicted the combination of organic and silica based inorganic coating as organo-silica coatings. Bakul states that due to the presence of an organic component, the organo silica coatings dry evenly and are more uniform and crack-free as compared to pure silica coatings. These results reveal that organo-silica coatings present an alternative technology, which may be easily adapted for commercial and mass production of anticorrosion coatings for different metallic surfaces.

Further studies are in progress to optimize the performance of these coatings (Bakul, 2004). Investigations show that introducing nano-silica into the composition of enamel increases the lifetime of glassy layer.

Corrosion tests with coated enamels were performed and the results show that crack and macro pore-free SiO_2 coatings significantly improve the chemical resistance of all the coated substrates against acidic environments, independent of the compositions of the enamels (Krzyzak, Frischat, Hellmold, 2007).

Fig. 5.3 shows SiO_2 coated stainless steel for easy cleaning purpose in order to reduce the requirements for cleaning agents for environmental protection.

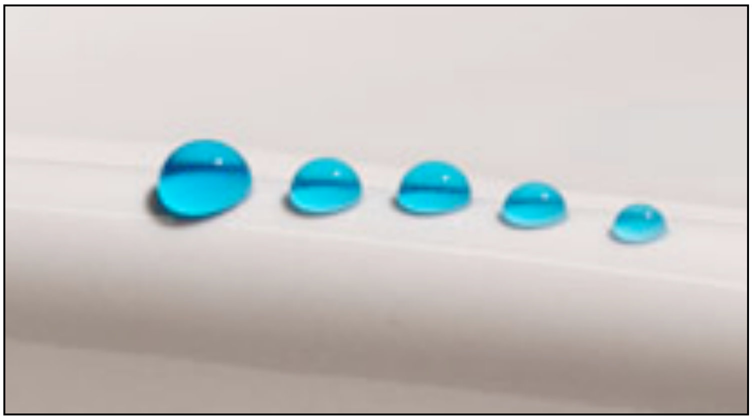

Fig. 5.3: SiO_2 coated stainless steel
(Source: www.nanocare-ag.com/mediathek)

Fürbert (2002) explains that with the usage of glass-forming oxides, nanostructured glass-like coating is developed in a way similar to enamel coating. That is why, it is called nano-enamel, which is the result of investigations aimed to get purely inorganic coatings. The investigations show that synthesis of enamel coating is possible by sol-gel technology (Chepik, Mashenko, Troshina, 2006). The sol-gel process provides a new approach for the preparation of glasses and ceramics with many advantages over conventional methods (Rosa-Fox, Pinero, & Esquivias, 2003).

Sol-gel method is ideal for the coating of metal applied at room temperature and offers a low-cost method (Romano, Gandra, Da Silva, 2000). Further, the sol-gel method is an environmentally friendly technique of surface protection and it showed the potential for the replacement of toxic pretreatments used for corrosion resistance of metals such as Cr^{4+} which has a carcinogenic nature of (Wang, Bierwagen, 2009).

Fig. 5.4: Nano-glass coated cooking plate for gas burners
(Source: www.inm-gmbh.de)

Fig. 5.4 and fig. 5.5 show the examples of glass-like coating which combines wear protection, oxidation and corrosion protection at high temperatures (up to 600 °C) on steel, metals and alloys. Synthesis of thin glass-like coatings on metals with tarnish and corrosion-protection at high temperatures, scratch and wear resistance, flexibility, and the ability to be applied by common coating techniques gives additional opportunities to the replacement of hardening and chromium coating.

Particularly, sol-gel process is very useful for thin film deposition because of the capability to coat materials of various shapes and large area, to control the composition easily for obtaining solutions of homogeneity and controlled concentration without using expensive equipment (Nishio, & Tsuchiya, 2004).

Fig. 5.5: Nano-glass coated manifolds
(Source: www.inm-gmbh.de)

Fig. 5.6: Half-coated aircraft model
(Source: www.inm-gmbh.de/wp-content/uploads/2009/03/INM_Corrosion-protection-through-Chemical-Nanotechnology_0111.pdf)

Fig. 5.6 shows half-coated aircraft model of zinc die- casting after corrosion test. Chromate-free, transparent corrosion protection coating consists of organic-inorganic hybrid materials with embedded metal-oxide nanoparticles (TiO_2, ZrO_2, CeO_2, SiO_2 etc.) and the coating is synthesised through sol-gel process. The surface provides scratch and abrasion resistance, hydrophilicity, hydrophobicity, UV protection, and photocatalysis. Transparency enables to show the metallic surface and low coating thickness enables reduced material consumption.

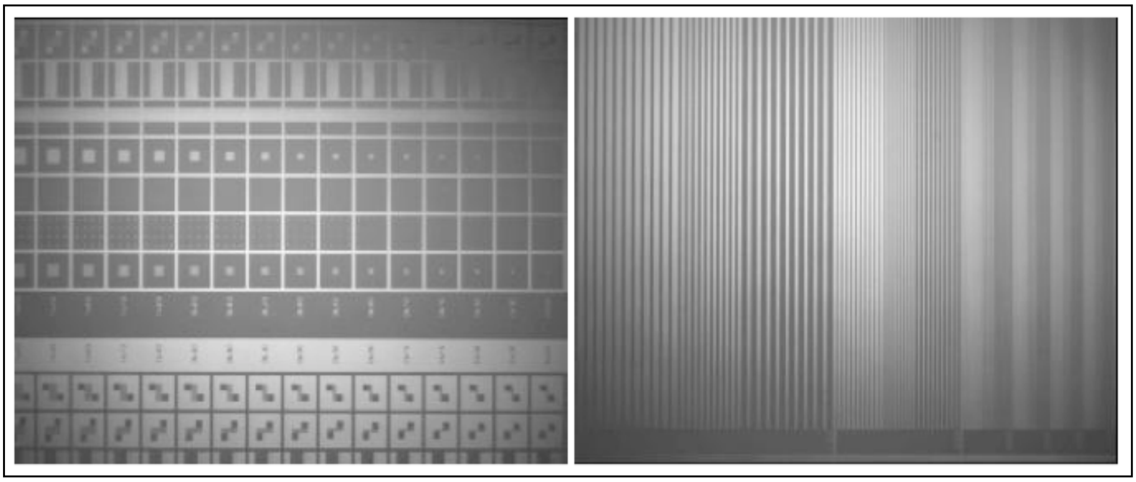

Fig. 5.7: Micrographs of various patterns generated by photolithography
(Source: www.inm-gmbh.de/wp-content/uploads/2009/03/ INM_Photopatternable-Nanomer-coatings_0111.pdf)

Fig. 5.7 shows the generation of patterns (up to 80 μm height) by photolithography with an adequate photo mask on optically transparent coatings based on organic-inorganic nano composites on metals. Transparent layer ensures optical appearance for different designs on visible surfaces in architecture and public areas.

Fig.5.8: Pigmented glass-like coatings
(Source: www.e-p-g.de/Links/EPG-17-Flyer.pdf)

Fig. 5.8 shows samples of Nanoseal pigmented glass like coatings on metals with high abrasion resistance (500 cycles Scotch Britt sponge without any scratch) and high temperature tarnish protection (>1000 h at 400 °C). Nanoscale coatings are much more tougher than classical enamel. In opposition to enamels, they are moldable and bendable, making them convenient to be used for complex shaped parts as furniture, containers, tubing, etc.

Variety of colors and ensures the attractiveness for aesthetics therefore colored nano coatings have increasing interest for industrial applications. Minimized coating thickness (4 – 8 μm) allows low material consumption and low cost. For the industrial applications, especially for the large surface areas, when the glassy appearance is compared with original glass, the shiny appearance is not equivalent as glass, as seen in the figure 5.9. Figure 5.9 shows kitchen furniture produced by layered glass, which comprises two plates of glass bonded together with a thin layer of plastic material. Impact strength is very high and, if struck by a foreign body, breakage is localised at the point of impact to avoid the risk that the structure may collapse.

Fig.5.9: Layer glass kitchen furniture
(Source: www.lago.it/36e8cucina-qualita.html?&L=1)

For the future studies in industrial application, further development is necessary to reach the perfect glassy surface together with base metal's durability.

CONCLUSION

In this study it has been attempted to emphasize that material properties of surface coatings at long time usage have very important role for extreme environmental condition.

Applications of enamel as glass like coating are analyzed and advantages are explained. Technical properties of enamel are investigated by the result of industrial trials and scientific researches.

		Corrosion Resistant	High-temperature stability	Scratch and abrasion resistance	Impact Resistance	Resistance to changed in temperature	Chemical resistance	Environment friendly	Resistance to cleaning products	Color stability	Hygiene and ease of cleaning	Luminosity	Ease with which graffiti can be cleaned	Fire resistance	Longevity
Art & Craft	Jewelry	•						•		•		•			•
	Watch	•						•		•		•			•
	Art object	•						•		•		•			•
Exterior Architecture	Exterior wall cladding	•		•	•		•	•		•			•	•	•
	Signage	•		•	•		•	•		•			•	•	•
	Mural	•		•	•		•	•		•			•	•	•
Domestic Appliances	Kitchenware	•	•	•	•	•	•	•	•	•	•	•		•	•
	Stoves	•	•	•	•	•	•	•	•	•	•			•	•
Interior Architecture	Elevator doors	•		•	•		•	•	•	•					•
	Bathtubs	•		•	•		•	•	•	•	•				•
	Furniture	•		•	•		•	•	•	•	•				•
Industry	Water heaters	•	•		•	•	•	•							•
	Heat Exchangers	•	•		•	•	•	•							•

Table 5: Summary of enamel applications by properties

At the end of thesis, nano structured glass like coatings compared with industrial enamel. Results show that nanostructured glass like coatings give best performance to the metal surface as well as supplying aesthetic demands of applied markets. Industry and architecture have been already applying enamel and glass like coatings for desired metal surfaces. However, enamel and glass like coatings do not have comman usage in industrial design objects.

Nanoscale glass like coatings will enlarge creativeness of designers, and will simplify the coating applications to the surface in terms of applied temperature and surface thickness.

As a result, my study suggests that enamel and nanostructured glass like coatings should more be recognized for industrial design and architecture where glassy appearance is demanded.

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