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DEVELOPMENT OF HIGH REFLECTANCE GLAZE

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **"Development Of High Reflectance Glaze".** I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABBREVIATIONS

EDX	-	Energy Dispersive X-ray Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscope
ICDD	-	Internasional Centre for Diffraction Data
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Fluorescence
CTE	-	Coefficient Thermal Expansion
OM	-	Optical Microscopy
UV-Vis	-	Ultraviolet-Visible

LIST OF SYMBOLS

%	-	Percentage
wt%	-	Weight percent
Ǻ	-	Armstrong
℃	-	Celsius
T	-	Temperature
μ	-	Micron
θ	-	Angle
λ	-	CuKα radiation

PENGHASILAN LICAU PANTULAN TINGGI

ABSTRAK

Jubin seramik dengan fungsi penyejukan dipercayai menjadi salah satu penyelesaian yang mampu untuk mengurangkan penggunaan tenaga elektrik dalam bangunan untuk penyejukan. Banyak pigmen telah dikaji sebagai bahan penyejuk dan di antara mereka, titanium dioksida (TiO_2) menunjukkan sifat yang dimahukan. Oleh itu, TiO_2 telah dipilih dalam kajian ini untuk membangunkan licau pantulan tinggi untuk jubin dengan fungsi penyejukan. Saiz partikel yang berbeza TiO_2 (0.9μm, 1.2μm dan 1.4μm) telah ditambah ke dalam pelbagai jenis licau komersial; putih dan vetrosa yang dibekalkan oleh Guocera Sdn. Bhd. Kedua-dua licau disalut pada jubin menggunakan kaedah celupan selama 5 saat. Kemudian, apabila jubin yang disalut licau putih dibakar pada suhu 1130 ° C selama 15 minit manakala jubin yang disalut licau vetrosa dibakar pada suhu 850 ° C selama 15 minit. Sampel kemudiannya dicirikan menggunakan Pembelauan Sinar-X (XRD), Mikroskop Imbasan Elektron (SEM), pekali pengembangan haba (CTE), pemerhatian fizikal dan analisis UV-Vis. Analisis SEM menunjukkan taburan saiz partikel TiO_2 yang lebih halus tersebar lebih seragam membawa kepada permukaan licau menjadi lebih sekata berbanding dengan saiz partikel yang lebih besar. Oleh itu, dapat meningkatkan penampilan legap licau. Peningkatan kelegapan licau dapat meningkatkan pantulan licau. UV-Vis analisis menunjukkan dengan penambahan TiO_2 boleh meningkatkan pantulan sampel. TiO_2 dengan saiz partikel yang lebih kecil (0.91μm) ditambah dalam licau putih memberikan pantulan yang tinggi iaitu 91% dengan penampilan legap licau yang baik. Ini membuktikan bahawa dengan mengubah sifat-sifat serbuk TiO_2 dapat meningkatkan sifat-sifat pantulannya.

DEVELOPMENT OF HIGH REFLECTANCE GLAZE

ABSTRACT

Ceramic tiles with cooling function were believed to be one of sustainable solution for reducing building electrical energy consumption for cooling. Many pigments have been studied as cooling materials and among them, titanium dioxide (TiO_2) showed promising properties. Therefore, TiO_2 was selected in this study to develop high reflectance glaze for cooling tile application. Different particle size of TiO_2 (0.9µm, 1.2µm and 1.4µm)were added in different types of commercial glazes; white and vetrosa supplied by Guocera Sdn. Bhd. Glazing were perform using dipping method for 5 seconds. Then, the dried glaze tile using white glaze was fired at temperature 1130°C for 15 minutes while dried glaze tile using vetrosa glaze was fired at temperature 850°C for 15 minutes. Samples were then characterized using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), the coefficient of thermal expansion (CTE), physical observation and UV-Vis analysis. SEM analysis show the distribution of finer particle size of TiO_2 dispersed more uniformly lead to smoother glaze surfaces compared to bigger particle size added. Thus, increase the opaque appearance of the glazes. As the opacity of glaze increase, the reflection is also increase. UV-Vis analysis show with addition of TiO_2 can increase the reflectance of samples. TiO_2 with smaller particle size (0.91μ) in white glaze gave high reflectance which is 91% with good opaque appearance. This proves that by altering the properties of TiO_2 powder will improve its reflectance properties.

CHAPTER 1

INTRODUCTION

1.1 Development of Cooling Tiles

Ceramic industry is constantly seeking to the market amplification by perfecting the quality of the products and increases the variety of functions of products. One of the ceramic product that have been develop is ceramic tiles that widely used possessing technical and aesthetic functions (Effting et al. 2007). Ceramic tiles are heterogeneous materials, consisting mainly of natural raw materials with wide range in composition. The properties of ceramic tile products consist of low water absorption and high mechanical strength. Ceramic tiles are classified by the type of clay, mineral composition and manufacturing method. The combination of different clays with different physical properties gives variation tile products depending on the application such as floor tile, wall tile and porcelain tile (Postell, 2011).

Glazed ceramic tiles are the most common building material for floor and wall coverings. Glazed tiles were produced from frits, which mixed with water and organic additives to yield glaze slips. The glaze were applied on the surface of green tiles and subjected to a firing process (Casasola et al. 2012). Functions of glaze applied onto the exposed tile surface which is to make it waterproof, tougher and more resistant to dirt, as well as to improve its esthetic aspect. Glaze composition was extremely variable and complex. It consist mainly of frits and other additional components in variable percentages such as kaolin, ball-clay, bentonite, opacifiers, pigments, or additives to control the glaze rheology during application (Ferrari et al. 2013).

Over the past years, there are increases of demand in ceramic tile industry that inspire many manufacturers to produce ceramic tiles that have variety of functions. One of the manufacture in Malaysia's Guocera Tile Industry Sdn. Bhd., that known as one of Malaysia's largest manufacturers and exporter of tiles. There are three types of tiles were produced in Guocera Tile Industry Sdn. Bhd.; wall tiles, floor tiles and porcelain tiles. Every type of tile has different body formulation that gives different properties depending on the applications. The properties of the ceramic tile resulted from its low porosity due to the processing conditions which were longer milling time of raw materials, high force compaction and sintering temperature (Acchar, et al 2015). Wall tiles were widely used in architecture for covering internal walls and decorative work especially for kitchen and bathroom due to water resistance, wear resistance and provide good image of building. The wall tiles body made of SiO_2, Al_2O_3, Fe_2O_3, Na_2O, CaO, K_2O, MgO, MnO, TiO_2, P_2O_5 and fluxing material (Richerson, 2006).

During the past few years, the urban areas either in Malaysia or other country were experienced rapid population growth. Forests and open spaces covered with low natural vegetation are being replaced by residential buildings. As a result, solar energy is was absorbed by concrete and paved surfaces, causing the surface temperature of urban structures to become several degrees higher than ambient air temperatures (Synnefa et al. 2007). The increased urban temperatures exacerbate the consumption of energy for cooling purposes, increases the peak electricity demand, increase the urban footprint and cause human discomfort and health problems (Santamouris et al. 2011).

Therefore, several techniques have been proposed to preserve lower exterior surface temperatures of buildings and one of it was development of cooling tile. This situation of increasing temperature within residential area has encouraged many tile manufacturers to produce tile with cooling function. The main properties of ceramic tiles with a cooling function consist of high solar reflectance around 0.80– 0.90. These tiles are able to absorb less radiation, reducing the envelope overheating and consequently the building cooling load. Given these features, cooling tile techniques have already been acknowledged as valid ways to reducing peak electricity demand and energy requirements for cooling in buildings (Pisello et al. 2014).

Cooling tiles products were made by incorporated highly reflective cool materials (normally pigments) into ceramic tiles. These pigments such as titanium dioxide (TiO_2) rutile, zinc oxide, antimony oxide, zirconium oxide, zirconium silicate have been used as white coatings to create cooling tiles in order to decrease the temperature in the interior of the house (Jovaní et al. 2016). Cool materials that mainly refer to inorganic pigments which have high near-infrared (NIR) solar reflectance or low NIR solar absorbance have been widely used as a coating in manufacturing of cooling tiles. It was considered as one of the most effective techniques to reduce energy requirements for cooling (Hedayati et al. 2015).

Many pigments have been studied as cooling materials and among them, titanium dioxide (TiO_2) rutile showed promising properties. (TiO_2) were found to be NIR-reflecting colorants, showing both strong NIR backscattering and weak NIR absorption in a binder of refractive index 1.5. In addition, rutile phase of (TiO_2) has the highest refractive index in the visible light which is about 2.7 and (TiO_2) scattering power is about 1.9 and therefore known to be the best visible scattering pigments. If used to improve the NIR reflectance of cool non-white coatings, it will modify the reflectance curve and the visual appearance of the coatings (Song et al. 2014).

1.2 Problem Statement

Rapid population of human beings resulting in rapidly increasing energy consumption, particularly by air conditioners, which are widely used in big buildings and residential area. Air-conditioning energy saving can be achieved by reducing the temperature of the building envelope, which in turn reduces the heat penetrating into the building. This situation cause human discomfort, health problems and also prompted higher energy consumption for cooling purpose (Thongkanluang et al. 2011).

The uses of cooling tile believed to be able substantially lower the surface temperature, thus provide comfort and cost reduction. By using a cooling tile solutions with high capacity to reflect incident solar radiation, can provide an effective answer to increasing temperature in buildings and residential areas. In 2016, Ferrari et al. investigate the development of solar reflective materials which can be integrated on tiles. The addition of pigment into ceramic glaze was believed to be able to enhance the solar reflectance of the glaze. Therefore, an attempt was made to develop new glazed for cooling tile application by using pigments for external tile systems and analyse their behaviour once embedded in ceramic glazes with different finishing and subjected to traditional ceramics heating treatment. However, the production of ceramic tiles still require detailed analysis in developing a cool glaze that have high reflectance.

In previous studies, Libbra et al. (2011) reported on the development of cool coloured glaze tile coverings by using the titanium dioxide (TiO_2) as the basecoat in order to simplify the application of glaze. They were concluded that titanium dioxide (TiO_2) white pigment used, able to strongly reflect solar radiation. However, this pigment is also a weak absorber and non-reflected radiation is thus transmitted towards the substrate. As a result, many layers need to be sprayed to achieve an adequate thickness of the basecoat and a satisfactory solar reflectance.

In other study by Casasola et al. (2012), state that the most suitable candidate for zircon ($ZrSiO_4$) replacement is titanium dioxide (TiO_2) which can crystallise in different polymorphs. Among phases of TiO_2, rutile found as the only stable phase, while the two metastable phases; anatase and brookite were irreversibly transform to rutile on heating. The high refractive indices for rutile (2.76) and anatase (2.52) make titania polymorphs excellent candidates to zircon replacement in glazes. TiO_2 is a bright white powder with high opacity and excellent covering power, chemical and physical resistance. These excellent optical characteristics, coupled with its high refractive index, make it a valuable pigment and opacifier into glaze application.

Therefore, the aim of this study was to observe and determined the effectiveness of titanium dioxide (TiO_2) pigment as cooling materials when embedded in ceramic glaze. In addition, it was believe that the particle size of the pigment used significantly influence the refractive index. Hence, this study was focusing on the influence of different particle size of TiO_2 added into ceramic glaze towards the effectiveness as cool coatings. The influences of different particle size of TiO_2 were also observed on the different types of glazes application which is as single layer and double layer glaze coating. TiO_2 pigment has been selected in this study since it has a high refractive index, which means that it was able to scatter and reflect light strongly. This study was collaboration between School of Materials and Mineral Resource Engineering, Universiti Sains Malaysia and Ceramic Research Company, Guocera Tile Industry Sdn. Bhd. to investigate further developing a cool glaze that have high reflectance for cooling tile application.

1.3 Research Objectives

The objectives of this research are as follows:

a) To investigate the influence of different particle size of titanium dioxide (TiO_2) in the preparation of cooling tile.
b) To determine the effect of titanium dioxide (TiO_2) as cooling materials on different type of glaze.

1.4 Scope of Research

In this research, mixture of raw material for wall tile powder was obtained from Goucera Tile Industry Sdn. Bhd. Industry. The mixture raw materials were in powder form and pressed into a button shape. Then, preparation of glaze with addition of TiO_2 was done to enhance the reflectance of the glaze. The ceramic glazes used; white glaze and vetrosa glaze were the commercial glazes obtained from Goucera Tile Industry Sdn. Bhd. Industry.

Then, different particle size of TiO_2 powder (0.9 µm, 1.2µm and 1.4 µm) was added into the white glaze. Then prepared glaze is applied on green body of wall tile. Sample was glazed using dipping method for 5 seconds. Then, the similar steps were repeated for preparation of glaze using different glaze finishing which is vetrosa glaze. The prepared glaze is applied on glazed tile as second layer coating glaze .The dried glaze tile using white glaze was fired at temperature 1130°C for 15 minutes while dried glaze tile using vetrosa glaze was fired at temperature 850°C for 15 minutes.

The fired glazed samples were characterized to investigate the effectiveness of the sample as cooling tile. The characterizations methods used were UV-Vis analysis, Coefficient of Thermal Expansion (CTE) test. While physical observation of glaze was done such as colour of glaze and whiteness analysis. Optical microscopy (OM) was also used to measure thickness of glaze. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX) were used to examine the phases, microstructure and elements that present in the glazed sample. The overall process in preparation of cooling tile was presented in Figure 1.1.

Raw materials

Weighing

Powder pressing (Button shape sample)

Drying

Glazing

White glaze: applied on green body of wall tile
Vetrosa glaze: applied on the fired glazed tile as second layer glaze

Firing
White glaze: 1130°C, 15 minutes
Vetrosa glaze: 850°C, 15 minutes

Characterizations

- X-Ray Diffraction (XRD) Analysis
- Scanning Electron Microscopy (SEM) Analysis
- Energy Dispersive X-Ray (EDX) Analysis
- Physical Analysis
- Coefficient Thermal Expansion (CTE)
- Optical Microscopy (OM) Analysis
- UV-Visible (UV-Vis) Analysis

Figure 1.1: Flowchart of overall process in preparation of glazed tile

CHAPTER 2

LITERATURE REVIEW

2.1 Ceramics

Ceramics are known as solid compounds that are most frequently oxides, nitrides, and carbides. The compound is formed by the application of heat, and sometimes heat and pressure, comprising at least two elements provided one of them is a non-metal or a non-metallic elemental solid (Michel Barsoum, 2003). The word “ceramic” is come from the Greek word keramikos, which means roughly “burnt stuff”. Also it can be defined as the art and science of making and using solid articles formed by the action of heat on earthy raw materials to achieve desirable properties (Richerson, 2006).

The time-temperature transformation of the constituent mineral into mixture of new minerals and glassy phases is induced during firing of ceramic bodies. Therefore, characteristic properties of ceramic product are relatively stiff and strong that is comparable to those of the metals in term of mechanical behaviour. Ceramics are typically very hard, but in the other hand, they are extremely brittle and are highly susceptible to fracture. Ceramics may be transparent, translucent, or opaque, and some of the oxide ceramics exhibit magnetic behaviour (William, 2007).

Ceramics have been produced for centuries and recent attempts have been made to classify into two parts which are traditional and advanced ceramic. The traditional ceramics have a close relationship with those materials that develop at earliest civilizations. The examples of traditional ceramic product are pottery, structural clay products, clay-based refractories, cements, concretes and glasses (Rahaman, 2005). Through traditional ceramics, discovery of old science and technology, particularly pottery, has been of interest in archaeology and history as well as in modern ceramics due to development of characterization methods and various applications (Kim & Kim 2002).

Traditional ceramic raw materials consist of raw material of distinctive characteristics. Raw material such as clay with main function is to provide plasticity to the mass and green resistance to the body. The main flux materials used like feldspar, talc and pyrophyllite, whose main role is to produce a liquid phase during sintering. While quartz is undoubtedly the most common used as inert materials, due to its immense availability Therefore, by careful selection of materials, desired properties are acquired for the final output (Acchar, 2015).

Whereas advanced ceramics were developed from chemical synthetic routes or from naturally occurring material that have been highly refined. The purity of ceramic powder is very important in advanced ceramics industry compare to traditional ceramics (Segal, 1991). Even though traditional ceramics still represent a major part of the ceramic industry, the interest more was focusing on development of advanced ceramics. These advanced ceramics are normally traditional ceramic that properties have been enhanced and newly developed for high performance. There are several examples of advanced ceramics application such as electrical, magnetic, electronic and optical application (Rahaman, 2005).

The examples of modern ceramic materials were silicon carbide and tungsten carbide. Both are valued for their abrasion resistance and hence find use in applications such as the wear plates of crushing equipment in mining operations. Advanced ceramics were also used in the medical applications that have high strength, such as alumina for artificial hip joint, rejuvenation of bone and carbon surgical implants (Segal, 1991).

2.2 Ceramic Tiles

Ceramic tiles are thin slabs made from clays and other inorganic materials, generally used as coverings for floors and walls after fired at high temperature. There are several types of ceramic tiles available on the markets which were shaped through dust pressing or extrusion. For example, ceramic tile with porous, compact or vitrified bodies, with white (whitish) or colour (reddish) bodies, unglazed or glazed (Stone et al., 2000). The manufacturing of ceramic tiles using dust pressing is developed in the middle of the 19th century. Dust pressing is a process that compresses the nearly dry clay (5-7% humidity) together with the rest of the tile components. Sufficient pressure is applied to compact the powder into the desired tile shape depending on application of ceramic tile (Casasola et al. 2012).

Excellent technical properties of ceramic tiles are achieved through careful control of the entire ceramic process, which begin with the careful selection of raw materials and final inspection for packaging and shipping of the product. Therefore, precise knowledge of the properties is essential for the consumer to achieve the desired and anticipated value of the tile. This is because a lot of tiles are installed in the area, which contain water. Ceramic tiles are porous materials that can absorb the moisture and unwanted organism. Therefore the absorption of moisture is one of the important properties because in wet-area application which can involve health and safety issues (Byrne, 2008).

Other important property of ceramic tile was chemical resistance which is capability of the tile to against the chemical and not effected with the chemical during services. While, abrasion resistance is the ability of surface of tile to resist to the wear caused by human’s foot or equipment. As for thermal shock resistance is the ability of ceramic tile to thermal shock created by severe temperature changes might be found near a fireplace or stove surround. Mechanical properties for ceramic tile have good compressive strength which is ten times more than the tensile strength. Therefore, ceramic has a good structural material under compression stress but not under tensile stress, such as under flexure (Byrne, 2008).

2.2.1 Type of ceramic tiles

Ceramic tiles can be classified by the raw material; type of clay, mineral composition and by their method of manufacturing such as glazed and non-glazed tiles, pressed and extruded tiles. However one cannot decipher quality variations based on what the products are called such as ceramic, quarry, paver, porcelain and terra-cotta, because these are ambiguous marketing that can describe tiles made of a combination of different clays with different physical properties. Ceramic tile also been sorted according to the different in technical characteristics that are depending on application, could be wall lining or floor covering, interior or outdoor usage (Postell, 2011).

There are several types of ceramic tiles used for different commercial applications. One of the examples is quarry tile which is unglazed ceramic tiles. It usually used a lot in industrial, commercial and other tile application since quarry tile is inexpensive and also durable to be used outdoors. Other types of ceramic tile is porcelain tile which are less porous and more stain resistant compared to ceramic tiles since porcelain is fired at higher temperature which resulting in more dense and moisture resistant. Therefore, most porcelain can be used either for indoor and outdoor tile (Sánchez et al. 2010).

Whereas for floor tile and wall tile types usually have attractive decoration compared to other types of ceramic tiles. Floor tile have higher strength and durability since it usage needs to withstand heavy weight, foot traffic and high impact. Most of floor designed to be able to tolerate these kind of stress. Meanwhile, the wall tile is more thinner, have finer finishes, and also be less expensive compared to floor tile due different properties and application. Wall tile usually designed to be smaller and lighter than other types of tile because it does not have the to bear the burden of heavy weight or withstanding heavy weight (Postell, 2011).

Glazed ceramics tile was a type of tile that made from clay presses into a pattern by a machine, glaze and then burned in a kiln. Generally, glazed tile absorbs very little or no water, making it easy to maintain and mildew resistant. While unglazed ceramic tile is distinguished by its integral colour throughout the wear layer, which indicates that the pigment has been added to the clay mixture prior to firing (Casasola et al. 2012).

2.2.2 Development of ceramic tile for cooling application

Over the past few years, optimizing building energy efficiency through sustainable passive strategies has become a crucial issue for both designers and researchers, given the huge energy demand required by the built environment and the concomitant potential for energy saving. Hence, by using cool materials and cool roofs was able to represent an interesting passive cooling technique. This was aimed to be able to reduce building energy requirement for cooling as cool materials stay cool under the sun because of high solar reflectance and thermal emittance (Zinzi, 2010).

The effect of cool roofs in determining cooling load and thermal comfort conditions was investigated by Synnefa et al. (2012) for residential buildings. The study consisted of an integrated experimental and numerical assessment aimed at estimating the effect of cool colored materials for envelopes in 27 cities around the world. They investigated cool roof potentialities in different climatological conditions. The main findings show that the value of roof solar reflectance is increase by 0.65 which is able to reduce cooling loads, discomfort hours and peak temperature.

Huge research effort was dedicated to investigate cool roof. In fact, important cool roof effects were also carried out through other larger scale studies, in particular considering the effect of high reflective surfaces in improving urban climate condition (Synnefa et al. 2012). In order to be able to apply such a technique to existing buildings located in urban area, new less impacting strategies and materials and roof elements were developed, where infrared reflectance is optimized, but visible aspect is maintained as traditional roof covering or tiles for example (Santamouris et al. 2011).

Important studies that also took into account are the use of cool pavements. It has become one of the most important proposed mitigation solutions by presenting substantially reduced surface temperature and lower sensible heat flux to the atmosphere. As heat island phenomenon rises the temperature of cities, increases the energy demand for cooling and deteriorates comfort conditions in the urban environment. The use of pavements show a very high fraction of the urban areas which means it highly contribute to the development of heat island in cities. The existing results of this study clearly show that the mitigation and cooling potential of cool pavements is very significant and can highly contribute to decrease temperature on the urban environment (Santamouris 2013).

Pisello et al. (2013) have revealed that roofing solutions with high capacity to reflect incident solar radiation that can provide an effective answer to overheating of either individual buildings or whole urban areas. Therefore, Ferrari et al. (2013) makes a contribution to research on cool tile by developing ceramic tiles with high solar reflectance through the development of a functional engobe. This research shows the procedure to develop a traditional white engobe and a glazed tile with high solar reflectance by adding suitable pigments. Different glazes were applied on engobed samples and were found to slightly affect the reflectance and improve the resistance to mechanical stress or weathering.

In 2014, Pisello et al. indicated that cool roof techniques have already been acknowledged as valid ways to reduce building energy consumption for cooling. Due to the fact the main properties of a cool roof consist of high solar reflectivity and high thermal emissivity. The study shows how this type of roof element optimisation could reduce the roof external temperature when the sloped roof is directly impacted by sunbeams. However, the proposed innovative brick tiles have been produced through the same industrial process of the other existing tiles and the actual colour is basically light beige-white. In addition, the coating durability is the same of other commercialized tiles with classic engobes.

A research was conducted to study the development of high reflective coatings with the purpose to elaborate "cool" tiles with the same visual appearance of traditional tiles for application to historic buildings. Therefore, all the analysis of the reflectance spectra is undertaken to evaluate the effect of different mineral pigments, binders, and an engobe basecoat. The main results present the developed coatings are able to increase the overall solar reflectance by more than 20% with acceptable visual appearance, suitable for application in historic buildings. In order to increase of the overall reflectance characteristics, substrate engobe layer have allows some further contribution about it (Pisello et al. 2013).

Previous studies of solar-reflective ceramic tile still have not able to deal with industries' needs and easily create a product that can be used as replacement for traditional clay roof tile. Solar-reflective surfaces represent an effective counter measure to Urban Heat Island (UHI). Hence, an increasing attention was paid recently to development of solar reflective materials which can be integrated on tiles. This lead to study of development of new glazed and engobed solar reflective on ceramic tiles. The behaviour of most used pigments for production of ceramic tile was analysed once embedded in differences ceramic glazes. This cool tile has been exploited to develop a cool ceramic tile that can be produced in the same production facilities of common products to create a whole tile by merging technological results and industrial production needs, to achieve a compromise between performance and costs (Ferrari et al. 2016).

Cool coatings, which were traditional research field of cool materials, usually prepared using an inorganic high-reflectance compound, organic solvent, and several additives, which are not environmentally friendly during the producing process. Meanwhile, cool tiles are one of most promising solutions to reduce both the heat absorption of building surfaces and pollution from the manufacturing processes of traditional cool coatings. One such cool tile structure is made of three layers which is a green body support, a high-reflectance engobe, and a transparent glaze top coat. There are two kinds of engobe, which respectively consist of rutile or zirconium silicate, provide a solar reflectance of around 0.80– 0.90. However, in this research, ceramic tiles with single solar- reflective titanium-based glaze layer on green body support were produced in order to simplify preparation process (Li et al. 2017).

2.3 Glaze

Ceramic tiles commonly used as tiles for building facades that first undergo a conventional manufacturing process and in sequence, a layer of glaze can be applied on their surfaces, giving them some properties making them functional coatings (Tezza et al. 2015). Glazes are stable glassy coatings applied to ceramic earthenware. This layer of glazes formerly obtained by cooling oxides or minerals applied and melted on the surfaces of ceramic objects. Glazes were an important innovation for earthenware because besides sealing the porous ceramic surface to avoid evaporation of liquids, this coating also made possible a great variety of decorations (Casasola et al. 2012).

Casasola et al. (2012) explain about the history of glaze which the first glazes already developed around 3500 BC in Eastern Mediterranean countries by potters. Therefore, small beads were sculpted from steatite ($Mg_3Si_4O_{10}(OH)_2$) and then coated with azurite or malachite powders, natural ores of copper with blue and green colours to generate a thin layer of colour glass when fired. Afterwards, potters consequently discovered mixtures that completely covered the surfaces of their earthenware with a watertight glassy layer after experimenting with different combinations of crushed and ground rock mixed with water. By using multiple firing cycles at different temperatures, the potters started learning to manufacture many different colours of glazes and textures and even in multiple layers.

Glaze can be defines as a glass that is formulated to fit on a ceramic surface and is made of a network or glass former (silica), network modifiers (metallic oxides), and intermediates (oxides that replace part of silica). Network formers create the largely unordered structure of the glass by combining oxygen atoms with certain cations into oxides. While network modifier acts as flux by lowering silica's high melting point. As for intermediate function, is to increase the viscosity of the glaze and strengthen the glaze in firing. Commonly, glaze is made of silica, alumina and flux. Alumina is a refractory material that helps make the glaze's expansion and contraction coefficient the same say the ceramic work, thereby aiding the glaze fit to the clay work (Rice, 2015).

Traditionally, the zircon or zirconia was use to opacify the industrial glazes for ceramic tiles, therefore become opacity agents for coatings, due its lower cost. However, it has been established that a large amounts of zircon are required to achieve adequate opacity which is more than three times the amount of zircon compared with other opacifiers such as titania and tin oxide. Hence, many search for new compositions of non-bearing zircon frits were conducted to gain opaque white glazes. One useful candidate for zircon replacement is titanium dioxide, which can crystallise in different polymorphs rutile and anatase (tetragonal) as well as brookite (orthorhombic). These high refractive indices titania polymorphs make it an excellent candidates to zircon replacement in glazes (Casasola et al. 2012).

Teixeira & Bernardin (2009) reported on the use of titania polymorphs (rutile and anatase) as the main component for producing white opacity in ceramic glazes for tile coatings. Total zirconia about 12% mass fractions that contained in a glaze frit system was replaced by rutile and anatase in different mass fractions which are about 5%, 10% and 15%. The basic of all glazes were composed of sphene and rutile crystals. The main difference between glazes is that the sphene phase was more developed in glazes compared to rutile phase. The study concluded that glaze frit compositions system are able to produce opaque white glazes, but such glazes present lower gloss than those obtained with ZrO_2 containing frits.

2.3.1 Properties of glazes

The properties of glazes and chemical composition of different ceramic products vary within a wide range by complicating their simple classification. It is essential to be able to estimate their most fundamental properties from chemical properties when comparing different glazes. Also, for some properties such as raw glazes, are to great extent dependent on the mineralogical composition of the raw material used. In addition, different plant-specific parameters are also affecting the final glaze quality (Carty, 2001).

A glaze composition is best expressed in terms of the constituent oxides which can be classified as basic oxides, amphoteric oxides and acidic oxides. Example of acidic oxides may be silica and boric oxides that able to control the maturing temperature of the glaze, give craze resistance and lower the thermal expansion of a glaze. Meanwhile alumina is added to prevent devitrification and can increases viscosity of the glaze at its maturing temperature. Basic oxides such as soda and potash may be introduced as feldspar. They are used as secondary fluxes in relatively small proportion since their compound are reactive and would give unstable glazes if present in high proportion (Ryan, 1978).

Application of glaze coating on ceramic tile body provides the underlying ceramic body with a waterproof, abrasion and chemical resistant covering. Also, glazes serve to eliminate surface porosity, increase the mechanical strength of ceramic tile, and confer aesthetic qualities to decoration systems and can consist of a glassy or vitreous phase, heterogeneous phases, or glass–ceramic phases, with the glassy matrix corresponding to 80–90% of the layer and the remainder to one or more crystalline phases (Silva et al., 2012).

2.3.2 Glazing

There are many manufacturers of tile; dinnerware and sanitary ware have begun to be more efficient in production processes to remain competitive in producing ceramic products. As part of these initiatives, some companies in ceramic industry have improved new glazing equipment, modified existing kilns or installed new kilns to optimize energy efficiency, developed new glaze and body formulations, investigated and/or implemented new glaze application processes, developed specially treated glaze materials or combined different application processes (Britt, 2004).

2.3.2.1 Glazing Method

There is a lot of glazing method that can be used to apply glaze on ceramic body. Regardless of the method used, the amount of glaze picked up by the product depend on the size, shape, surface area, temperature of the product, amount of water and the glazing time. As for the surface of the ceramic tile, glazing consists of the application of one or more layers of glaze with a total thickness between 75 and 500 microns. Glazing is performed to confer to the fired product a series of technical and aesthetical properties, such as being watertight, cleanable, glossy, coloured, textured and chemically and mechanically resistant (Peligrad et al. 2001).

For glazing method, a variety of different application methods are used in the industry to achieve the desired results. Waterfall, disc and spray application are the most commonly used wet methods, while dry pressing and dry glazing are the most widely used dry methods. There were also traditional glaze applications such as dipping, painting, pouring, and brushing that are mostly applied to either biscuit-fired or green pottery (Britt, 2004).

In wet method, the waterfall method is the most widely used glaze application method in the industry. The liquid glaze is allowed to fall freely through a defined opening onto the surface of the ceramic body. Hence, in order to improve the glaze quality and ensure perfectly smooth surface. Newer bell glazing machines and high-density glazes were eventually been developed. Therefore, the glazing process was faster and more uniform, and even low-density glazes could be used. Meanwhile the disc method can be used to apply glaze to the ceramic body when a perfectly smooth surface is not required. Spray guns are widely used to overspray the first coat with a cover coat of either a colored or clear glaze. Spraying method is the excellent way to apply an even coat of glaze without touching the piece (Parise, 1990).

The most commonly used in floor tile production is dry glazing which consists of a dry glaze powder (granulated glaze) being scattered over a wet base glaze. During firing, the base glaze and dry powder smelt into each other and produce beautiful effects on the surface. This type of glazing usually undergoes third firing at low temperature just to soften and melt the glaze. The final tile surface is typically harder and more durable than surfaces obtained using traditional wet glaze application methods (Parise, 1990)

As for traditional glaze application, dipping is common method of glaze application that very simple and the result is an even, consistent coat. While, pouring is particularly useful on large piece that cannot be dipped into the bucket. Sometimes combinations of these both methods resulting in variation of decoration. Brushing requires a bit of practice, but the result can be indistinguishable for dipping or pouring. It is useful with glaze that melt smoothly or when brushed texture is desired (Britt, 2004).

2.3.2.2 Glaze Formulation

Glaze can be made from only three necessary elements which are silica, the glass former, a flux or glass; and alumina, the refractory element. The compounds employed by the potter are usually those mineral that are abundant in nature in a relatively pure state. As example, the lower fire glaze consist of Kaolin ($Al_2O_3 . 2SiO_2 . 2H_2O$) potash and feldspar ($K_2O.A1_2O_3.6SiO_2$) and red lead (Pb_3O_4) or borax (Na_2O-$2B_2O_3 . 10H_2O$) as the flux. In order to gain an understanding of the qualities imparted to the glaze by silica, alumina and the flux, the several tests with varying proportions of feldspar, kaolin and borax should be done (Nelson, 1978)

A new glaze can be an easy way to bring a unique look to a new or existing product and also create new application. However, a new glaze developed for the intended application needed to be rigorously tested in a lab to identify any potential problem areas before been used. As new formulation of glaze need to be provided with information such as the type of product on which the glaze will be applied, the thermal expansion of the ceramic body, the firing process, the firing time and temperature, and the equipment that will be used for glaze application (Rhodes, 2015).

2.3.2.3 Batching

The quality, application of the final glaze and also the overall efficiency of the production process can be affected by glaze preparation method. Wet grinding using a conventional ball mill is one of the most popular glaze preparation methods. The glaze used usually contains frits, raw materials such as clay and feldspar and colouring agents. The grinding media is typically alumina ballsand different-sized balls or stones are used to optimize grinding efficiency. The glaze is then dried after it thoroughly mixed, and sent through a second dispersion process to ensures any agglomerates formed in the drying process is removed. The differences in glaze properties were obtained when various sizes of ball mills were used to prepare the same glaze due to differences in variables such as batch size, grinding time, particle size distribution and/or the amount of water and suspension materials used. For this reason, all parameters must be carefully defined and rigorously followed to ensure the highest glaze quality and consistency (Rhodes, 2015).

As for dry blending process, all of the glaze ingredients are milled to a small particle size and are thoroughly mixed into a homogeneous glaze powder. In most cases, the finished glaze powder is ready to use in a dry application process or can be easily converted into a slip using high-speed dispersion equipment. An additional wet grinding step using a ball mill usually required if the raw materials used in the dry blending process are coarse. Meanwhile, to prepare a liquid glaze, all of the glaze ingredients are wet milled in a ball mill. Then, when the glaze slurry achieve the desired particle size, it will pass through a screen and a magnetic filter to remove any impurities. The density and viscosity of the glaze are then adjusted to fit the application, and the finished glaze is ready to be used in production (Weber, 2010).

2.3.2.4 Firing of glaze

One of the most important steps in the manufacturing process is the firing of ceramic products because it significantly influences the technological properties of ceramic tiles. Earthenware materials can be fired once, twice or a greater number of times. Unglazed ceramic tiles are fired only once, while glazed tiles can be fired once (single firing process) or twice depending on type of glaze and tile application. In the first firing, the biscuit that will act as a support is fired, and then the glaze is applied and fired in a second thermal cycle (double firing process). A further firing at lower temperatures may be necessary (third firing) in some decorated earthenware materials, (Casasola et al. 2012).

There are two types of glaze firing, the one in which glaze and body mature together and the one in which the body is already matured and only glaze is affected. An example for the first type was porcelain; the body matures and becomes translucent together with glaze during firing. While, the example of the second type is raku which the body is already fired to a temperature equal to or higher than the glaze firing. Therefore, this type is unaffected by the heat of the glaze firing but only the glaze is changes completely. These type of firing usually used for overglaze decoration firing and can be done at a faster rate than for other firings (Hamer, 2014).

2.4 Cooling Materials

Cooling materials can be defined as are highly reflective cool materials that able to stay cool under the sun due to high solar reflectance and thermal emittance. Therefore, cool materials are mainly used in coatings for construction materials since it able to improve the solar and thermal performance of the roof and buildings. This solution is effective in reducing the cooling demand and ensuring thermal comfort conditions in the built environment (Zinzi 2010).

Thermal comfort condition refer to the comfortable thermal sensation based on the environmental conditions and material properties including its microstructure and surface. The uncomforting thermal condition can be characterized by heated floor surfaces in external environments which are exposed to sun radiation or by cold floor surfaces in internal environments. The property named thermal effusivity which defines the interface temperature when two semi-infinite solids are putted in perfect contact.