DEVELOPMENT OF ENGOBE COMPOSITIONS FOR LOCAL ROOF TILES

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ABSTRACT

DEVELOPMENT OF ENGOBE COMPOSITIONS FOR LOCAL ROOF TILES

Engobes can be described as a coating layer on ceramic surfaces to produce the desired color. In this thesis a commercial roof tile, which was taken from a company, was used. For good fitting between the engobe and the roof tile their coefficients of thermal expansion (CTE) should be almost the same. One way of adjusting the CTE values, the chemical analysis of the roof tile was analyzed and based on these different engobe recipes with high purity raw materials and frit that was made in the laboratory with high purity raw material were prepared. The roof tiles were rich in SiO_2, Al_2O_3, $(Na+K)_2O$. Therefore, by changing the percentage of these oxides new engobe recipes were prepared to find the most suitable composition for roof tiles. After application on surfaces of roof tiles, the samples were fired at 1000^oC for 75 min. 70% SiO_2, 20% Al_2O_3, 10% $(Na+K)_2O$ with 10% laboratory frit and 70% SiO_2, 20% Al_2O_3, 10% $(Na+K)_2O$ with 30% laboratory frit were found to be two of the most proper engobe compositions for the roof tile. Later these engobe recipes were prepared with lower purity industrial grade raw materials and industrial frit because the cost of producing frit is high for a roof tile manufacturer. The low purity engobes were applied successfully on the surface. However, lower purity raw materials containing little Fe and Ti led to a slightly darker color compared to higher purity engobes. The life cycle of the products were tested with different kinds of acids and temperature tests. And the results showed that the engobe samples were durable against the environmental effects. Finally, metal oxides were used up to 5% in the engobe compositions to give different colors to the roof tiles.

ÖZET

YEREL KİREMİTLER İÇİN ENGOB KOMPOSİZYONLARININ GELİŞTİRİLMESİ

Son günlerde inşaat sektörünün gelişmesi ile renkli kiremitler kullanılmaya başlanmıştır. Doğal kil esaslı hammaddeleri kullanan ticari bir üreticiden alınan yarı mamül kiremitlere uygun ve düşük maliyetli engob kompozisyonları bu çalışmada geliştirilmiştir. Kiremite en uygun engob komposizyonunun hazırlanması için kiremit bünyesi analiz edilmiştir. Engob ile bünyenin ısıl genleşmelerinin benzer olması amacıyla uygun engob reçeteleri geliştirilmiştir. Kimyasal olarak benzeyen bu iki malzemenin pişirme esnasında benzer davranışlara sahip olması engob - yüzey etkileşimleri sırasında hataların oluşmaması için önemlidir. Bu çalışmada engob uygulanacak kiremitin XRD ile analizleri yapıldıktan sonra yüksek saflıktaki malzemeler kullanılarak engob komposizyonları oluşturulmuştur. Analizlere göre kiremitlerin yapılarında bol miktarda silika, alümina, sodyum oksit ve potasyum oksit içerdikleri saptanmıştır. Bu doğrultuda engob numunelerinin SiO_2, Al_2O_3, $(Na+K)_2O$ oranları değiştirilerek en etkili kompozisyon bulunmaya çalışılmıştır. Yüksek saflıktaki malzemelerden ve özel olarak laboratuarda üretilen yüksek saflıktaki frit ile yapılmış en uygun engobun başarıyla kiremit yüzeyine kaplanmasının ardından düşük saflıktaki ve endüstriyel frit ile benzer engob kompozisyonları hazırlanmıştır. Hazırlanan yeni engob kompozisyonlarıyla da başarıya ulaşılmış ve değişik asit baz gibi kimyasal malzemelere maruz bırakılarak performans deneyleri yapılarak bunlardan da olumlu sonuçlar alınmıştır. Hazırlanan engob reçetesine farklı miktarda renklendiriciler katılarak renklendirilmesi sağlanmıştır. İstenilen renkler renklendirici oranları değiştirilerek elde edilebilmektedir.

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CHAPTER 1

INTRODUCTION

Since centuries, the roof tiles have protected their important place as the roof cover for buildings. The Romans were the first to make and use the roof tiles. Other people also used roof tiles because of the convenience, low cost and aesthetic properties. When the population growth is concerned, it is understood that there is a huge potential in the roof tile industry worldwide. The main reason roof tiles have such popularity is because of their physical, thermal and hydrous properties (Genç and Başkıran 2001, Kornmann 2007). Roof tiles are sometimes exposed to hard weathering conditions like freeze-thaw cycles, rain, snow, wind, UV radiation from sunlight. In order to produce roof tiles of sufficient strength, low porosity, and resistance to weathering the manufacturers are nowadays more technical and sophisticated. Besides the research on improving the technical quality of roof tiles a new aspect has emerged; appearance of the roof tiles. With increasing variety of architectural techniques, artistic affects and customer choices, many more alternative roof covering materials appeared in the market. Examples are steel panels, aluminum panels, concrete panels, mineral pressed covers, shingle. In addition, different colors for roof tiles are increasingly sought for in the market (Karasu, Kaya and Özkaya 2002, Poyraz, Erginel and Ay 2006). Especially in Japan, EU, USA there is a big demand for colored roof tiles. In the last decade Turkey too has been affected by this variation and some manufacturers have tried to find new engobe compositions (Karasu and Kara 2001). Roof tiles are colored by applying a thin layer of coloring material on the surface of green roof tile before drying and firing at high temperatures to mature the product. A colored and partially glassy surface layer of ceramic quality which is quite resistant to frosting and weathering effects is obtained. This layer is known as engobe or slip. Sometimes another layer is applied on top of engobe to give bright appearance. This final layer is known as glaze which is completely vitreous (glassy). If there is a final glaze layer then the engobe acts as an intermediate layer to hide the color of the substrate. For roof tiles glaze coating is generally not applied as a final coating, only a 100-500 micrometer thick layer of engobe is used.

The best coloring method of roof tiles is engobe because it is a ceramic layer fired at high temperatures and well-integrates with the substrate. Other techniques like painting and silicone have long term durability problems under UV radiation of sunlight and freeze/thaw cycles.

The fit of engobe is the most important point for ceramic coating. The substrate and engobe must bond together very well and must not be damaged easily. A good fit is obtained when the two materials of substrate and the engobe have similar coefficients of thermal expansion (CTE). Ceramic bond between substrate and engobe develops during firing around 1000oC. Engobe layer is partially vitrified and a chemically durable and mechanically strong product is obtained (Kornmann 2007, Eppler 2000).

The goal of this work was to develop the most suitable engobe composition for a commercial roof tile to provide different colors for more pleasing appearance. The use of natural minerals and industrial frit to produce engobe by manufacturer easily was also investigated. Because making frit is both expensive and difficult for a roof tile company.

This thesis consists of five chapters. Information obtained from the literature is summarized in Chapter II, experimental procedure and materials are presented in Chapter III, results and discussions are given in Chapter IV and conclusions are explained in Chapter V.

CHAPTER 2

ENGOBE AND ROOF TILES

In this chapter roof tiles, engobes, their chemistry, coating properties for matching engobe and roof tile, colorants (metal oxides), application methods and defects are explained.

2.1. Roof Tile

Roof tiles were first used for their buildings and were introduced to the rest of the world by Romans and Greeks (Genç and Başkıran 2001, Overbeck 1969) as shown in Figure 2.1.

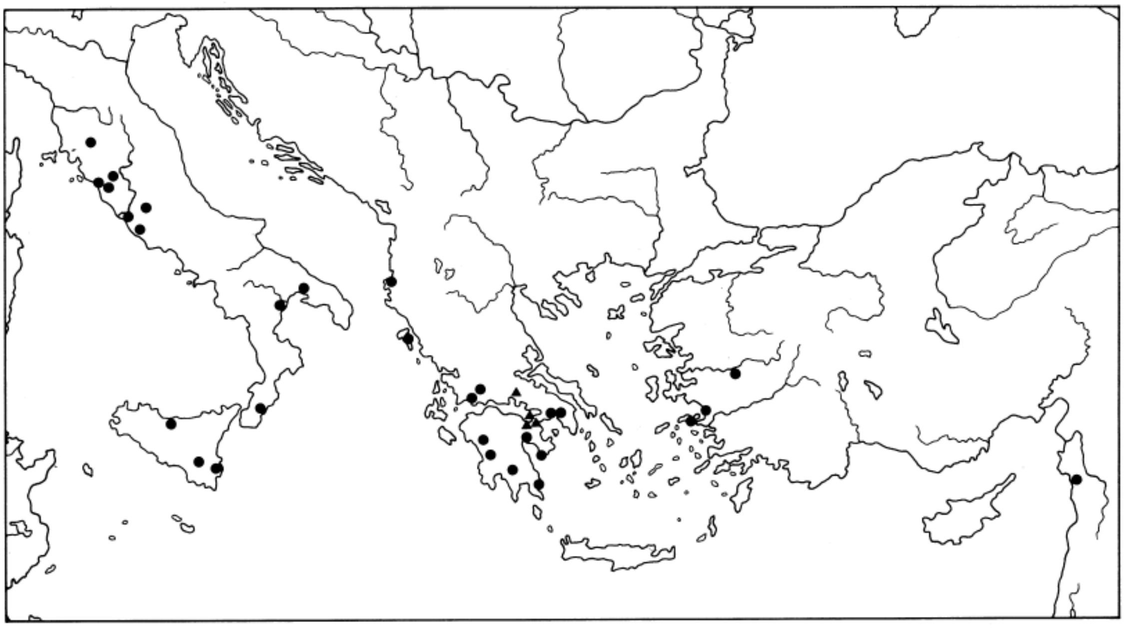

Figure 2.1. Distribution of the use of roof tile (700-650 B.C. triangle, 650-600 B.C.round) (Source: Wikander 1990).

With this distribution it can be said that roof tiles are one of the most widely used materials for covering the ridges. The frequent use of the roof tiles is based on the following reasons;

- They have an aesthetic view- both historical and modern.
- They are light and waterproof.
- They have good frost resistance.

As most ceramics, roof tiles are made from oxides that can be found in large quantities in nature. Clay is the base material of roof tile. Clays are removed from the upper top layer of the earth. They are formed in a long period by weather effects and by physical erosion. The minerals in roof tile clay can be estimated by three components of its environmental conditions as illustrated in Figure 2.2 (Kornmann 2007). Generally clays consist of between 40-65% SiO_2 (silica), 1-25% Al_2O_3 (alumina) and 3-9% Fe_2O_3 (iron oxide). Apart from these, K_2O (potassium oxide), Na_2O (sodium oxide) and $CaCO_3$ (calcium carbonate) are also found in the roof tile in different ratios. Iron gives the roof tile its natural red color. According to the amount of iron the color can be changed from orange to pale brown. Also the color is derived from the minerals contained in the tile (Eppler and Eppler 2000). Alumina and silica increase the firing temperature but they also increase the strength of the roof tile. Therefore, they are the basic materials of the roof tiles (Yanık 2003).

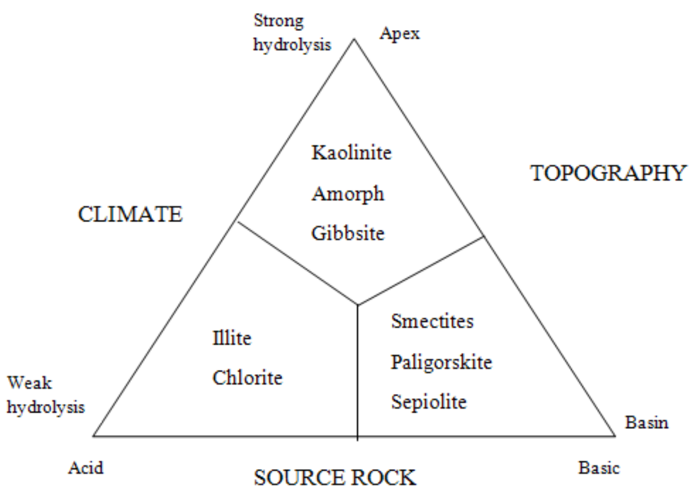

Figure 2.2. Formation of clay according to environmental effects (Source: Kornmann 2007).

For producing a roof tile, clay that is taken from the earth is ground to decrease its particle size which is one of the important properties for the roof tile. If the particle size of the roof tile is large, cracks can form on the product. Also the characteristic properties of the roof tiles affect the firing temperature of the clay. Especially the strength and color maturation of the tile occurs during the firing process. A typical roof tile is fired between 900 to 1000 ^{o}C (Genç and Başkıran 2001, Lyons 2006). Fired earthenware products have a traditional red color. Sometimes a thin layer of clayey paste (slip or engobe) is applied on the surface to impart lighter colors to the ware. This clayey paste contains much lower percentages of iron than the base material which generally has 4-9% Fe.

2.2. Engobe

Engobe is a layer for covering the surface of the clay bodies with a different color. It gives a smooth surface to the tile after application. The color is provided to the engobe composition by addition of small amounts of metal oxides. Therefore the tile can have an aesthetic appearance with different colors. Engobes are sometimes also called as slip or as an intermediate layer between clay body and glaze (Grimshaw 1971). Glaze layer is applied on the engobe layer as a final coating layer to impart a shiny appearance to the clay body. A low-melting additive of frit is often incorporated into the engobe mixture to assist earlier vitrification upon firing. There is often less proportion of frit in engobe than in glaze. The latter is more glassy than the former. The amount of frit adjusts the hue of the engobe color and the surface brightness. This is the reason why the engobes are less shiny than glazes. This property of the engobes also provides the diffusion of the gas. In other words engobes have a porous structure as shown in Figure 2.3. Since the melting of the engobe eventuates locally during the firing process (Zanger 2002). Porous structure of the engobe allows passage of gases that may form during firing of the ware. If the engobe layer is completely vitreous then gases cannot escape and blowholes can from, marring the surface of the ceramic.

For a good covering of the substrate, engobe composition should be carefully designed. First the body and the engobe should be compatible together during both drying and firing. This shows the quality of the engobe. In addition, the firing temperature of engobe should be near the firing temperature of the substrate. The roof tiles have a low firing temperature. Therefore this condition is very important for making an engobe for roof tile. Secondly, the color of the substrate should be covered completely. The color of the engobe is affected mainly by the amount of the iron in the engobe. So, the raw material for making an engobe should be chosen according to their purities. Finally, engobe should cover the substrate well without peeling. Defects on the surface are not desired for engobes (Rhodes 2000).

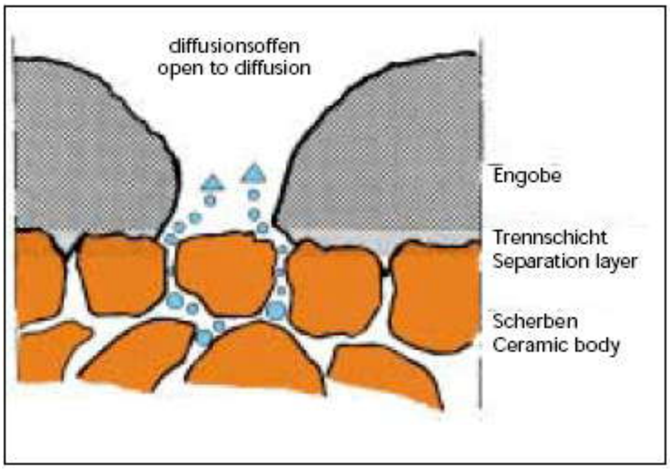

Figure 2.3. Cross section of the engobe and clayed body
(Source: Zanger 2002).

2.3. Properties for Matching Engobe and Roof Tile

As mentioned in section 2.2, the engobe and substrate (roof tile) should satisfy conditions like properly adjusted thermal expansion, particle size distribution (PSD) and viscosity.

2.3.1. Thermal Expansion

For best fit of the engobe on the substrate the thermal expansion coefficient (CTE) value of the former must be equal or slightly smaller than that of the latter. In order to predict the CTE value of a ceramic its chemical composition must be known. The most practical approach to match the CTE of the roof tile and the engobe was to match their chemical compositions because each oxide has a thermal expansion coefficient. To calculate the thermal expansion coefficient of the engobe the thermal expansion coefficient is multiplied by the weight percentage of the oxide in the composition as shown in Equation 2.1. But this theoretical calculation has moderate accuracy (Eppler and Eppler 2000).

$$CTE_{(engobe)} = \sum CTE_{(oxide)} * w(\%)_{(oxide)} \quad (2.1)$$

The exact coefficient of thermal expansion can be measured by dilatometer as shown in Figure 2.4. The device measures the expansion of the sample length during desired heating temperature range. For finding CTE of a sample reversible thermal expansion measurement should be done. That means the fired sample is measured not unfired (Dinger 2005).

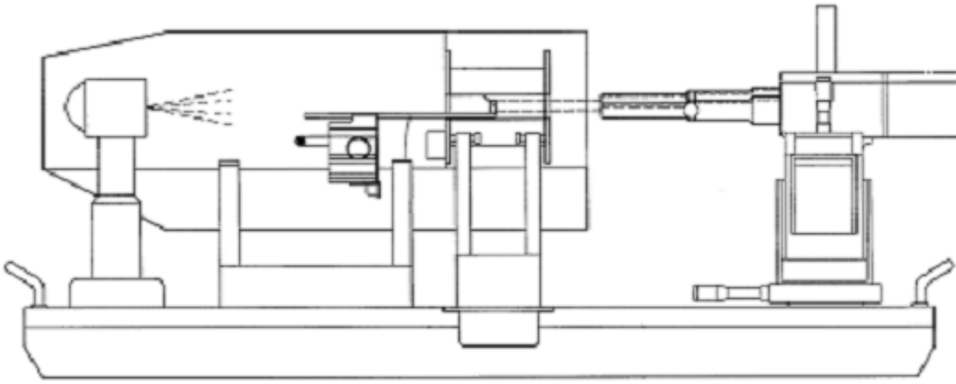

Figure 2.4. Schematic of a dilatometer
(Source: Free patents online 2010).

After measurement the elongation of the sample and temperature graph is drawn to calculate CTE value. This calculation is based on linear expansion of the material. The coefficient of thermal expansion (CTE) on a graph can be calculated with Equation 2.2 (Brown 2001).

$$\frac{\Delta L}{\Delta T} = \frac{dL}{dT} = L_1 \alpha \quad (2.2)$$

where;

α: the slope of the curve (CTE)

L1: initial length

dL/dT: elongation in unit temperature

2.3.2. Particle Size Distribution

Particle size is important for a smooth surface. Especially it is effective for preventing the crawling defect because the uniform particle size produces a homogeneous engobe layer. In addition for a good compositional homogeneity of the mixture, a well distributed particle size is needed. When the particle size of the engobe decreases the reaction during the heat treatment is accelerated. Also the amount of water for preparing the engobe mixture is adjusted according to the particle size (Wattanasiriwech and Wattanasiriwech 2006, Bernardin 2009). Moreover it is an important control parameter for viscosity of the engobe. Particle size distribution can be measured by many methods. One of the most accurate ways is sedimentation. Although this is an automatic PSD (particle size distribution) analysis it has an analysis range. The size of the particle should be between 300 µm and 0,1 µm for using this analysis. Another way for finding the PSD is sieve analysis as in the Figure 2.5. The mechanism has a simple system. There are many sieves that are placed from coarse to fine mesh. For illustration, distribution histograms are used. In this graph the mass percentage of particle is used as data according to their size class (Dinger 2005).

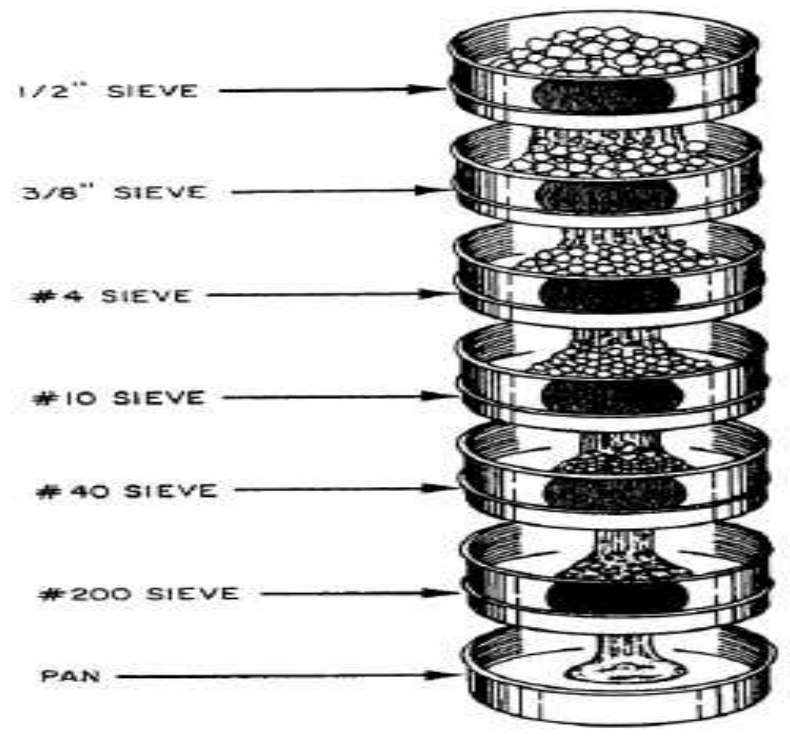

Figure 2.5. Laboratory sieve device.

2.3.3. Viscosity

As explained in chapter 2.3.2 the particle size affects viscosity. The viscosity increases with decreasing particle size because the specific surface of the power increases in fine particle. In addition they need more water to bind. The viscosity is the ratio of shear force to rate of flow. The fluids are separated into two groups that are Newtonian and Non-Newtonian as shown in the Figure 2.6. If the shear stress and rate of deformation is linear, the fluid is named as Newtonian. If not, the fluid is called as Non-Newtonian. In some Non-Newtonian fluids the viscosity decreases with increasing shear rate. They are called as shear thinning or pseudoplastic. The opposite of shear thinning is also called as shear thickening or dilatant (Reed 1994, Phan-Thien 2002). In ceramic suspensions shear thinning rheology is desirable. Dilatant suspensions lead to processing problems as most fluid transport processes involve high shear rates. For example, during spraying of an engobe suspension onto the roof tile body the shear rate is very high and clogging of the nozzle may occur if the engobe suspension is dilatant.

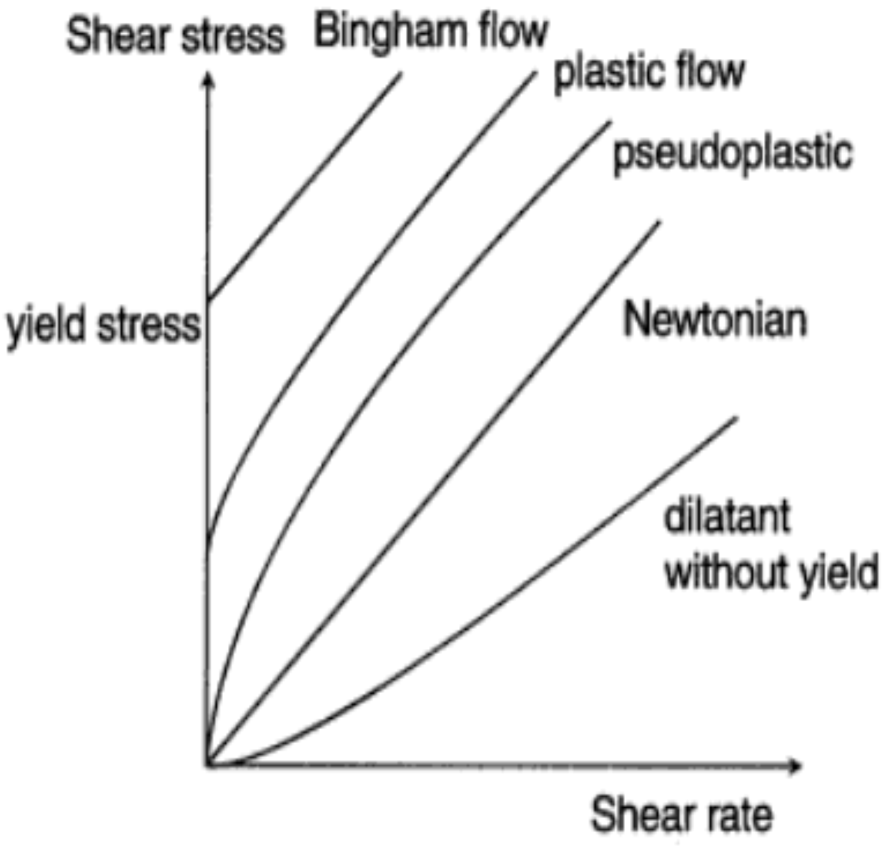

Figure 2.6. Different types of flow behavior of fluids as a function of shear rate (Source: Phan-Thien 2002).

The surface of the roof tile is not flat. When the viscosity of the engobe is too small the engobe may run off the uneven surface and the thickness of the engobe would be uneven. So, defects can occur on the surface which is an unwanted situation for the engobe (Britt 2004).

2.4. Oxides

Roof tiles and engobes are all made of oxides which are naturally occurring materials available at reasonable cost at large quantities. In order to properly design an engobe composition one has to understand the properties that these oxides can provide. The oxides are separated into three groups; stabilizer, glass former and fluxes as illustrated in the Table 1.1. The stabilizers prevent the engobe from being water soluble and also not to flow on the surface. Furthermore it helps to increase opacity and the durability of the engobe. The glass former provides a glass structure. The fluxes are used to reduce the firing temperature (Bailey 2004)

Table 1.1. Oxide types.

Stabilizers	***Glass former***	***Flux***
Al_2O_3	SiO_2	K_2O
	B_2O_3	Na_2O
	P_2O_5	MgO
		CaO

Silica, which is the major oxide for engobes, forms the skeleton of the engobe structure. In addition the percentage of the silica is more than the other oxides in an engobe composition. It is glass former at high temperatures. Although they have high melting temperatures (approximately 1700^{o}C) they decrease thermal expansion, fluidity and the shrinkage of the engobe. Because of low thermal expansion coefficients they reduce surface defects. In addition they help increase hardness. Furthermore they have a good resistance to water and chemical effects. With increasing SiO_2 the transparency of engobe increases. It has a good resistance to thermal shock. SiO_2 can be obtained from silica, feldspar, talc and ball clay (Eppler and Eppler 2000, Çetin 2005).

Alumina is added to the composition through ball clay and feldspar. It reduces crazing defect while increasing the melting temperature of the engobe. Therefore, the amount of the alumina is adjusted according to the desired firing temperature of the engobe. It reduces the thermal expansion of the engobe. Moreover it helps to increase the hardness, viscosity, opacity and the resistance to acid and water (Grimshaw 1971).

Calcium oxide (CaO) is used in the form of calcium carbonate, dolomite. Calcium carbonate ($CaCO_3$) is affective to get white color in the engobe. It provides a matte appearance when used too much in the engobe composition because of increasing the refractory inclination. It decreases the viscosity and increases hardness and durability.

Contrary to calcium oxide, magnesium oxide (MgO) helps to give a shiny appearance. It is effective to decrease the thermal expansion and to prevent crazing. Magnesium hydroxide ($Mg(OH)_2$) and talc are the sources of magnesium oxide (Çetin 2005).

Alkali oxides and B_2O_3 are needed to vitrify the engobe and to act as a flux to reduce the melting point of the engobe. Some of the raw materials used for making engobe are water soluble. Examples are Na_2O, B_2O_3, and K_2O. These materials need to be transformed into a water-insoluble form because engobe is coated on the surface of the roof tile by spraying which involves a water based suspension. They quickly dissolve in water but a little of them positively affects the suspension. It helps the recrystallization in the suspension during drying. Therefore, surface of the engobe prevents the damage because of its hardness (Rhodes 2000). A frit, which is a water-insoluble glassy material, needs to be made from engobe raw materials. The frit, which is usually quite rich in B_2O_3, is a strong flux and helps vitrify the engobe. Borax is used as a source of B_2O_3. Na_2O, B_2O_3, and K_2O which are used for lowering the melting temperature of the engobe affect negatively the engobe because of high thermal expansion. The properties of the Na_2O and K_2O are almost the same. Na_2O is added as a form of feldspar, Na_2CO_3 and K_2O are obtained from K_2CO_3 (Britt 2004).

Fe_2O_3 is not used due to staining which is the coating of red or black depending on the firing atmosphere (McVay and Parmelee 1937). They are also called as impurity of the raw materials to change the color of the engobe which is undesirable situation.

The oxide combination with laboratory frit and with industrial frit to get desired oxide is two of important reason for preparing engobe as in the Table 1.2. Generally the natural raw materials are used for making engobe in lieu of pure (laboratory) materials. So the cost of engobe can be decreased by this way (Eppler and Eppler 2000).

Table 1.2. Melting temperature of the oxides and their source.

Oxide	*Melting Temperature (^{o}C)*	*Raw Material*	
		Quartz	*Natural*
		Feldspar($Na_2O.Al_2O_3.6SiO_2$)	*Natural*
		Ball clay	*Natural*
SiO_2	*1723*	*Talc($Mg_3Si_4O10(OH)_2$)*	*Natural*
		Feldspar($Na_2O.Al_2O_3.6SiO_2$)	*Natural*
Al_2O_3	*2050*	*Ball clay*	*Natural*
		Sodium Carbonate (Na_2CO_3)	*Laboratory*
Na_2O	*860*	*Feldspar($Na_2O.Al_2O_3.6SiO_2$)*	*Natural*
		Calcium Carbonate ($CaCO_3$)	*Laboratory*
CaO	*2500*	*Dolomite ($CaCO_3.MgCO_3$)*	*Natural*
		Magnesium Hydroxide ($Mg(OH)_2$)	*Laboratory*
		Dolomite ($CaCO_3.MgCO_3$)	*Natural*
MgO	*2800*	*Talc($Mg_3Si_4O10(OH)_2$)*	*Natural*
B_2O_3	*700*	*Borax ($Na_2B_4O_7.10H_2O$)*	*Natural*

2.5. Colorant (Metal Oxides)

CIE system is the most widely used system for the description the color. Of course the color can be described with eye roughly: red, yellow, green, etc. However their accurate hue, lightness cannot be separated with eye. In CIE, the color is represented in an L – b – a coordinate system to identify color as illustrated in Figure 2.7. In the color system diagram the coordinates are named as L, b, a. (+) a refers to the redness and (-) a refers to the greenness of the color. (+) b shows the yellowness and (-) b shows the blueness. The last coordinate L means the lightness from light (+) L to dark (-) L (Nassau 1998).

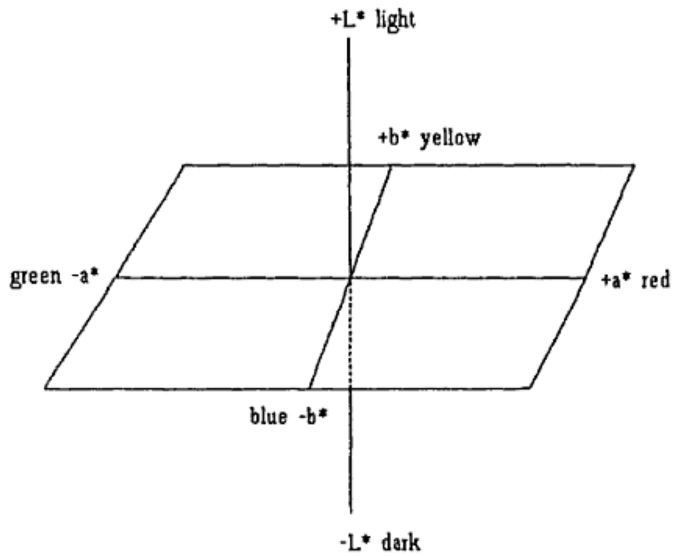

Figure 2.7. Color system diagram in the CIE L – b – a system (Source: Nassau 1998).

The color can be given to the engobe by addition of small amounts of some metal oxides. With different metal oxides various colors can be obtained. Iron oxide (Fe_2O_3) can be used for giving red to black color according to its amount. Cobalt oxide (CoO) produces blue color in the engobe. Chromium oxide (Cr_2O_3) leads to green color. Manganese dioxide (MnO_2) is also used for obtaining a color range from purple to brown. For yellow color titanium dioxide (TiO_2) is chosen in the engobe compositions. Apart from the amount of the colorant (metal oxide) the color is affected by the atmosphere, time, temperature and thickness of the engobe (Cooper 2004). Effect of reducing atmosphere is to modify the oxidation state of the color-making cations which is most strongly manifested in raku glazes (Eppler and Eppler 2000, Çetin 2005). The mixing of the engobe and colorant is also important to produce a uniform color.

2.6. Application Methods

Application of the engobe to the surface is important as much as the production of the engobe. Dipping, spraying, waterfall and brushing are the most widely used methods in the industry as illustrated in the Figure 2.8. The desired thickness of the engobe, ease of application and type of ware are major selection parameters for choosing the application method. Generally a thin and uniform coating is desired for the engobe. Dipping method is used for thin ceramics such as tableware. In this method the ceramic ware is dipped in a bucket of engobe. The time of the immersing adjusts the thickness of the engobe. The spraying is generally an ideal method for ceramics that has a big surface in order to cover the surface easily. Also a thin layer can be obtained by this way. A spray gun, container and trigger mechanism (air) is needed. If the surface of the ware is big the waterfall is suitable for applying the engobe. Generally the floor tiles are covered by this way. When the ware is moving on a belt with a constant speed, the engobe is poured from the engobe container. The brushing is always used for artistic works. It is a painting process on the surface of the ware with a brush. Prevention of brush marks and adjustment of a constant thickness are very difficult. So, it is not preferred method for serial manufacture (Eppler and Eppler 2000, Çetin 2005).

Figure 2.8. Application methods of the engobe: a) dipping b) spraying c) waterfall and d) brushing (Source: MEGEP 2007).

2.7. Defects

Although a perfect compliance is expected between engobe and tile some undesired defects like crazing, peeling, bubbles and crawling can occur.

The reason for crazing and peeling is the thermal expansion mismatch of body and engobe. There can be two conditions. First condition is if the engobe thermal expansion is much larger than the substrate ware thermal expansion, crazing occurs on the surface because of a high difference between the CTE values as illustrated in Figure 2.9.a. The engobe cannot balance the tensile stress so it cracks. If the CTE difference between them is not too much the shape of the ware is concave. Second condition is when the engobe thermal expansion is much less than the ware thermal expansion, the engobe will peel as shown in Figure 2.9.b. This defect is called as peeling or shivering. Contrary to crazing, a compressive force occurs. And if the CTE difference is less the ware and engobe can be shaped convex (MEGEP 2007).

A bubble defect occurs during the firing process. After the material in the engobe or body reacts with each other gases are produced. These gases try to separate from the surface. If the engobe layer doesn't permit the exit of the gas, the air bubble shapes are observed on the surface as shown in Figure 2.9.c. If the viscosity of the engobe and the temperature rate are decreased, formation of the bubbles can be prevented (MEGEP 2007).

If the engobe pulls together and the bonding between ware and the engobe rupture, crawling and tearing defect occurs as in Figure 2.9.d. It is related to lack of wetting. Therefore, too fine particle size can cause these defects. Decreasing the thickness of the engobe is a good way not to form crawling and tearing. The surface should be clear for preventing this defect (Bernardin 2009).

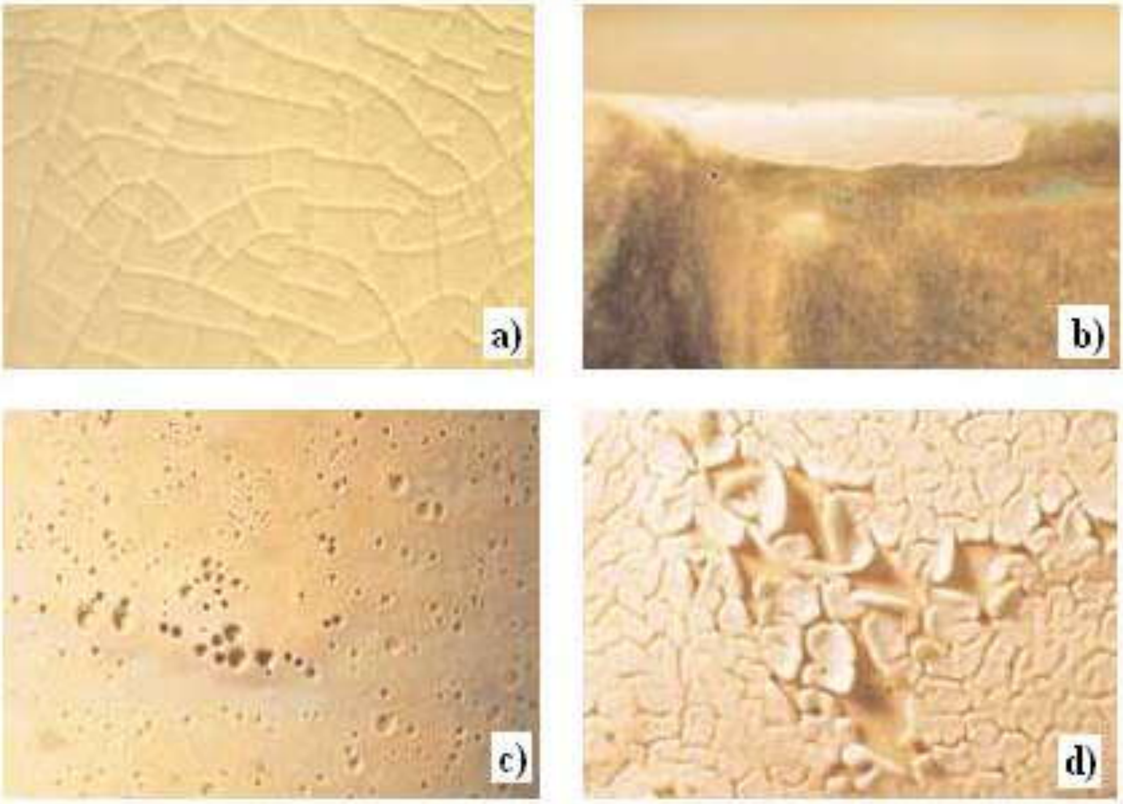

Figure 2.9. Typical defects of the engobe a) crazing defect, b) peeling defect, c) bubble defect and d) crawling and tearing defect (Source: Ceramic art daily 2010).

CHAPTER 3

EXPERIMENTAL

In this chapter, the chemical and physical characteristics of raw materials, methods for making engobes, frit and techniques for characterization of products are explained. In this thesis a glaze layer was not applied on any of the samples.

3.1. Raw Materials

In this section information on chemical and physical characteristics of the raw materials are given. The substrate material, which is a commercial roof tile body, was analyzed for its chemical and physical characteristics in order to collect information to be used for identifying the composition of the engobe. Because the engobe and the substrate must fit together during drying and firing processes their CTE values must be matched.

3.1.1. Roof Tile Body

In this study a commercial roof tile which was in the green state was used as a substrate for coating with the engobe. Supplier of the green roof tile samples was Yüksel Toprak A.Ş., Turgutlu, Manisa. Details of the production of these shaped roof tiles are given in section 3.2. The chemical composition of the roof tile raw material as measured by XRF (X-Ray Fluorescence, Spectro IQII) is given in Table 3.1. The measurement was performed on pellets of the raw material prepared by fusion in platinum crucibles. Particle size distribution, thermal expansion behavior, thermal gravimetric behavior (TGA) of the raw material along with the color measurement of the fired roof tiles are given in Chapter IV. The raw material was an aluminosilicate composition with about 8% Fe which gives the well-known red color to the roof tile.

Table 3.1. Chemical analyses (XRF) of the roof tile sample used in this study.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
51.8%	19.1%	7.3%	7.4%	8.4%	1.0%	2.7%	0.6%	0.0%	0.1%

3.1.2. Engobe

Engobe was prepared in two stages. First stage involved the use of higher purity laboratory grade raw materials while the second stage involved making the engobe with natural mineral raw materials.

In the first stage of engobe development relatively higher purity analytical grade oxides were used to eliminate problems from impurities. Therefore. a relatively pure frit was made in the laboratory to be used. This type of engobe was named HP Engobe. Once success was achieved with engobe development. lower purity materials were adapted for production of the engobe. An industrial grade frit (6116 Kalemaden) was used together with the lower purity engobe. This type of engobe was named LP Engobe indicating the low purity of its raw materials. Below are given information on the raw materials used in this study.

As mentioned in Chapter 2. each oxide has different properties like flux. stabilizer. glass former. For calculations such as CTE. Seger formula. the oxide composition should be known. In this study the chemical composition of each raw material was either obtained from their manufacturers or was analyzed by SEM-EDS. XRF was occasionally also employed for chemical analysis. The chemical analyses of the raw materials are given in Table 3.2. In addition suppliers of these materials are also summarized in Table3.3. Compositions of engobes were calculated in order to have their CTE values equal to or larger than that of the roof tile. This was achieved by matching the chemistries of the substrate (roof tile) and the engobe. CTE values of roof tiles and engobes could have been matched by other techniques as well (Eppler and Eppler 2000).

Table 3.2. Chemical analysis of the raw materials.

Raw Material	SiO_2	Al_2O_3	Fe_2O_3	***CaO***	***MgO***	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
*$Mg(OH)_2$**	NA	NA	NA	NA	63.6%	NA	NA	NA	NA	NA
*Na_2CO_3**	NA	NA	NA	NA	NA	57.5%	NA	NA	NA	NA
*$CaCO_3$**	NA	NA	NA	55.3%	NA	NA	NA	NA	NA	NA
*Borax**	0.0%	0.0%	0.0%	2.4%	0.0%	16.0%	0.0%	0.0%	33.3%	0.0%
*Quartz***	99.4%	0.2%	NA	NA	NA	0.1%	NA	NA	NA	NA
*Feldspar**	70.3%	18.3%	NA	0.3%	0.1%	10.5%	0.2%	NA	NA	NA
*B. Clay***	51.5%	33.0%	1.7%	0.2%	0.2%	0.1%	0.5%	1.5%	0.0%	0.0%
*Dolomite**	7.0%	2.4%	12.3%	30.2%	13.3%	0.0%	0.0%	0.0%	0.0%	0.0%
*E. Talc**	54.1%	0.0%	17.2%	5.3%	23.5%	0.0%	0.0%	0.0%	0.0%	0.0%
*Ind. Frit***	25.3%	5.3%	0.0%	3.6%	0.0%	9.6%	0.0%	0.0%	56.1%	0.0%

NA: Not Analysed
* Published chemical analysis
** Measured chemical analysis

Table 3.3. Supplier product codes of the raw materials.

Raw material	***Product code No.***	***Supplier***
$Mg(OH)_2$	M-8511	Sigma
Na_2CO_3	106.398.500	Merck (Eksper)
$CaCO_3$	C-3174	Sigma
Borax ($Na_2B_4O_7.10H_2O$)	Boraks Dekahidrat	Eti Maden İşletmeleri. Turkey
Quartz	Q.75	Kaltun madencilik A.Ş. Çine. Turkey
Feldspar	1005	Akmaden Madencilik A.Ş.. Çine. Turkey
Ball Clay	Mask-I	Matel Maden Hammadde A.Ş. Turkey
Dolomite	-	Boğaziçi A.Ş. Tire. Turkey
Egyptian Talc	ET 5	Omya Madencilik. İzmit. Turkey
Ind. Frit	6116	Kale Maden. Turkey

3.2. Method

In this thesis an engobe composition in the form of a suspension was prepared from oxide raw materials and frit. The engobe was applied on the surface of the green roof tile using a high pressure spray system. Details are provided below. This type of coating system is the most widely adapted technique in the industry.

Roof tile samples used in this study were made by Yüksel Toprak A.Ş. Therefore. more information about the manufacture of roof tiles is given in this section. Turgutlu is very rich in clayey raw material for roof tile which are brought to the factory by trucks (Yanık 2003). Conveyor belts carry the raw material within the factory through a number of machines that either sort out large pieces of rock or compress large chunks of earth to reduce the particle size to less than 3 mm. Some homogenization is also achieved in the process. Before being fed to the extruder (a.k.a. vacuum press) some moisture is added to the raw material to adjust the moisture to roughly 18-24%. The mud should be vacuumed before extrusion or else air packets in the product will explode during firing. harming the product. Once the roof tile is extruded out and shaped in presses into molds they are stacked in racks to dry them for extended periods of time depending on the humidity in the air. A major portion of the total shrinkage of the product occurs during drying while little shrinkage occurs during firing. Drying process must be slow to allow shrinkage without cracking. In Figure 3.1 the processing details are illustrated step by step.

In this study. semi finished product of green roof tile was obtained from the manufacturer in the form of rectangular pieces (230mmx410mm) that were just extruded. The green roof tile sample was then divided into small pieces of 60mm x 60mm as shown in Figure 3.2. Later they were measured for dimensions. dried for five days at 50^{o}C. Dry samples were ready for engobe coating.

Figure 3.1. Manufacturing of roof tiles
(Source: Wienerberger 2009).

Figure 3.2. Green roof tile samples that were wire-cut.

Engobe Mixture Preparation:

In Figure 3.3 the processing of engobe in İYTE Mechanical Engineering. ceramic laboratory is shown. For calculation of a proper engobe composition a MS Excel worksheet was formulated. The oxide percentage of each raw material was fed to this worksheet. Engobe compositions were prepared by adding 10-30wt% frit to the engobe. The frit supplied low-melting and water insoluble components to the engobe. The production of frit and engobe in the laboratory are explained step by step below.

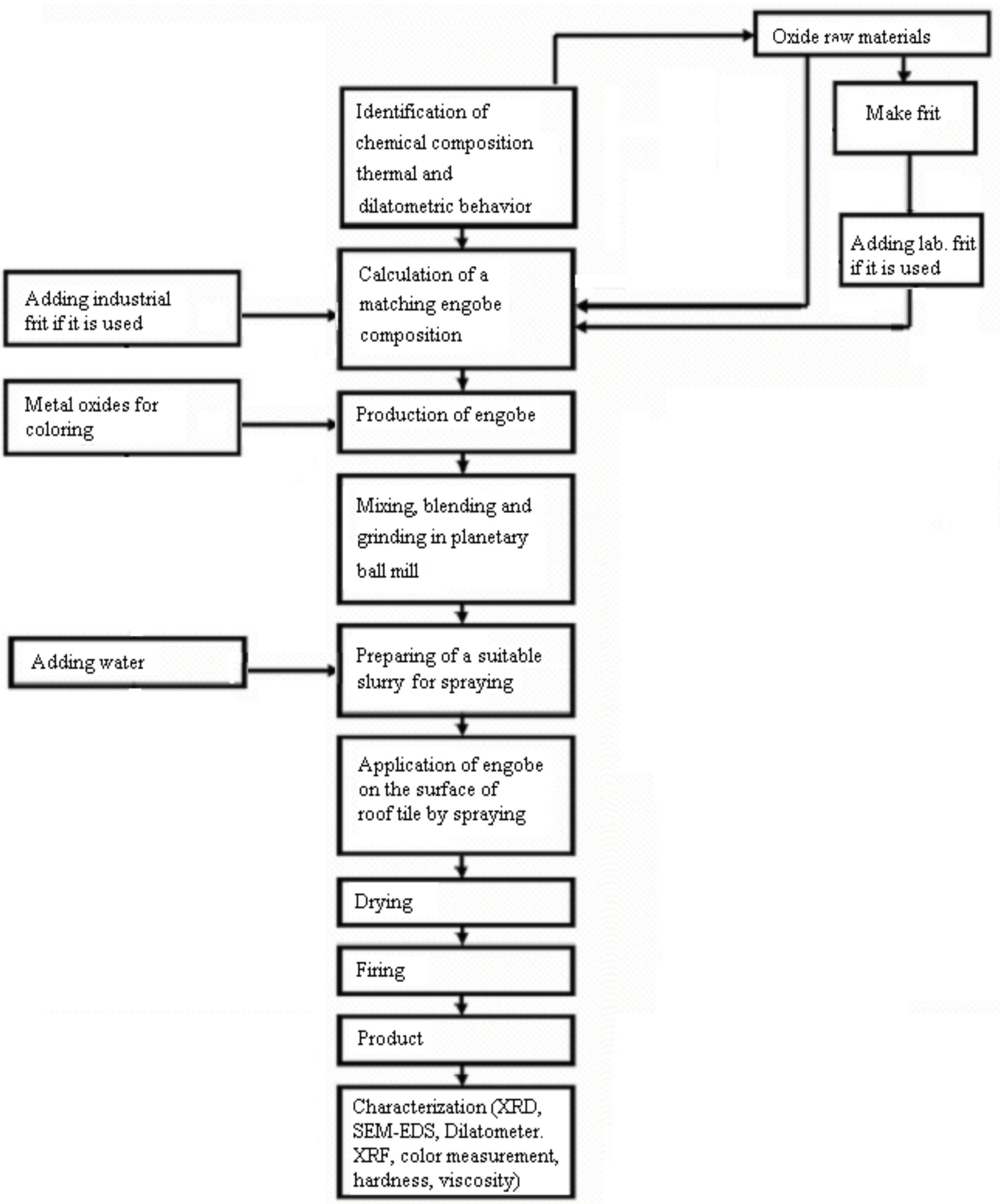

Figure 3.3. Flow chart for engobe production.

First step was making the lab frit. The most important mineral for frit was borax because it has low melting temperature. For this reason three different trials were done by changing the percentage of the B_2O_3 in the frit composition. Three different frit samples were prepared with 14%. 18% and 22% B_2O_3 as shown in Tables 3.4-6. Chemical compositions of these frits were almost identical apart from their B_2O_3 contents. Frit mixtures were weighed into a high density alumina crucible before being heated at 10^{o}C/min of heating rate to 1200^{o}C at which it was soaked for 2 hours as shown in Figure 3.4.a. Later they were poured into cold water in order to produce glass as illustrated in Figure 3.4.b. The high cooling rate during rapid cooling in water was sufficient to produce completely amorphous glass with good homogeneity. All frits were ground in Fritsch Pulverisette 6 planetary ball mill machine as illustrated in Figure 3.5 to convert them into fine powder form. 50 grams of frit was ground in 250ml tungsten carbide pot with 24 tungsten carbide balls of 10 mm diameter.

Table 3.4. Composition of lab frit containing 14% B_2O_3.

Chemical Composition of RawMaterials

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
45.6%	9.6%	0.0%	6.6%	0.0%	24.0%	0.1%	0.0%	14.0%	0.0%

Table 3.5. Composition of lab frit containing 18% B_2O_3.

Chemical Composition of RawMaterials

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
42.0%	8.8%	0.0%	6.0%	0.0%	24.7%	0.1%	0.0%	18.2%	0.0%

Table 3.6. Composition of lab frit containing 22% B_2O_3.

Chemical Composition of RawMaterials

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
38.6%	8.1%	0.0%	5.6%	0.0%	25.3%	0.1%	0.0%	22.3%	0.0%

After making the frit the next step was to find out which laboratory frit was suitable for the proper engobe composition. As shown in the flowchart in Figure 3.6. two different frits were used in this thesis. First frit was produced in the lab (Lab Frit) while the second was an industrially available frit (Industrial Frit).

Figure 3.4. Making of frit a) melting in box kiln and b) quenching in water.

Figure 3.5. Fritsch Pulverisette 6 planetary ball mill for dry grinding.

The grinding process of the engobe was the same for all samples and the same procedure with frit was used for size reduction. After grinding. a 50wt% suspension of engobe and the colorant oxides was prepared in water. The purpose was to produce a stable and homogenous aqueous suspension of engobe that could be sprayed onto the roof tile surface effectively. A compressor was used to deliver pressurized air for spraying the engobe through a nozzle. The pressure was adjusted at about 3-4 bars. As shown in Figure 3.7. the distance between the gun and the sample was about 50 cm to avoid uneven surface coating.

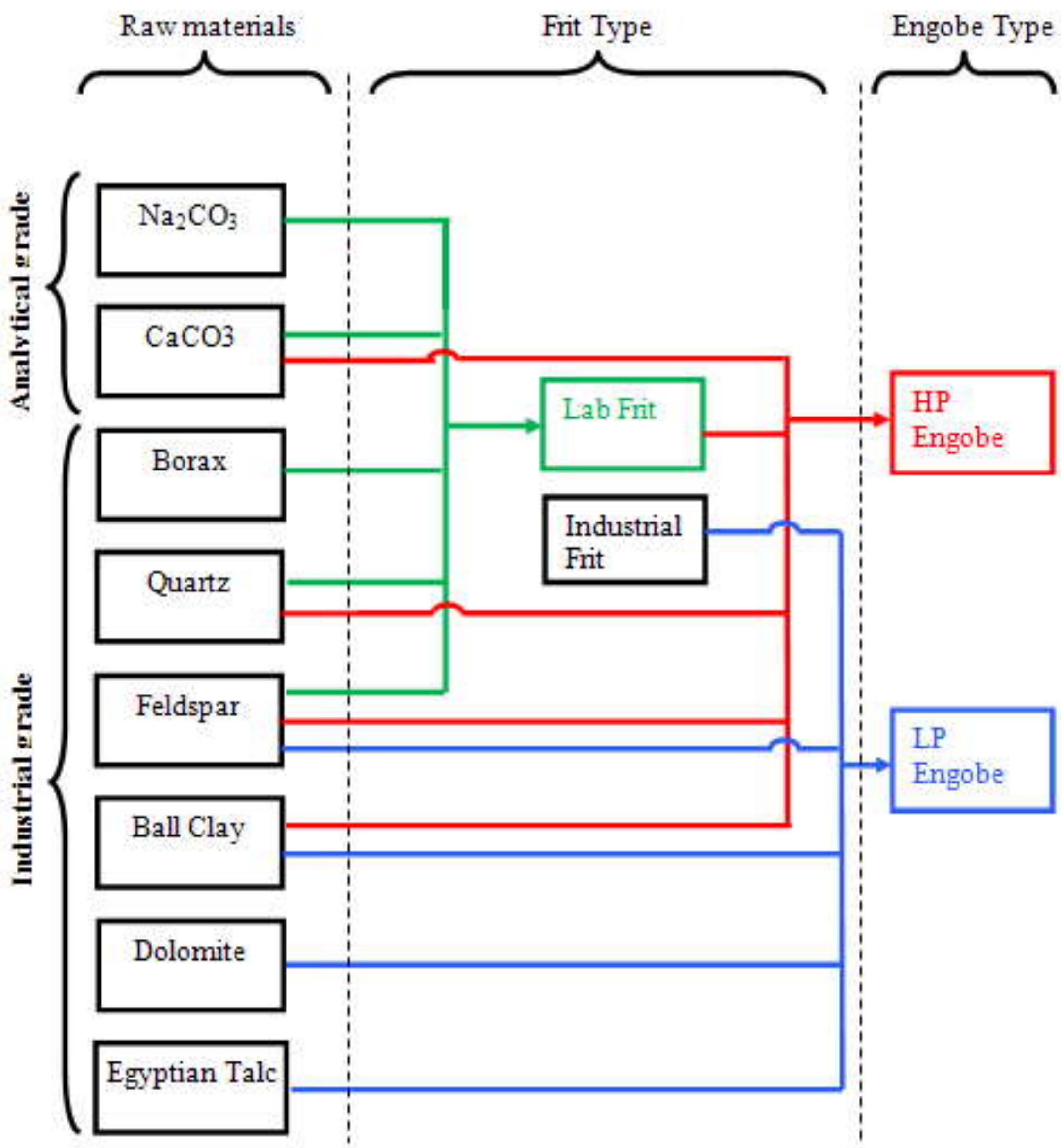

Figure 3.6. The use of raw materials for different frit and engobe production.

Figure 3.7. Application of engobe with a spray gun.

Variable amounts of colorants (metal oxides) were used in order to get different hues and colors. Before spraying onto the roof tile surface. the engobe suspensions were blended in the low speed lab type tumbling ball mill in a cylindrical plastic container for one hour at 30 rpm (Figure 3.8). There were a total of 8 pieces of balls with 12mm of diameter in the container to help with blending. The ball mill was not used for size reduction of the powder but was rather used for homogenization of the powder.

Figure 3.8. Lab type tumbling ball mill.

HP engobe:

High purity (HP) engobe was made by using high purity raw materials in order to adjust the oxide percentages easily. The percentages of quartz. feldspar. ball clay. lab frit. $CaCO_3$ used in the HP engobes were calculated. Therefore the engobe trials that contained 5%wt frit were made according to the chemical analysis of the substrate. Only the percentage of B_2O_3 was changed for each HP engobe as shown in Table 3.7. The following sample coding system was used in this thesis: EHP-14LF indicates a High Purity Engobe prepared with 14% B_2O_3 Lab Frit. Another example would be *EHP-18LF* meaning that High Purity Engobe prepared with 18% B_2O_3 Lab Frit.

Table 3.7. Chemical compositions of the HP engobe samples.

No	SiO_2	Al_2O_3	Fe_2O_3	***CaO***	***MgO***	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
EHP-14LF	61.0%	22.5%	0.8%	8.7%	0.1%	4.9%	0.3%	0.7%	0.9%	0.0%
EHP-18LF	60.9%	22.6%	0.8%	8.7%	0.1%	4.6%	0.3%	0.7%	1.2%	0.0%
EHP-22LF	60.8%	22.4%	0.8%	8.7%	0.1%	4.6%	0.3%	0.7%	1.5%	0.0%

In the third stage a number of sample sets of different engobe compositions with different percentages of SiO_2. Al_2O_3 and (Na_2O+K_2O) were prepared as shown below. These tests were designed in a triangular plot to investigate the most suitable engobe composition (Figures 3.9-11). This triangular plot was created by neglecting all components except SiO_2. Al_2O_3 and (Na_2O+K_2O) because these three are already the most abundant of all. A small amount of error is expected in these compositions since only these three are taken into consideration in setting up the different compositions. Such plots are useful in locating the best compositions for such studies. In addition. the experiments were done by changing the percentages of the lab frit to observe its effect on engobe formation. In all these tests the lab frit that was added to the engobe contained 18% B_2O_3. Samples are coded in such a way to indicate their lab frit contents. For example. sample coded EHP1-10 was prepared by mixing approximately 70%SiO_2 + 20%Al_2O_3 + 10% (Na_2O+K_2O). The meaning of the EHP1-10 code is the first sample of high purity engobe with 10%w lab frit which contains 18% B_2O_3. In Tables 3.8-10 the overall chemical compositions of the final engobe including the frit are given.

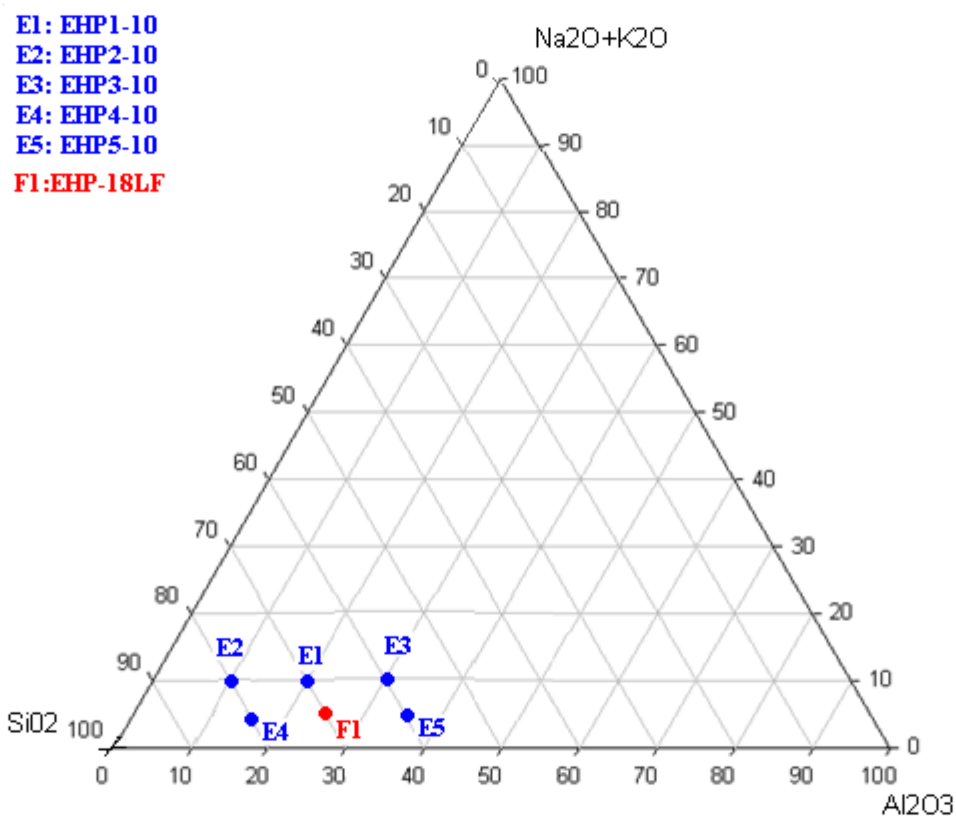

Figure 3.9. Engobe samples according to SiO_2-Al_2O_3-(Na_2O+K_2O) triangle design for 10%wt lab frit. B_2O_3 content of the lab frit was 18% for this design.

Table 3.8 Engobe compositions for 10%wt lab frit

No	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
E1/10	62.9%	17.9%	0.5%	8.1%	0.1%	7.5%	0.2%	0.4%	2.3%	0.0%
E2/10	72.7%	9.1%	0.0%	8.2%	0.0%	7.6%	0.1%	0.0%	2.2%	0.0%
E3/10	54.0%	27.2%	1.2%	8.4%	0.1%	5.3%	0.4%	1.0%	2.4%	0.0%
E4/10	67.7%	17.0%	0.8%	7.9%	0.1%	3.2%	0.3%	0.7%	2.3%	0.0%
E5/10	51.5%	30.5%	1.5%	8.4%	0.2%	3.5%	0.5%	1.3%	2.5%	0.0%

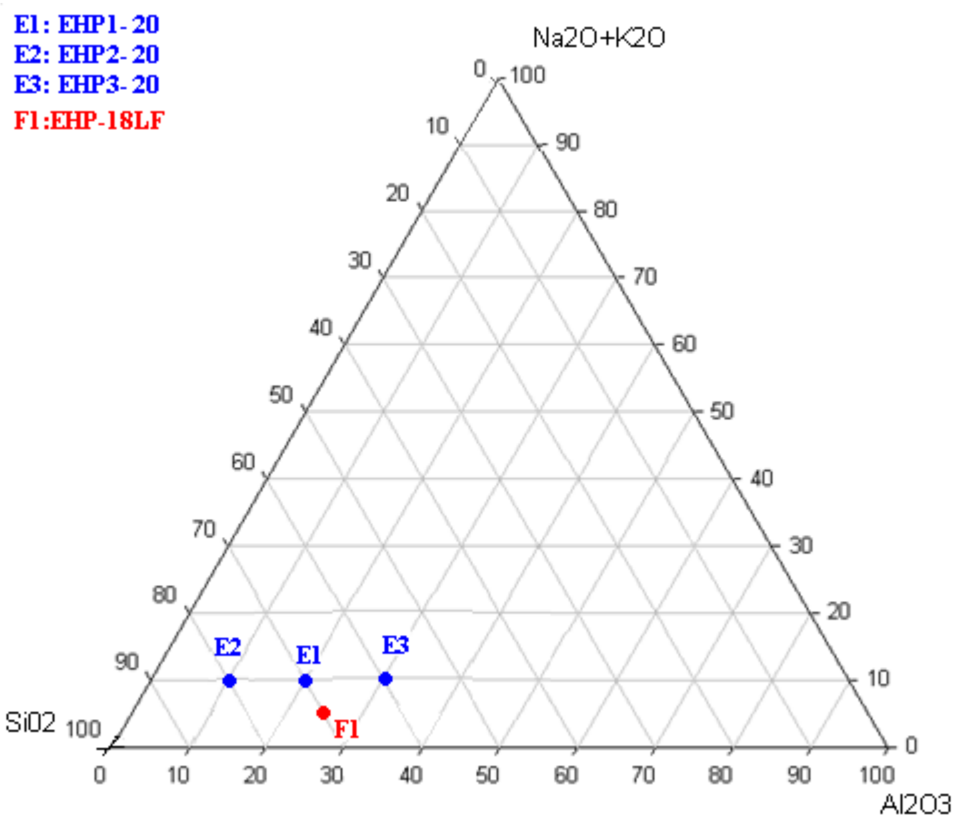

Figure 3.10. Engobe samples according to SiO_2-Al_2O3-(Na_2O+K_2O) triangle design for 20%wt lab frit. B_2O_3 content of the lab frit was 18% for this design.

EHP4-20. EHP4-20 cannot be obtained with the desired composition (SiO_2+Al_2O_3+Na_2O+K_2O=100%). The amount of the Na_2O is come from frit. So the decreasing the percentage of the Na_2O cannot be achieved.

Table 3.9 Engobe compositions for 20%wt lab frit.

No	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
E1/20	63.8%	15.5%	0.5%	7.2%	0.1%	8.1%	0.2%	0.4%	4.1%	0.0%
E2/20	71.1%	8.9%	0.2%	8.3%	0.0%	7.0%	0.1%	0.2%	4.1%	0.0%
E3/20	50.5%	25.2%	1.1%	7.9%	0.1%	7.3%	2.3%	1.0%	4.6%	0.0%

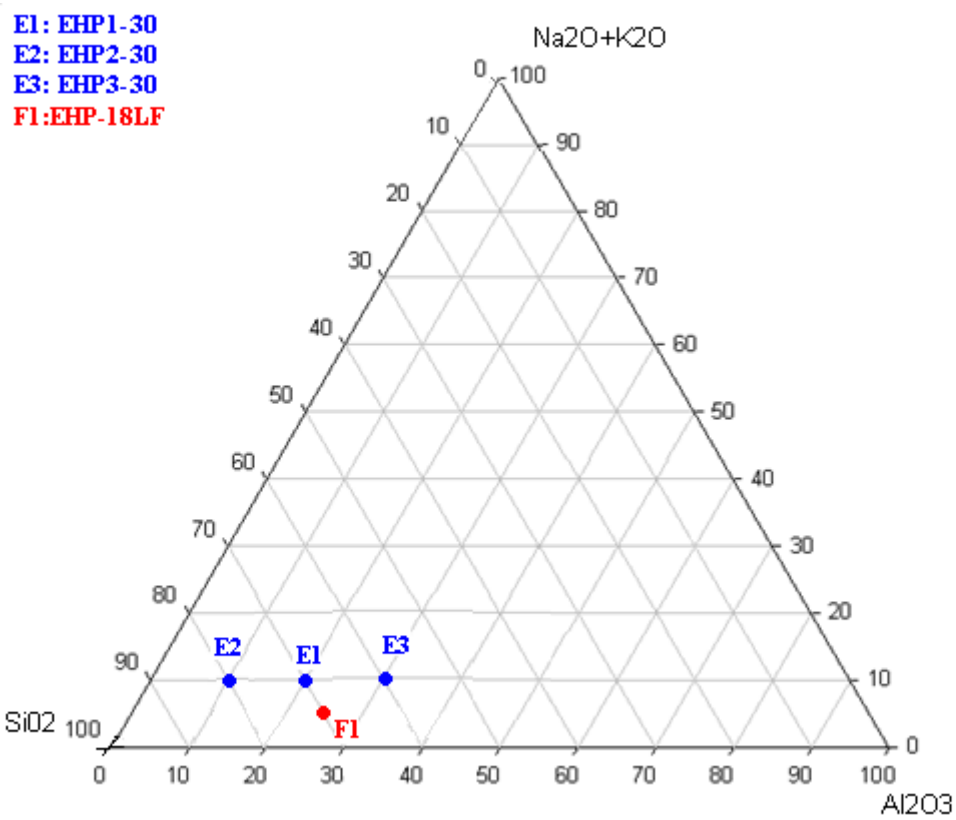

Figure 3.11. Engobe samples according to SiO_2-Al_2O_3-(Na_2O+K_2O) triangle design for 30%wt lab frit. B_2O_3 content of the lab frit was 18% for this design.

Table 3.10 Engobe compositions for 30%wt lab frit.

No	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
E1/30	57.1%	16.3%	0.5%	7.7%	0.1%	11.2%	0.2%	0.4%	6.5%	0.0%
E2/30	66.8%	8.4%	0.2%	7.9%	0.0%	9.8%	0.1%	0.2%	6.5%	0.0%
E3/30	49.2%	23.9%	1.0%	7.9%	0.1%	9.7%	0.3%	0.9%	6.9%	0.0%

LP engobe:

Last step was done by using natural minerals and the industrial frit instead of making lab. frit that was prepared with high purity materials. Different percentages of feldspar. ball clay. quartz. dolomite. talc and industrial frit were used in this stage. These raw materials were all available in tonnage quantities at reasonable prices. These samples were prepared by first mixing in powder form of almost 70%SiO_2. 20%Al_2O_3 and 10% (Na_2O+K_2O) and then by adding 12 and 32% of industrial frit to these blends. The engobe composition that contained 12%wt industrial frit is named ELP-IF-12. The other one is named ELP-IF-32. Compositions of mixtures using low purity raw materials and industrial frit are given in Table 3.11.

Table 3.11. Oxide compositions of LP engobe.

No	SiO_2	Al_2O_3	Fe_2O_3	*CaO*	*MgO*	Na_2O	K_2O	TiO_2	B_2O_3	P_2O_5
ELP-IF-12	51.5%	14.4%	6.2%	7.3%	7.4%	5.0%	0.2%	0.3%	7.6%	0.0%
ELP-IF-32	43.4%	11.0%	6.3%	7.0%	7.7%	5.0%	0.1%	0.3%	19.1%	0.0%

For investigating the effect of grinding speed and frit addition on final product quality some experiments were done as given in Table 3.12.

Table 3.12. Experiments for different grinding RPM and time.

No	SiO_2*	Al_2O_3*	Na_2O+K_2O*	*Ind. Frit*	*Grinding*	
					RPM	*Time (min.)*
ELP-IF-12	72.6%	20.3%	7.4%	12.0%	400	10
ELP-IF-32	72.9%	18.5%	8.6%	32.0%	400	10
ELP-IF-12-G200	72.6%	20.3%	7.4%	12.0%	200	10
ELP-IF-32-G200	72.9%	18.5%	8.6%	32.0%	200	10

$(SiO_2+Al_2O_3+NaO_2+K_2O=100\%)$

The effect of 5wt% addition of colorant oxides to an engobe sample (see sample ELP-IF-12. ELP-IF-32) were also studied. Cr. Mn. Ti. Fe. Co and Cu oxides were used as colorants.

3.2.1. Drying and Firing

After applying the engobe. the products were dried at ambient conditions for 3 days. If they were not dried well. cracks could occur during firing. Firing time and temperature affect the formation and maturation of the engobe. Many chemical reactions occur at this stage. Therefore. a great deal of defects results from these chemical reactions. The products were fired in a Protherm PLF160/5 laboratory furnace. The firing conditions are given in Table 3.13.

Table 3.13. Engobe compositions for different firing temperatures.

				Ind.	*Grinding*		*Firing*	
No	***SiO_2****	***Al_2O_3****	***Na_2O+K_2O****	***Frit***	***RPM***	***Time***	***Temp.***	***Time***
ELP-IF-12	72.6%	20.3%	7.4%	12%	400	10min.	1000°C	75min.
ELP-IF-32	72.9%	18.5%	8.6%	32%	400	10min.	1000°C	75min.
ELP-IF-12-970	72.6%	20.3%	7.4%	12%	400	10min.	970°C	75min.
ELP-IF-32-970	72.9%	18.5%	8.6%	32%	400	10min.	970°C	75min.
ELP-IF-12-1030	72.6%	20.3%	7.4%	12%	400	10min.	1030°C	75min.
ELP-IF-32-1030	72.9%	18.5%	8.6%	32%	400	10min.	1030°C	75min.
ELP-IF-12-150	72.6%	20.3%	7.4%	12%	400	10min.	1000°C	150min.
ELP-IF-32-150	72.9%	18.5%	8.6%	32%	400	10min.	1000°C	150min.

*($SiO_2+Al_2O_3+NaO_2+K_2O=100\%$)

3.2.2. Characterization

In order to obtain particle size distribution of engobe powder Sieve Analysis (ASTM C136) was made. Particle size distribution analysis of the roof tile raw material was made by a Laser Scattering Particle Size Analyzer (Malvern Instruments). The phase analyses of prepared engobes are investigated by powder XRD (X-Ray Diffraction) using Philips X'pert Difractometer with Cu-Kα radiation at 45kV. Also Phlilps XL-30S FEG Scanning Electron Microscope and Nikon L-150 Optical Microscope were used. The samples for SEM and OM were polished before analysis to observe the thickness of the engobe and its penetration and bonding to roof tile.

The thermal expansions of the samples were measured by using Linseis Dilatometer. For this analysis the powder engobe samples were pressed into a small pellet whose diameters were 15 mm. In order to prevent cracks 1wt% of PVA was added. Later they were fired at 800°C with 10°C/min rate for 75 minutes not to melt and deteriorate their shape. After firing they were cut into 6x6x12mm rectangular prisms. The CTE of the samples were measured at 600°C with 10°C/min rate.

Color measurements of the samples were done by using a spectrophotometer instrument (Spectrocam. Avantes). In addition the powder density was measured by using pycnometer.

Besides these analyses. temperature cycling resistance test was applied. The soaked products were heated to 185°C for 4 hours. Later they were quenched in 20oC water (B. Karasu & E. Gerede). This process was made to observe how the response of product against climate changes would be. Later the cracks on the surface were investigated.

For the acid resistance 5% NaOH. 5% H_2SO_4. 5% HCl. 5% HNO_3 solutions were applied on the surface of the engobes for a week. Later the surfaces were investigated.

Qualitative scale:

A qualitative scale was proposed and used in this thesis to evaluate the success of the engobe coating on the roof tile samples. The following basic quality criteria were used: cracks. degree of bonding. degree of vitrification. color and aesthetically pleasing. Each of these criteria was issued different levels.

- The crack. for example. was identified as many. moderate or no. depending on the frequency of observation of the cracks. as well as their sizes.
    - Many: If there are large cracks or if the cracks are small but count more than 10 per 4 cm^2. it is in the many group.
    - Moderate: If the number of cracks is between five and ten per 4 cm^2. the engobe is placed in the moderate group.
    - No: Engobe has no crack at all.
- For estimating the degree of bonding of the engobe. the surface was scratched with a sharp tool about 1 cm.
    - Good: If the engobe is not scraped from the surface or the length of the scratch is less than 3 mm. it is labeled as good.
    - Average: If the length of the scratch is between 3 and 6 mm. it is named as average.
    - Poor: If the surface is significantly affected more than 6 mm by the sharp steel tool. it is located in the poor group.
- The degree of vitrification is classified in two groups.
    - Transparent: If the surface of the roof tile (red color) can be seen the engobe is transparent.
    - Opaque: If not it is opaque.

- The color is determined according to the whiteness of the surface such as well or poor. It was defined according to percentage of the Fe_2O in the composition.
  - Well: If the percentage of the Fe2O is smaller than 1%. the color of the engobe is well.
  - Poor: If not. the color of the engobe is specified as poor.
- The aesthetic appearance is used as a general criteria to name the quality of the coating by comparing the samples according to the bubbles on the surface.
  - Good: If the number of the bubbles on the surface doesn't exceed 2 per 4 cm^2. the aesthetic appearance of engobe is determined as good.
  - Average: If the number is between 2 and 6 per 4 cm^2. it is labeled as average.
  - Poor: In other cases the engobe is named as poor.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter results of experimental studies on the production and application of engobe on roof tile are given. First the findings on the roof tile are given and then those for the engobe and frit are presented and discussed.

4.1. Roof Tile

The roof tile was a commercial product with the composition (Table 3.1) which was presented in section 3.1. In this section particle size distribution (PSD) analysis (Figure 4.1), the thermal expansion (dilatometric) behavior (Figure 4.2), color analysis (Figure 4.3), XRD analysis (Figure 4.4), and TGA analysis (Figure 4.5) results are given. The average particle size (D_{50}) of the roof tile was 16 μm. Thermal expansion coefficient of the roof tile was found to be 8 $x10^{-6}$ 1/^{o}C according to the Figure 4.2. Color data of the roof tile are L = 42.72, a = 21.00, b = 24.07. Location of the roof tile color is also shown in Figure 4.3. The color of the roof tile was red because of the Fe in the roof tile. According to XRF data (Table 3.1) the roof tile was very rich in SiO_2 and Al_2O_3. When the roof tile was heated up to 1000^{o}C the weight loss of the roof tile was about 18% according to TGA analysis. The reason of the weight loss can be the removal of physical water from the tile up to 100^{o}C, oxidation / burning of the organic compounds, loss of CO_2 from calcite and loss of chemically bound water from clay minerals like illite and kaolinite (Yanık 2003).

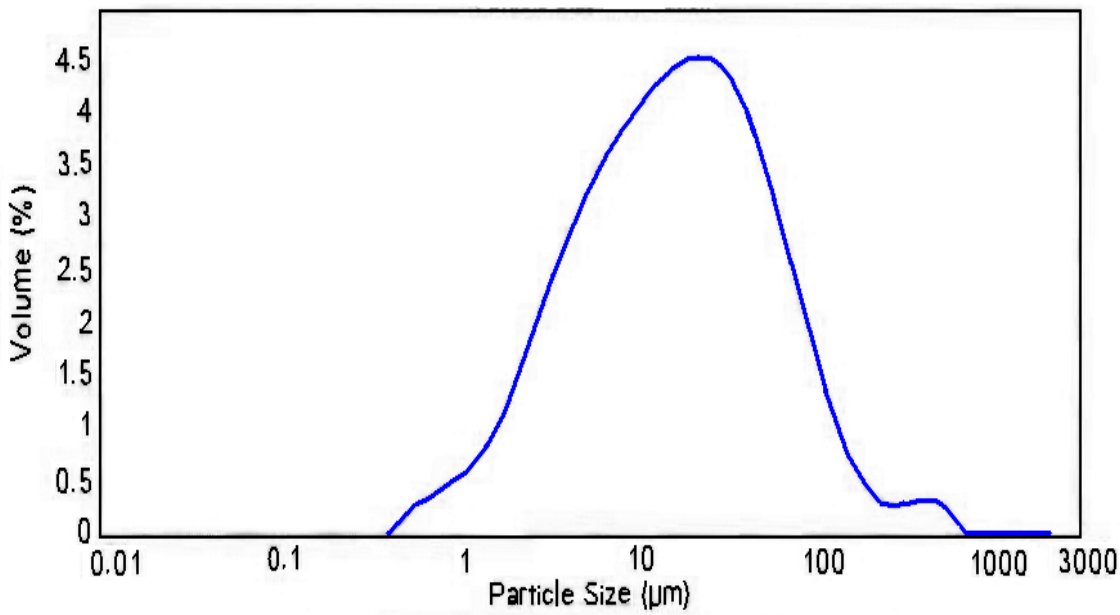

Figure 4.1. Particle size distribution (PSD) analysis as measured by Laser Scattering technique.

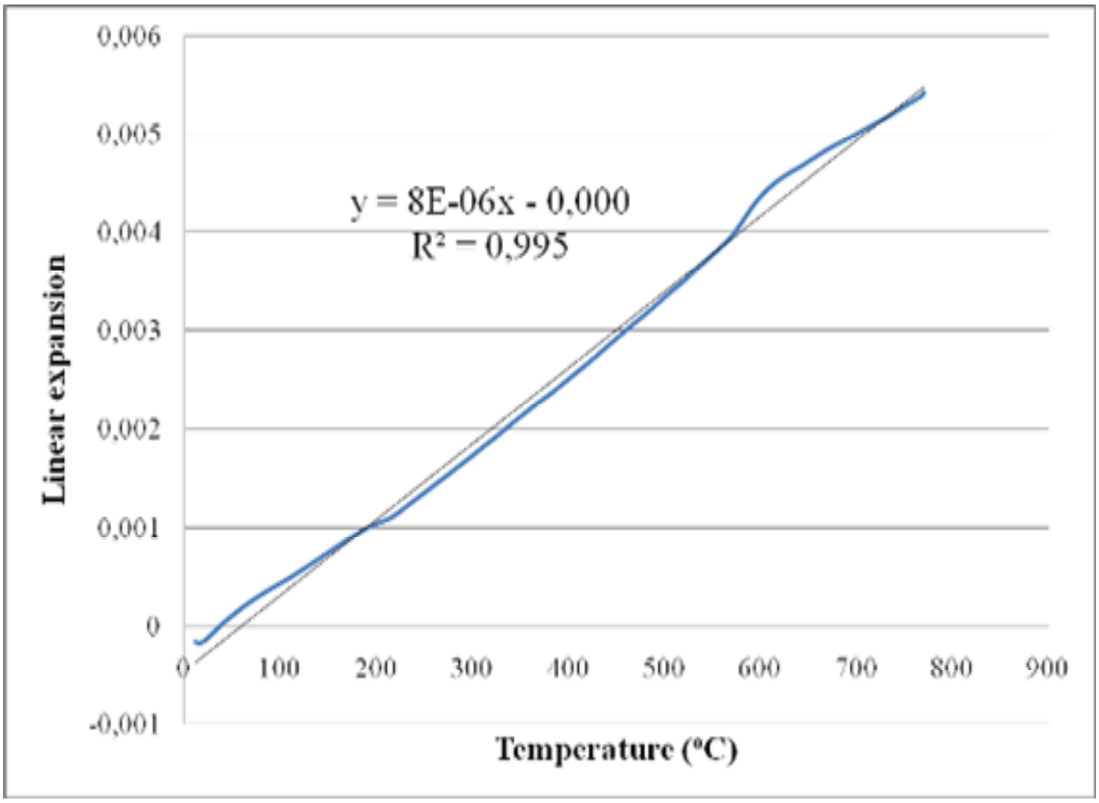

Figure 4.2. Thermal expansion behavior of the roof tile as measured by dilatometer.

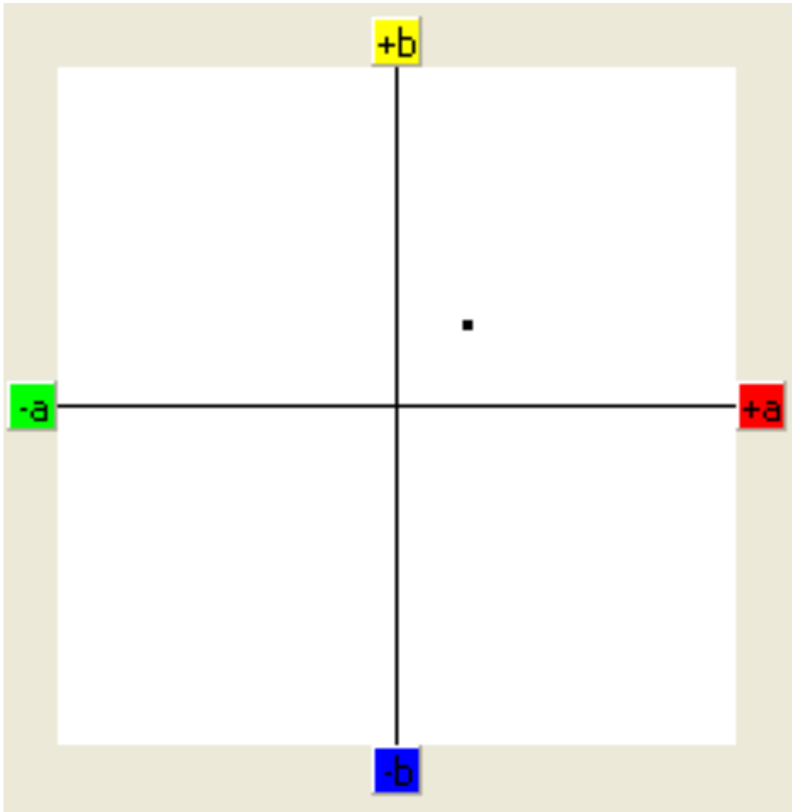

Figure 4.3. Location of the roof tile color on L – b – a diagram.

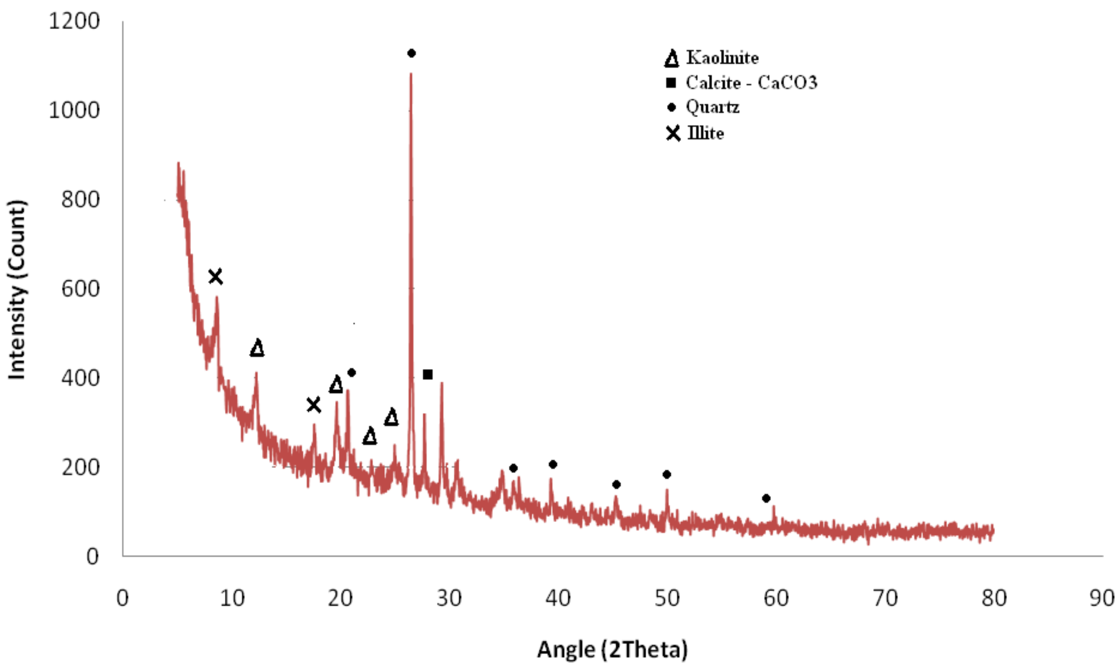

Figure 4.4. XRD analysis of the roof tile as measured by CuKα radiation.

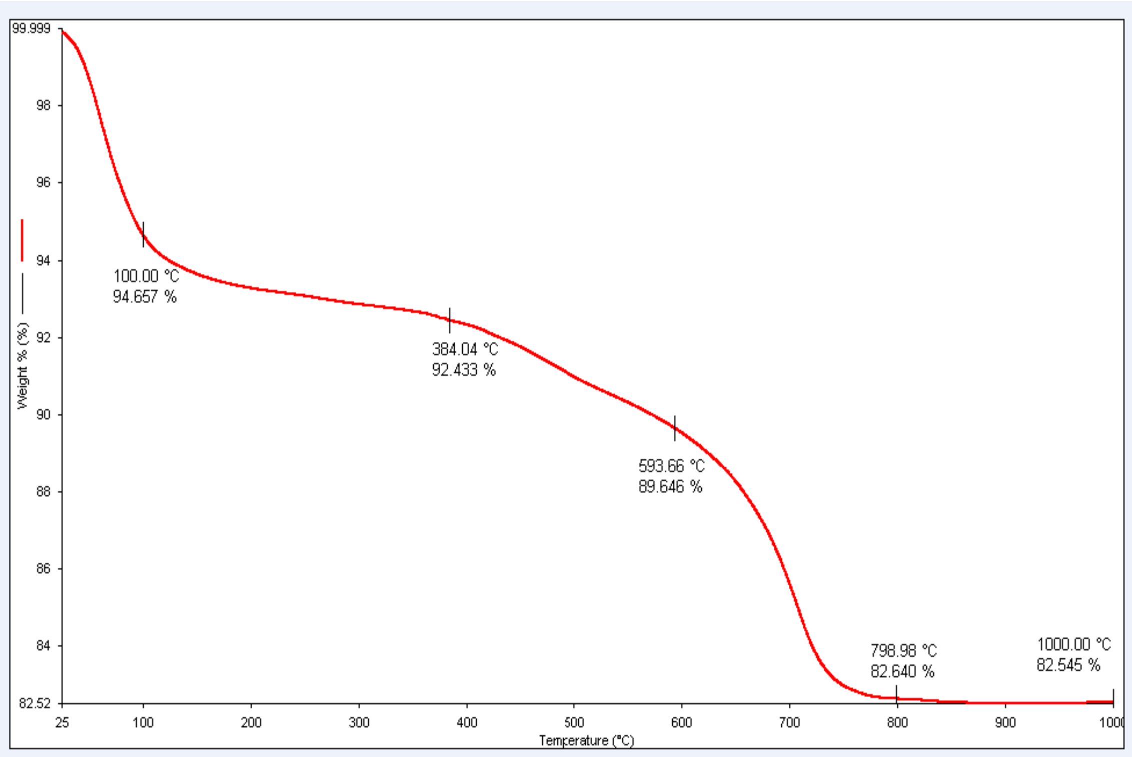

Figure 4.5. TGA analysis of the roof tile.

4.2. Characterization of the Raw Materials Used in Engobe

Results of characterization of each material which was used for making engobes and frit are given below. The chemical analysis of the raw materials was given in Chapter 3.1 so they are not given in this part.

Quartz (SiO_2):

Quartz, which is a source of highly pure SiO_2, is abundantly available on earth at low cost. It was used as the major component of the engobe and frit compositions. The SEM image of the quartz is also given in Figure 4.6.

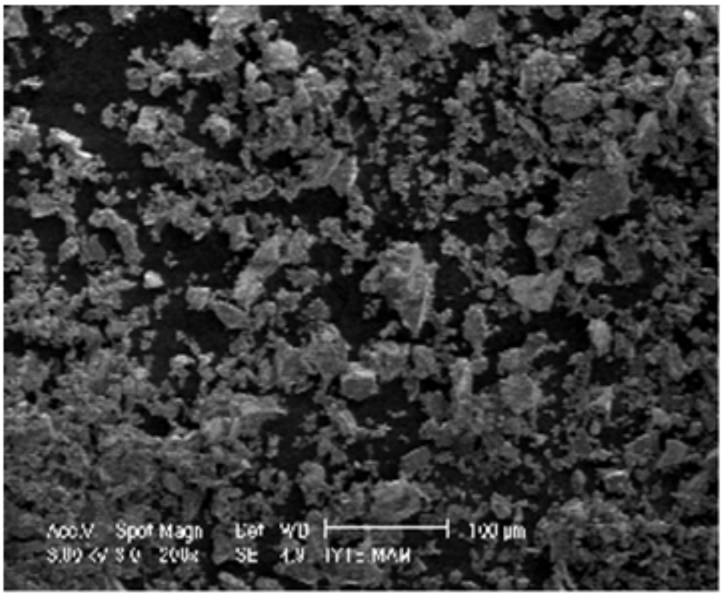

Figure 4.6. SEM image of the Quartz.

The sodium feldspar (Akmaden code 1005):

The color of the feldspar is an indication of its impurity content. The higher the amount of impurities like Fe and Ti, the darker is the color from white to pale or darker brown. Sodium feldspar with a code number 1005 was white due to its high purity. The published average particle size of the powder was 30 µm (Çine Akmaden Catalog 2009). SEM image and XRD analysis pattern are illustrated in Figures 4.7-8. As the name implies, it consists of mainly sodium feldspar and XRD results also confirmed this.

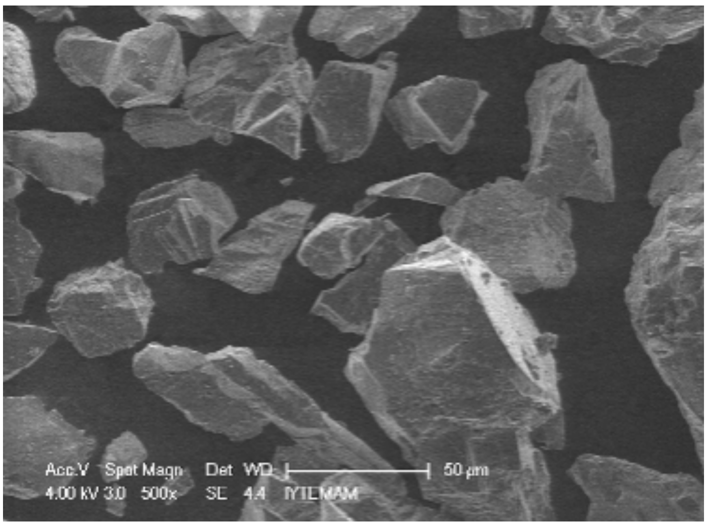

Figure 4.7. SEM image of the Sodium Feldspar 1005.

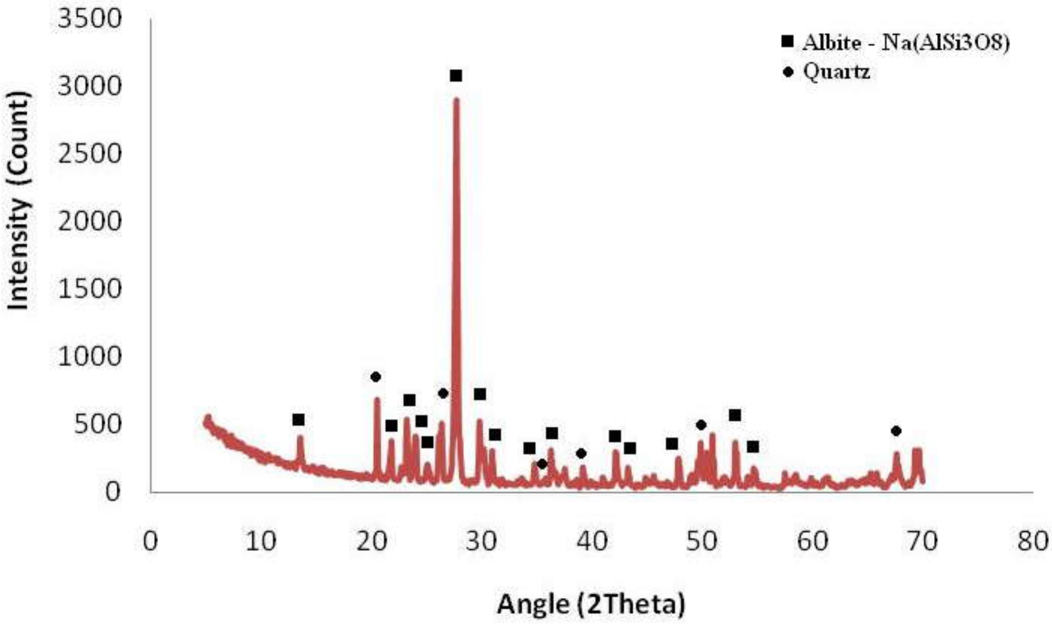

Figure 4.8. XRD analysis of the Sodium Feldspar 1005.

Ball clay :

This clay contains some iron and titanium which can change the color of the engobe as in Figure 4.9 (Table 3.2). LOI (loss on ignition) value of the clay is approximatelly 12% (Matel 2009). In addition, the SEM image and XRD analysis of the mineral are presented in Figures 4.10 and 4.11. According to XRD results the material obtained was good quality clay with more kaolinite than quartz.

Figure 4.9. Ball clay.

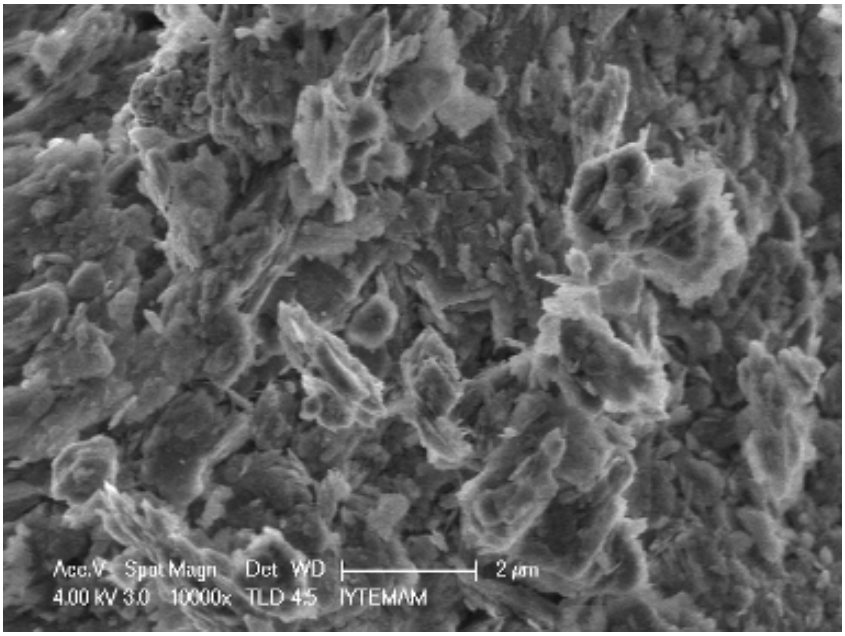

Figure 4.10. SEM image of the ball clay.

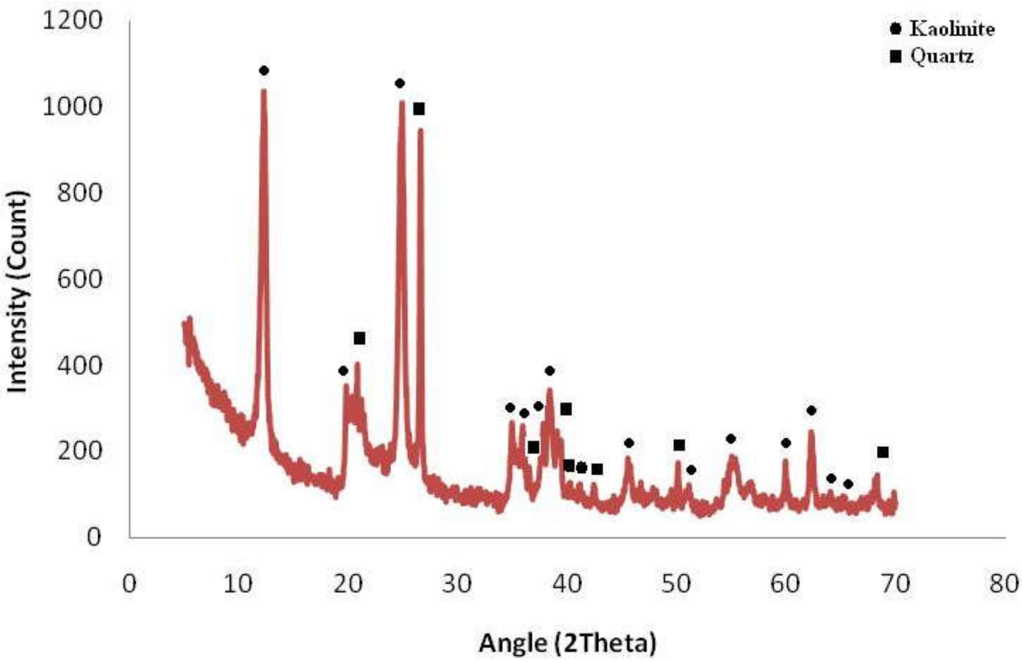

Figure 4.11. XRD analysis of ball clay.

Egyptian Talc:

The published average particle size of the Egyptian talc (Omya A.Ş., İzmir) was 13 µm. Also the percentage of powder finer than 2 µm was 3.2%. SEM image, the particle size distribution and XRD analysis are given in Figures 4.12-14.

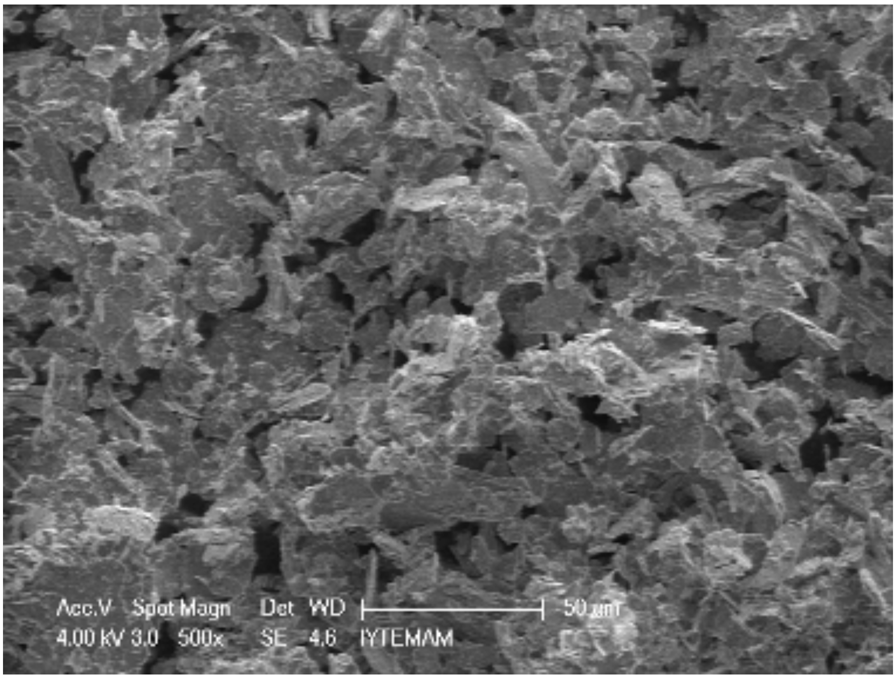

Figure 4.12. SEM image of Egyptian talc.

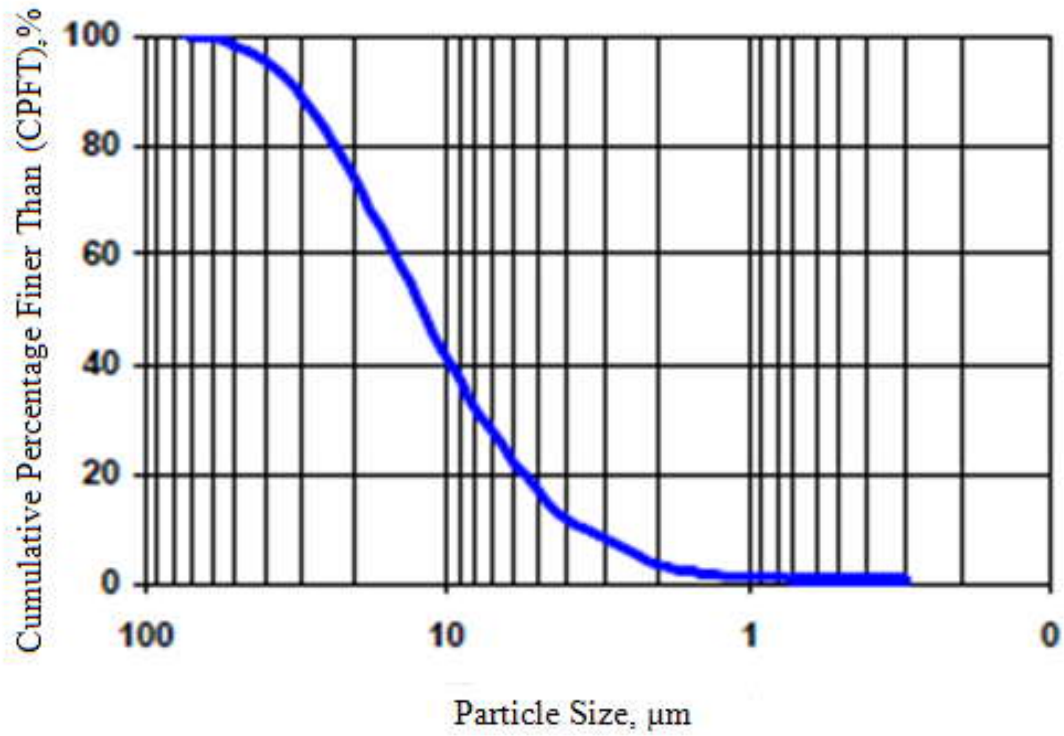

Figure 4.13. Published particle size distribution of Egyptian talc.

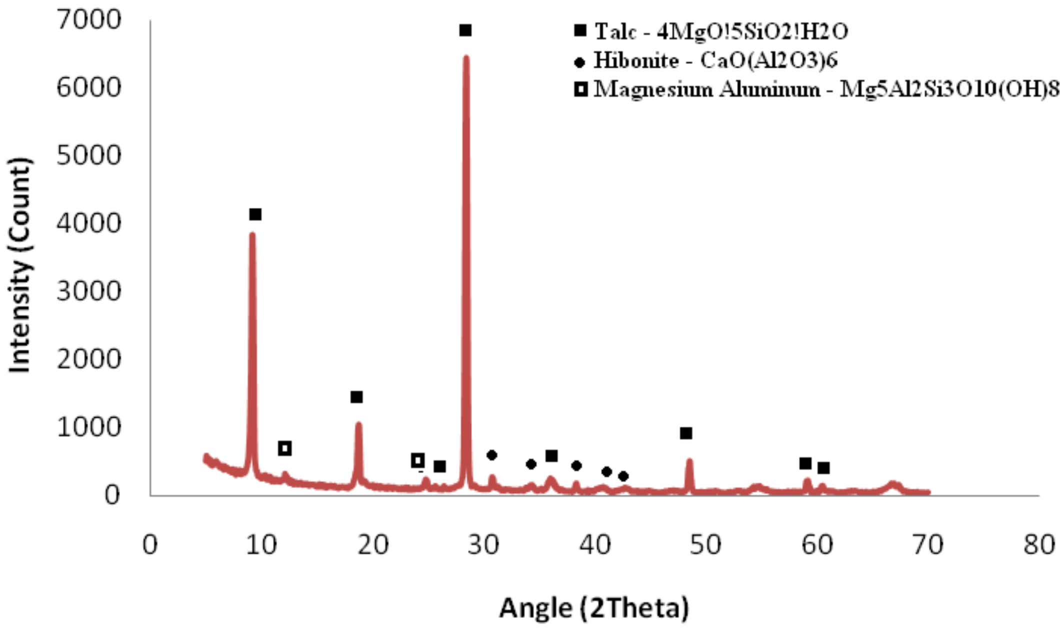

Figure 4.14. XRD analysis of Egyptian talc.

Dolomite:

Dolomite is named as double carbonate mineral of calcium and magnesium therefore it is one of the most widely used mineral for making engobe (Eppler 2000). Figure 4.15 shows SEM image and Figure 4.16 illustrates XRD analysis of the mineral.

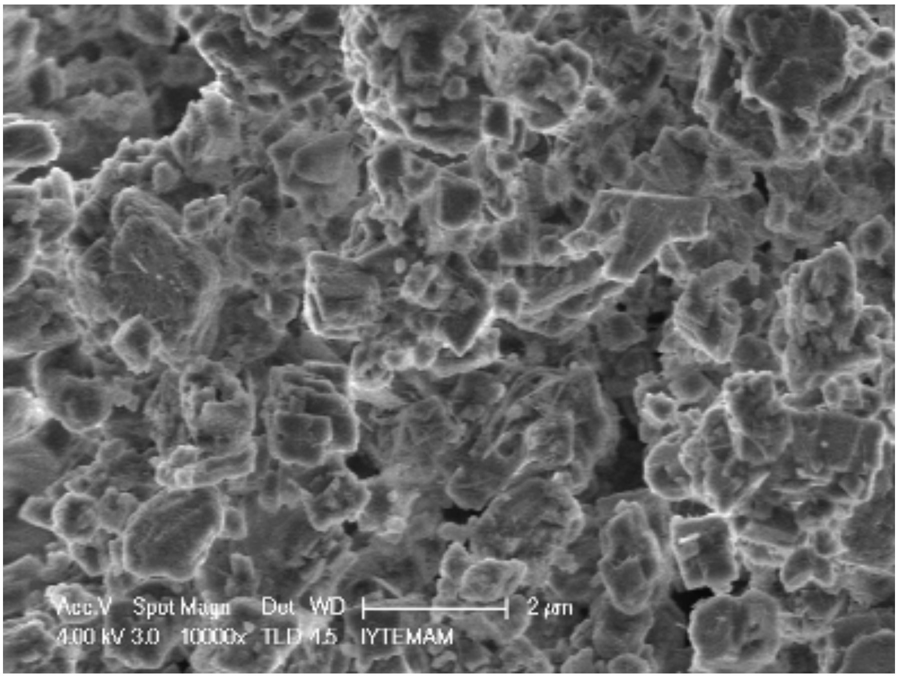

Figure 4.15. SEM image of Dolomite.

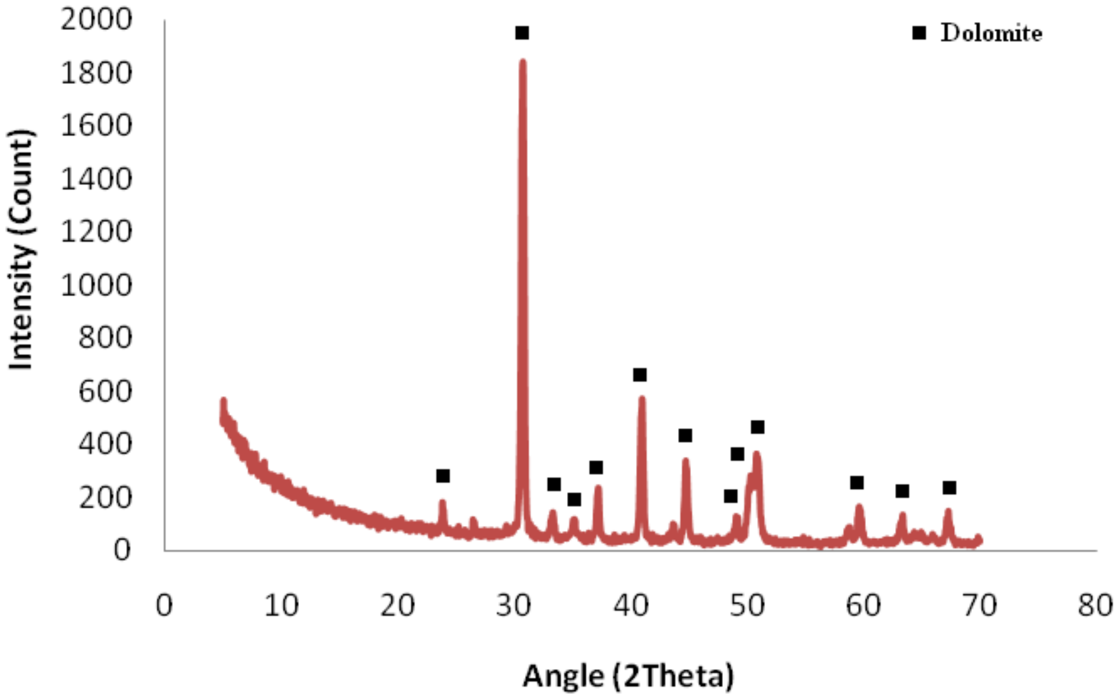

Figure 4.16. XRD analysis of Dolomite.

Borax ($Na_2B4O_7.10H_2O$):

Borax was soluble in water therefore it could not be used in engobe in the as-received form. Hence, it was incorporated into a frit melt in the lab. The published particle size of as-received borax was 50% smaller than 63 µm (Eti Maden 2009). In addition the SEM analysis was illustrated in Figure 4.17.

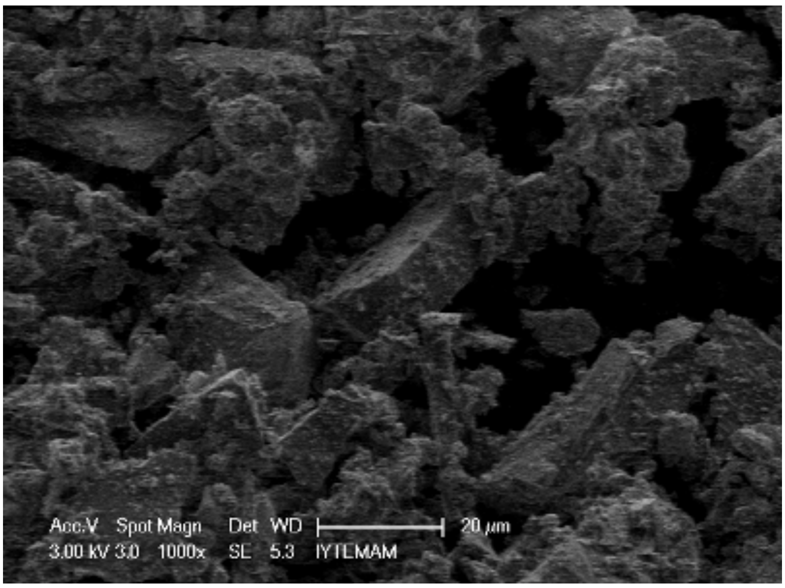

Figure 4.17. SEM image of Borax powder.

Industrial frit (Frit 6116):

For engobe compositions low temperature frit is an important constituent that helps improve penetration of engobe to roof tile surface. Hence a better mechanical contact is achieved. Frit 6116 (Figure 4.18) was chosen due to its low maturation temperature and lack of lead oxide (PbO) which is an undesirable constituent in roof tiles. The published melting point of frit 6116 was 647^{o}C. Figure 4.19 shows the analysis of the particle size distribution. Furthermore Figure 4.20 shows SEM image of the industrial frit.

Figure 4.18. The Industrial Frit – 6116.

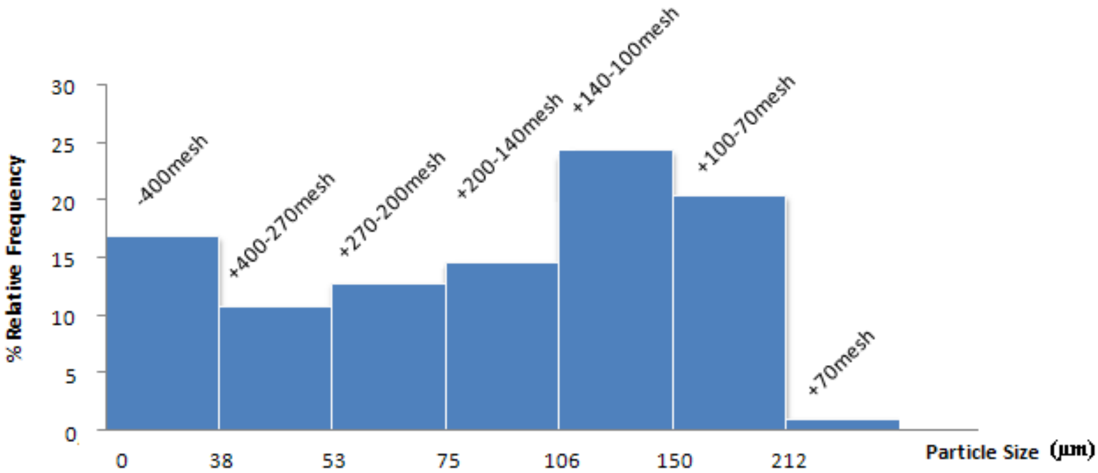

Figure 4.19. Sieve Analysis of industrial frit 6116.

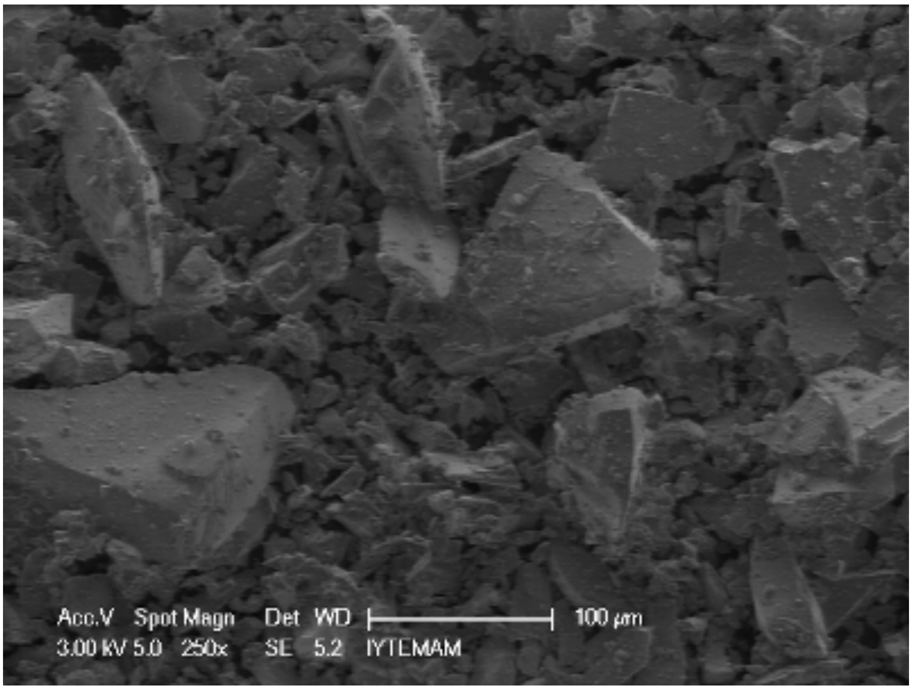

Figure 4.20. SEM image of industrial frit 6116.

Lab frit:

Three different frits were made in the lab. They contained 14, 18 and 22% B_2O_3. All three of them were used in engobe compositions but the lab frit with 18% B_2O_3 was the most suitable for the engobe as illustrated in Figure 4.21. Therefore the sieve analysis of the lab frit with 18% B_2O_3 is given in Figure 4.22.

Figure 4.21. The Laboratory Frit (18% B_2O_3) removed from water was glassy.

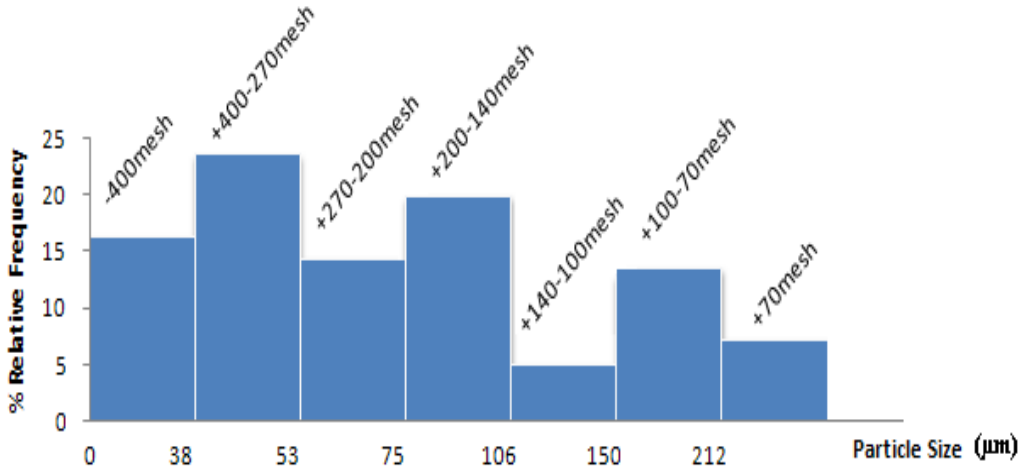

Figure 4.22. Sieve Analysis of Laboratory Frit (18% B_2O_3).

4.3. Results of Studies with Engobe

4.3.1. Development of Engobe by Using Higher Purity Chemicals and Different Types of Laboratory Frit

For development of proper engobe composition by using higher purity chemicals (EHP: Engobe High Purity), 5% by weight of lab frit was added. Different compositions of this lab frit with 14, 18 and 22% B_2O_3 were tested (Table 3.7). The results of these experiments are summarized in Table 4.1. All of the engobe surfaces had a matte shade possibly due to the low amount of the lab frit. Although they had the same chemical composition there were many cracks on the samples except for *EHP-18LF* which was also very well bonded to the roof tile (Figure 4.23). It was not easy to scratch the engobe from the surface with a sharp metal tool. Since 18% B_2O_3 lab frit gave the best result for the engobe composition, the remaining tests were made by using 18% B_2O_3 lab frit.

Figure 4.23. Photograph of the engobe samples with different kinds of lab frit.

Table 4.1. Properties of the engobe samples prepared by different percentages of lab frit.

	Presence of cracks			*Degree of bonding*			*Degree of vitrifying*		*Color*		*Aestatically pleasing*		
No	***Many***	***Modarate***	***No***	***Poor***	***Average***	***Good***	***Transparent***	***Opaque***	***Poor***	***Well***	***Poor***	***Average***	***Good***
EHP-14LF	+			+				+		+	+		
EHP-18LF			+			+		+		+			+
EHP-22LF	+			+				+		+	+		

4.3.2. HP Engobes (EHP)

Once the 18% B_2O_3 containing frit was chosen as the best frit, it was added in different proportions to different engobe compositions in eleven different HP engobe samples. Each composition contained different weight percentages of SiO_2, Al_2O_3, (Na_2O+K_2O). Results of these tests are given in Table 4.2. The quality rating of the fit of the engobe on roof tile was graded in discrete qualitative levels.

According to Table 4.2 transparency of the engobe was parallel to the percentage of the lab frit in the engobe. Because frit encourages glass formation (vitrification) that gives a transparent shade to the engobe (Figures 4.24-26). Besides engobe and roof tile interface was stronger because the melting point of the engobe decreases with increasing proportion of lab frit which in turn produces a more fluid and more penetrating engobe at high temperature.

In addition ball clay was used as an alumina source in the engobe compositions. Therefore the color of the HP engobe became darker when the amount of the alumina was increased as shown in Figure 4.27. The change in color depends on the amount of Fe2O3 in the ball clay.

EHP1-10 (High purity engobe sample number 1 containing 10% lab frit that has 18% B2O3) and EHP1-30 engobe samples gave the best results with a good bond and smooth surface. For engobe sample number 1 the reader is referred to Figure 3.9 and 3.11.

Table 4.2. Properties of the HP engobe samples.

	Presence of cracks			*Degree of bonding*			*Degree of vitrifying*		*Color*		*Aestatically pleasing*		
No	***Many***	***Modarate***	***None***	***Poor***	***Average***	***Good***	***Transparent***	***Opaque***	***Poor***	***Well***	***Poor***	***Average***	***Good***
EHP1-10			+			+		+		+			+
EHP2-10			+			+		+		+		+	
EHP3-10		+		+				+	+			+	
EHP4-10	+			+				+		+	+		
EHP5-10	+			+				+	+		+		
EHP1-20			+			+		+		+		+	
EHP2-20			+		+			+		+		+	
EHP3-20	+				+			+	+		+		
EHP1-30			+			+	+		+				+
EHP2-30		+				+	+		+		+		
EHP3-30		+			+		+		+				+

Figure 4.24. Images of the EHP engobe samples prepared with 10%w lab frit. These results are to be compared to Figure 3.9. a) EHP1-10, b) EHP2-10, c) EHP3-10, d) EHP4-10 and e) EHP5-10.

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Figure 4.24. (cont.)

(cont. on next page)

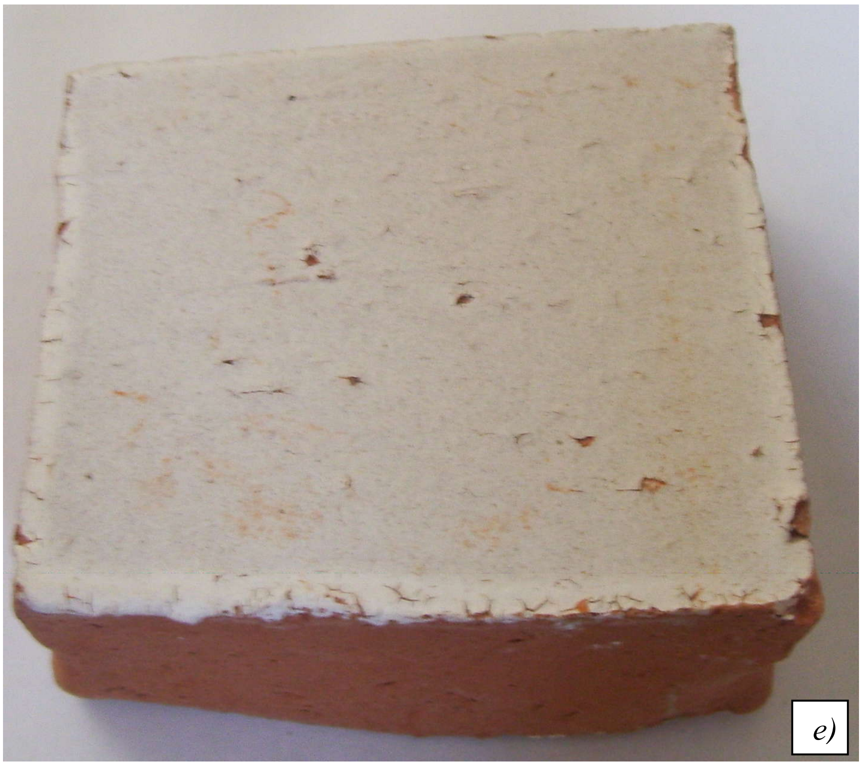

Figure 4.24. (cont.)

Figure 4.25. Image of the HP engobe samples prepared with 20%w lab frit. These results are to be compared to Figure 3.10. a)EHP1-20, b) EHP2-20 and c) EHP3-20

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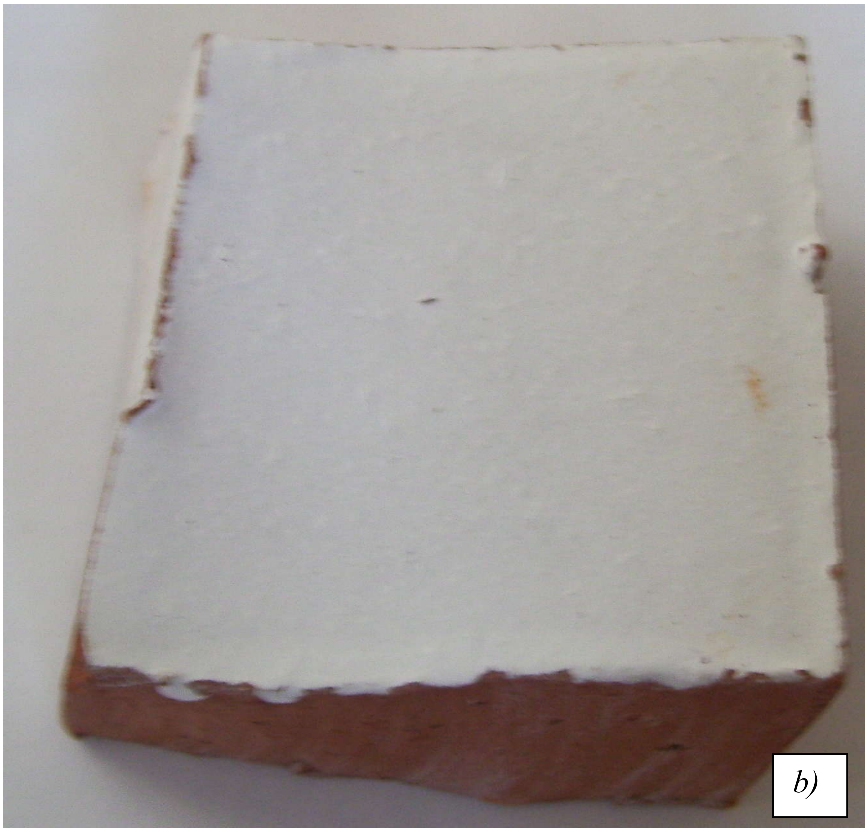
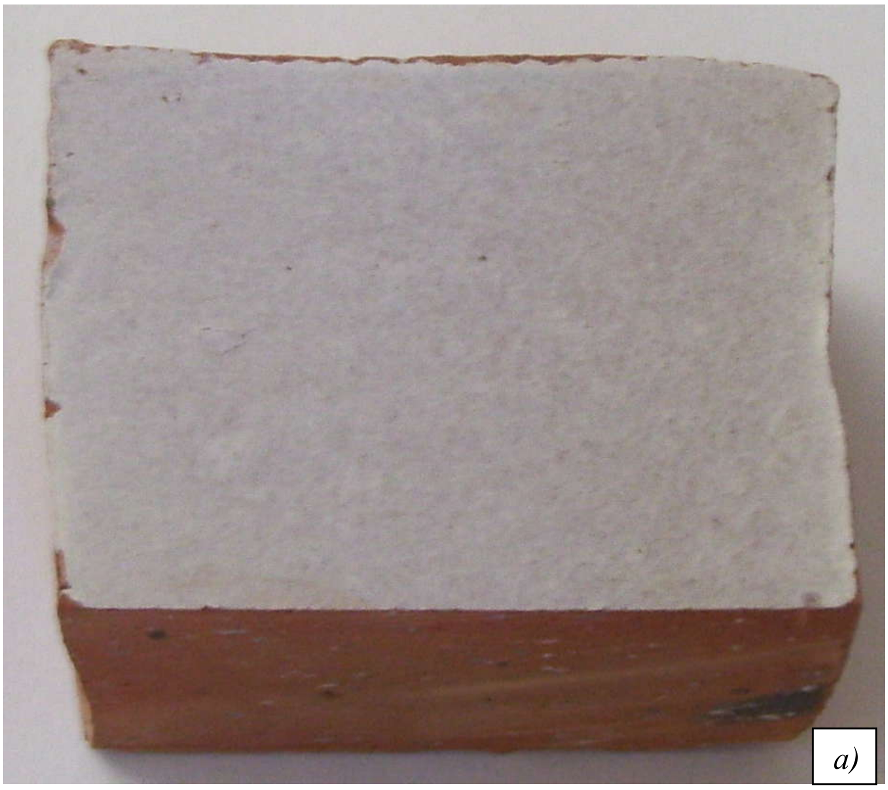


Figure 4.25. (cont.)



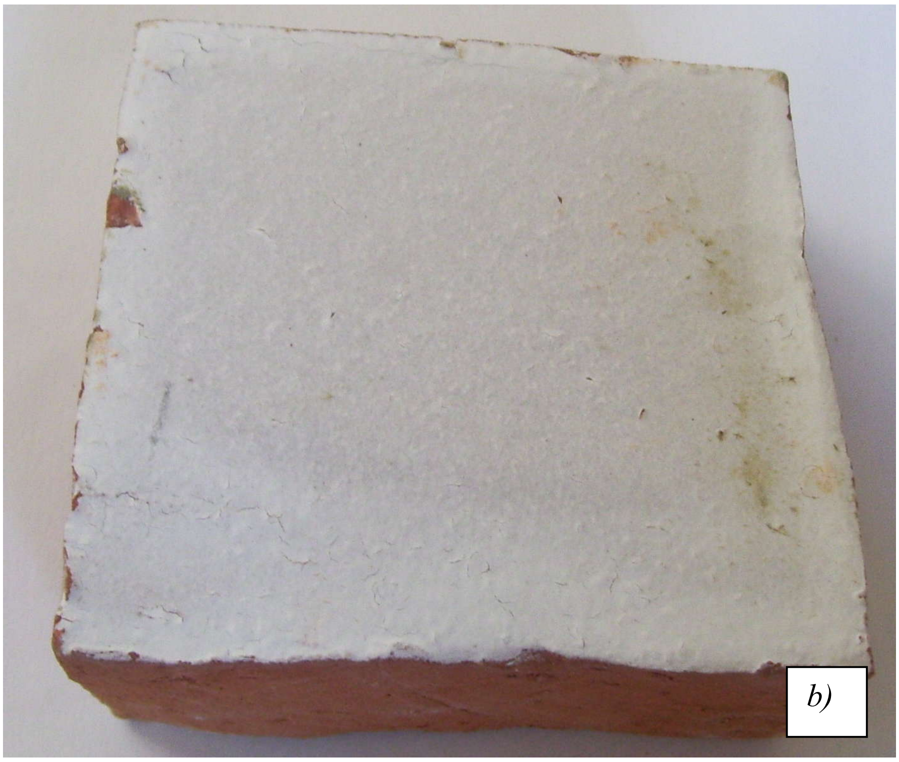


Figure 4.26. Image of the HP engobe samples prepared with 30%w lab frit. These results are to be compared to Figure 3.11. a)EHP1-30, b) EHP2-30, c) EHP3-30

(cont. on next page)

Figure 4.26. (cont.)

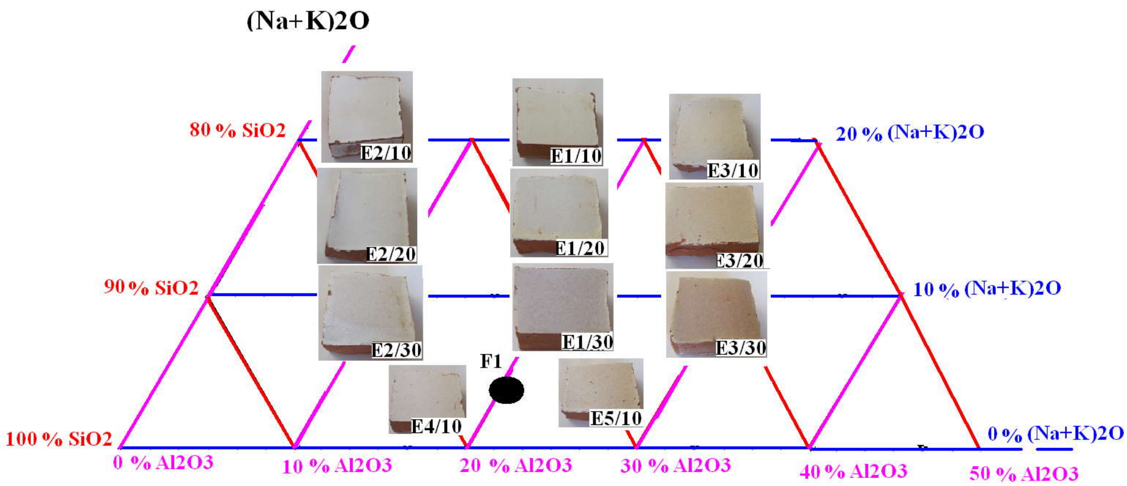


Figure 4.27. All EHP samples laid out on a triangular plot for comparison. The effects of the oxides and frit to the HP engobe can be seen here.

Thermal expansion of each engobe was calculated to analyze the fitting of the engobe and roof tile because thermal expansion is one of the most effective properties for elimination of defects. So, the CTE values of EHP1-10 (Figure 4.28) and EHP1-30 (Figure 4.29) were measured. The slope of the curve shows the CTE of the material.

The CTE of EHP1-10 was 9 x10^{-6} 1/^{o}C and the CTE of EHP1-30 was 7 x10^{-6} 1/^{o}C and these two results were close to the CTE of the roof tile.

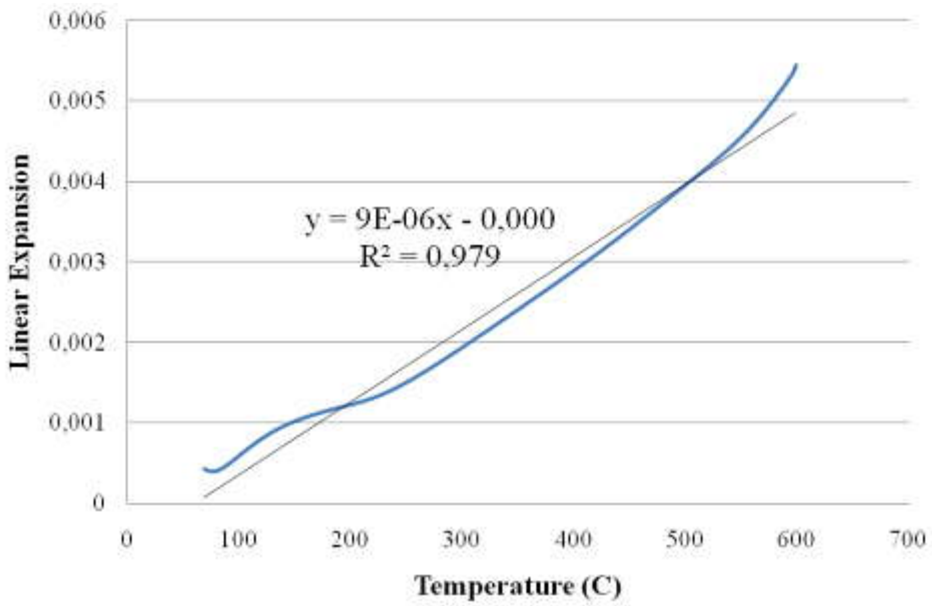


Figure 4.28. Thermal expansion graph of EHP1-10.

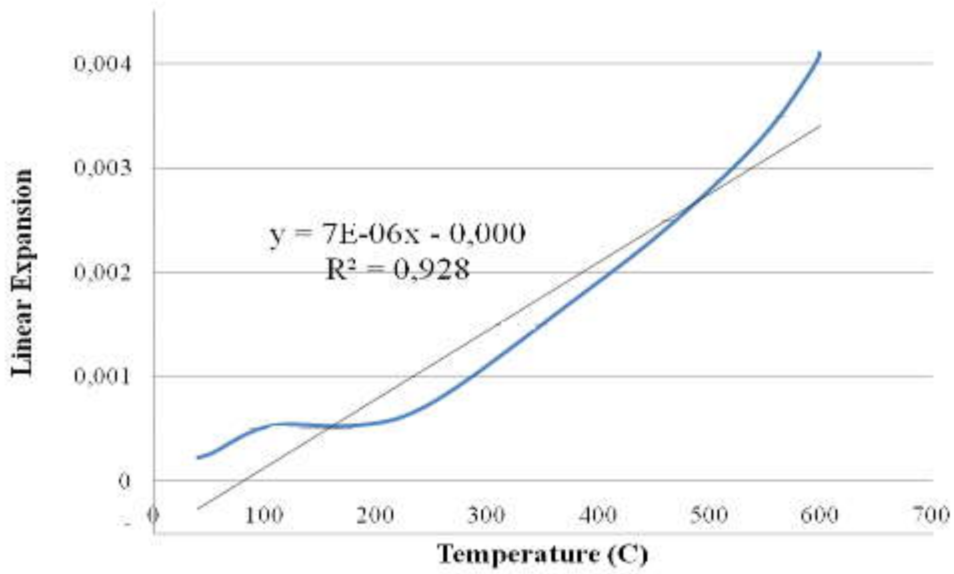


Figure 4.29. Thermal expansion graph of EHP1-30.

To observe the penetration of the engobe and roof tile they were analyzed by OM and SEM. The OM image of the EHP1-30 and EHP1-10 are given in Figures 4.30-31 the glass structures of the engobes of 250 μm thickness were easily observed by these images. Quality of bond of the engobe layer onto the body was good in both EHP1-10 and EHP1-30 samples. SEM images of the EHP1-30 sample (Figure 4.32) showed that engobe was glassy and well attached to the roof tile body. The roof tile part was horizontal due to the extrusion effect of the shaping.

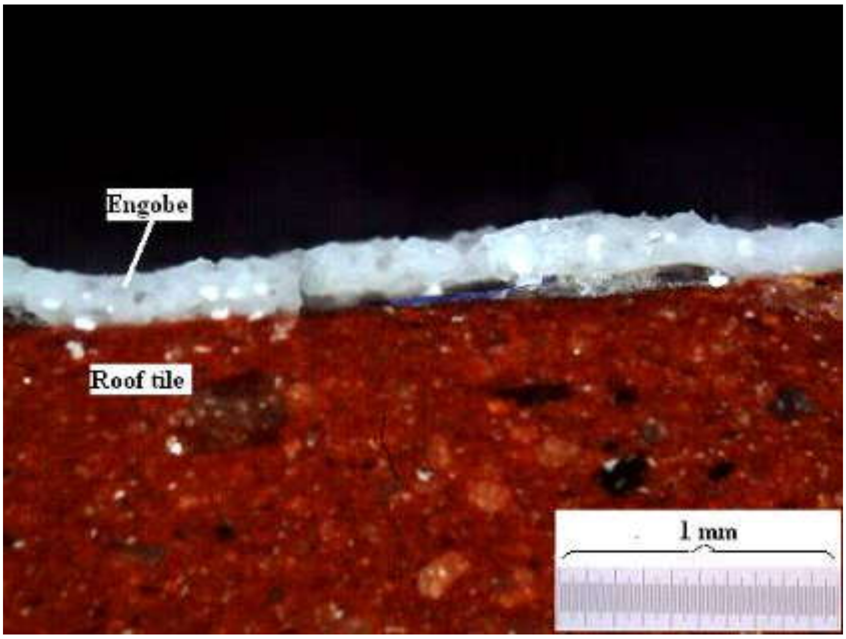


Figure 4.30. The OM image of the EHP1-10.

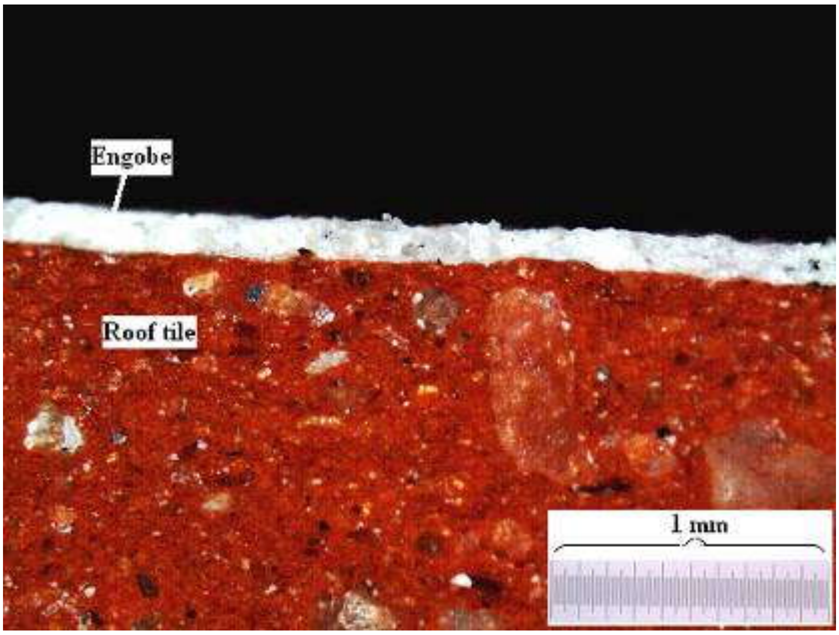


Figure 4.31. The OM image of the EHP1-30.

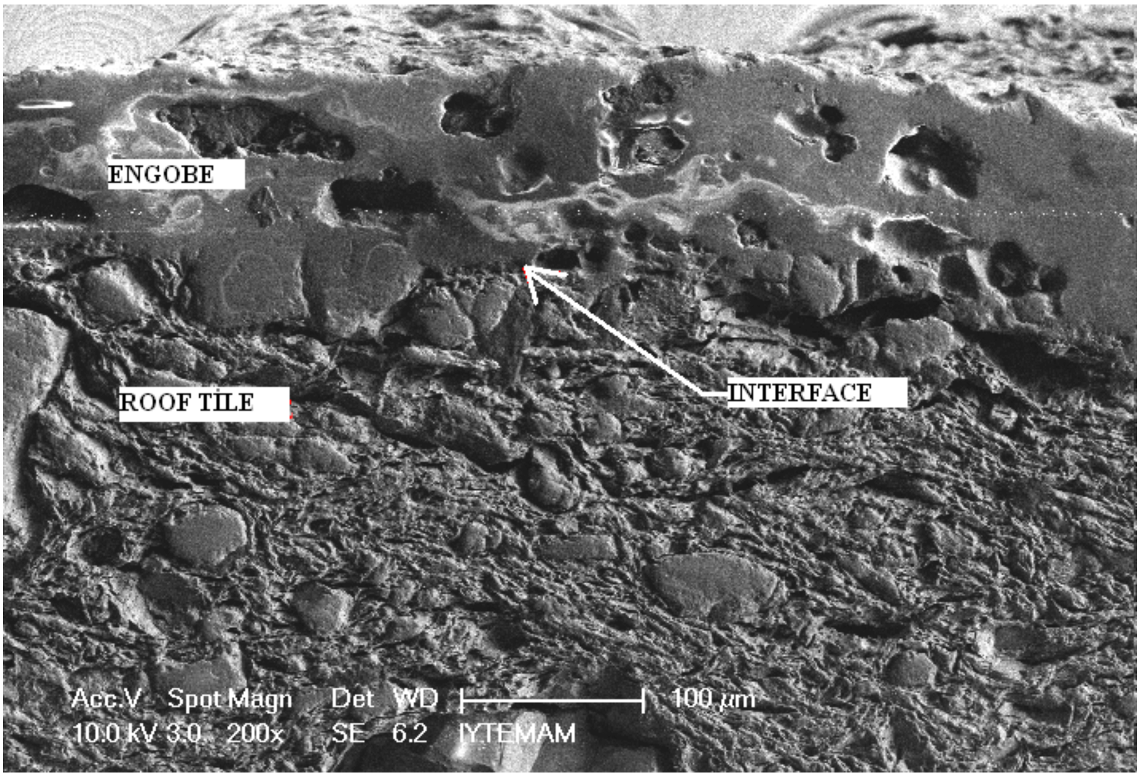


Figure 4.32. The SEM image of the EHP1-30. Roof tile body was well bonded to the engobe layer which was glassy.

The XRD results of the EHP1-10 and EHP1-30 are given in Figures 4.33-34.

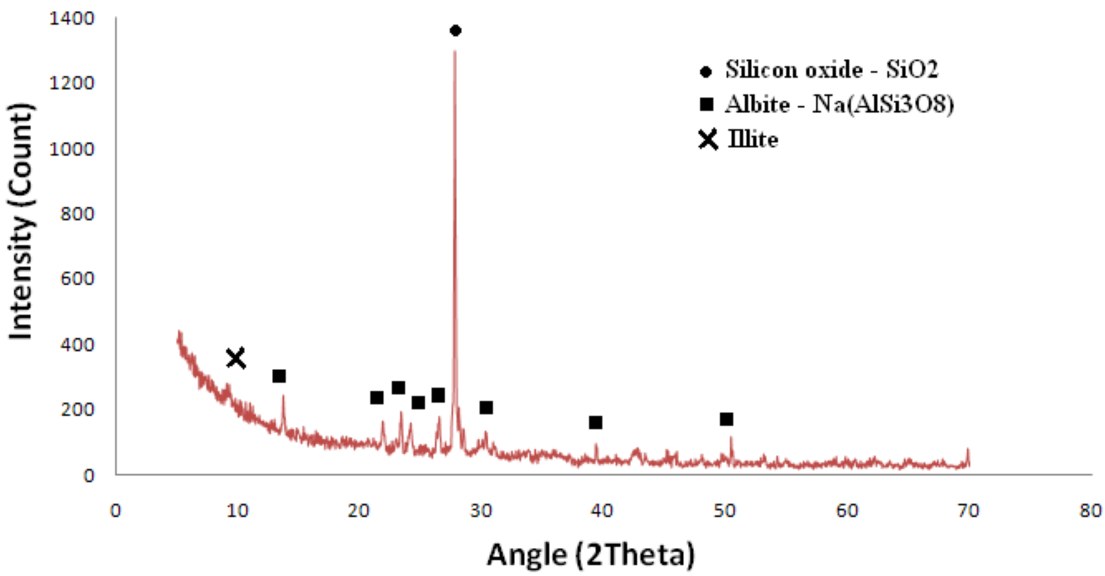


Figure 4.33. XRD analysis of EHP1-10.

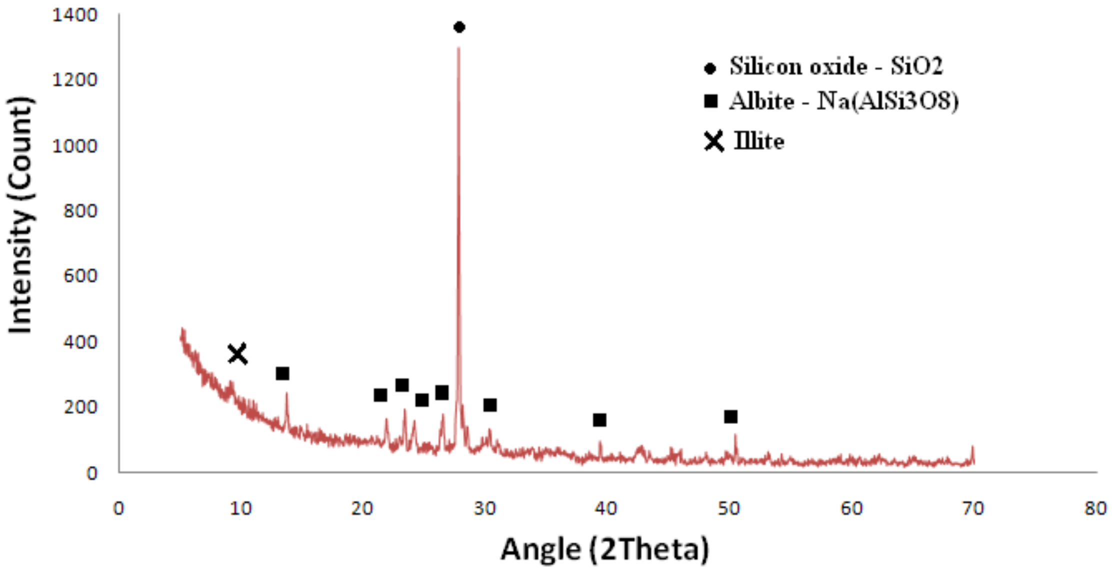


Figure.4.34. XRD analysis of EHP1-30.

4.3.3. Low Purity Engobe (ELP)

Two EHP samples were identified as the best engobe samples above. These same engobe compositions were this time tried to be made from low purity raw materials and industrial frit to produce a reasonably low cost product that may have potential for marketing in roof tile industry. ELP engobe samples were prepared from compositions with 12% and 32% of industrial frit (IF). ELP-IF-12 was the low purity engobe equivalent of EHP1-10 and ELP-IF-32 was the low purity version of EHP1-30. The average density of the ELP-IF-12 sample in powder form was 2.62 g/cm^3 and for the ELP-IF-32 sample it was 2.65 g/cm^3 these measurements were done with a pycnometer. Weights of 1 liter 50% solids suspensions of the ELP-IF-12 and ELP-IF-32 were 1370 and 1400g, respectively.

Viscosity of the fluid was also analysed. The engobe suspensions were non-newtonian because they did not have a constant viscosity independent of the shear rate. Viscosity of the engobe suspension decreased with increasing shear rate. So, both ELP-IF-12 and ELP-IF-32 had shear thinning rheologies which was desirable during spray coating process.

The particle size and its distribution are important because they affect the rheological behavior of the engobe suspension and the firing behavior of the engobe. This latter factor helps improve penetration of the engobe to the roof tile during firing.

Therefore; the particle size of the engobe powders were analyzed by Sieve method. As shown in Figure 4.35 the average particle size of ELP-IF-12 was 142 µm. Besides; the particle size of ELP-IF-32 was 131 µm according to Figure 4.36.

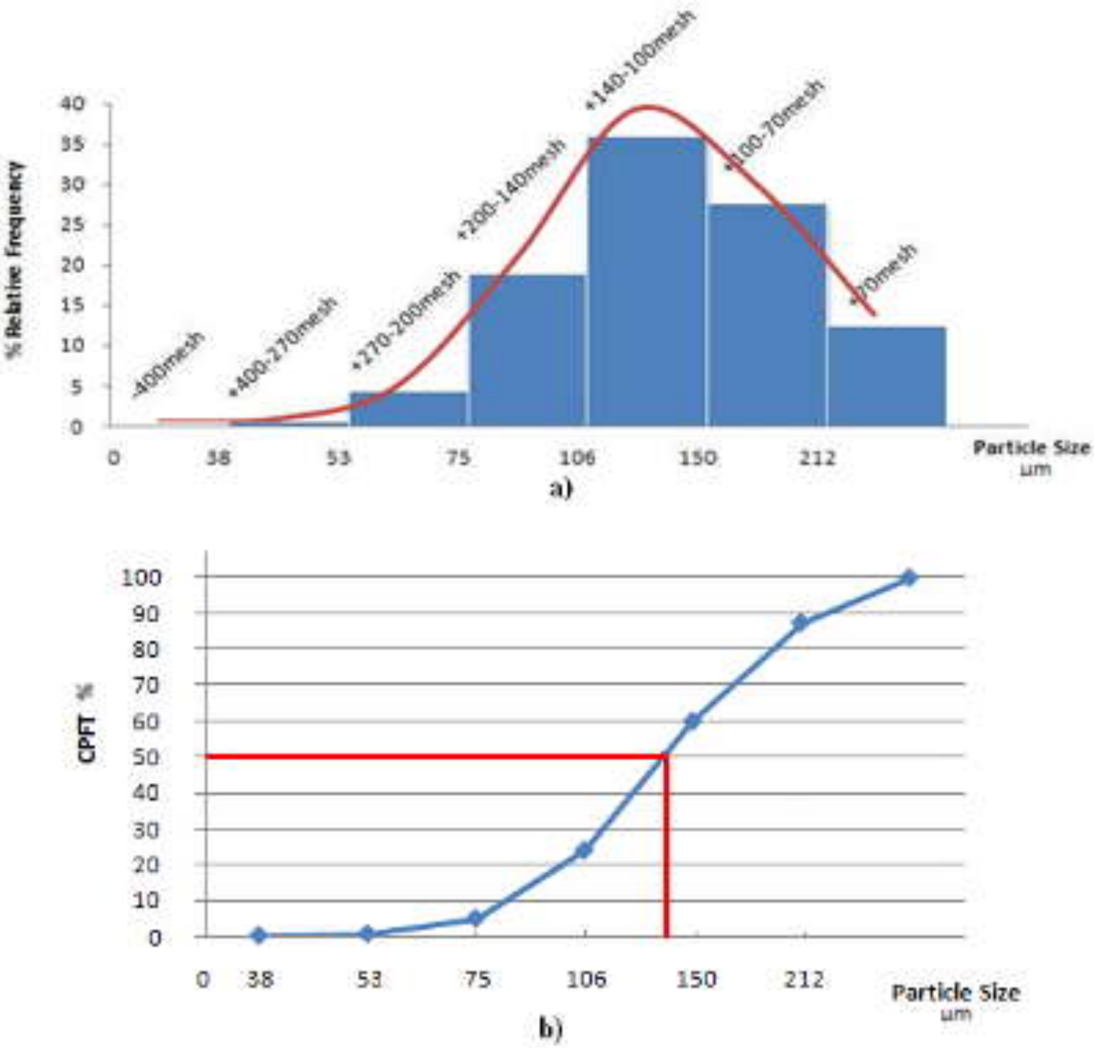


Figure 4.35. Particle size distribution of the ELP-IF-12 engobe sample a) Histogram and b) Cummulative Percentage.

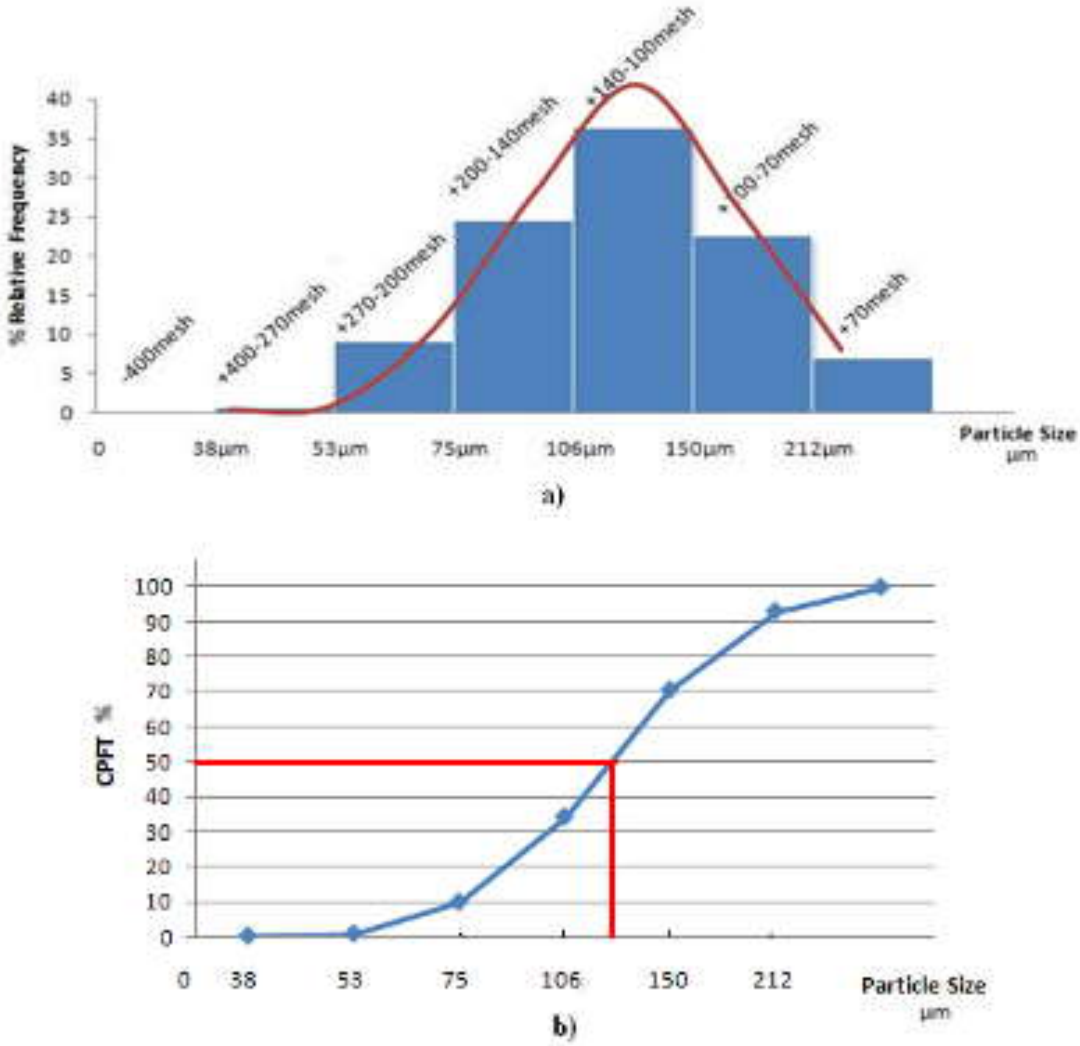


Figure 4.36. Particle size distribution of the ELP-IF-32engobe sample a) Histogram and b) Cummulative Percentage.

Application of both engobes was achieved without any defect on the surface. As illustrated in Figure 4.37, ELP-IF-32 had more transparent shade than ELP-IF-12 as a result of the high amount of the B_2O_3 in the LP engobe composition (Table 3.8, 10). Properties of the samples were very good for all criteria (Table 4.3). The colors of the LP engobes were a little darker than HP engobes because of the impurity of the raw materials.

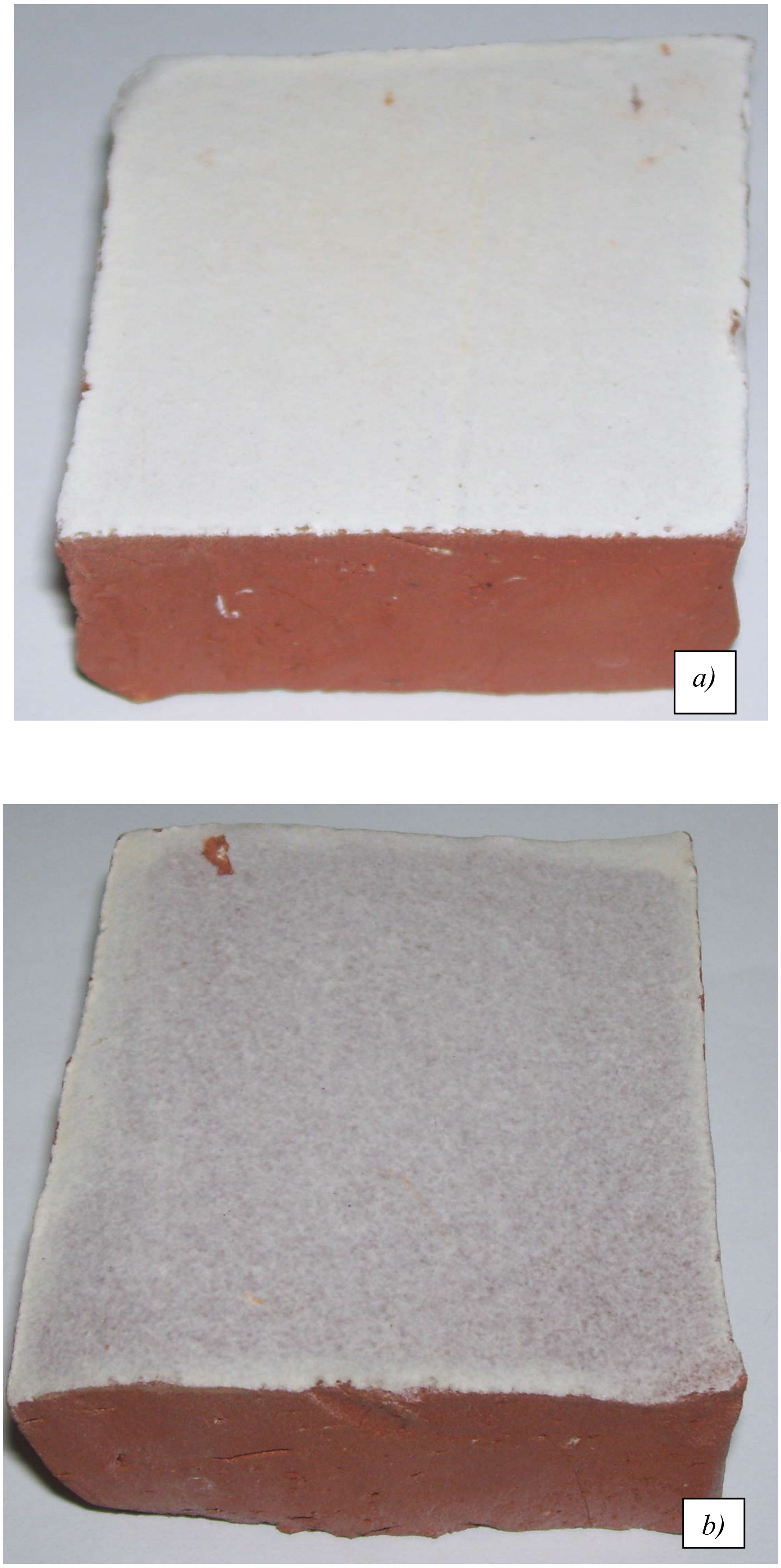


Figure 4.37. Photographs of LP engobe samples coded ELP-IF-12 (a) and ELP-IF-32(b)

Table 4.3. Properties of the ELP-IF-12 and ELP-IF-32 engobe samples

No	*Presence of cracks*			*Degree of bonding*			*Degree of vitrifying*		*Color*		*Aestatically pleasing*		
	Many	***Modarate***	***No***	***Poor***	***Average***	***Good***	***Transparent***	***Opaque***	***Poor***	***Well***	***Poor***	***Average***	***Good***
ELP-IF-12			+			+		+	+				+
ELP-IF-32			+			+	+		+				+

The CTE values of ELP-IF-12 and ELP-IF-32 were 9 $x10^{-6}$ 1/^{o}C and 7 $x10^{-6}$ 1/^{o}C, respectively as shown in the Figure 4.38-39. Both CTE values were almost equal with the CTE of the roof tile suggesting a good match between the body and the top engobe layer.

The OM images of the ELP-IF-12 and ELP-IF-32 are also analyzed as illustrated in Figures 4.40-41. These engobes had a shiny appearance meaning further vitrification. According to the image thicknesses of the engobes were about 150-200 µm. The SEM images of the ELP-IF-12 (Figure 4.43) and ELP-IF-32 (Figure 4.44) indicated that the engobe bonded well to the body like the sample EHP1-30. Therefore, a strongly bonded layer of engobe on roof tile body was successfully produced using low purity raw materials and engobe.

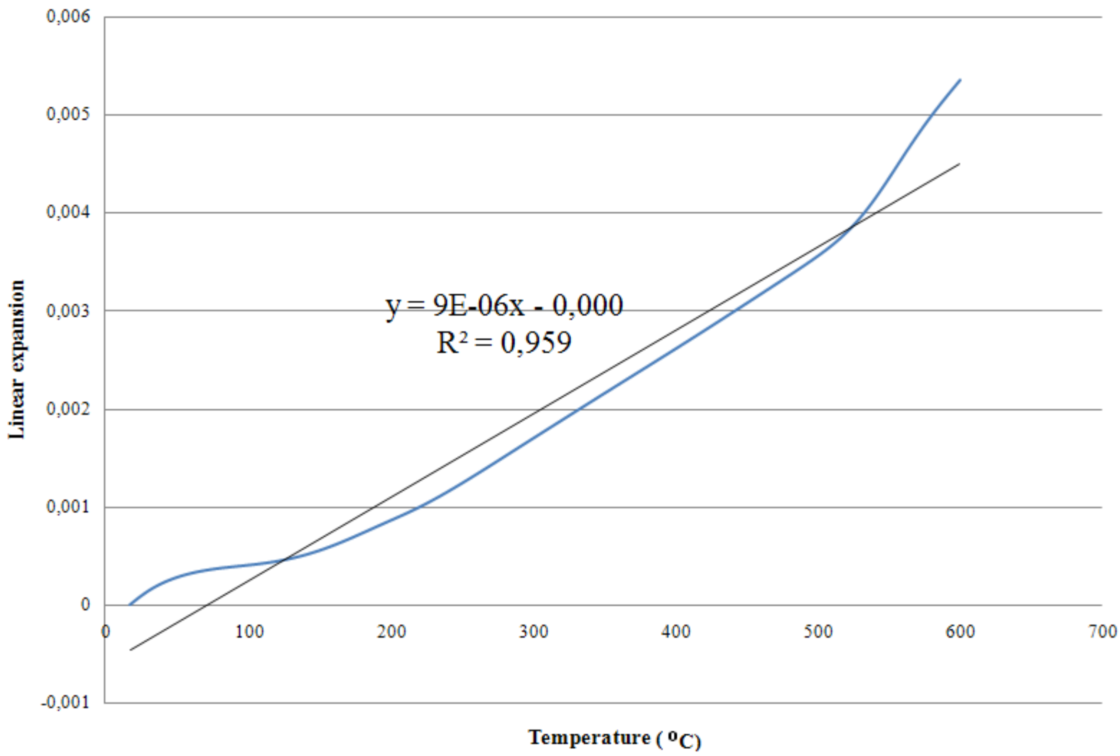


Figure 4.38. Thermal expansion graph of ELP-IF-12.

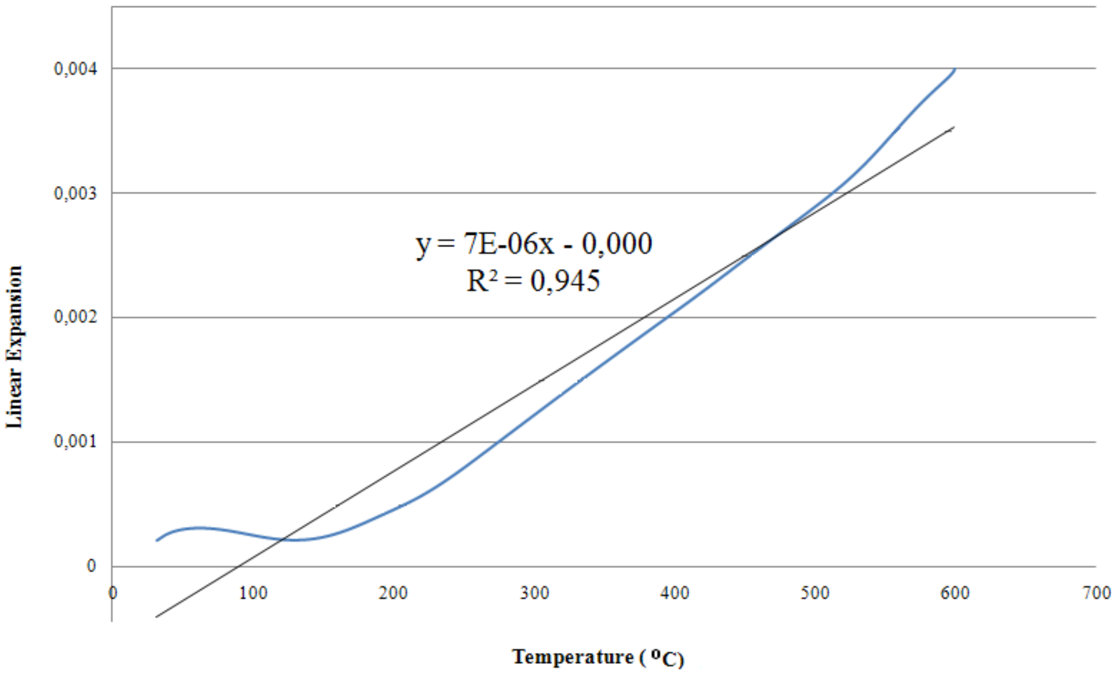


Figure 4.39. Thermal expansion graph of ELP-IF-32.

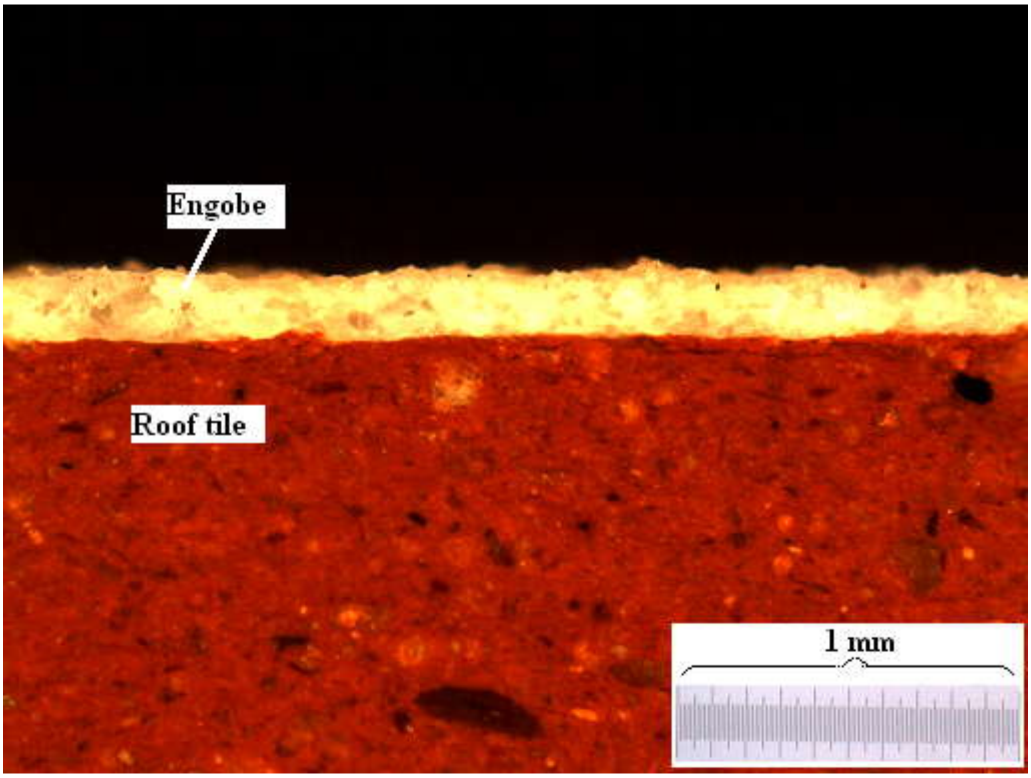


Figure 4.40. The OM image of the ELP-IF-12.

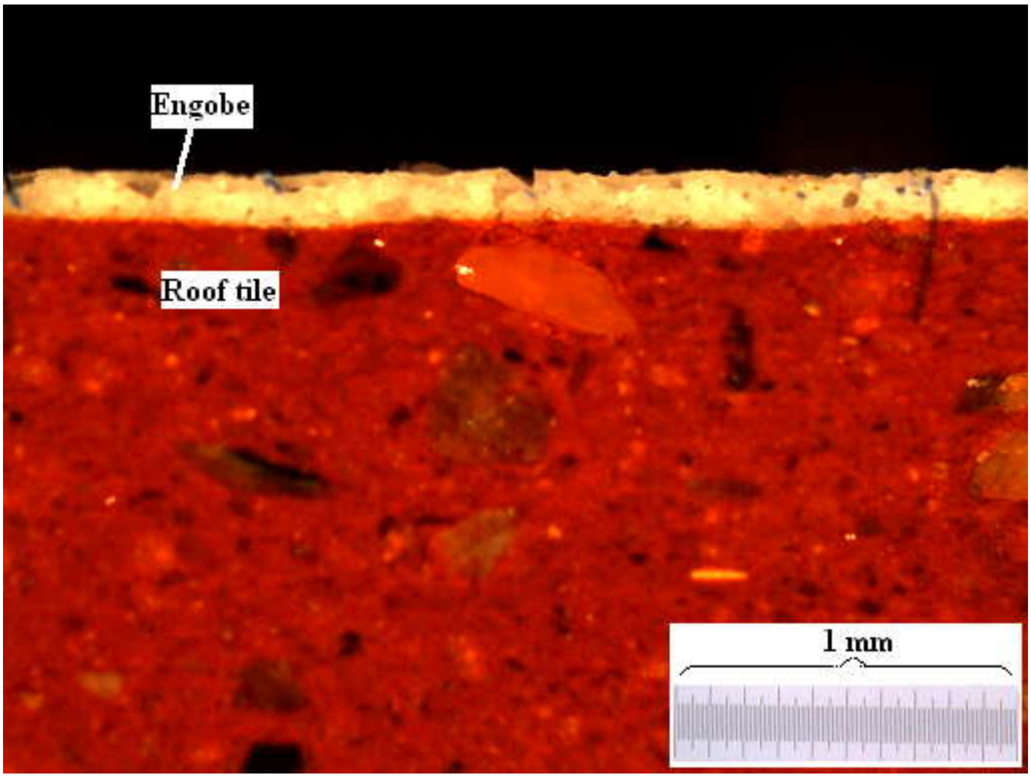


Figure 4.41. The OM image of the ELP-IF-32.

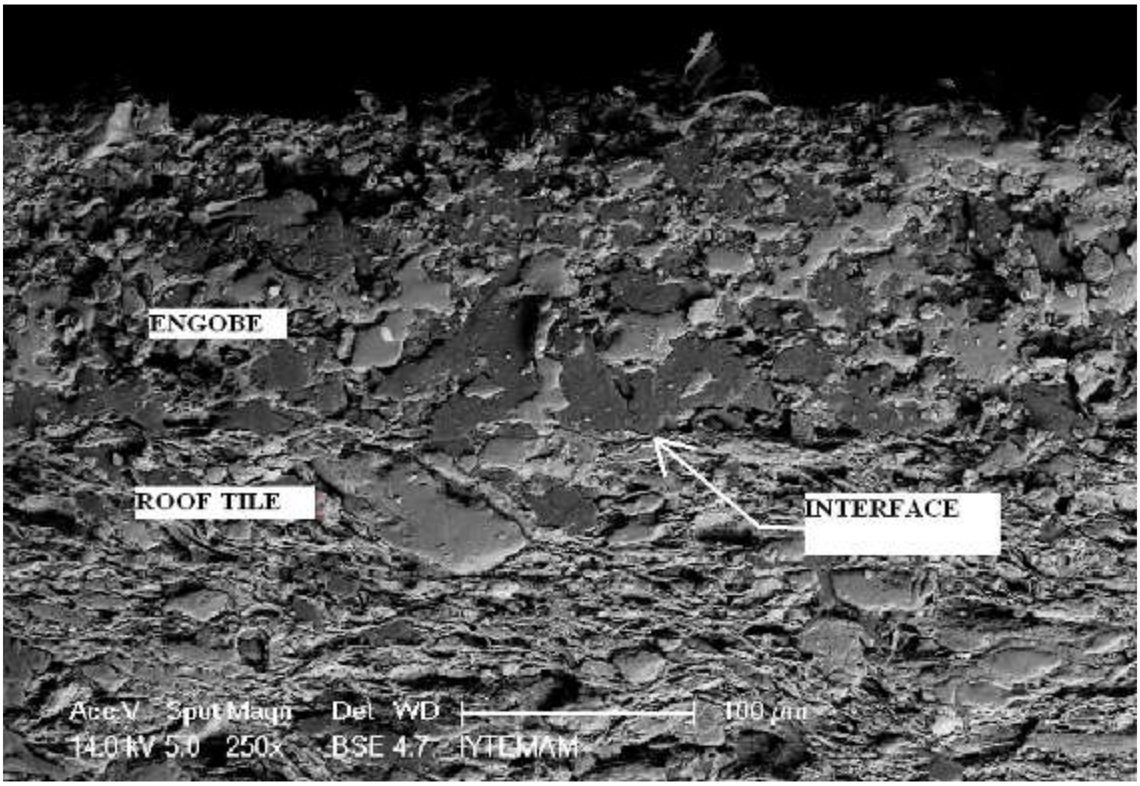


Figure 4.42. The SEM image of the ELP-IF-12.

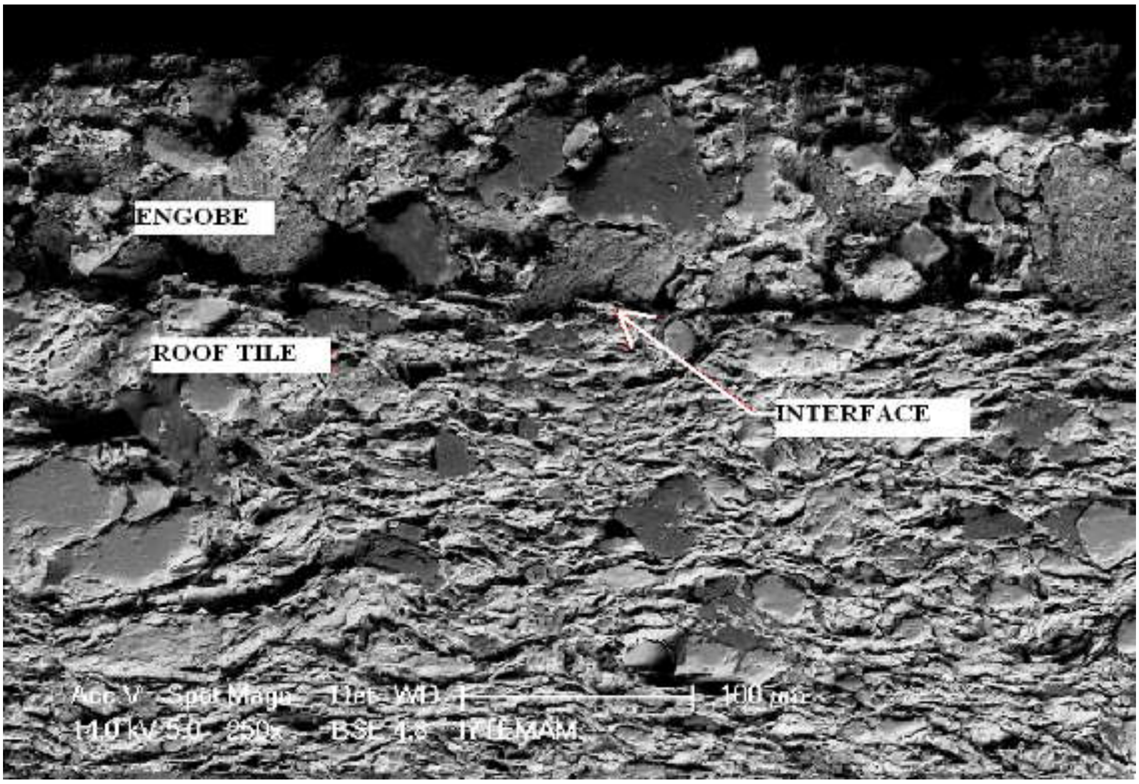


Figure 4.43. The SEM image of the ELP-IF-32.

XRD results of the ELP-IF-12 and ELP-IF-32 are given in Figures 4.44-45. Albite and SiO_2 phases were observed in both ELP samples.

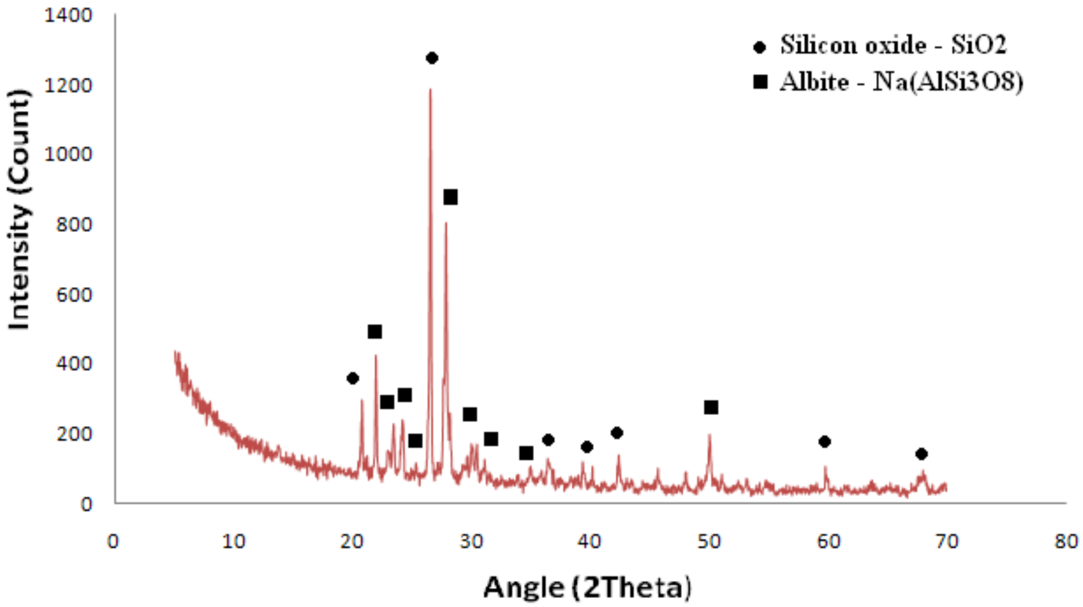


Figure 4.44. XRD analysis of the ELP-IF-12.

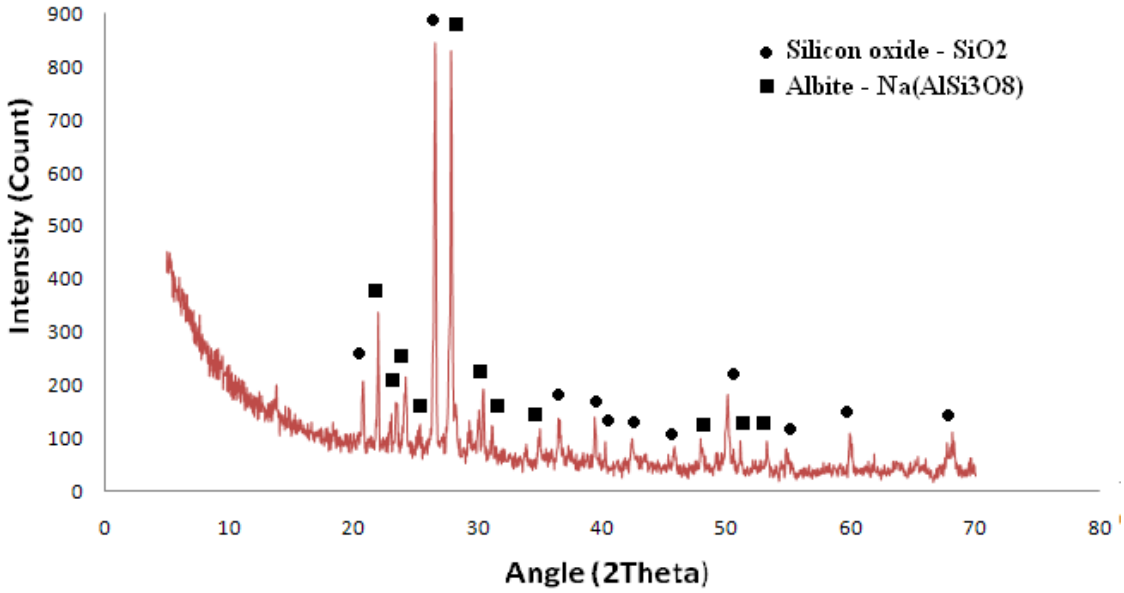


Figure.4.45. XRD analysis of the ELP-IF-32.

The particle size of the engobe samples was also investigated. ELP-IF-12 and ELP-IF-32 samples were ground at different speeds and times as given in Table 3.12 and were named as ELP-IF-12-G200 and ELP-IF-32-G200. The results which are given in Figures 4.46-47 showed that the particle sizes of ELP-IF-12-200 and ELP-IF-32-200 were generally between 150 and 212 µm, respectively. When the speed and time increased the curve of ELP-IF-12 and ELP-IF-32 shifted to the left as expected. The average particle size of both of the engobe samples were about 180 µm. A test was done to reduce the grinding speed from 400 to 200rpms. The ELP-IF32-200 engobe produced some bubbles on the surface of the roof tile after firing as shown in Figure 4.48. The surface quality is also given in Table 4.4. This was probably due to insufficient vitrification and distribution on the roof tile surface due to large particle size of the engobe.

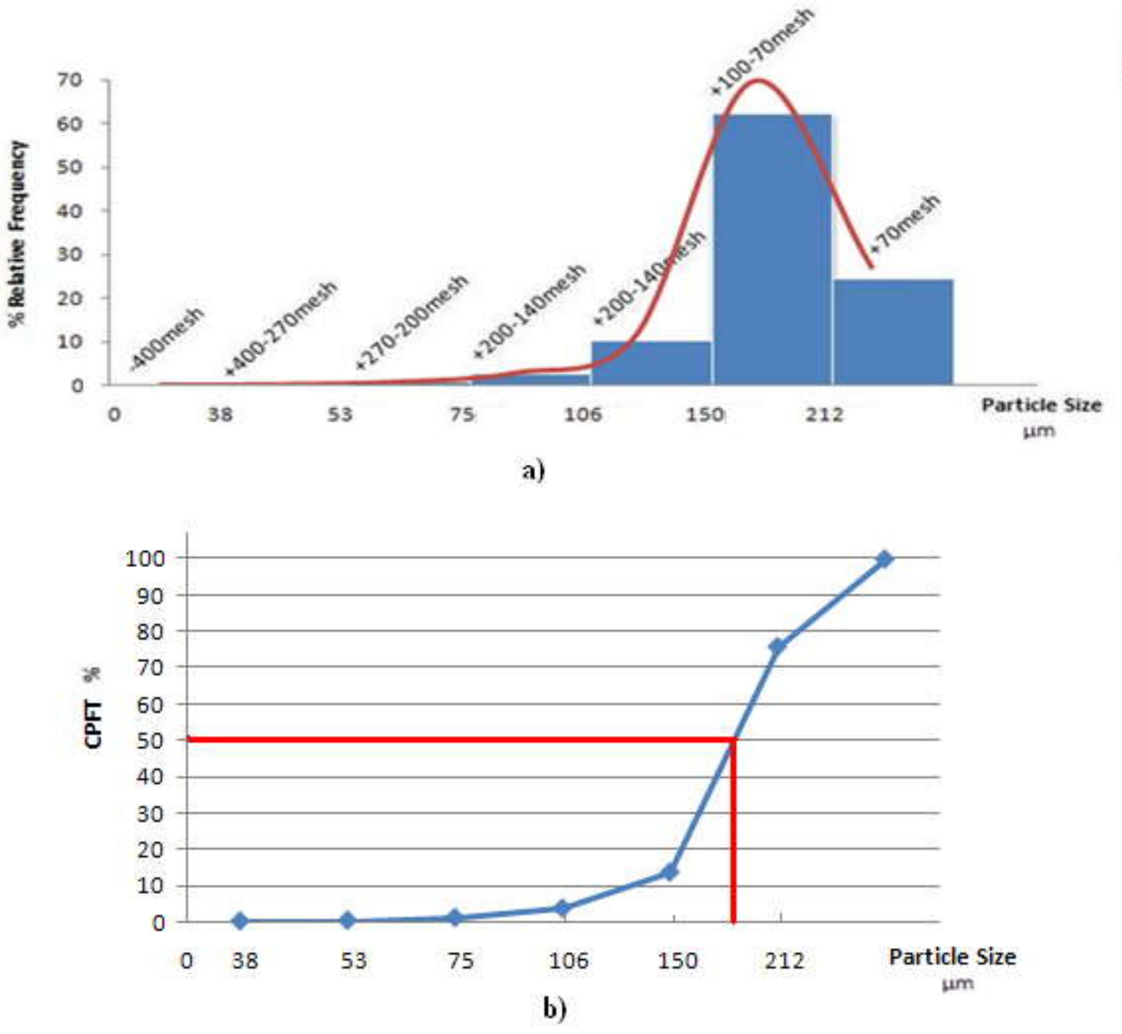


Figure 4.46. Particle size distribution of the ELP-IF-12-200 engobe sample a) Histogram and b) Cummulative Percentage.

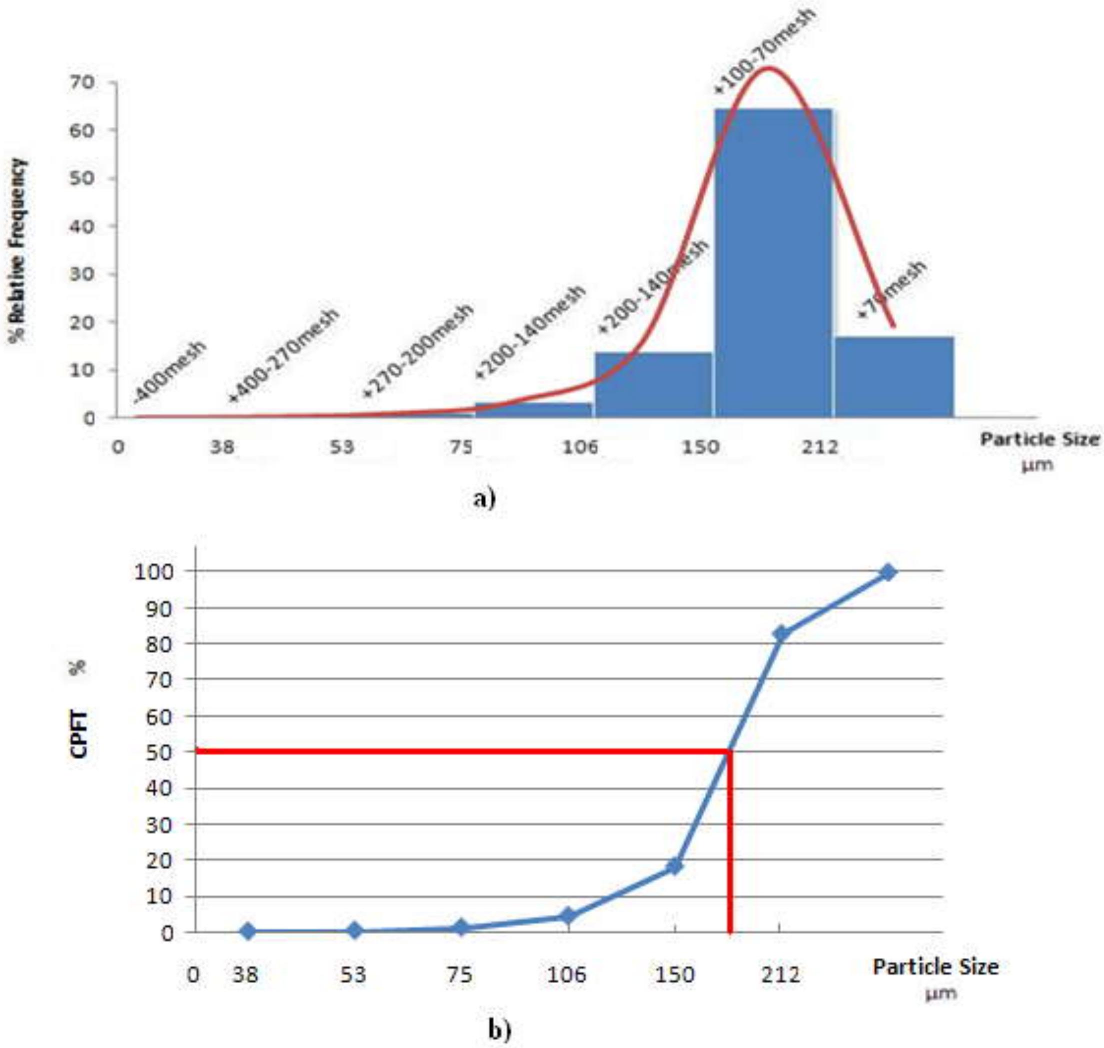


Figure 4.47. Particle size distribution of the ELP-IF-32-200 engobe sample a) Histogram and b) Cummulative Percentage.

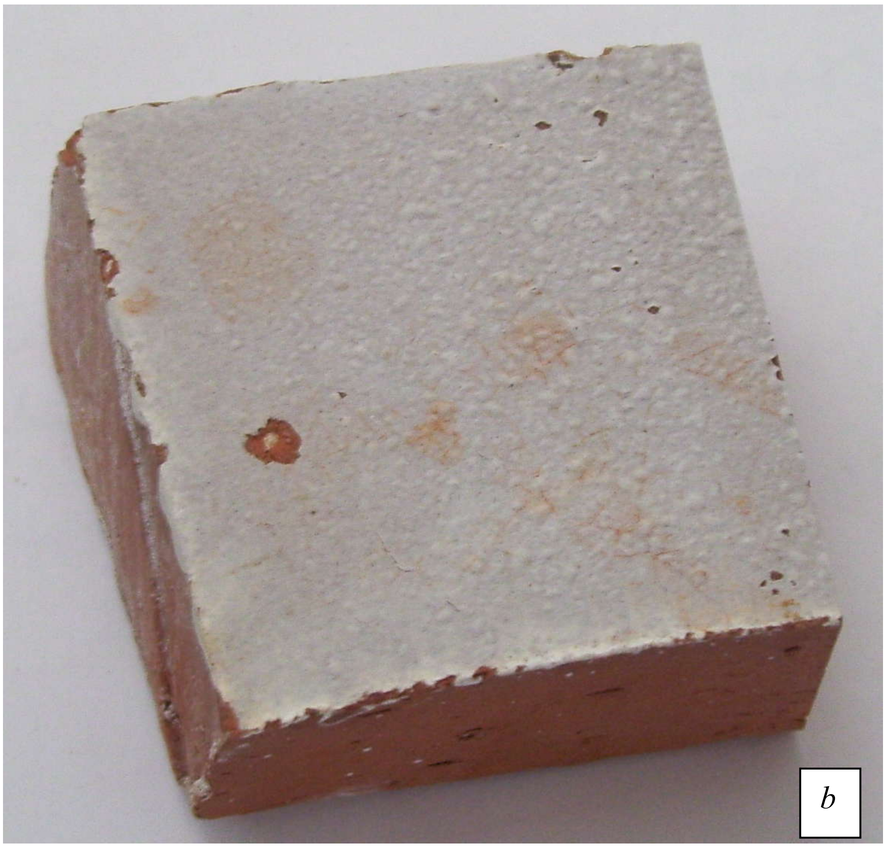
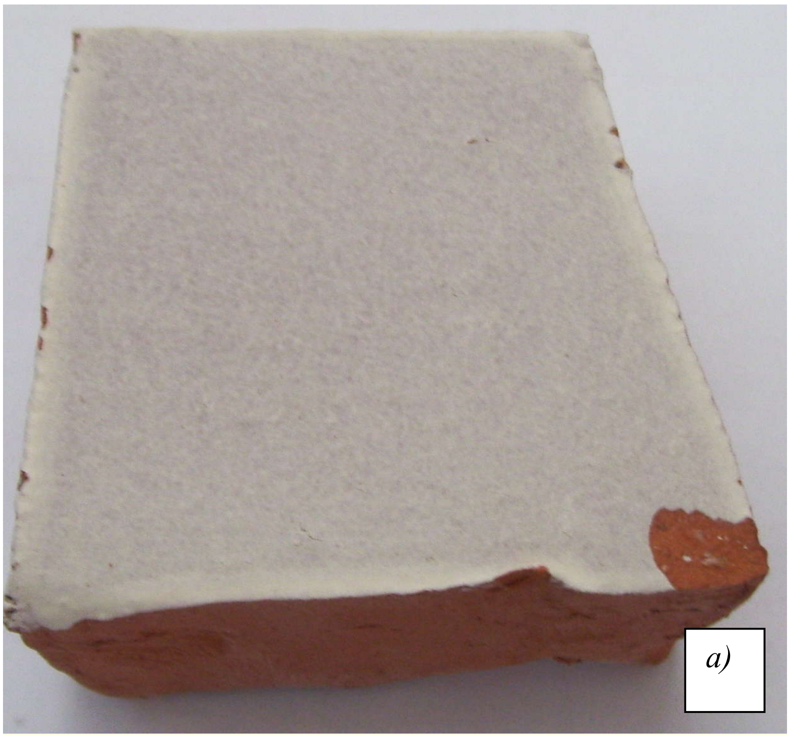


Figure 4.48. Image of the LP engobe samples ground at different speeds a) ELP-IF-12-200, b) ELP-IF-32-200.

Table 4.4. Properties of the ELP samples that ground at 200 RPM.

No	*Presence of cracks*			*Degree of bonding*			*Degree of vitrifying*		*Color*		*Aestatically pleasing*		
	Many	***Modarate***	***None***	***Poor***	***Average***	***Good***	***Transparent***	***Opaque***	***Poor***	***Well***	***Poor***	***Average***	***Good***
ELP-IF-12-G200	+			+				+	+			+	
ELP-IF-32-G200		+			+		+		+		+		

Maturation of the engobe is effected by its chemistry as well as firing time and temperature. But the firing temperature of the roof tile is fixed at 1000^{o}C due to manufacturer requirements. In this thesis, the firing temperature of engobe was matched with the firing temperature of the roof tile so that the engobe-coated roof tiles can be produced in a single step firing schedule. A second step firing process for engobe would not be economically feasible. Roof tile industry is already suffering from poor profit margins due to significant energy bills. The firing conditions for engobe are given in Table 3.13. Specks on the surface of the engobe were observed after firing at the high temperature (1030 ^{o}C) as shown in Figure 4.49. According to Table 4.5 when the temperature and time of the firing increased the quality of the surface became worse.



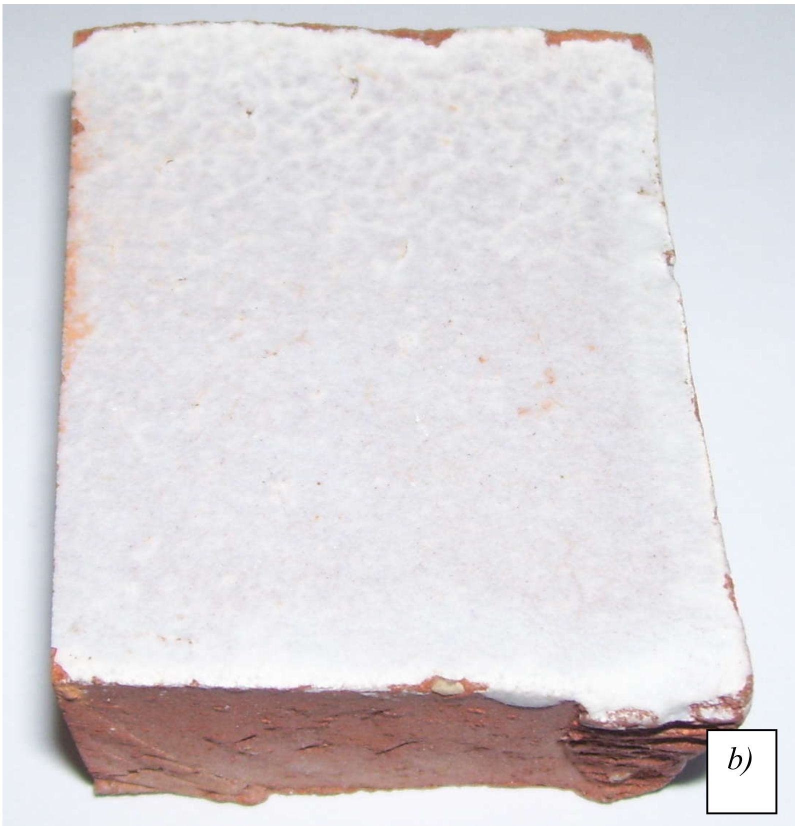


Figure 4.49. Images of the LP engobe samples fired at different temperatures a) ELP-IF-12-970, b) ELP-IF-32-970, c) ELP-IF-12-1030, d) ELP-IF-32-1030, e) ELP-IF-12-150 and f) ELP-IF-32-150.

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Figure 4.49. (cont.)

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Figure 4.49. (cont.)

Table 4.5. Properties of the ELP samples fired at different temperatures and durations.

No	*Presence of cracks*			*Degree of bonding*			*Degree of vitrifying*		*Color*		*Aestatically pleasing*		
	Many	***Modarate***	***None***	***Poor***	***Average***	***Good***	***Transparent***	***Opaque***	***Poor***	***Well***	***Poor***	***Average***	***Good***
ELP-IF-12-970			+		+			+	+				+
ELP-IF-32-970			+		+		+		+		+		
ELP-IF-12-1030			+			+		+	+				+
ELP-IF-32-1030		+				+	+		+		+		
ELP-IF-12-150			+		+			+	+				+
ELP-IF-32-150			+			+	+		+		+		

The life of the engobe is an important point for usage of roof tiles. So the acid resistance was investigated with 5% HCl, 5% HNO_3, 5% NaOH, and 5% H_2SO_4 solutions for ELP-IF-12 and ELP-IF-32. Few milliliters of acid were dropped onto the surfaces of engobe coated roof tiles. No significant degradation was observed on the surfaces after application of the acid-water solution on the surface for a week. SEM images of the samples ELP-IF-12 and ELP-IF-32 confirmed this observation. (Figure 4.50-54) Temperature change is one of the other effects for the life of the engobe so the samples were heated to 185^{o}C. Later they were quenched in cold water in order to inflict thermal shock. But the samples survived the test without observable damage.

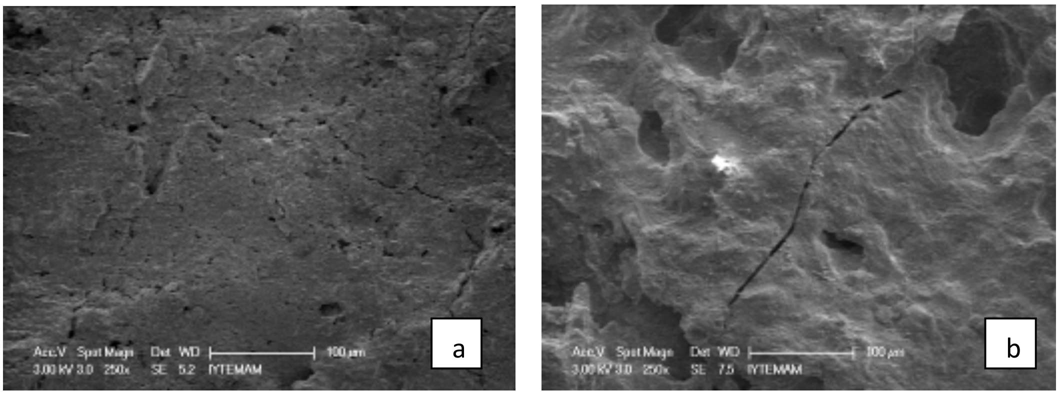


Figure 4.50. The SEM images of the 5% HCl - water solution applied engobe surfaces a) ELP-IF-12 and b) ELP-IF-32.

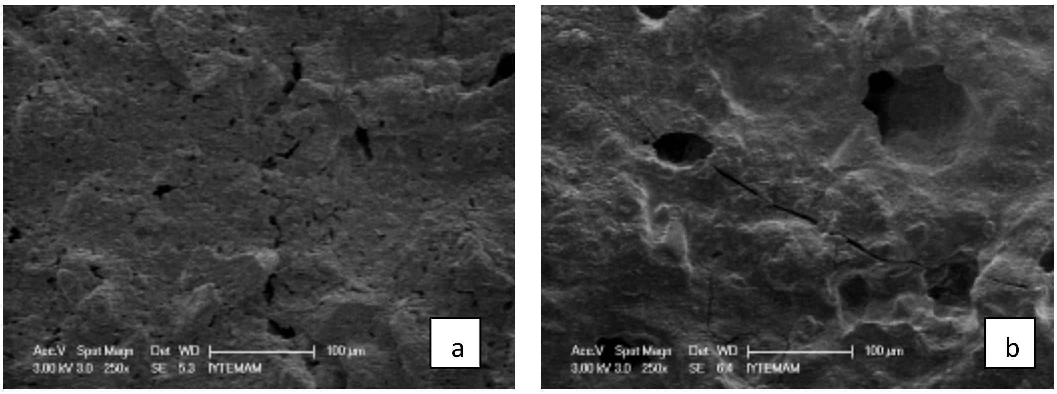


Figure 4.51. The SEM images of the 5% HNO_3 - water solution applied engobe surfaces a) ELP-IF-12 and b) ELP-IF-32.

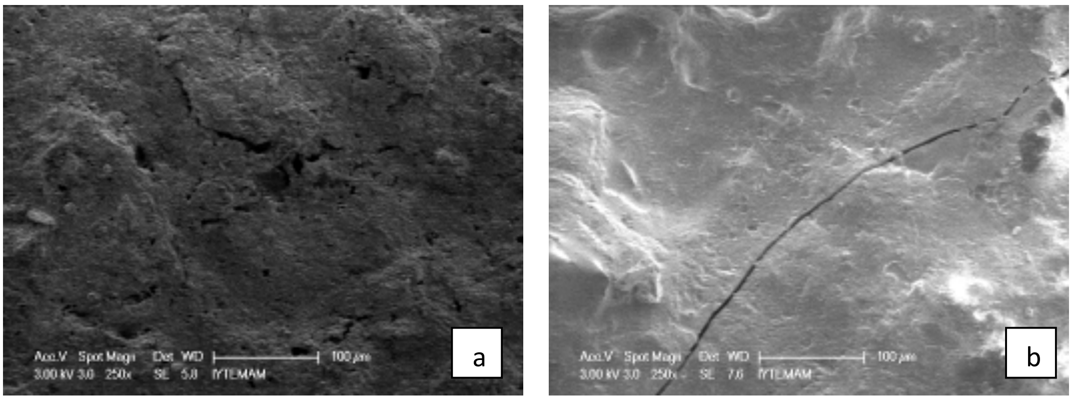


Figure 4.52. The SEM images of the 5% NaOH - water solution applied engobe surfaces a) ELP-IF-12 and b) ELP-IF-32.

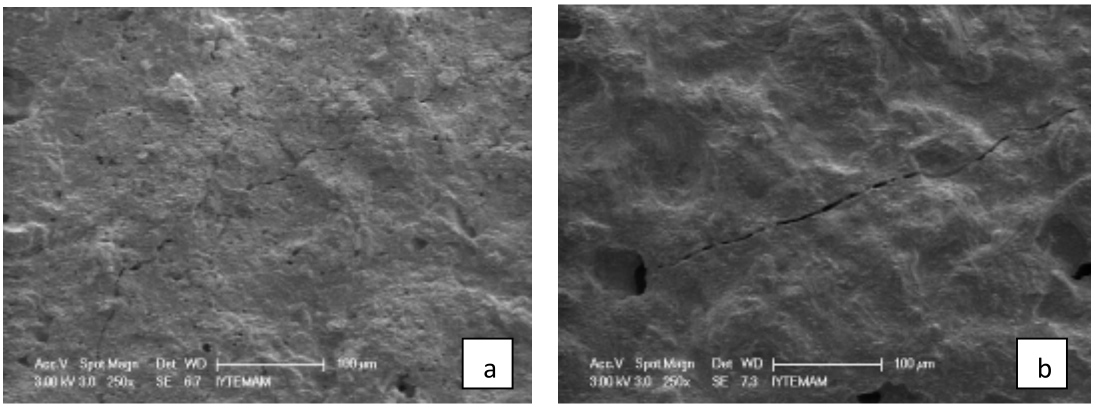


Figure 4.53. The SEM images of the 5% H_2SO_4 - water solution applied engobe surfaces a) ELP-IF-12 and b) ELP-IF-32.

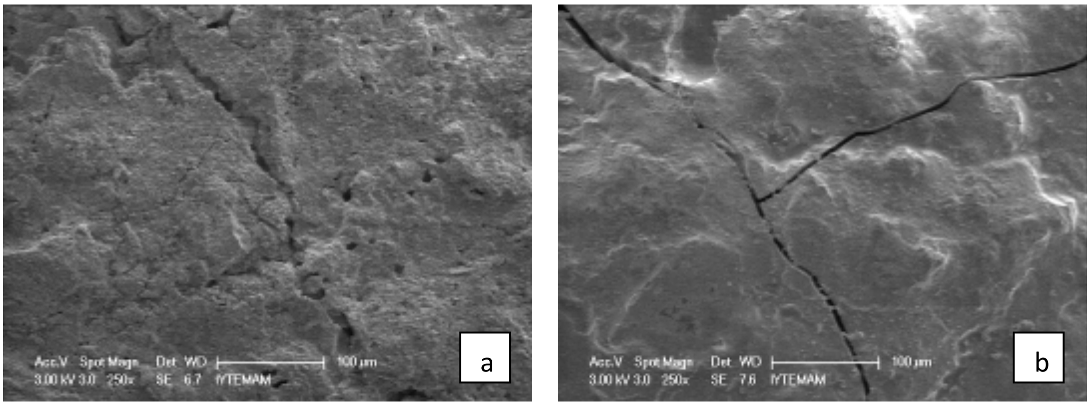
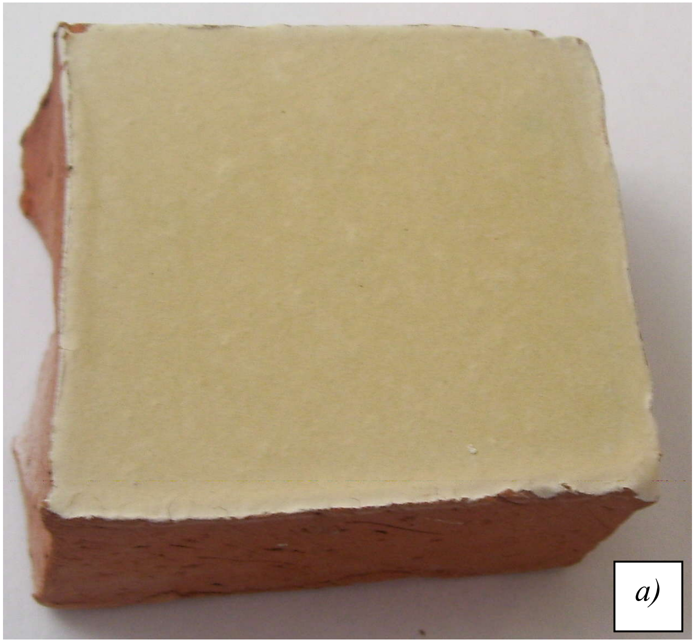


Figure 4.54. The SEM images of the engobe surfaces after heating test a) ELP-IF-12 and b) ELP-IF-32.

4.3.4 Color Analysis

The color tests were done by using ELP-IF-12 and ELP-IF-32 engobe compositions. To adjust the amount of the colorant (metal oxide) 1%wt of chromium (III) oxide was added to the engobe compositions. ELP-IF-12 containing 1% chromium oxide yielded poor results as shown in Figure 4.55. Chromium oxide gave green color as expected. Therefore colorant addition was increased to 5% in all remaining runs. It was possible to obtain a brown or purple color by using manganese oxide but the color of ELP-IF-32-Mn5 was pale purple. The Titanium was used to give the engobes a yellow color however the results shows that the color of ELP-IF-32-Ti5 was light yellow like cream. Iron oxide affected the color of engobe (ELP-IF-32-Fe5) in red color as expected. However yellow points were observed on the surface. The color of ELP-IF-

32-Co5 was green. Copper oxide (ELP-IF-32-Cu5) also was used as a blue or green pigment and a green color was obtained. L – b – a values of each colored engobe samples is given in Table 4.6. Also their L – b – a diagrams are shown in Figure 4.56.



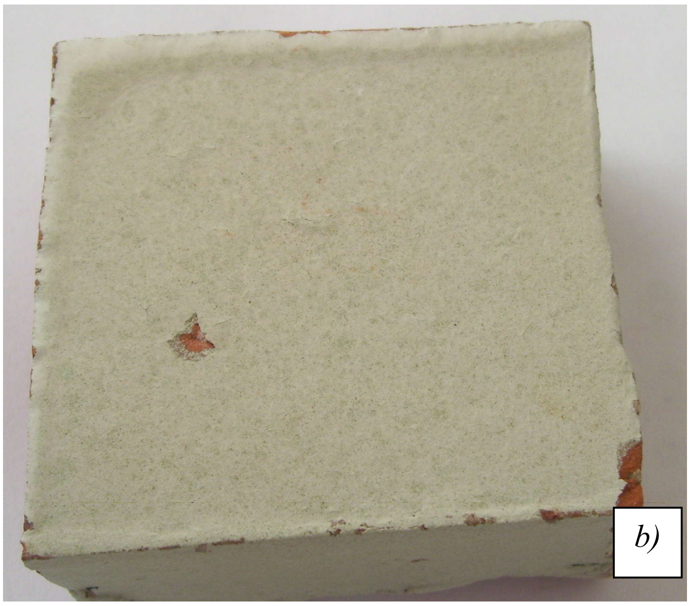


Figure 4.55. Image of the LP engobe samples with different colorant a) ELP-IF-12-Cr1, b) ELP-IF-32-Cr1, c) ELP-IF-32-Cr5, d) ELP-IF-32-Cr5, e) ELP-IF-32-Mn5, f) ELP-IF-32-Ti5, g) ELP-IF-32-Fe5 and h) ELP-IF-32-Co5, i) ELP-IF-32-Cu5.

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Figure 4.55. (cont.)

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Figure 4.55. (cont.)

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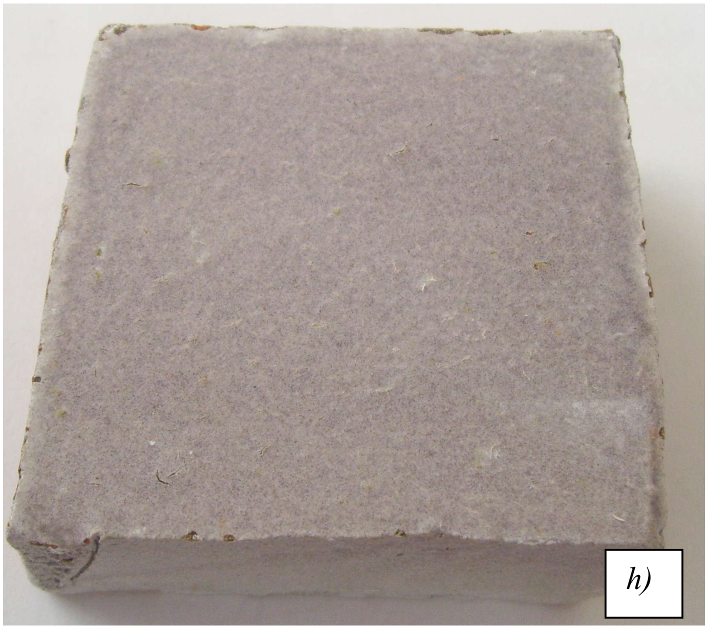

Figure 4.55. (cont.)

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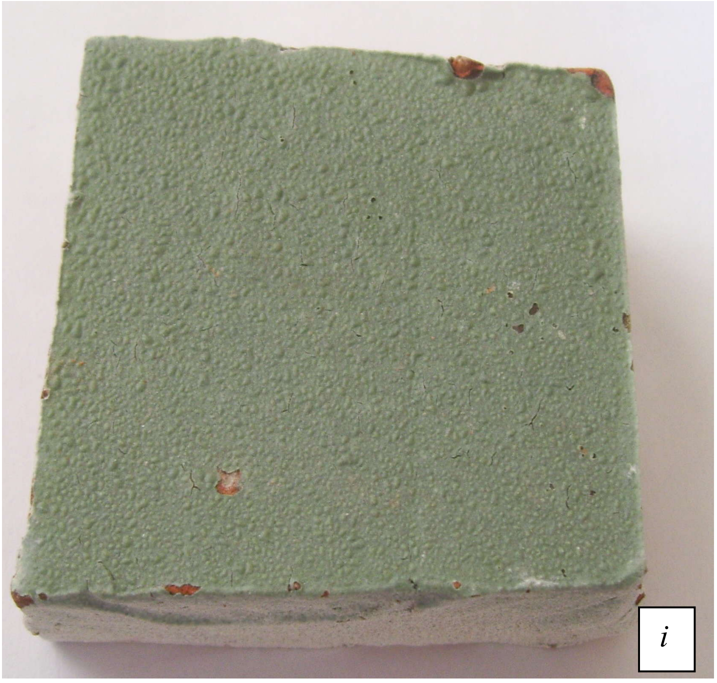

Figure 4.55. (cont.)

Table 4.6. Color measurement for the engobe samples.

No	***Colorant***		***Frit (%)***	***L***	***b***	***a***
	Amount	***Type***				
ELP-IF-12-Cr1	1%	Chromium(III) Oxide	12	77.23	13.04	-0.37
ELP-IF-12-Cr5	5%	Chromium(III) Oxide	12	71.56	12.68	-1.37
ELP-IF-32-Cr1	1%	Chromium(III) Oxide	32	68.69	17.43	-11.35
ELP-IF-32-Cr5	5%	Chromium(III) Oxide	32	48.5	17.16	-9.88
ELP-IF-32-Mn5	5%	Manganese(IV) Oxide	32	52.88	11.2	4.37
ELP-IF-32-Ti5	5%	Titanium(IV) Oxide	32	76.96	7.7	-0.47
ELP-IF-32-Fe5	5%	Iron(III) Oxide	32	45.74	21.88	18.36
ELP-IF-32-Co5	5%	Cobalt(III) Oxide	32	58.93	-0.62	5.42
ELP-IF-32-Cu5	5%	Copper(III) Oxide	32	50.37	5.37	-6.09

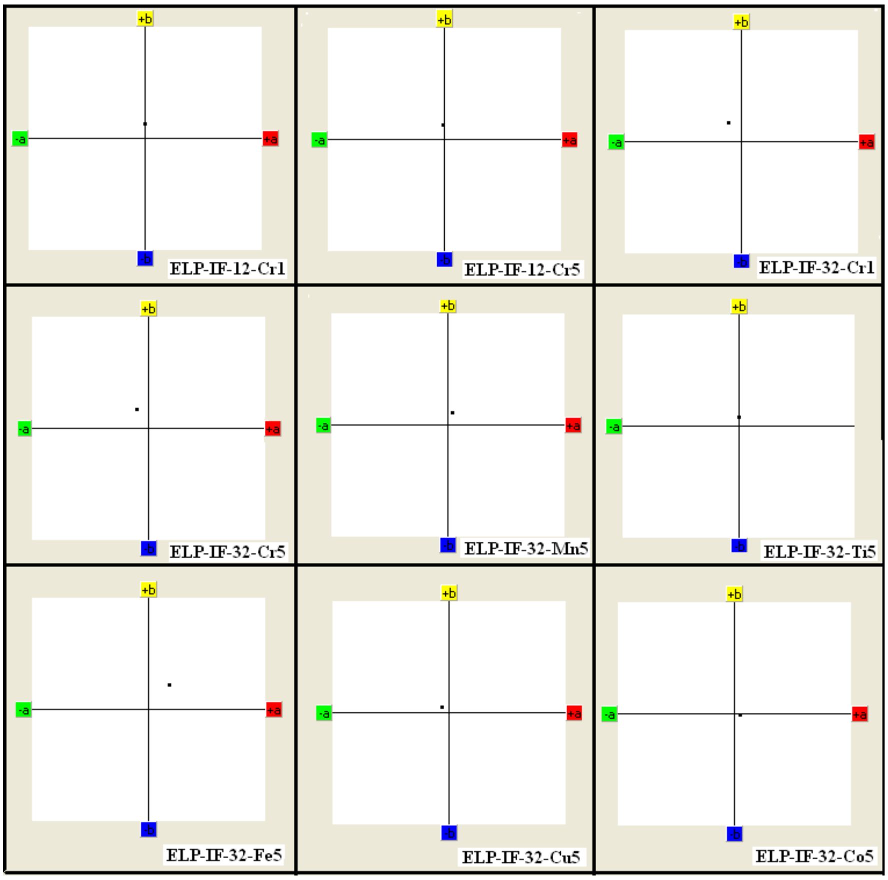

Figure 4.56. Location of color on the L - b – a diagram.

4.3.5. Working on Industrial-size Roof Tile

The ELP-IF-32-Cr5 was also applied to industrial size roof tile. After firing the cracks were observed on the surface as in the Figure 4.57. The roof tiles were fired in the manufacturer furnace. The temperature of the furnace is not stable and the temperature was not measured. These can be the reason of the crack on the surface.

Figure 4.57. ELP-IF-32-Cr5 on industrial - size roof tile.

CHAPTER 5

CONCLUSIONS

Development of an engobe composition for a commercial roof tile was successfully achieved. For developing a proper HP (high purity) engobe composition the commercial roof tile was analyzed. According to the roof tile chemical analysis a number of HP engobe compositions were prepared with different weight percentages of lab frit containing 18% B_2O_3. Two of the HP engobe compositions for the roof tile were identified as the most suitable: EHP1-10 and EHP1-30. EHP1-30 was more transparent than EHP1-10 because of the higher amount of frit. The high purity materials are very expensive to be used by industry. In addition, making a lab frit can be difficult for a roof tile company. Therefore, two new engobe compositions were prepared which had almost the same compositions with EHP1-10 and EHP1-30 by using low purity materials and an industrial frit. The ELP-IF-12 which had similar chemical composition with EHP1-10 and the ELP-IF-32 which had similar chemical composition with EHP1-30 were also successful. The most important difference between the HP engobes and LP engobes was that LP engobe samples were a little bit darker than HP engobe samples. The reason was probably the higher amount of Fe_2O_3 in the LP engobe samples. However, it is not expected to be a big problem for coloring of the engobe as low iron raw materials are also available in the industry. There was no defect on the surface of the engobe as might be expected form CTE values of the engobes and roof tile. Small differences in CTE values were therefore not effective. The grinding speed was also decreased to observe the effect of the PSD for engobe compositions. When the speed of grinding was reduced the surfaces became less smooth and some bubbles formed. Formation of bubbles was also observed when the firing temperature was increased. Slurries containing 50 weight percent solids showed shear thinning rheology which enabled easy application on surfaces by spraying thorough a nozzle. The life of the engobe coated roof tile was another important point. So, for testing the environmental effects on the engobe coated roof tile, acid and base tests and quenching tests were applied on the surface of the engobes. They were tested to be durable against the climate change or natural events. Industrial scale tests showed some cracks on the engobe coating probably as a result of furnace atmosphere fluctuations.

The following are recommended for future study on this topic:

- Sintering and densification behavior of co-pressed clay and engobe can be measured using a vertical dilatometer.
- Effect of different additives for reducing the viscosity of the engobe at high temperature can be studied.
- Production of low purity engobe can be done with better color by using industrial grade raw materials containing a lower amount of iron.
- Different engobe suspension application techniques like waterfall and dipping can be tested against spraying.

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