THE PREPARATION OF LOW-TEMPERATURE FUSION ENAMELCOATINGS FOR CORROSION CONTROL USING LOCAL RAW MATERIALS

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DECLARATION

I hereby declare that this submission is my own work towards the MSc and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any degree of the University, except where due acknowledgement has been made in the text.

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ABSTRACT

An attempt has been made in this study to formulate materials for low-temperature fusion enamel coating from local raw materials and borax that can be applied directly onto steel substrate for corrosion control. Mfensi and Afari clays, and the Mouri feldspar were mixed in various proportions with borax to form various batches. The batches were mixed with water to form slips which were used to coat already prepared steel surfaces and were allowed to dry in the open. The coated steel plates were again dried in the oven and fired at temperatures of $800^{o}C$, $850^{o}C$ and $900^{o}C$ to mature. The coatings were observed and also physico-chemical tests were conducted to evaluate some properties of the coatings.

The coatings matured and adhered very well to the substrate at $850^{o}C$ and $900^{o}C$ and showed good hardness and thermal shock resistance as well as good corrosion resistance in brine and 10% nitric acid. The coatings hardness at the above temperatures were between 7 and 8 on the Mohs scale and 70-90 on the BHN(1/60). The coatings thickness at these temperatures was between 0.42mm and 0.5mm. They were able to resist fifteen cycles of heating and quenching from $400^{o}C$. The coatings prepared with the Afari clay with its higher content of iron oxide showed better results in terms of hardness and thermal shock resistance than those prepared with the Mfensi clay. However the coatings fired at $800^{o}C$ did not fuse properly and hence did not show good adhesion to the substrate. They showed a hardness of 4-6 on the Mohs scale and failed on the Brinnel Hardness Tester.

ACKNOWLEDGEMENT

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CHAPTER ONE

1. INTRODUCTION

1.1 BACKGROUND

Corrosion in metals may be defined as the deterioration of a metal by chemical or electrochemical interaction with its environment. It can also be defined generally as the deterioration of a material or its properties because of reaction with its environment. The second definition recognizes that materials other than metals may deteriorate or corrode and that corrosion is also directed to the idea that properties as well as the material itself can and do deteriorate.

For metallic materials, corrosion is normally electrochemical; that is a chemical reaction in which there is transfer of electrons from one chemical species to another. In an aqueous environment, some metals characteristically give up electrons and dissolve in a reaction called dissolution or corrosion. Once corrosion is set up in a material, its progress is determined mainly by resistance to the continued action of the corrosion by-products. The rate in aqueous media also depends on the electrochemical potential, which varies with the environment.

Corrosion in aqueous environment accounts for the greatest amount of corrosion. Corrosive aqueous media include the atmosphere, fresh water and the soil. Others are alkalis, acids and salt solutions. It is clear that the start and progress of corrosion in an aqueous media is determined by many factors. They include acidity (pH), the presence of oxidizing agents, the formation of protective film and its stability and temperature. Other factors are the relative velocity of the aqueous medium around the surface and the heterogeneity of the solution or the metal.

The corrosion of metals and alloys can be reduced or prevented in various ways. These include the formation of a protective oxide or insoluble film on the surface of the metal, sacrificial anodic protection with a less noble metal connected to the metal in a galvanic circuit and the use of organic, inorganic and metallic coatings. All the various options have their advantages and disadvantages. Inorganic or oxide coatings provide additional advantage of chemical inertness, high temperature stability and superior mechanical properties as compared to other coatings currently in use that is metals, polymers, paints among others [*Majundra and Sunimal, 1995*].

The choice of option depends on the particular situation. Apart from economic and other technical considerations, three very important factors for good protection in terms of coatings include good adhesion, similar thermal coefficient of expansion of the coatings and the metal and low conductivity and diffusion coefficient across the coating.

Methods of application of protective materials to the surface include dipping, spraying, painting and connection to galvanic circuit. Enamel and ceramic coatings are generally applied using spraying or dipping techniques. In the thermal spraying technique the ceramic material are heated in a gun and propelled onto the substrate surface.

1.2 MAIN OBJECTIVE

The main objective of this project is to formulate an appropriate low-temperature fusion inorganic (enamel) coating from local clays and feldspar that could melt in a modified spray gun and used for corrosion control on steel substrates**.**

1.3 SPECIFIC OBJECTIVES

1. To review literature on corrosion control coatings especially enamel coatings on steel substrates.

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2. To formulate materials for low-temperature enamel coatings from local clays and feldspar suitable for application on steel substrates.

3. To produce and test for some physical properties of the formulated coating(s)

1.4 JUSTIFICATION

The problem of metallic corrosion is one of significant proportions to any nation. In economic terms it has been estimated that approximately 5% of an industrialized nation's income is spent on prevention and the replacement of products lost or contaminated as a result of corrosion reactions. Even though there is no specific data on the cost of corrosion damage in Ghana it can be inferred from above to be substantial. That of the US is estimated to be about $700 billion a year *[Narang, 1998]*.

Iron, steel and their alloys are used extensively in Ghana as construction materials for various structural and fabrication purposes including pipes, poles, steel rods, sheets and sections. These materials are used in the food, brewery, chemical processing, thermal power plants, metallurgical and other industries. Equipment and structures in these industries placed in areas near the sea deteriorate rapidly if proper protective schemes are not employed to protect them. Presently the principal method used for controlling corrosion in some of the industries includes the use of organic paints, which do not give lasting protection. In this case the equipment is repainted after a short time at a great cost. Also some of the industries simply replace machine parts at a great cost due to corrosion damage. Some advertising bill boards have also been found to corrode which often become an eyesore and a hazard and are therefore replaced after a short time.

Protecting these ferrous substrates mentioned above with good coating is therefore of utmost importance. The use of inorganic coatings such as enamels or properly fused ceramic coatings on these surfaces can produce a more lasting solution to the problem

of corrosion as these coatings are chemically inert and also possess superior mechanical properties. They protect by acting as a barrier between the environment and the metal surface and thus substantially minimize the corrosion process. Also because of their chemical inertness they do not pose any danger to the environment and are therefore considered to be environmentally friendly.

1.5 METHODOLOGY

1. Review Literature on corrosion processes and corrosion prevention /control techniques

2. Selection and collection of local raw materials such as clay and feldspar suitable for forming coating batches.

3. Chemical analysis of the samples

4. Formulation of mixtures, its use in coating steel plate surfaces and heating to various temperatures.

5. Analysis of the coatings

1.6 ORGANIZATION OF REPORT

The report of this thesis is organized into five main chapters namely Introduction, Literature Review, Materials and Methods, Results and Discussion, and Conclusion and Recommendation.

CHAPTER TWO

2   LITERATURE REVIEW

2.1   CORROSION AND CONTROL

2.1.1   The Corrosion Process

Corrosion may be defined as the physicochemical interaction between a metal and its environment which results in changes in the properties of the metal and which often leads to impairment of the function of the metal, the environment or the technical system of which these form a part*[ISO 8044-1999]*. It may also be defined as the natural deterioration that results when a surface reacts with its environment *[NACE, 2012]*.

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Corrosion of metals is mostly electrochemical, that is a chemical reaction in which there is transfer of electrons from one chemical specie to another. Metal atoms characteristically lose or give up electrons in what is called an oxidation reaction. For example the hypothetical metal M that has a valence of n electrons undergoes oxidation according to the reaction below in which M becomes an n+ positively charged ion and in the process losses n valence electrons.

$$M \longrightarrow M^{n+} + ne$$

The site where oxidation takes place in the metal is called the anode and this reaction is sometimes called anodic reaction or dissolution. The electrons released from the anode move through the metal to adjacent site where they combine with both oxygen and water to form either hydroxyl ions $(OH)^-$, or hydrogen ions (H^+) depending on the nature of the solution to form hydrogen gas as follows:

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- \qquad \text{neutral}$$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad \text{acid}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \text{acid}$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2\,OH^- \quad \text{alkaline}$$
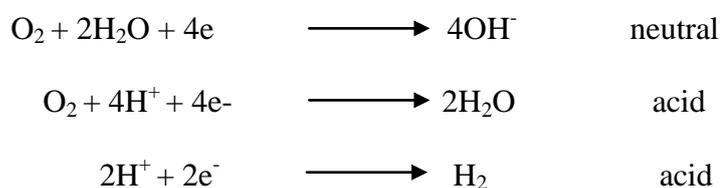
The location at which the above reaction may occur is called the cathode. An overall electrochemical reaction consists of at least one oxidation or anodic reaction and one reduction or cathodic reaction and there is no net accumulation of charges as the electrons generated from dissolution are consumed by reduction. For example the rusting of iron in water containing dissolved oxygen is shown according to the reaction below.

$$Fe \longrightarrow Fe^{2+} + 2e \qquad \text{Anodic}$$

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^- \qquad \text{Cathodic}$$

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe\,(OH)_2 \qquad \text{Overall}$$
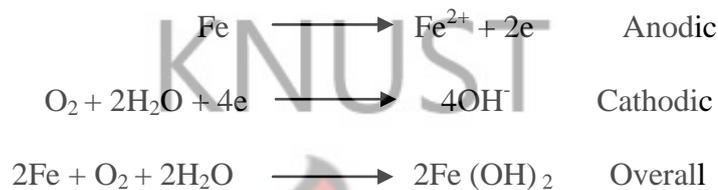
Thus for iron or steel to corrode, it is necessary to have the simultaneous presence of water and oxygen. In the absence of either, corrosion does not occur and also all the corrosion occurs at the anode and none at the cathode *[Callister, 2006]*.

Corrosion environments include the atmosphere, aqueous solutions and soil. The rest are acids, basis, inorganic solvents, molten salts, liquid metals, and the human body. On a tonnage basis, atmospheric corrosion accounts for the greatest losses. Moisture containing dissolved oxygen is the primary corrosive agent, but other substances including sulphur compounds and sodium chloride may also contribute. This is especially the case for marine environments which are highly corrosive because of the presence of chloride ions and industrial environments with dilute sulphuric acid (acid rain) can also cause serious corrosion problems *[Callister, 2006]*.

The rate of corrosion of metal is affected by a number of factors which include: time of wetness, type and concentration of pollutants, fluid velocity, temperature and the design

and manufacturing process of which the part is made of. In some specific environments however some normally active metals lose their chemical reactivity and become extremely inert and this phenomenon is termed Passivity. It is believed that this passive behaviour results from the formation of a highly adherent and very thin oxide film on the metal surface which serves as a protective barrier to further corrosion *[Callister, 2006]*.

2.1.2   Forms of corrosion

The two broad forms of corrosion are the uniform attack and localized corrosion. In the uniform attack the electrochemical corrosion occurs over the entire exposed surface with equivalent intensity and often leaves behind a scale. It is the most common and is typified by steel in air and the tarnishing of silverware. Corrosion at anodic areas becomes stifled over a period of time and new anodic areas adjacent to the original ones become active and over a long period the entire surface becomes covered with corrosion products *[Callister, 2006]*.

Localized corrosion however occurs when a particular site becomes anodic and undergoes deterioration while the entire surface becomes cathodic. The factors that are likely to cause localized corrosion are established and must be taken into consideration in the design of a structure. Examples of localized corrosion include: pitting, crevice corrosion, differential aeration, selective leaching, intergranular corrosion and erosion corrosion. Other types of corrosion are stress corrosion which is due to the combined action of an applied stress and a corrosive environment which causes damage and corrosion fatigue which is the failure of a material under the influence of both fatigue and corrosion together. Bimetallic or galvanic corrosion takes place when two metals or alloys of different compositions are electrically coupled while exposed to an electrolyte in which the less noble metal in the specific environment undergoes corrosion.

2.1.3   Methods of Preventing /Controlling Corrosion

In most practical situations corrosion attack cannot be prevented but can be controlled so that a useful life is obtained from a structure or an item. There are three significant stages in the life of a component namely design, manufacture and use. Corrosion control must be taken into consideration in all these stages. The failure of this will lead to premature failure of the component *[Diamant, 1971]*.

Corrosion control may be exercised in a number of ways but most important are; selection of materials, modification of design, modification to the environment (inhibition), cathodic or anodic protection and the application of barrier coats.

The use of barrier coats especially paints are the principal method of controlling corrosion as the other methods are either not suitable or inadequate because of economic and technical considerations. Barrier coatings are applied to metal substrates, either to separate the environment from the metal or to control the micro-environment on the metal surfaces. Many types of coatings are used for these purpose and they include paints, organic films, metallic coatings and enamels *[Diamant, 1971]*.

 Enamel coatings like other glass-ceramic coatings are generally chemically inert, have high temperature stability and good mechanical properties compared to other coatings such as metals, polymers paints rubbers etc. [Majundra and Sunimal, 2001]. Table 1 below compares qualitatively the properties of selected coatings used in industrial and engineering applications.

Table 2.1: Properties of various coating materials [*Majundra and Sunimal, 1995*]

Property	*Enamel coatings*	*Stainless Steel*	*Plastic*	*Anodized aluminium*	*Paint*
Colour performance	Very good	Poor	Good	Poor	Good
Cleanliness	Excellent	Very good	Fair	Fair	Fair
Resistance to heat and light	Excellent	Excellent	Poor	Good	Fair
Resistance to corrosive attack	Very good	Very good	Very good	Good	Poor
Resistance to scratch and abrasion	Excellent	Very good	Poor	Good	Poor
Resistance to brittleness and chipping	Good	Very good	Poor	Good	Fair
Hygienic	Very good	Fair	Fair	Good	Poor

2.2   GLASS MATERIALS

Since enamels coatings are coatings of glass material that has been fused onto a metal substrate a general description is made in this section on glass material structure and properties.

2.2.1   Definition of Glass

A glass may be defined as an inorganic product of fusion which has been cooled to a rigid condition without crystallization [*ASTM, 2004*].

According to Zachariassen, glass is a substance which can form extended three-dimensional network lacking periodicity with energy content comparable with that of the corresponding crystal network. In essence, the density and mechanical properties of a glass are solid-like however; the atoms form a continuous random network such that

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the unit cell is infinitely large, containing an infinite number of atoms. Thus a glass is solid with a liquid-like structure.

Unlike a crystal, glass may not be represented by a simple chemical formula. There are no restrictions with regard to relative numbers of chemically different atoms other than the fact that the valence and or coordination requirements may need to be satisfied. Unlike a crystal, glass does not have a sharp melting point when heated. The seemingly rigid solid gradually softens and flows at a higher temperature. At ambient temperatures, however the viscosity of glass may be sufficiently high that measurable flow does not occur over millennia.

Glass and amorphous solids are X-ray amorphous and make up a class of materials called non-crystalline solids. Glass is however distinguished from amorphous solids in that the latter appears to crystallize before transformation into the liquid state. Again care should be taken not to confuse a glass with an amorphous powder, a term commonly used to refer to a random assemblage of finely divided crystals *[Harper, 2001]*.

2.2.2 Glass Transition Temperature

As stated above the solidification behaviour of a glass is different from that of a crystalline solid, as illustrated in Figure 2.1 *(Wyatt and Dew-Hughes,1974)* as plot of specific volume (reciprocal of density) versus temperature for these two types of materials. A liquid that forms a crystalline solid upon solidifying (i.e. pure metal) will normally crystallize at its melting point with a significant decrease in specific volume, as indicated by path ABC (*Figure 2.1*). In contrast, a liquid that forms a glass upon cooling does not crystallize but follows a path like AD in Figure 2.1. Liquid of this type becomes more viscous as its temperature is lowered and transforms from a rubbery, soft

plastic state to a rigid, brittle glassy state in a narrow temperature range where the slope of the specific volume versus temperature curve is markedly decreased. The point of intersection of the two slopes of this curve defines a transformation point called the glass transition temperature (T_g). This point is structure-sensitive, with faster cooling rates producing higher values of (T_g).

Figure 2.1 Solidification of crystalline and glassy materials showing changes in specific volume.

T_m is the melting temperature of the crystalline material.

2.2.3   Structure of Glasses

2.2.3.1 Glass-forming oxides (network formers)

 These are oxides that can form polyhedra (e.g. silica) which can connect with a SiO_4^- network associated with vitreous silica. The fundamental subunit in silica-based glasses is the SiO_4^{4-} tetrahedron in which silicon is bonded to four oxygen atoms. In crystalline silica, e.g. crystoballite, the Si-O tetrahedral are joined corner to corner in a regular arrangement, producing a long range order. In a simple silica glass however the

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tetrahedral are joined corner to corner to form a loose network with no long-range order [*Smith and Hashemi, 2006*].

Boron oxide, B_2O_3, is also a glass-forming oxide and by itself forms subunits that are flat triangles with the boron atom slightly out of the plane of the oxygen atoms. However in borosilicate glasses that have additions of alkali and alkaline earth oxides, BO_3^{3-} triangles can be converted to BO_4^{4-} tetrahedral, with the alkali or alkaline earth cations providing the necessary electroneutrallity. Boron oxide is an important addition to many types of commercial glasses such as borosilicate and aluminoborosilicate glasses. Other oxides that can form the glass skeleton on their own are GeO_2, P_2O_5 [*Smith and Hashemi, 2006*].

2.2.3.2 Glass-modifying oxides (network modifiers).

These are oxides that break up the glass network. They are the alkali oxides such as Na_2O, Li_2O and K_2O and alkaline earth oxides such as CaO, BaO and MgO. These are added to silica glass to lower its viscosity so that it can be worked and formed more easily. The oxygen atoms from these oxides enter the silica network at points joining the tetrahedral and break up the network, producing oxygen atoms with an unshared electron. The Na^+ and K^+ ions from the Na_2O and K_2O do not enter the network but remain as metal ions ionically bonded in the interstices of the network. By filling some of the interstices, these ions promote crystallization of the glass *[Smith and Hashemi, 2006]*.

2.2.3.3 Intermediate oxides in glasses (intermediates)

These are oxides that do not form glass networks by themselves but can join into an existing network. For example, aluminium oxide, Al_2O_3, can enter the silica network as AlO_4^{4-} tetrahedral, replacing some of the SiO_4^{4-} groups. However since the valence of Al

is +3 instead of the necessary +4 for the tetrahedral, alkali cations must supply the necessary other electrons to produce electrical neutrality. Intermediate oxides are added to silica glass to obtain special properties e.g. aluminosilicate glasses can withstand higher temperatures than common glasss. Other intermediate oxides that are added to silica glass are lead oxide, ZrO_2, BeO and TiO_2 *[Smith and Hashemi, 2006]*.

2.2.4   Viscous Deformation of Glasses

A glass behaves as a viscous (super-cooled) liquid above its glass transition temperature. Under stress, groups of silicate atoms (ions) can slide past each other, allowing permanent deformation of the glass. Interatomic bonding forces resist deformation above the glass transition temperature but cannot prevent viscous flow of the glass if the applied stress is sufficiently high. As the temperature of the glass is increased above its glass transition temperature, the viscosity of the glass decreases and viscous flow becomes easier. The effect of temperature on the viscosity of glass follows the Arrhenius-type equation given by

$$\eta^* = \eta_o \, e^{Q/RT}$$

Where η^* = viscosity of the glass in poise, η_o = pre-exponential constant, Q = molar activation energy for viscous flow in J/mol; R = universal molar gas constant; and T = absolute temperature (K) *[Harper, 2001]*.

The various steps of forming glass are essentially determined by using viscosity-temperature curves from which four different viscosity reference points are used as guidelines. These are working, softening, annealing and strain points and they are defined as follows;

Working point is the temperature at which the viscosity is 10^4 poise. This is the viscosity at which a machine is able to work on glass without losing control.

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Softening point is the temperature at which the viscosity is $10^{7.6}$ poise. This is the approximate viscosity at which a glass will deform under its own weight on the time scale of manufacturing operations. Glass temperatures must be lower than this before the glass leaves the forming machine.

Annealing point is the temperature at which the viscosity is 10^{13} poise. Stresses that form in the glass object are relieved at this viscosity in a matter of minutes.

Strain point is the temperature at which the viscosity is $10^{14.5}$ poise. Stresses that form in the glass object are relieved at this viscosity in a matter of hours *[Harper, 2001]*.

2.3   ENAMEL COATINGS

An enamel coating is a coating of a glassy substance which has been fused onto the basis metal to give a tightly adherent hard finish resistant to many abrasive and corrosive environments *(Shrier, Jaman and Burstein, 1994).* The ASTM defines porcelain enamel as a substantially vitreous or glassy inorganic coating bonded to metal by fusion at a temperature above 425°C [*Geiger (PEI), 2006*].

Ceramic coatings however consists of glass-ceramic materials which are polycrystalline solids prepared by controlled crystallization of the glass. Ceramic coatings are often formulated and designed to contain mainly crystalline rather than glassy material. Crystallization is accomplished by subjecting the glass composition to carefully regulated heat treatment schedule which results in nucleation and growth of crystalline phases within the glass [*Friedberg, 1977*].

The purpose of an enamel coat is twofold, first to confer corrosion protection to the metal substrate and secondly to provide a permanent colour, gloss and other aesthetic values. Most of the corrosion resistance and other mechanical properties of the enamel coatings are determined by the enameller's raw material called *frit,* although other

factors can influence them to a minor extent. Enamel frits consist of alkaline alumina-borosilicate to which other inorganic substances may be added to provide desirable physical properties such as resistance to acid and alkaline solutions, heat, corrosion and abrasion *[Shrier, Jaman and Burstein, 1994]*.

2.3.1   Uses of enamels

Porcelain enamels protect against corrosion, decorate and resist the attack of alkaline, acids and other chemicals. Because of these they are adopted as suitable material for bathtubs, laundry appliances, sinks and refrigerator liners. They are also used in architectural panel applications. They are also used in the dairy, pharmaceutical, brewing and other chemical industries. Enameled tanks and Vessels made of heavy gage steel or cast iron are commonly used in the above industries. Cooking utensils, architectural panels, signs, silos, storage tanks, roofing tiles, gasoline service stations, guard rails, chalk board and many other products of commerce indicate the broad use of enamel coatings on iron and steel which is among the most desirable of composite system of materials. Figure 2.2 below shows some of the common areas of application of enamel coatings.
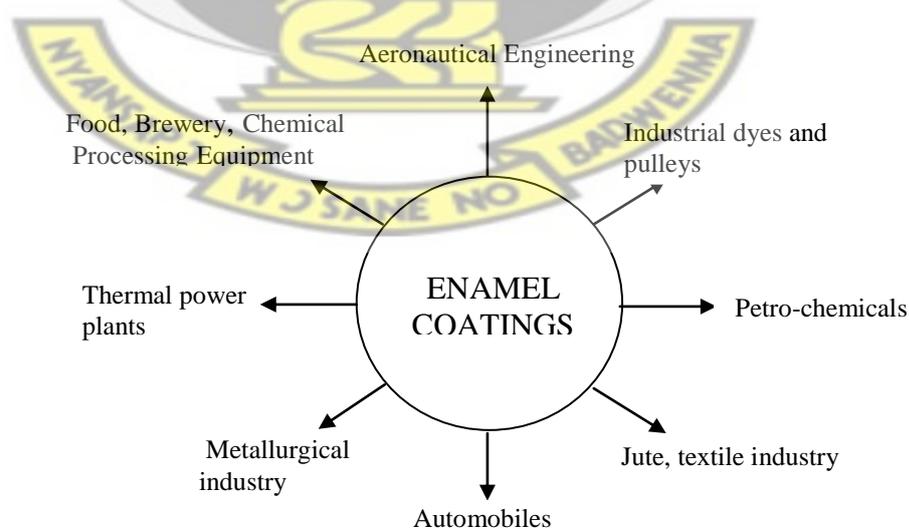
Figure 2.2: Areas of application of enamel coatings [Majundra and Sunimal, 2001]

2.3.2   The Enamel Oxides

A listing of all the commonly used enamel oxides includes the following boric oxide (B_2O_3), silicon (IV) oxide (SiO_2), aluminum oxide (Al_2O_3), titanium oxide (TiO_2) and potassium oxide(K_2O). The rest are Sodium oxide(Na_2O), calcium oxide(CaO), magnesium oxide(MgO), barium oxide(BaO), lithium oxide(Li_2O), strontium oxide(SrO), antimony oxide(SbO) and zinc oxide(ZnO) *[Rhodes, 1965]*.

2.3.3   The function of some of the oxides in enamel

Something should be said here in a general way about the oxides which have been listed as entering into enamel composition. For one thing, no two of them behave exactly alike. Each oxide has a particular contribution to make to the enamel. Calcium and strontium behave more nearly alike than any other pair, and sodium and potassium are similar. The only oxide which is indispensable to enamel making is silica, and all the rest are oxides which may, or may not, appear in any particular enamel. Sources for the various enamel oxides are abundant and relatively cheap *[Rodes, 1965]*

2.3.3.1   Silica, (SiO_2)

Silica is the fundamental oxide of glass. Enamels are preponderantly made up of silica, and the other ingredients which are put into enamel are really put in to modify it towards a lower melting point, or to lend to it some other properties such as alkalinity, opacity, or matness.

About 60 percent of the crust of the earth is made up of silica, a fact which is attributed to the hardness, durability, and resistance to chemical change or solution of this oxide. These are the desirable properties which it adds to enamel. Vitreous silica has a low coefficient of expansion, and for this reason its presence in the enamel controls the fit of the enamel to the body. Silica has no undesirable properties when used in enamel,

except that, when present in excessive amounts, it may cause the enamel to be under-fired at the intended temperature. An excess may cause devitrification or the formation of crystals in the cooling enamel. No enamel colours are adversely affected by silica *[Harper, 2001]*.

2.3.3.2 Alumina (Al₂O₃)

Although alumina is used in relatively small amounts in enamel, it contributes importantly to the working properties of the enamel, and the only enamels which are commonly made up without alumina are those which are intended to develop crystals during cooling. Alumina is refractory and does not melt by itself until about 2040°. For this reason, not much alumina can be added to enamel without causing it to be under-fired and dry in appearance.

The presence of alumina in enamel makes the melted enamel more viscous and less apt to run down off vertical surfaces. This is an indispensable property of enamels for most useful purposes. Another valuable function of alumina is the prevention of recrystallization during the cooling of the enamel. Without alumina, many enamels would devitrify on cooling and would have rough surfaces, opacity, or mottled textures. Alumina in the molten glass acts as a retardant in keeping the other materials from getting together in the crystalline state. Alumina also adds to the hardness, durability, and tensile strength of enamels *[Rhodes, 1965]*.

2.3.3.3   Sodium Oxide (Na₂O)

The oxide of sodium is very active chemically and functions in enamels as a strong flux or melter. It is a very useful oxide in enamel from the lowest temperature range to the higher-fired enamel. Soda has the disadvantage of having a very high coefficient of expansion which causes enamels that are high in soda to craze after firing. Other dis-

advantages of high soda enamels are their tendency to be soft and easily scratched their high solubility in acid, and their tendency to weather and deteriorate. Used in moderate amounts and in combination with other fluxes, soda is a very useful oxide in enamels over a wide range of temperatures. Soda is an important constituent of ordinary glass, which is largely composed of silica, soda, and lime. *[Rhodes, 1965]*

2.3.3.4 Potassium Oxide (K_2O)

Potassium oxide is very similar to sodium in its action in enamels. Actually, these two oxides behave so much alike that they are frequently described by the symbol "KNaO", which means a blend of sodium and potassium in any proportion. Potassium has the same advantages and the same disadvantages as sodium. It has a slightly lower coefficient of expansion than sodium, but it is still very high and causes crazing. Potassium is a very active flux and is useful in enamel at all temperatures. Its only natural source in insoluble form is feldspar, and when considerable amounts of potassium are required in enamel, a frit is used *[Rhodes, 1965]*.

2.3.3.5 Calcium Oxide (CaO)

Most enamels contain calcium oxide. Since it is a common and inexpensive material and contributes only desirable properties to enamel, it is one of the most valuable enamel ingredients. Its principal function in enamel is that of a flux. Calcium contributes to the hardness and durability of enamels. It causes no difficulty in firing, and few enamel faults can be traced to it. [*Rhodes, 1965*]

2.3.3.6 Boric Oxide (B_2O_3)

Boric oxide is a low-melting-point substance with strong fluxing power comparable to lead oxide or sodium oxide. It is a very useful enamel ingredient which has come into common use in modem times. The only natural source of boric oxide is colemanite, which is not soluble and except where this material is used, boric oxide is introduced

into the enamel in fritted form (*Rhodes, 1965*). Boric oxide can be used as the main flux in enamel, or as an auxiliary flux, and it can be used from the lowest to the highest temperatures. It forms borates that reduce the expansion of the enamel, and so is useful in the correction of crazing.

2.4 RAW MATERIALS FOR ENAMEL COATINGS

Even though the compositions of enamels are given in terms of oxides, most often oxides are not directly used. Rather a mixture of naturally occurring minerals is used, which are complemented with oxide additives. Some of these include flint, feldspar and borax among others. Tables 2.2 and 2.3 below present the oxide composition and batch compositions of selected substrates.

Table 2.2 Oxide compositions of selected enamels and substrates [*Friedberg, 1977*].

Oxide % composition	Sheet steel *Ground coat*	Sheet steel *Titania cover*	Cast iron *Ground coat*	Cast iron *Cover coat*
(KNaO)	19.7	(14.0)	(11.4)	20.8
K_2O	-	3.5	7.1	4.4
Na_2O	-	10.5	4.3	16.4
B_2O_3	14.6	14.0	6.9	2.6
Al_2O_3	7.2	-	11.3	6.0
SiO_2	50.5	45.0	51.8	48.9
CaF_2	5.1	-	-	3.2
CoO	0.6	-	-	-
MnO	1.9	-	-	-
TiO_2	-	20.0	-	-
P_2O_5	-	2.0	-	-
PbO	-	-	18.4	-
$Sb_2O+NaF+AlF_3$	-	-	-	21.2

Table 2.3: Batch composition of selected enamels and substrates [*Friedberg, 1977*]

Batch	Sheet steel *Ground coat*	Sheet steel *Titania cover coat*	Cast iron *Ground coat*	Cast iron *Cover coat*
Feldspar	30.3	-	35.0	22.6
Borax(hydrous)	31.6	-	23.0	16.7
Borax(anhydrous)	-	19.1	-	-
Quartz	20.0	42.0	15.0	26.0
Soda ash	6.7	-	-	3.0
(NaNO$_3$)	3.8	7.8	4.0	4.5
Fluorspar	4.6	-	-	2.3
Phosphate	-	3.2	-	-
Manganese oxide	1.5	-	-	-
Boric acid	-	-	-	-
Titania	-	20.2	-	-
Cryolyte	-	-	-	10.7
Red lead	-	-	23.0	-
K$_2$SiF$_6$	-	7.8	-	-
NaSiO$_3$	-	1.2	-	-
BaCO$_3$	-	-	-	-
NaSbO$_3$	-	-	-	11.4
Clay	-	-	-	2.4

2.4.1 Flint (SiO2)

Flint is used in enamel as the main source of silica. In mineralogy, flint is a variety of quartz usually grey, black, or brown, which has an extremely small crystalline structure (cryptocrystalline). Potter's flint may be made by grinding any form of crystalline quartz into a fine powder. Flint is insoluble and chemically inert. It is abundant and cheap [*Rhodesl, 1965*].

2.4.2 Feldspar (SiO$_2$.AlO$_2$.CaO.K$_2$O.NaO)

Feldspar is one of the most important enamel materials. It is used in almost all enamels and it is often the principal material and provides the principal flux. Feldspar is one of

the constituents of granite and it is one of the most common and wide-spread minerals. Feldspar is made up of an alkaline portion (consisting of sodium, potassium, or calcium, singly or in combination), alumina and silica [*Rhodes, 1965*].

2.4.3 Borax (Na$_2$O. 2B$_2$O. 10H$_2$O)

Borax is one of the principal ingredients of porcelain enamels. Borax may be used in enamels as a source of both sodium and boric oxide .It is one of the most active of all fluxes in enamels. It has a low melting point and vigorously attacks other components and thus accelerates the rate at which the enamel is brought to a uniform molten state. Borax also imparts important thermal properties necessary to assure proper fit of the enamel to the base metal.

Borax imparts high luster, strength, toughness and durability and assists in obtaining deep brilliant colorings, though it shortens the firing range of most enamels. Increasing the boric oxide content of mill liquor decreases the scumming of enamel caused by firing at too low temperature. Pitting caused by crystallization of borax on the surface of enamel during drying will burn out in firing. Borax helps to prevent crazing, but excessively large amounts will cause tearing and crawling and will reduce the efficiency of mill-added opacifiers. The amount of borax in the frit batch for sheet-steel ground-coat enamels varies from 20-45%, for sheet-steel cover coats from 15-40%, and for dry-process ground coats from 20-45%.

Theoretical composition of borax is 16.25% Na$_2$O, 36.6% boric acid, 47.2% water of crystallization. The water of crystallization is eliminated during fusion with the ceramic material, leaving 52.7% of Na$_2$O and boric oxides to form part of the ceramic composition. Borax begins to melt in its water of crystallization at 60.8°C and it is soluble in water, acids, glycerol and other solvents. Borax is obtained in large crystals,

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powder and granular form the last being regarded the most practical and economical for glass/ceramic use *[Harper, 2001].*

2.4.4 Clays

Clays are products of the decomposition and alteration of feldspathic rocks. It consists of a mixture of particles of widely differing physical, chemical and mineralogical properties. The non plastic portion consists of altered and unaltered rock particles of which the most common and abundant substances are quatz, micas, feldspars, iron oxides and calcium and magnesium carbonates. Organic matter is also usually present in greater or smaller amounts and plays a role in determining clay properties. The essential constituents of clays are hydrated silicates of aluminium, of which there are several but the most important and widely spread are the Kaolinite group, $Al_2O_3.2SiO_2.2H_2O$, and montmorillonite group $(Mg.Ca)O.Al_2O_3.SiO_2.H_2O$. Clays may be designated as residual or secondary, according to their geologic history. Residual clays are those occurring in the same location as originally formed by weathering whereas secondary clays are those that have been transported by water, ice or wind and redeposited, alteration usually occurring during the transportation process.

Clays are introduced into the enamel batch to serve as suspending and binding agents in the unfired state, and as an intrinsic part of the unfired enamel. In general enamel clays are very clean with minimal impurities, selected for their ability to hold the finely ground enamel frit particles in water suspension so they will dip and spray evenly. Clay also aids the opacity of the fired coating. Amounts of clay ranging from 2-15%, based on dry weight of frit, have been added to the mil, the usual amount is about 7%. Enamel clays are usually of ball clay characteristics *[Harper, 2001].*

2.5   ENAMEL PROPERTIES

2.5.1   Physical Properties of Enamel Coatings

The porcelain enamel coating, the metal substrate and the design of the part to be coated all contribute to the mechanical and physical properties of the porcelain enamel. However, since porcelain enamel is glass, the glasslike properties are most influential. Porcelain enamels, regardless of thickness, provide outstanding wear resistance and abrasion resistance, while contributing to the strength of the metal substrate *[Geiger, PEI, 2006]*.

2.5.1.1   Hardness

Depending on composition, hardness of porcelain enamels range from 3.5 to 7 on the Mohr's scale of mineral hardness. Most porcelain enamels for steel substrates fall in the range of 4 to 5.5. Organic finishes commonly fall in the 2 to 3 range. As a rough approximation, a typical porcelain enamel on steel has about the same hardness as plate glass. Rather uniquely, hardness of porcelain enamel does not vary greatly from one composition to another. Porcelain enamel surfaces are unaffected through the range of pencil hardness scratch tests commonly used to evaluate organic finishes. Comparable values on the Knoop scale range from 149 to 560. The Sward rocker rating is 100, the same as plate glass. The surface hardness property of porcelain enamel contributes a durability quality that is essential to a broad range of long-lasting products *[Geiger, PEI, 2006]*.

2.5.1.2   Abrasion and Wear Resistance

Porcelain enamel coatings provide excellent abrasion and wear resistance, with every formulation being substantially more abrasion resistant than the hardest organic coating. Porcelain enamels frequently provide better wear and abrasion resistance than metals. This is attested to by their use on bunker and silo discharge chutes, coal chutes, water

lubricated bearings, screw conveyors and chalkboards. Sinks, lavatories, bathtubs and range tops are further examples where good abrasion and wear resistance is an important service requirement *[Geiger, PEI, 2006]*.

2.5.1.3 Adhesion

Adhesion may be viewed as (1) resistance to mechanical damage by impact, torsion, and bending or heat shock; (2) "attraction" of enamel and metal; and (3) a relationship to substrate design. Good adhesion is produced by reaction and fusion of the porcelain enamel coating with the base metal at relatively high temperatures that may fall within $500^{o}C$ to $900^{o}C$ ranges. Glass is very strong in compression *[Geiger, PEI, 2006]*.

When the porcelain enamel coating (glass) is applied to the metal substrate, the formulation of the coating is such that it has a lower coefficient of expansion than the substrate and thus is always in compression. The bond has many characteristics of a true chemical bond in combination with mechanical bond developed by fusion flow of the coating over the surface roughness of the substrate. Since moisture or rust cannot penetrate beneath the porcelain enamel coating, it will not flake away from exposed edges or damaged areas. The coating does not tend to "creep" under service conditions as can be shown by salt spray testing. Porcelain-enameled metal will flex with the metal providing resistance to stresses that cannot be obtained in solid glass.

2.5.1.4 Thickness

Porcelain enamel can be applied in a wide range of thickness, from 0.25mm or less on steel or aluminum substrates to 0.5mm or more on cast iron or heavy gage steel or plate. Optimum thickness depends on compositions of the porcelain enamel coating and the base metal and -particularly-on the expected service conditions. In general, thinner porcelain enamel coatings are more flexible and have greater resistance to fracture.

Thicker coatings have better electrical properties; they also withstand chemical attack for longer periods *[Geiger, PEI, 2006]*.

For applications on steel, a base or ground coat of porcelain enamel 0.2mm thick is commonly applied and followed with one or more finish coats. However, with modified pretreatment of steel substrates and decarburized steel quality, a one-coat porcelain enamel finish coat of 0.3 to 0.5mm may be applied directly to the steel. If more than one cover coat is applied, each may be 0.2 to 1.0mm thick. Multiple coats can be applied that interfuse to form a single heavy layer. Normally, a white cover coat (titania opacified) should be at least 0.3mm thick to provide adequate opacity to hide light scratches in the metal. Certain colors and textural effects can be obtained with relatively thick coatings *[Geiger, PEI, 2006]*.

However, purely functional coatings such as those for high temperature protection are usually applied quite thin (as thin as 0.1mm) using special base metals. Thickness over 1.5mm is not generally recommended for sheet metal parts because of warpage or chippage problems. Normally, heavier coatings are used on cast iron or steel plate where rigidity of the substrate resists deformation and reduces the danger of fracture. Such coatings are sometimes desirable to hide rough spots on the metal or to provide longer service life. Porcelain enamels for aluminum sheet are usually applied at a target thickness of 0.3mm. However, thickness of 0.5 to 0.7mm may be required for specified appearance or use requirements *[Geiger, PEI, 2006]*.

2.5.1.5 Resistance to weather

The weatherability of porcelain enamel is usually measured by the degree to which the coating retains its original gloss and color. In general, acid resistance porcelain enamels have better weather resistance than those that are non-acid resistant.

Porcelain enameled signs have been known to be still in good condition after 50 years exposure. According to exposure tests conducted by Porcelain enamel Institute, UK, porcelain enamels of even the poorest weather resistance can protect metal from outdoor atmospheric corrosion for 15 years. To achieve this performance, the metal substrate must receive good initial coverage and there must be no pinholes or mechanical damage *[Geiger, PEI, 2006]*.

2.5.1.6 Acid resistance

The acid resistance of porcelain enamels can vary widely depending on composition and, to some extent, the processing used. Special formulations can provide porcelain enamels with excellent corrosion protection against aqueous solutions of alkalis, salts and most acids except hydrofluoric. Even such corrosive media as molten metals and vapor phases present in hot gases have been confined within porcelain enameled structures. The degree of attack by acid solution on porcelain enamels appears to depend less on the type of solution than on its pH.

The highest degree of acid resistance is obtained by sacrificing other desirable properties such as alkali resistance. To achieve maximum service conditions, a proper balance of acid resistance, alkali resistance and other properties is necessary. Such a balance is achieved for the porcelain enamel coatings used on such applications as home laundry equipment, dishwashers (or self-cleaning) oven liners and architectural panels. Test references include ASTM C282 Citric Acid Spot Test and ASTM C283 Boiling Acid Test *[Geiger, PEI, 2006]*.

2.5.1.7 Salt spraying resistance

Many evaluations have shown that porcelain enamels with complete coverage will withstand the standard ASTM B117-571 salt spray test for days and even weeks without evidence of corrosion. In addition, experience has shown that porcelain enamels provide

excellent service in applications involving salt air exposure or intermittent or continuous exposure to sea water *[Geiger, PEI, 2006].]*.

2.5.2 High Temperature Resistance

Abrupt and severe temperature changes do not affect porcelain enamels applied at normal thicknesses. Porcelain enamel's thermal properties are excellent in the range of temperature from below freezing to high heats up to about 200°C below firing temperature. Because of this thermal stability and thermal shock resistance, porcelain enamel is a suitable coating for many heat-related applications. The thermal properties of porcelain enamel provide a coating that readily withstands the expansion and contraction of the base metal under changing temperature conditions.

2.5.2.1 Thermal shock resistance

Thermal shock resistance of a porcelain enamel varies inversely with its thickness. Thermal shock failure is caused by the rapid chilling of the surface. It manifests itself in a crack and occurs when the thermal gradient perpendicular to the surface is large enough to cause excessive differential shrinkage and tensile stress. Important considerations are the porcelain enamel's thickness and its coefficient of thermal expansion. Thermal shock resistance is also affected by the design and thickness of the part. Flexing of the metal due to localized thermal gradients parallel to the surface can produce bending and tensile stresses in the coating. Thus, any increase in the strength or rigidity of a part helps increase the coatings resistance to thermal shock. Most porcelain enamels applied at conventional thickness can be expected to take abrupt temperature drops of 400°C to 149°C without damage. Thinner coatings have a proportionately higher thermal shock resistance. Other things being equal, the best thermal shock resistance is achieved with coatings of 5-mills or less. Special ceramic coatings will

successfully undergo repeated tests of heating to 927°C and quenching in water *[Geiger, PEI, 2006]*.

2.6   ENAMEL DEFECTS

The various flaws which develop in enamels are not easy to get under control, particularly in small-scale production where numerous enamels are used and there is not the opportunity for sustained experimentation and control work *[Rhodes, 1965]*.

The reasons for most of the defects which develop in enamel are well known and careful compounding, application, and firing can ensure good results. The common enamel defects include crazing, shivering, crawling, pitting or pinholes and blistering or blebbing.

2.6.1   Crazing

Crazing is a common enamel flaw, but one which is rather easily corrected in many cases. Crazing is the development of a fine network of cracks in the finished enamel. These cracks may be present when the ware is first taken from the kiln, or they may develop days or months after the ware has been fired. Ware which is crazing when it comes from the kiln makes a tinkling sound each time a new crack appears. Crazed ware may be unsightly and unsanitary, and may permit leaking or seepage through ware which is used to contain liquids *[Rhodes, 1965]*.

2.6.2   Shivering

Shivering occurs when enamel is under too great compression, which causes it to separate from the clay and peel or shiver. The effect might be compared to a sidewalk which buckles and rises from the ground in places as a result of expansion. Shivering is certainly a serious flaw, but it is easily corrected. The remedy is to increase the high expansion oxides in the enamel and thus make it contract more when it is cooling. This decreases the compression in the enamel which causes the trouble. In practice, the flint

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in the enamel is decreased and the feldspar or other alkali-bearing materials are increased. If the cure is to be effected in the body, a decrease in the flint content of the clay usually takes care of the difficulty.

2.6.3 Crawling

In crawling, the enamel parts during melting and leaves bare spots of metal exposed. The crawl may expose only few tiny places, or it may leave a pattern of exposed areas resembling the cracks in dried mud. In extreme cases, the enamel may roll up into droplets or blobs, or it may crawl off most of the piece and be found in a melted puddle on the kiln shelf below the piece *[Rhodes, 1965]*.

2.6.4 Pitting and Pinholing

Pitting and pinholing are, by all odds, the most annoying and difficult enamel flaws to cure. The enamel may come from the kiln covered with minute pits or pinholes. These pinholes may be small, or they may be larger, resembling miniature volcano craters. Re-firing may only serve to make the pinholes larger or more frequent *[Rhodes, 1965]*.

2.6.5 Blistering and Blebbing

Lead enamels, if accidentally subjected to reducing atmospheres in the kiln, are apt to blister. The enamel is grayed and blackened and the surface may be covered with large blisters and craters. Lead oxide is sensitive to atmosphere and is easily reduced. Care must be taken, therefore, when firing lead-enamel ware, to protect it from direct impingement of the flames from burners. Enamel which contain lead in fritted form only are less subject to blistering from reduction than are enamel which contain raw lead compounds *[Rhodes, 1965]*.

2.7   THE PROCESS OF ENAMELLING

The process of applying an enamel or glass-ceramic coating to a material commonly

called enameling broadly comprises of the following steps:

- Preparation of coating material

- Selection of proper substrate

- Metal surface preparation

- Application of coating material

- Drying of coating material and

- Maturing/firing of the coated material.

Figure 2.3 below shows a flow diagram of the process of applying enamel to metallic

substrates.
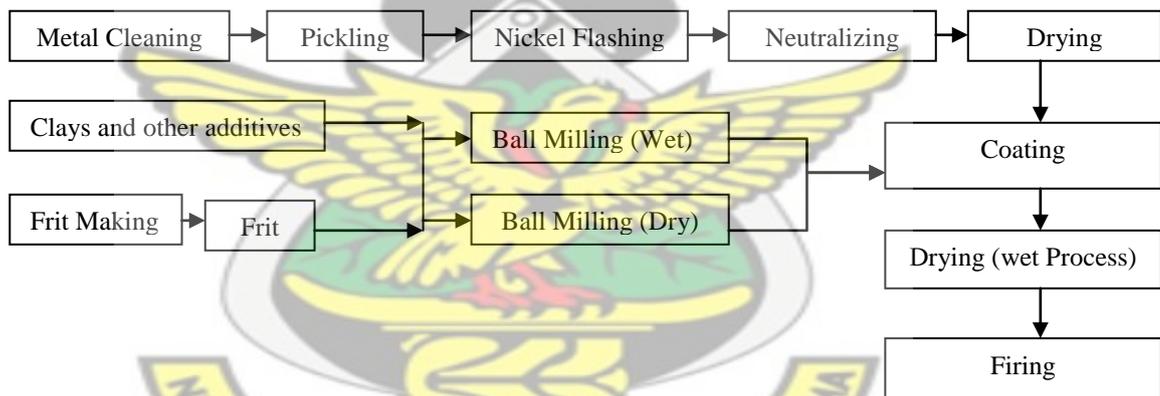
Figure 2.3: Flow diagram of the enamel coating application process on metallic substrate *[Friedberg, 1977 and Majundra and Sunimal 1995]*

2.7.1   Preparation of Coating Material

The basic ingredients of enamel finishes are the oxides SiO_2, B_2O_3 and P_2O_5 called the

network formers and Na_2O, K_2O and CaO called network modifiers. Other oxides like

TiO_2 and CoO are added as colourants. A desired composition of the oxides for a

particular end use application is obtained by smelting together carefully selected glass

material (batch) and quenching rapidly to produce frit. Table 2.2 and 2.3 gives the oxide and batch compositions for selected enamels and their substrates. The frit is ground in a mill in dry or wet condition. In the case of wet milling other additives usually clay electrolytes and colour oxides are incorporated to form a thick creamy suspension called slip which is used to coat a clean metal surface *[Friedberg, 1977]*.

2.7.2 Selection of Proper Substrate

Normally steel and cast iron are enameled but occasionally aluminium and its alloys are also coated with enamels. Sheet steel to be selected for enameling should have the following criterion [*Andrews 1972]*.

- Low carbon content (not more than 0.2%)

- Freedom from harmful gases in the metal(vis CO_2, SO_2)

- Low hydrogen collection during coating and

- Uniform composition and structure.

For cast iron enameling the so called gray iron is preferred *[Andrews, 1972]*. Its composition varies somewhat depending on the type and thickness of casting but falls within the following limits 3.2-3.6%C, 2.25-3.0%Si, 0.45-0.65%Mn, 0.60-0.75%P, and 0.05-0.10%S *[Shrier, Jaman and Burstein, 1994]*.

2.7.3 Surface Preparation

The quality of the coating depends largely on the nature of the surface to which the coating is applied (*Shaw, 1968*). The cleaning of a metal surface can be accomplished mechanically or chemically.

2.7.3.1 Mechanical cleaning

This is accomplished by blasting for large shapes or heavy stocks. The metal surface is exposed to a jet of an abrasive material such as sand, alumina or steel shots to remove

scale, rust and dirt. The surface becomes clean and slightly pitted which helps promote good bonding. Removal of material from the surface should not be excessive and can be controlled by adjusting the air pressure and the exposure time of blasting *[Majundra and Sunimal, 2001]*.

2.7.3.2   Chemical Cleaning

This is carried out to remove oil, grease and other organic impurities by using organic solvents or more commonly alkaline solutions. The animal and vegetable fats are saponified by alkalis and the soap formed is washed off while mineral oils are removed as emulsions. Mixing of the solution and the heating to about $80\text{-}100^{o}C$ accelerates the process. The pH of the solution is maintained at about 8-13 depending on the degree of contamination. After cleaning the wares are rinsed with water for complete removal of traces of the adherent cleaning solution and they are ready for pickling, nickel flushing and neutralizing *[Shaw, 1968]*.

2.7.3.3   Pickling

After chemical degreasing, the rust and scales are removed from the metal surface by immersing the articles in a solution. Pickling in HPO_4 improves the quality of surface but is generally not done because of high cost of the acid. Generally pickling is done in $6\text{-}8\%H_2SO_4$ or HCL. The parameters to be controlled here are the acid strength, iron content in solution, sludge and pickling time (which should be short to avoid hydrogen absorption) *[Shaw, 1968]*.

2.7.3.4   Nickel Flushing

After pickling, occasionally the metal items are immersed in a 2% solution of $NiSO_4.6H_2O$ at a pH of 3.2-3.6 and a temperature of $65\text{-}75^{o}C$. This is done in order to deposit a thin layer of metallic nickel on the metal surface which prevents fish scale and copper head formation and promotes adhesion *[Shaw, 1968]*

2.7.3.5 Neutralizing

This process removes the acidic residue adhering to the metal surface during drying. An alkaline solution for this purpose contains 0.3-0.4% Na_2O and it is prepared by dissolving Na_2CO_3 and $Na_2B_4O_7.10/5H_2O$ in the ratio 2:1 in water. The solution is maintained at 60-70°C during the neutralizing process. After neutralizing, the moisture is removed from the clean metal surface by heating in a chamber at 150-200°C and dried quickly to avoid rusting *[Shaw, 1968,]*.

2.7.4 Application of Coating Material

The common method of applying an enamel slip to metal substrate are dipping, draining and spraying. The usual method of applying dry powders to metal substrate is by the method of electrostatic spraying in which the enamel leaves a spray gun and passes through a high intensity direct current fields of 100kV. The negatively charged enamel particles are attracted to the metal surface which is at ground potential. This method of coating which is usually automated produces a uniform coating thickness and good coverage around corners.

Electrophoresis is also employed commercially to provide a dense uniform coating. In this process the metal surface is positively charged and the negatively charged electrodes are located in the slip. The metal particle is immersed in the slip and attracts the frit particles which parch into a tightly adherent coating layer.

Dry process cast iron enameling involves the application of the cover coat by dusting the drying glass powder onto the heated cast iron article using long-handled vibrating sifter. The cast iron which has been previously ground coated is removed form the furnace at 870°C or higher for dusting operation and then returned to the furnace.

Generally, only two dusting and heating are required for the development of a uniform coating *[Shaw, 1968 and Friedberg, 1977]*.

2.7.5   Drying

After application of the coating slip by any of the mentioned processes, the coated item is dried in a stove maintained at a temperature of $100^{o}C$. This is done to prevent moisture removal during firing at higher temperatures which can cause boiling or "pop off" defects. Low clay content and coarse particles in the slip leads to quick drying *[Shaw, 1968 and Friedberg, 1977]*.

2.7.6   Maturing/Firing

Firing of the coated material is the last operation in the enameling process. Firing temperature depends on the fusion characteristics of the coating material and the type of metal substrate. Enamels for aluminum are fired at $500\text{-}540^{o}C$, where as coatings for high temperature alloys may be fired at $900^{o}C$ or more. Uniformity in heating and cooling of the coating items is of great importance for the prevention and control of ceramic defects like chipping, hairlines and cracking.

Two types of furnaces – the box type and continuous furnaces are generally used. The batch or box-type is the oldest and is still efficient for low-production schedules or where a variety of shapes and sizes are to be fired in the same furnace (though not at the same time). The continuous furnaces are preferred when high production schedules are called for and when long runs of identical parts are to be fired. Two advantages of using the continuous type are that it can incorporate the dryer on the furnace chain and also can be adapted to the desirable progressive heating and cooling of the parts. Both types of furnaces can be fueled by gas, oil and electricity but electrically fired heated muffle furnaces are commonly used *[Shaw, 1968 and Friedberg, 1977]*.

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 MATERIALS

The raw materials considered in this study for the formulation of the enamel coatings include the Mouri feldspar, from the town of Mouri in the Central region of Ghana; Mfensi clay from Mfensi a town near Kumasi in the Ashanti region of Ghana and the Afari clay from the town of Afari also near Kumasi in the Ashanti region. Analytical grade sodium tetraborate decahydrate ($Na_2 B_4O_7.10H_2O$) was used as a source of boric oxide. The first three which were major constituents of the coatings are local materials and are readily available *[Kesse, 1985]*. Sodium tetraborate decahydrate was selected as the source for boric oxide.

The steel plate used was of the mild steel type and was obtained from the local market.

3.2 MATERIAL PREPARATION

3.2.1 Material Analysis

Samples of the local raw materials namely the Mfensi clay, Afari clay and the Mouri feldspar were analyzed for their elemental compositions using X-ray fluorescence (XRF) machine at the Geological Survey Department, Accra, after which their oxide compositions were calculated. (Table 3.1 and 3.2 present results of the analysis and the oxide composition of the sodium tetraborate decahydrate used).

For the XRF analysis a sample each of the Mfensi and Afari clays and the Mouri feldspar were first ground and sieved to all particles passing through 180µm (i.e. BS 410 mesh size). After sieving, 4g of each of the samples were measured and placed in

already cleaned steel dish and 0.9g of wax powder (Licowax) was added to each of the samples in the dish together with two small milling balls. The dish with its contents was placed in a vibratory mill and milled for about 3 minutes to further reduce the particle size. After milling the sample/wax powder, the mixture were transferred into an already cleaned die and pressed into pellets under a load of 10 tonnes.

The pellets were then put into the computer controlled X-ray fluorescence machine and machine settings done to conform to the pellets configuration. The settings were cross-checked again to ensure everything was in order. The machine was put on and it automatically analyzed the samples. The analytical results of the various oxides present were displayed on the computer monitor and were later printed. (Figure 3.1 and 3.2, presents the samples of the pellets and how they were placed on the sample tray for analysis)
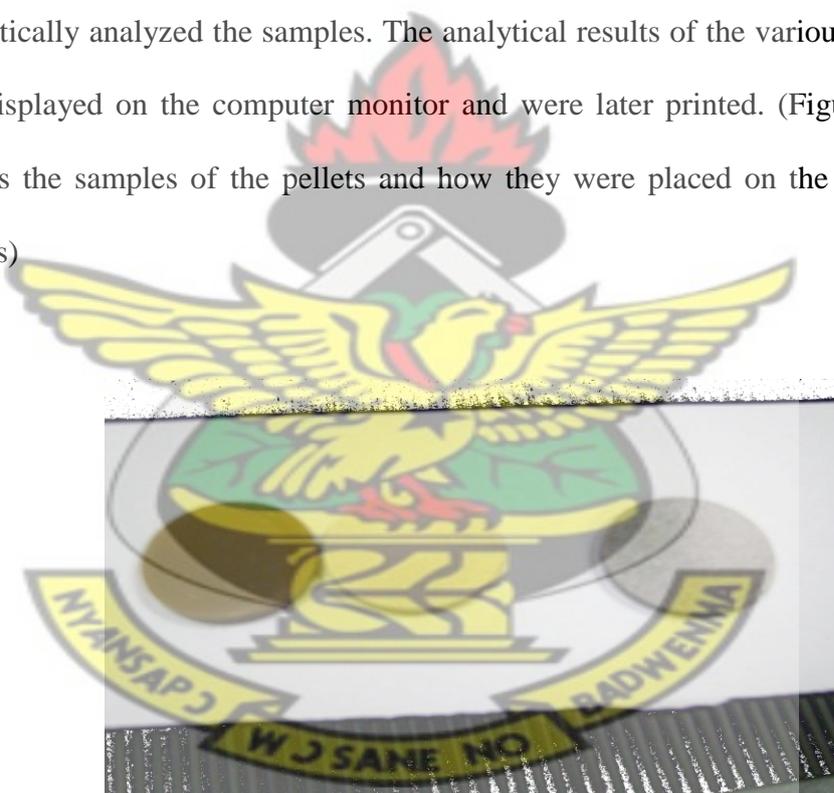
Figure 3.1: The compressed pellets of the samples

Figure 3.2: Placing the Pellets into the X-ray Fluorescence machine

Table 3.1: X-ray Fluorescence Results of the raw materials

Element	Afari Clay, %	Mouri Feldspar, %	Mfensi Clay, %
Na_2O	1.78	4.61	1.91
MgO	2.70	0.94	1.09
Al_2O_3	15.17	16.15	18.47
SiO_2	38.63	63.33	47.56
P_2O_5	0.09	0.31	0.07
SO_3	0.18	0.16	0.19
Cl	0.00	0.01	0.01
K_2O	0.34	7.42	1.09
CaO	0.69	2.15	0.15
TiO_2	0.89	0.00	0.87
MnO	0.22	0.03	0.03
Fe_2O_3	8.74	2.19	2.85
L.O.I	29.90	1.00	25.49
TOTAL	99.33	98.31	99.77

Table 3.2: Percentage composition of the sodium tetra borate decahydrate crystal

COMPONENTS	% COMPOSITON
B_2O_3	36.51
Na_2O	16.26
H_2O	47.2

3.2.2 Drying and Milling

Four kilogram samples each of the Afari Clay, Mouri Feldspar and Mfensi Clay were dried in an oven at a temperature of 105^oC for twelve hours to remove moisture to enable fine dry milling with a vibratory mill. The clays were then milled to fineness. Each sample was milled separately and collected in different containers. Care was taken to avoid contamination by one another or dust.

The raw clay materials after milling were sieved to all particles passing through 90μm sieve. The sieves were washed and dried after each use to prevent contamination. The sodium tetra-borate deca-hydrate sample was also pulverized and sieved to all passing through a sieve size of 90μm.

3.2.3 Formulation of enamel batches

Four different batches of enamel coatings were formulated based on information on enamels from the literature (*Frieberg, 1977*) by mixing the various raw materials to achieve four different ground coating batches suitable for applying directly onto steel plates. The expected compositions of the coatings of the various batches after firing were calculated from the chemical composition of the raw materials and are listed in Tables 3.3 to 3.6.

3.2.3.1 Mouri feldspar (F), Mfensi clay (M) and Sodium tetraborate (B) batch in the ratio 8:1:5. (FMB: 8:1:5)

This batch was formed by mixing 8 grams of Mouri feldspar, 1 gram of Mfensi clay and 5 grams of the sodium tetra borate by carefully weighing amounts and mixing them to give a mass ratio of 8:1:5 (FMT: 8:1:5). The expected percentage oxide composition of the mixture in the resultant coating after heat treatment were calculated as before and is presented in Table 3.3

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Table 3.3: Percentage composition of the FMB: 8:1:5 batch after heat treatment

Oxide	8g of Mouri Feldspar	1g of Mfensi Clay	5 g borax	Total, g	% Oxide
B_2O_3	0.0000	0.0000	1.8255	1.8255	16.35
Na_2O	0.3688	0.0191	0.8130	1.2009	10.76
MgO	0.0752	0.0109	0.0000	0.0861	0.77
Al_2O_3	1.2920	0.1847	0.0000	1.4767	13.23
SiO_2	5.0664	0.4756	0.0000	5.5420	49.64
P_2O_5	0.0248	0.0007	0.0000	0.0255	0.23
SO_3	0.0128	0.0019	0.0000	0.0147	0.13
Cl	0.0008	0.0001	0.0000	0.0009	0.01
K_2O	0.5936	0.0109	0.0000	0.6045	5.41
CaO	0.1720	0.0015	0.0000	0.1735	1.55
TiO_2	0.0000	0.0087	0.0000	0.0087	0.08
MnO	0.0024	0.0003	0.0000	0.0027	0.02
Fe_2O_3	0.1752	0.0285	0.0000	0.2037	1.82
TOTAL	**7.7840**	**0.7429**	**2.6385**	**11.1654**	**100.00**

3.2.3.2 Mouri feldspar, Mfensi clay and Sodium tetraborate (borax) batch in the ratio 10:1:5 (FMB: 10:1:5)

This coating material was formed from carefully weighing Mouri feldspar (F), Mfensi clay (M) and sodium tetra borate decahydrate(B) in the ratio 10:1:5 and mixing thoroughly. This mixture gives an expected percentage oxide composition in the coating after firing as calculated from the oxide composition of the raw materials and presented in Table 3.4.

Table 3.4: Percentage composition of the FMB: 10:1:5 batch after heat treatment

Oxide	10g of Mouri Feldspar	1g of Mfensi Clay	5 g borax	Total, g	% Oxide
B_2O_3	0.0000	0.0000	1.8255	1.8255	13.92
Na_2O	0.4610	0.0191	0.8130	1.2931	9.86
MgO	0.0940	0.0109	0.0000	0.1049	0.80
Al_2O_3	1.6150	0.1847	0.0000	1.7997	13.73
SiO_2	6.3330	0.4756	0.0000	6.8086	51.93
P_2O_5	0.0310	0.0007	0.0000	0.0317	0.24
SO3	0.0160	0.0019	0.0000	0.0179	0.14
Cl	0.0010	0.0001	0.0000	0.0011	0.01
K_2O	0.7420	0.0109	0.0000	0.7529	5.74
CaO	0.2150	0.0015	0.0000	0.2165	1.65
TiO_2	0.0000	0.0087	0.0000	0.0087	0.07
MnO	0.0030	0.0003	0.0000	0.0033	0.03
Fe_2O_3	0.2190	0.0285	0.0000	0.2475	1.89
TOTAL	**9.7300**	**0.7429**	**2.6385**	**13.1114**	**100.00**

3.2.3.3 Mouri feldspar, Mfensi Clay and Sodium tetra borate batch in the Ratio 12:1:5 (FMB: 12:1:5)

Amounts of the Mouri feldspar, Mfensi clay and sodium tetraborate were weighed and mixed to give a ratio of 12:1:5 in the coating batch. The expected percentage composition of this batch was also calculated.

Table 3.5: Percentage composition of FMB: 12:1:5 batch after heat treatment

Oxide	12g of Mouri Feldspar	1g of Mfensi Clay	5 g borax	Total, g	% Oxide
B_2O_3	0.0000	0.0000	1.8255	1.8255	10.26
Na_2O	0.5532	0.0191	0.8130	1.3853	9.20
MgO	0.1128	0.0109	0.0000	0.1237	0.82
Al_2O_3	1.9380	0.1847	0.0000	2.1227	14.10
SiO_2	7.5996	0.4756	0.0000	8.0752	53.63
P_2O_5	0.0372	0.0007	0.0000	0.0379	0.25
SO3	0.0192	0.0019	0.0000	0.0211	0.14
Cl	0.0012	0.0001	0.0000	0.0013	0.01
K_2O	0.8904	0.0109	0.0000	0.9013	5.99
CaO	0.2580	0.0015	0.0000	0.2595	1.72
TiO_2	0.0000	0.0087	0.0000	0.0087	0.06
MnO	0.0036	0.0003	0.0000	0.0039	0.03
Fe_2O_3	0.2628	0.0285	0.0000	0.2913	1.93
TOTAL	**11.6760**	**0.7429**	**2.6385**	**15.0574**	**100.00**

3.2.3.4 Mouri feldspar, Afari clay and Sodium tetraborate Batch in the ratio 10:1:5 (FAB: 10:1:5)

The same preparation was done using the Afari clay (A) instead of the Mfensi clay. This last batch of material for coating was formed by mixing amount of samples of Mouri feldspar (F), Afari clay (A) and sodium tetraborate in the ratio 10:1:5 by mass. This mixture gave an expected composition in the resulting coating as calculated from the oxide composition of the raw materials.

Table 3.6:Percentage composition of FAB: 10:1:5 after heat treatment

Oxide	10g of Mouri Feldspar	1g of Afari Clay	5 g borax	Total	% Oxide
B_2O_3	0.0000	0.0000	1.8255	1.8255	13.97
Na_2O	0.4610	0.0178	0.8130	1.2918	9.89
MgO	0.0940	0.0270	0.0000	0.1210	0.93
Al_2O_3	1.6150	0.1517	0.0000	1.7667	13.52
SiO_2	6.3330	0.3863	0.0000	6.7193	51.44
P_2O_5	0.0310	0.0009	0.0000	0.0319	0.24
SO3	0.0160	0.0018	0.0000	0.0178	0.14
Cl	0.0010	0.0000	0.0000	0.0010	0.01
K_2O	0.7420	0.0034	0.0000	0.7454	5.71
CaO	0.2150	0.0069	0.0000	0.2219	1.70
TiO_2	0.0000	0.0089	0.0000	0.0089	0.07
MnO	0.0030	0.0022	0.0000	0.0052	0.04
Fe_2O_3	0.2190	0.0874	0.0000	0.3064	2.35
TOTAL	**9.7300**	**0.6943**	**2.6385**	**13.0628**	**100.00**

3.2.4   Preparation of substrate for coating application

Forty pieces of mild steel plates of dimensions 10x5cm were first washed with soap to remove dirt and oils. The samples were pickled in 6% H_2SO_4 dilute acid solution at 60°C for about thirty minutes to remove oxide scale from the surface. This pickling process significantly reduced the time needed to clean the plates mechanically. After the pickling process the plates were immersed in a rinsing water maintained at about 80-90°C and were quickly transferred to an oven maintained at 105°C. This produced a surface that was fairly clean and only traces of oxide were left.

The last traces of oxide were removed by using mechanical abrasion with emery paper followed by rinsing in alcohol and finally drying in the oven at 105°C. The substrates were removed from the furnace after drying and the coatings were immediately applied.

### 3.2.5 Preparation and application of the enamel slip

Samples of each of the four batches of the enamel coating were mixed with 20% by weight of water to form a slip suitable for application. Immediately a steel plate was removed from the oven, a slip of particular composition was applied by pouring a suitable quantity onto the substrate and adjusting the plate in such a way that the slip flowed to cover about 80% of entire surface of the plate. The thickness of the coatings was controlled by ensuring that the same amount of water was added to each batch and also by pouring the same quantity of the slip on each plate. After application of the coating the samples were allowed to dry over night in air and then transferred to the oven and allowed to dry further in the oven for twelve hours at $105^{o}C$. Eighteen samples each of the steel plates were coated with each of the four different enamel slips.

3.2.6 Firing of the enamel coatings

The temperature of firing was selected taking into consideration the objective of the project to prepare low melting temperature enamel. For a guide the binary phase diagrams $Na_2O.SiO_2$, $K_2O.SiO_2$ and the ternary phase diagram of $K_2O.SiO_2.Al_2O_3$ shown in Figures 3.3-3.5 were used. The estimated composition of the fluxing oxides and SiO_2 for the fired products is presented in Table 3.7. In these systems the fusion temperatures are expected to be in the range of $800^{o}C$ -$1000^{o}C$ *[Kingery, Bowen and Ulman, 1976].*

Table 3.7: Expected percentage composition of the fluxing oxides in the fired coatings.

Batch	$Na_2O +K_2O$, %	Fe_2O_3, %	B_2O_3, %	SiO_2, %
FMB 8:1:5	16.16	1.82	16.35	49.64
FMB 10:1:5	15.60	1.89	13.92	51.93
FMB 12:1:5	15.19	1.93	10.26	53.63
FAB 10:1:5	15.6	2.35	13.97	51.44

43
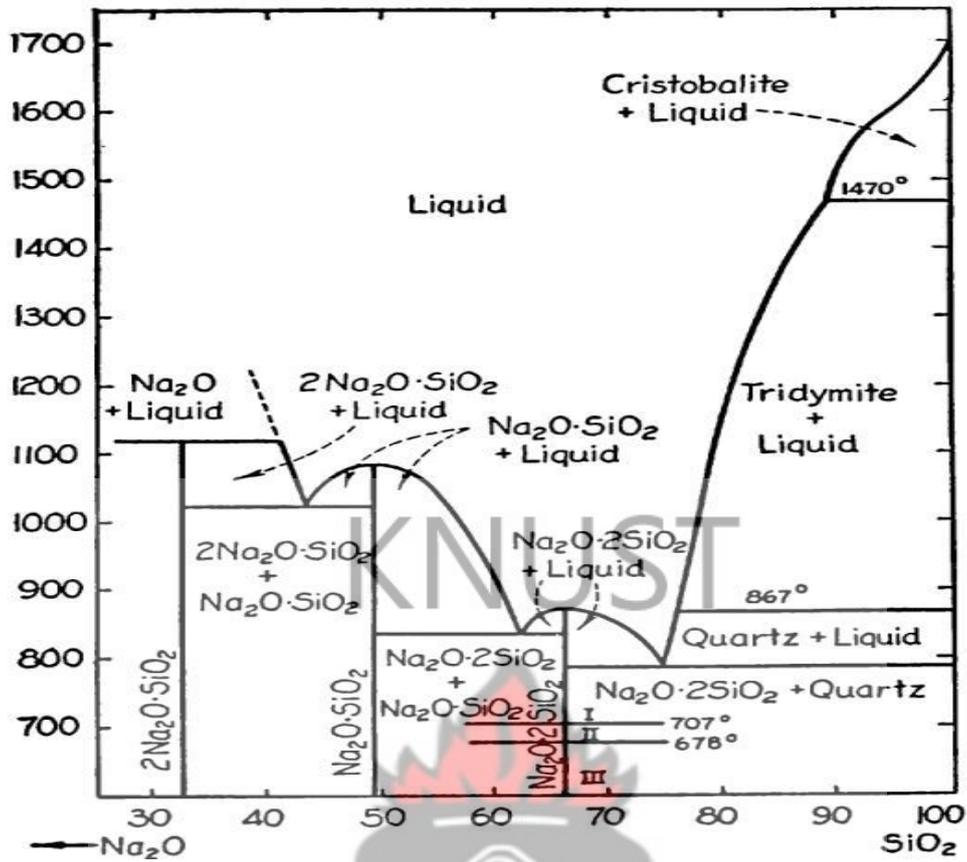
Figure 3.3: The Na₂O.SiO₂ system
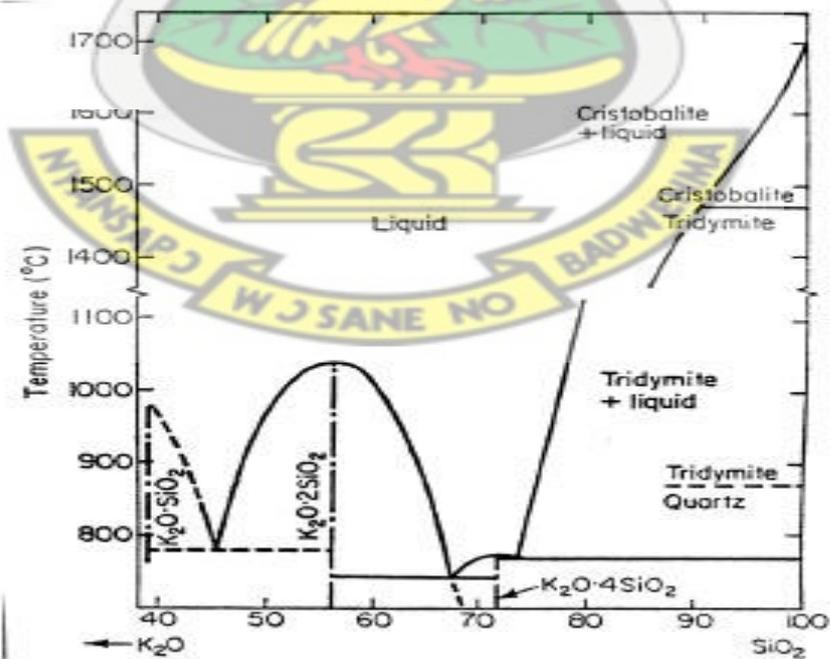
Figure 3.4: The binary K₂O-SiO₂ system
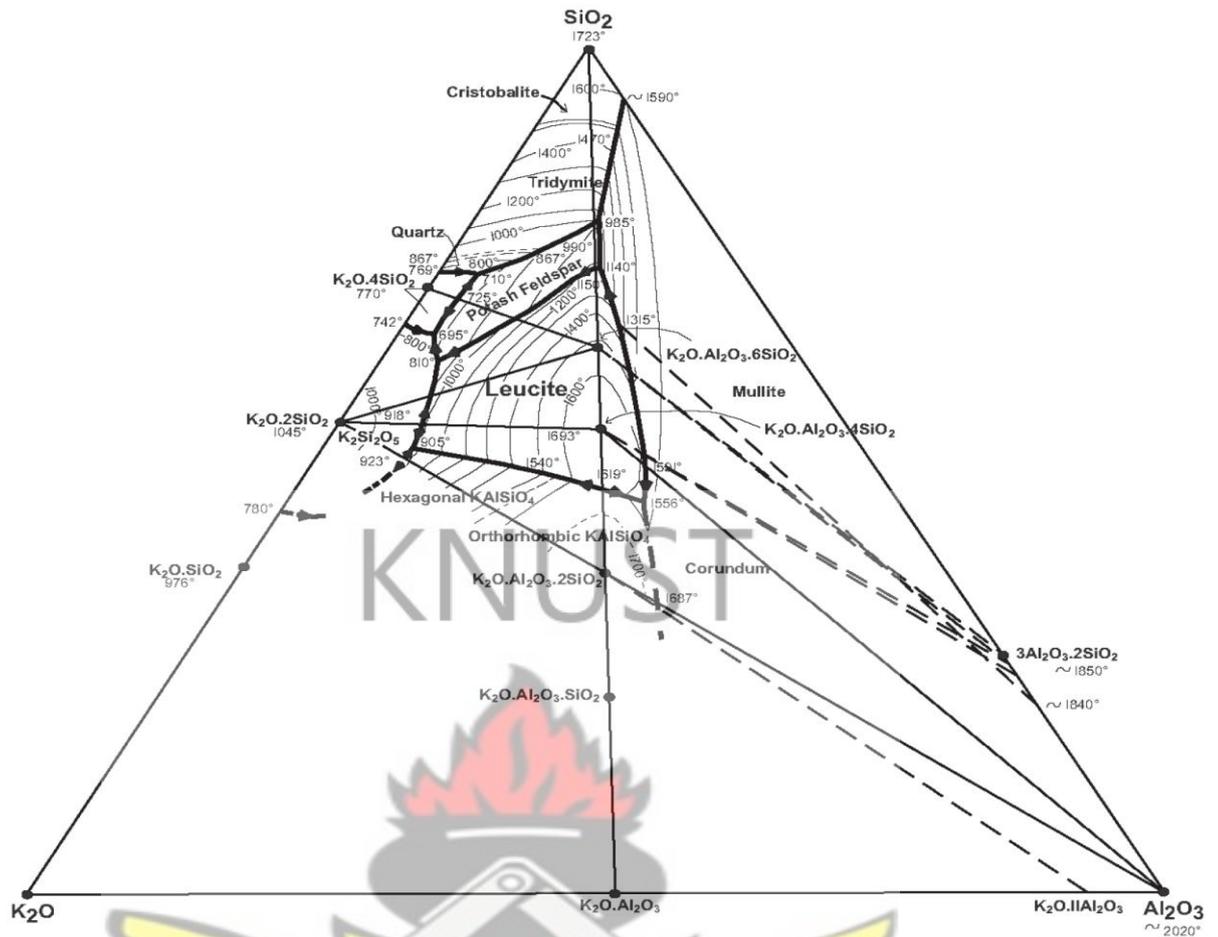
Figure 3.5: The SiO₂.Al₂O₃.K₂O ternary phase diagram.

The enamels, after drying in the oven to remove moisture, were transferred into a furnace where samples from the different batches were fired at 800°C, 850°C and 900°C respectively. Two samples each of the 10:1:5 FMB and 10:1:5 FAB were fired at 800°C and eight samples each of the coatings were initially fired at 850°C and 900°C respectively. Others were later fired at these temperatures. The samples were soaked at the firing temperatures for twenty minutes and allowed to cool in the furnace to room temperature.

This slow cooling was done with the aim of establishing some crystalline phases in the resultant coating so as to achieve some good physical properties of the coatings and also to prevent crazing of the coatings. After cooling to room temperature the samples were

removed from the furnace and taken for inspection and testing. Pictures of the various test pieces were taken and observations made.

3.2.7 Enamel testing

Various physical and some chemical test were performed on the coated steel plates to determine some of the physico-chemical properties of the fused enamel coatings. Because of lack of appropriate material/equipment some of the tests were only qualitative. These include resistance to corrosion in brine and acid resistance test.

3.2.7.1 Thickness of enamel coating

The thickness of the coatings was determined by finding the difference between the uncoated steel plate and the coated plate after firing using Vernier calipers.

3.2.7.2 Adhesion test

Qualitative adhesion test was conducted on the fused enamel batches by striking them with steel rods and observing the amount of coating material that remained on the coating. Equipment was not available to adequately determine the adhesion of the coatings according to standard measurement procedure.

3.2.7.3 Hardness test

Samples of the fired coatings of the enamels were scratched with samples of the minerals on the Mohs scale of hardness to determine their resistance to abrasion on the Mohs scale.

Again a sample each of the enamel coatings was also tested with Brinnel Hardness Tester under a load of 60kg and ball diameter of 1mm to determine their Brinnel Hardness Number. Five locations on each sample were tested and the average of the five results obtained was calculated and recorded as the hardness of that sample.

3.2.7.4 Thermal shock resistance test

The thermal shock resistance of the coatings was determined by soaking the coated steel plates for 30 minutes at 400$^{\text{o}}$C, 500$^{\text{o}}$C and 600$^{\text{o}}$C and dipped in water at room temperature. The soaking and dipping repeated until the 15$^{\text{th}}$ cycle or visible crack was seen. This was done according to test reference *ASTM C 385-58*

3.2.7.5 Resistance to corrosion in brine - Spot test

The surface of each of the four types of enamel coatings was smeared with 0.5ml of 10% by weight of salt solution. The surfaces were observed every day for one month to investigate the extent of attack of the salt solution on the coating and the extent to which the coating can protect the substrate from being attacked by the reactive salt solution. As a control a freshly cleaned surface of uncoated steel was also sprayed with the same amount of the prepared salt solution and was also observed within the period [Test reference *ASTM B117-57]*.

3.2.7.6 Acid resistance test – Spot test

The surface of each of the four types of enamel coatings together with a freshly cleaned uncoated surface were spotted with about 0.5ml of 10% citric acid at room temperature and the surface observed every day for a month. The loss of gloss or reaction products on the surface of the coating was observed for twenty eight days. Test reference *ASTM 283-67*

3.2.7.7 Sample preparation for Microstructural analysis

The fired coating samples selected for microstructural analysis were subject to a series of grinding i.e. rubbing with silicon carbide papers. Rough grinding was done starting with grit abrasive paper of size 1200 to 800. This was followed by fine grinding for each surface with silicon carbide paper size from 600 to 80 in series.

After grinding, the surfaces of the samples were polished with diamond paste of size 6 microns and 3 microns. The polishing was done by applying the paste on the rotating plate with polishing oil as lubricant.

The samples were observed under a microscope of magnification 20x and the structures observed were captured with a digital camera.

4 RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 Thickness and surface finish of the fused coatings

The thickness and surface characteristics of the coatings after treatment at 850^oC and 900^oC are presented in Tables 4.1 and 4.2.

Table 4.1: Thickness of the fused coatings.

Batch	Thickness(mm)	
	850^oC	900^oC
FMB: 8:1:5	0.45	0.42
FMB: 10:1:5	0.45	0.45
FMB: 12:1:5	0.47	0.46
FAB: 10:1:5	0.40	0.50

Table 4.2: Surface finish of the coatings.

Batch	Surface finish of fused coating		
	800^oC	850^oC	900^oC
FMB: 8:1:5	Light grey	Dark grey and glossy	Gray and glossy
FMB: 10:1:5	Light grey	Grey and glossy	Gray and glossy
FMB: 12:1:5	Light grey	Grey and glossy	Gray and glossy
FAB: 10:1:5	Light grey	Grey and glossy	Gray and glossy

4.1.2 Adhesion of the coatings

Qualitative adhesion results obtained are summarized in Table 4.3 below.

Table 4.3: Qualitative adhesion results of the fused coatings.

Batch	Qualitative adhesion result.		
	800°C	850°C	900°C
FMB: 8:1:5	Bad	Good	Good
FMB: 10:1:5	Bad	Good	Good
FMB: 12:1:5	Bad	Good	Good
FAB: 10:1:5	Bad	Good	Good

Bad = Less than 50% of the coatings remaining after striking with steel rod.
Good = More than 75% of coatings remaining after striking with steel rod.

4.1.3 Hardness of the fused enamel coatings

Results of test conducted for Mohs scale and Brinnel hardness for the coatings fired at various temperatures are presented in Tables 4.4 and 4.5.

Table 4.4: Mohs scale Hardness of the fused coatings

Batch	Mohs Scale Hardness		
	800°C	850°C	900°C
FMB: 8:1:5	4-5	7-8	7-8
FMB: 10:1:5	4-5	7-8	7-8
FMB: 12:1:5	4-5	7-8	7-8
FAB: 10:1:5	4-5	7-8	7-8

Table 4.5: Brinnel Hardness of the fused coatings

Batch	Hardness (Brinnel No.)		
	800°C	850°C	900°C
FMB: 8:1:5	Failed	80	76
FMB: 10:1:5	Failed	79	71
FMB: 12:1:5	Failed	74	76
FAB: 10:1:5	Failed	84	91

Failed* = Material failed under the load of the Hardness Tester.

4.1.4 Thermal shock resistance

Results of the thermal shock resistance test conducted on the fused coatings are presented in Tables 4.6 and 4.7

Table 4.6: Thermal Shock resistance of the coatings fired at 850°C at various soaking temperatures.

Batch	No. of cycles to failure		
	400°C	500°C	600°C
FMB: 8:1:5	15 (ND)	10	1
FMB: 10:1:5	15 (ND)	6	2
FMB: 12:1:5	15 (ND)	8	1
FAB: 10:1:5	15 (ND)	10	3

ND = No Damage.

Table 4.7: Thermal shock resistance of the coatings fired at 900°C at various soaking temperatures.

Batch	No. of cycles to failure		
	400°C	500°C	600°C
FMB: 8:1:5	15 (ND)	8	1
FMB: 10:1:5	15 (ND)	6	1
FMB: 12:1:5	15 (ND)	6	1
FAB: 10:1:5	15 (ND)	10	3

ND = No Damage.

4.1.5 Resistance to corrosion in brine

Table 4.8 shows the result of the corrosion resistance spot test conducted on the fused coatings using the aqueous 10% salt solution.

Table 4.8: Results of corrosion resistance spot test with 10% aqueous salt solution.

Batch	Corrosion resistance in 10% salt solution	
	850°C	900°C
FMB: 8:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days
FMB: 10:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days
FMB: 12:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days
FAB: 10:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days

4.1.6 Acid Resistance

Result for acid resistance spot test with 10% nitric acid is presented in Table 4.9 below.

Table 4.9: Results of the acid resistance spot test conducted on the coatings fired at 850°C and 900°C.

Batch	Acid resistance in 10% Nitric acid solution	
	850°C	900°C
FMB: 8:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days
FMB: 10:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days
FMB: 12:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days
FAB: 10:1:5	No Visible reaction after 28 days	No Visible reaction after 28 days

4.1.7 Microstructural analysis

Micrographs of the fused coatings under a microscope of magnification of 20x and captured with a Sony digital camera are presented in figures 4.1-4.12.
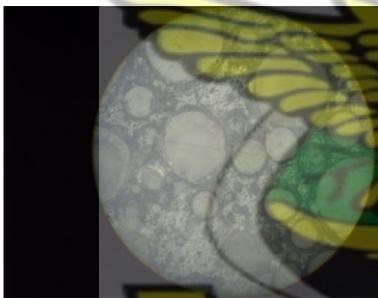


Figure 4.1: Micrograph of FMB 8:1:5 fired at 850°C

Figure 4.2: Micrograph of FMB 10:1:5 fired at 850°C
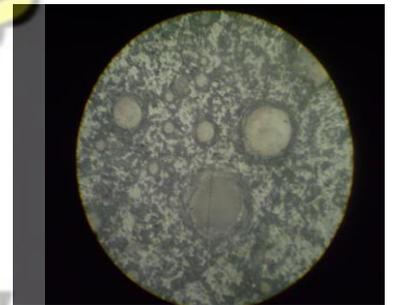
Figure 4.3: Micrograph of FMB 12:1:5 fired at 850 °C

**Figure 4.4: Micrograph of FMB 8:1:5 fired at 900°C**
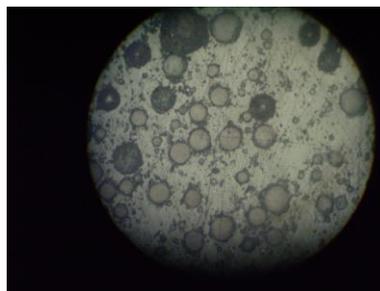
Figure 4.5: Micrograph of FMB 10:1:5 fired at 900°C
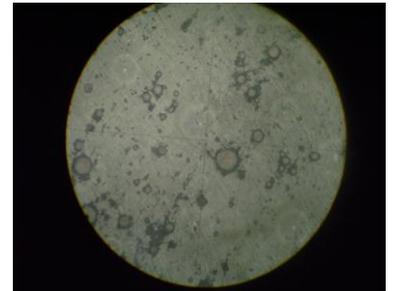
Figure 4.6: Micrograph of FMB 12:1:5 fired at 900°C
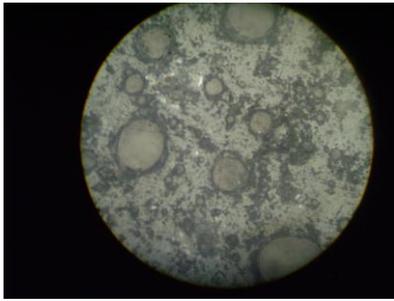
| Figure 4.7: Micrograph of FAB 10:1:5 fired at 850°C | Figure 4.8: Micrograph of FAB 10:1:5 fired at 900°C |
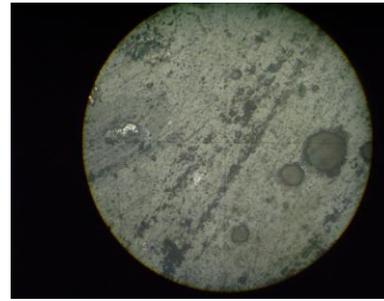
4.2   DISCUSSION

4.2.1   Thickness and surface finish

The thickness of the coatings varied between 0.40mm – 0.55mm. No inference can be made on the thickness because it depended on how much material was put on the plate and the plate dimensions which may differ for each case. Thinner coatings could have been obtained using slips of lower viscosities than the ones used in this project. The enamels fired at 800°C and 850°C had shades of grey colour with those fired at 900°C having a somewhat dark gray colour. Also those formulated with the Afari clay hard a slightly reddish-dark colour than those prepared with the Mfensi clay. The reddish colour may be attributed to the high content of iron-oxide in the Afari clay.

The enamel coatings fired at 800°C were found to have a whitish-grey colour. It was observed that the enamels did not fuse completely and therefore the surf aces were not smooth. The surface of the enamels fired at 800°C significantly lack gloss. Additionally, the coatings fired at 800°C had some of the coatings at the edges chipping off on cooling to room temperature and this can also be attributed to insufficient melting and thus inadequate wetting of the surface and adhesion by the coating at this temperature. Figures 4.9-4.10 present pictures of the coatings treated at 800°C, whilst those treated at 850°C and 900°C are shown in Figure 4.11- 4.18.

Figure 4.9: A picture of test piece prepared with FMB 10:1:5 fired at 800°C
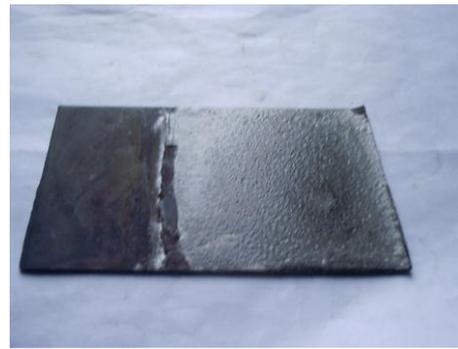
Figure 4.10 A picture of test piece prepared with FAB 10:1:5 fired at 800°C

The enamels fired at 850°C gave a very good surface in terms of texture, gloss and cleanability. The surfaces were grey of different shades and were very smooth with minutely gritty surfaces. This is because the enamels melted sufficiently at this temperature and therefore enough glassy phases were obtained.

Figure 4.11 A picture of test piece prepared with FMB 8:1:5 fired at 850°C

Figure 4.12: A picture of test piece prepared with FMB 10:1:5 fired at 850°C

Figure 4.13: A picture of test piece prepared with FMB 12:1:5 fired at 850°C

Figure 4.14: A picture of a test piece prepared with FAB 10:1:5 fired at 850°C

The enamels fired at 900°C gave the same results in terms of appearance, texture, gloss and cleanability as those fired at 850°C in terms of appearance. However their colours were slightly darker than those at 850°C. There were small defects such as pin-holes on the surfaces and this may be as a result of the entrapped gases in the enamels that escaped during firing at high temperatures.

Figure 4.15: A picture of test piece prepared with FMB 8:1:5 fired at 900°C

Figure 4.16: A picture of test piece prepared with FMB 10:1:5 fired at 900° C

Figure 4.17: A picture of test piece prepared with FMB 12:1:5 fired at 900°C

Figure 4.18: A picture of test piece prepared with the FAB 10:1:5 fired at 900°C

4.2.2 Adhesion

Quantitative adhesion values could not be obtained in order to compare with standards as such equipment for testing coating adhesion was not available. Qualitative adhesion testing was done on the coatings by hitting the fired coatings with small steel rod. The coatings fired at 850°C and 900°C remained significantly intact after striking with the rod by the hand whereas those fired at 800°C had most of the coatings scraping off the plate.

The coatings fired at 800°C did not seem to have good adhesion as some portions of the coatings chipped off after a while. This may be due to incomplete melting as enough liquid phases were not achieved to ensure proper wetting of the coating on the steel substrate to ensure good adhesion.

The enamels fired at 850°C and 900°C showed very good adhesion as the coating adhered to the substrate very well. This shows that the enamel coating melted well at these temperatures and the liquid phases attained at these temperatures were enough to wet the substrate well. Also, the slow cooling ensured less internal stresses in the glass and that the thermal expansion of the coating and substrate were close. Again the increase in adhesion of the coatings could also be attributed to the higher content of the

borax in the batches as it was the main source of boric oxide which is known to promote adhesion in enamels. The borax content of the batches was between 27.8% for the FMB 12:1:5 and 35.7% for the FMB 8:1:5 which is consistent with the range stated in the literature *[Harper, 2001 and Frieburg 1977]*.

4.2.3   Hardness

The values of the hardness of the enamels fired at 800^oC on the Mohs' scale were between 4 and 5 that is between the minerals Fluorite and Apatite. These were within the range specified by the Porcelain Enamel Institute (PEI, 2006) which is 3.5-6. Results on the Brinnel Scale of hardness for the 800^oC could not be obtained as the coatings failed during loading on the Brinnel Hardness machine.
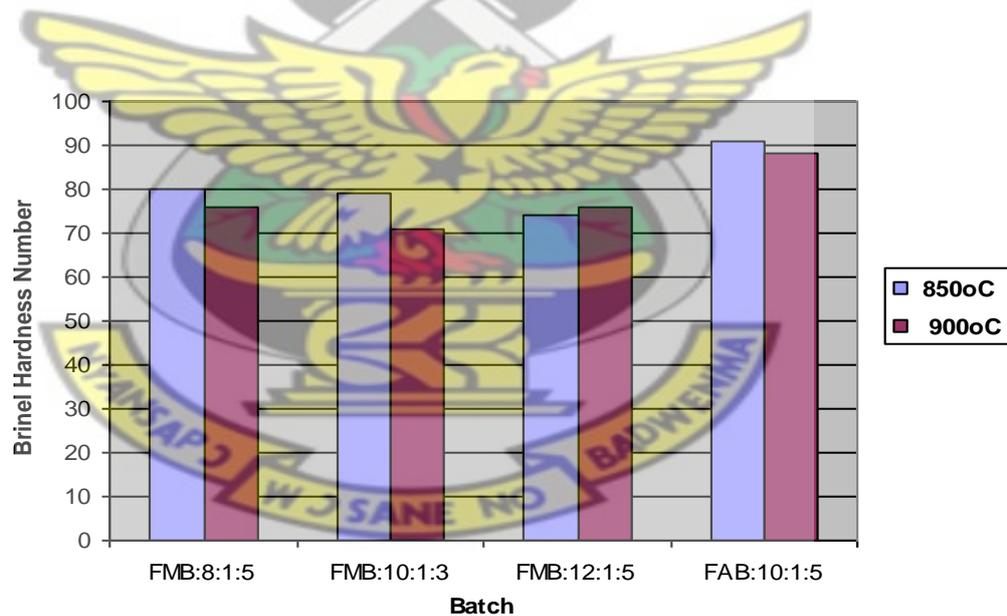

Figure 4.19: Brinnel Hardness No of the fused coatings

The hardness according to the Mohs scale of the enamels fired at 850^oC and 900^oC were between 7 and 8 which is higher than the range of 4 and 6.5 stated by the PEI. This shows that the enamels fired at 850^oC and 950^oC were harder than those fired at 800^oC.

The results show that the Mohs scale hardness practically remained constant irrespective of the ratio of materials used for the coatings fired at 850°C and 900°C. This may be due to the fact that the scale is not continuous and hence the difference in hardness within the various batches could not be manifested.

Values on the Brinnel Scale as presented in Fig.4.23 range between 71 and 91. The enamels prepared with the Afari clay (FAB) had higher BHN values than those of the Mfensi clay. This shows that these coatings are very hard and therefore can be applied to substrates for the use in areas where abrasion resistance is desired. The reason for the higher hardness could be due to the high content of the silica and the presence of iron oxide in the fired coating. Iron is known to reduce the melting point of silica and therefore gives a good flux at low temperatures. Increase in borax content did not seem to have any significant effect on the BHN and the best firing temperature seems to be 850°C. The enamels fired at 850°C seemed to have a slightly higher BHN values than those fired at 900°C.

4.2.4 Thermal shock resistance

Table 4.5 and 4.6 illustrated in Figure 4.20 show results of test conducted for the thermal shock resistance, thus the number of cycles of heating and soaking in water required for failure in adhesion, for the coatings fired at 850°C.Values for the coatings fired at 850°C and 900°C were almost the same (compare Tables 4.5 and 4.6) for each batch. The coatings were able to withstand fifteen cycles of heating and quenching at 400°C without damage. Values at 500°C range from six cycles to ten cycles. The coatings could not withstand rapid cooling from 600°C as they failed from the first quenching to maximum of three cycles. These values are consistent with those mentioned in the literature *[Geiger, PEI, 2006]*.
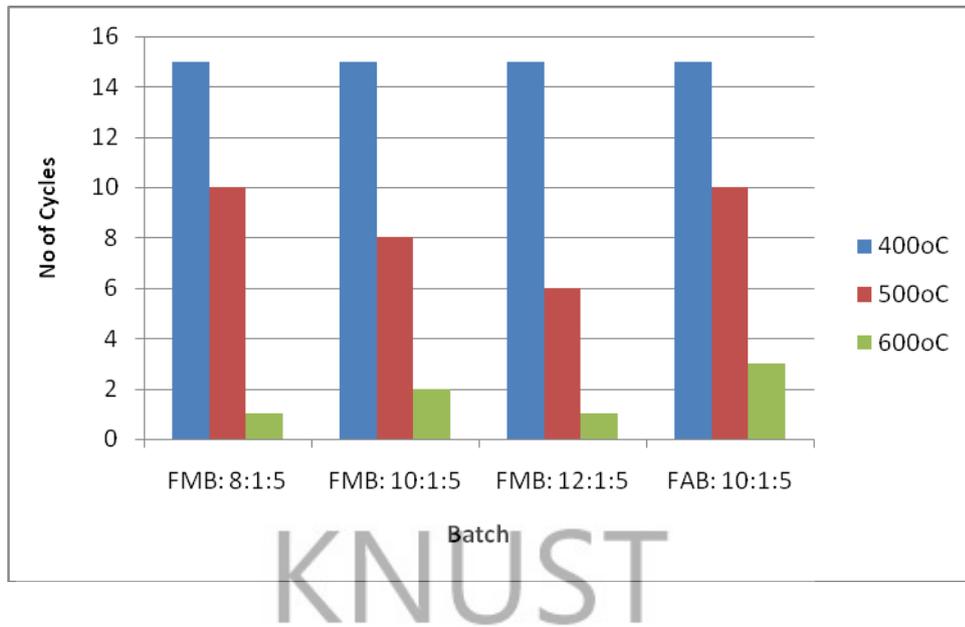
Figure 4.20: Thermal Shock Resistance of the enamels fired at 850°C

In the case of the Mfensi Clay, thermal shock resistance decreased as the temperature of soaking increased. Also thermal shock resistance at 500°C decreased as the amount of feldspar in the mixture was increased from 57.1% to 66.67% and the borax content decreased from 35.7% to 27.71%. It follows from these results that these coatings can only be used for application at temperatures lower than 400°C.

It seems that when Afari clay was used the shock resistance increased for samples treated at 850°C and 900°C. This can be seen by comparing FMB: 10:1:5 and FAB: 10:1:5 soaked at 500°C and 600°C from Figure 4.24. The number of cycles increased from 8 to 10 at 500°C and from 1 to 3 at 600°C when the Mfensi clay was replaced with Afari clay. This may be due to the higher content of iron oxide in the Afari clay as a small increase in the amount of iron oxide in ground coat enamels is known to increase adhesion of the coating to the substrate.

Figures 4.21 and 4.22 present a pictorial illustration of some of the results of the thermal shock resistance test.
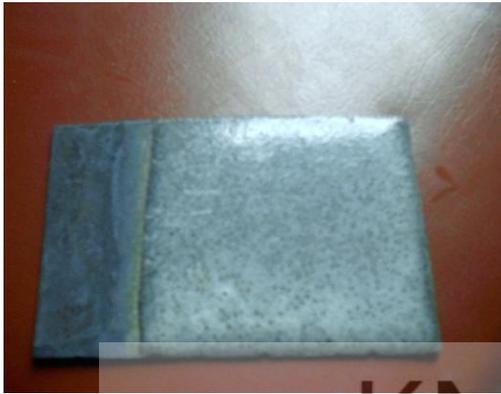
Figure 4.21: A picture of test piece prepared with FMB 10:1:5 (fired at 850°C) after 15 cycles of heating and quenching at 400°C

Figure 4.22: A picture of test piece prepared with the FAB 10:1:5(fired at 850°C) after 3 cycles of heating and quenching at 600°C

4.2.5   Acid resistance

Qualitative observations of the test carried out on acid resistance are presented in Tables 4.1-4.8. No corrosion products were observed on the surface of the enamels treated with 10% nitric acid for as long as twenty-eight days. Also the surfaces had their original clean gloss before they were eventually cleaned of the solution. These results indicate that surfaces coated this way could be used in acid corrosive environments similar to those tested.

4.2.6   Salt spraying resistance

No loss of gloss or colour was observed in the coatings treated with 10% salt solution for as long as 28 days. The drops of salt solution remained on the coated surface without causing any damage to the coating until it was cleaned. And the surface retained its original colour and gloss.   It was, however, observed that when an uncoated surface was also exposed to the same salt solution the surface colour changed into rust in a matter of minutes (Figures 4.23 and 4.24).

Figure 4.23: FAB 10:1:5 coated surface two weeks after being treated with 10% salt solution


Figure 4.24: An uncoated surface two weeks after being treated with 10% salt solution

4.2.7   Qualitative Microstructural Analysis

Equipment was not available for the quantitative and qualitative analysis for the phases present in the enamels consequently, only qualitative observations were made of the micrographs.

The micrographs observed under microscope at a magnification of 20x and captured with the digital camera are shown in Figures 4.1 to 4.8. The micrographs of the fused enamels show a structure of a vitreous matrix in which is dispersed secondary phases which resembles a bubble-like structure. It was observed that this secondary phase in the structure decreased as the borax content decreased and feldspar content increased. This can be seen by comparing Figures 4.1 to 4.3 for FMT 8:1:5, 10:1:5 and 12:1:5. This may be due to the release of water of crystallization in the borax which left bubbles in the resulting coating.

$$Na_2B_4O_7.10H_2O \rightarrow Na_2B_4O_7 + 10H_2O \xrightarrow{750^0C} Na_2O + 2B_2O_3 + 10\,H_2O$$
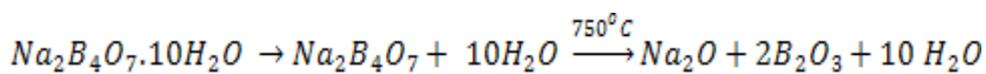
Also this secondary phase in the coatings appeared to decrease as the temperature increased from 850°C to 900°C for each batch of coating and this too can be seen by comparing Figures 4.1-4.3 and 4.3-4.6. Finally it was observed that the amount of the bubble-like structure was less in the coating prepared with the Afari clay than that prepared with the Mfensi clay. This can be seen by comparing Figures 4.2 and 4.7 as well as 4.5 and 4.8. This low content of the secondary phase in the Afari clay could account partly for the superior physical properties of this batch of coating as compared to the same ratio prepared with the Mfensi clay.

CHAPTER FIVE

5   CONCLUSION AND RECOMMENDATION

5.1   CONCLUSION

Four different enamel coatings were formulated from local clays using the Mfensi and Afari clays, feldspar from Mouri and borax. The coatings were successfully applied as a slip onto already prepared steel surfaces. The coated plates were then dried and fired at temperatures of 800°C, 850°C, and 900°C. The coatings after fusion were tested for some physical properties and protection against corrosion. Micrographs of the samples were also obtained under a microscope and were qualitatively analyzed.

Well matured coatings were obtained at the temperatures of 850°C and 900°C. Those fired at 800°C did not vitrify completely and thus had poor physical properties. Those fired at 850°C and 900°C had very good physical properties in terms of adhesion, thermal shock and hardness. The coatings fired at these temperatures showed good corrosion resistant properties by remaining unreacted after being smeared with 10% nitric acid and brine for as long as twenty eight days that they were tested. These results show that the coatings prepared can be used to protect steel substrates used in atmospheric and moist environments at temperatures of 400°C or less and also in areas close to the sea.

The hardness and thermal shock resistance of the coatings appeared to increase with increased borax content but this was offset by a corresponding increase in the bubble-like structure within the coating. It was evident that the coating prepared from the Afari clay was better in terms of hardness and thermal shock resistance than the one prepared

with the Mfensi clay. Also the coatings vitrified better and had less bubble structures at the temperature of $900^{\circ}C$ than at $850^{\circ}C$ as revealed by their microstructures

The results show that it is possible to formulate low fusion enamel coatings using the Mfensi and Afari clays, Mouri feldspar and borax that could be used for corrosion control on steel substrates.

5.2   RECOMMENDATION

I recommend the use of the coatings formulated in this project to protect steel for corrosion control in normal atmospheric condition as well as in environments close to the sea. In order to make the application of these coatings convenient to already installed equipments and structures I recommend the use of a thermal spray gun that can take the coating mixtures and deliver it to the substrate at the maturing temperature for melting and adhering to the substrate. This may involve fritting the batches before they are suspended with clays and used as a feed for the gun or they can be fed to the spray gun directly.

It may be possible to achieve similar or even better results from other clay and feldspar deposits in the country and I therefore recommend more research to uncover such information.

The use of local materials as opacifiers may also be employed in the coating mixtures to give them aesthetic appeal. Further work on microstructural analysis and heat treatment operations on the coatings may reveal more useful information.

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