

UNIT 1

Branch : Ceramics Engineering

Semester = Fourth

Subject : Ceramics Coating Technology

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Syllabus Covered: Introduction of Glaze: Definition of Glaze, Similarities & Dissimilarities between glaze and glasses. Classification of glazes, Definition and explanation of Raw glaze, Fritted glaze, Lead glaze, Leadless glaze, Vapour glaze, Opaque glaze, Matt glaze & Crystalline glaze.

Learning Objectives: After going through this unit student should be able to

- 1) Define glaze
- 2) Differentiate between glaze and glass
- 3) Classify different types of glaze
- 4) Explain different types of glazes.
- 5) Understand different types of coating
- 6) Explain purpose of coating
- 7) Define coating

UNIT -1 INTRODUCTION OF GLAZE

1.1 Coatings – A **coating** is a covering that is applied to the surface of an object. The surface is usually known as the **substrate**.

The coating may be an all-over coating, completely covering the surface (substrate) or it may only cover some parts of the surface (substrate).

1.1.1 Purpose

The purpose of applying the coating may be

Decorative : Paints and lacuers (e.g. wooden coating) are coatings are mostly used for protecting the substrate and decoration. Some coatings (by artists paints) are only for decoration, and the paint on large industrial pipes is for the function of preventing corrosion.

Functional Functional coatings may be applied to change the surface properties of the substrate, such as adhesion, wettability, corrosion resistance or wear resistance.

Both (Decorative and Functional) Some times coatings are applied for both purposes. For example glazes are applied on ceramics ware for decorations and to reduce permeability (porosity). An example of all of these types of coating is a product label on many drinks bottles- one side has an all-over functional coating (the adhesive) and the other side has one or more decorative coatings in an appropriate pattern (the printing) to form the words and images

1.2 Types of coatings

Oxide coating (ceramics coatings) , metal coating, rubber ,polymer, paints.

1.2.1 Ceramic coatings : are thin layers applied on ceramic wares, metal and glass. Ceramic coatings are also called oxide coating.

Oxide coatings are applied to improve

1. Chemical inertness
- 2 High temp. stability
3. Hardness
4. Mechanical strength
5. Lustre
- 6 Appearance

1.2.2 Types ceramics (oxide) coatings

Glaze - Glaze are thin glassy layers fused on surface of ceramic wares
e.g lead glaze , leadless glaze , Bristol glaze, matt glaze

Porcelain Enamels : are thin glassy protective coatings applied on metal surface. These are also called vitreous enamels. These are made by fusing powdered glass to a surface by firing at low temp (750-850 C°)

Glass enamels -These are lower melting decorative coatings on glass wares.

Engobe: It is surface coatings (not completely glass) given on ceramic ware in between body and glaze. This is applied to so that glaze is properly sticked to ceramic ware.

1.3 Definition of Glaze - Glazes are thin, homogeneous silicate mixture fused on the surface of ceramic wares. Or

Glazes are thin layer of glass fused on the surface of the ceramic body.

1.3.1 Purpose of Glazing :- The glazes are applied to ceramic bodies

1. To make them impervious to gases and water
2. To make them mechanically strong
3. To increase scratching resistance
4. To make the wares more chemically inert.
5. To make more pleasing to eyes ant to touch.

1.3.2 Properties / Characteristics of glazes:

1. Glazes are lustrous and highly reflecting, except matt glaze.
2. Glaze can be coloured or colourless.
3. Glaze can be translucent, transparent or opaque.
4. Glaze can be decorated over glaze, under glaze or in glaze.

1.4 Similarities between Glaze and Glass

1. Both glaze and glass can be transparent or translucent.
2. Glazes and glasses have same physical and chemical nature.
3. Both follow all principles of glassy state.
4. Both follow glass forming rules.
5. Both have compositions of oxides which are divided as glass network formers [SiO_2 , B_2O_3 , P_2O_5], network modifiers [Na_2O , K_2O , CaO , MgO , PbO] and intermediate glass formers like [Al_2O_3 , PbO , ZnO , ZrO_2]
6. For making glazes of low maturing temperature same considerations are used as that for lowering the softening point of glasses.
 - e.g i . introduction of B_2O_3 , [up to 12%] in place of SiO_2 .
 - ii. Partial replacing Si^{4+} by Al^{3+}
 - iii. Introducing of PbO in greater proportion.

1.5 Dissimilarities between Glazes and Glass

GLAZE	GLASS
1. Glaze is a thin coating on ceramic ware	1. Glass is ware itself
2. Glaze have Al_2O_3 in large quantity	2. Glass have Al_2O_3 in minor (less) quantity
3. The glaze are applied by dipping , Pouring, brushing, spraying etc	3. Glasses are made by blowing, rolling, drawing , press & blow etc.
4. Glazes can be transparent, translucent or opaque	4. Glasses are usually transparent.
5. Glazes are applied as protective covering on ceramic wares	5. Glasses are used as wares for domestic, laboratories etc
6. Examples: Transparent glaze, opaque glaze, coloured glaze etc	6. Examples: Bowls, glass, dinner set, tea set, conical flask, beaker etc.

1.6 Classification of Glazes

Glaze can be classified in various ways. The common methods of classification are

1.6.1 Based on fusibility:- Glazes can be classified as

- i) Easily fusible
- ii) Fusible with difficulty

Also based on fusibility these can be classified according to the increasing cone fusion temperature.

1.6.2 Based on main constituent :- Glazes can be classified as

- (1) Raw lead glaze
- (2) Leadless glaze
- (3) Tin enamel.

1.6.3 Based on application on ware type :- Glazes can be classified as porcelain Glaze , stoneware glaze, majolica glaze .

1.6.4 Based on place of origin :- Albany slip glaze, Bristol glaze

1.6.5 Based on use of Raw or fritted constituent :- Raw glaze or fritted glaze .

1.7 Raw Glaze :- The glaze which is made by using raw constituents are known raw glaze. A raw glaze is made from natural and synthetic compounds such as quartz, and clays.

Raw glazes are

- 1) Easy to make as compared to fritted glaze
- 2) Raw glaze cause more problems during firing as compared to fritted glaze.
- 3) These can assume (made) lesser variety of properties such as colour and texture as compared to fritted glaze.
- 4) Need high firing temp (glost) to mature.

Types of Raw Glaze

- (1) Porcelain Glaze (2) Bristol Glaze (3) Raw lead (4) crystalline glaze
(5) Semi conducting glaze

1.8 Fritted Glaze:- These glazes are made from previously melted glass. These glazes are made by melting natural and synthetic raw materials such as clay, quartz and feldspar. The glass obtained after melting is known as frit. The fritted glaze is made by mixing certain frit with addition of where necessary, raw materials, pigments, salts etc. The composition is then milled in ball mill and fritted glaze slip is obtained.

The fritted glazes are

- 6.1 Leadless Borsilicate glazes 6.2 Lead Borosilicate glaze

1.9 Types Of Glazes

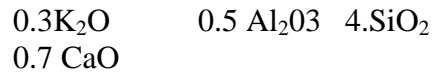
1.9.1 Porcelain Glaze : These are used on porcelain. These glazes are applied on raw piece for single firing. Due to dunting problem, these cannot be re-fired. These glazes are calcareous alumino- silicate (with some alkali). These are most refractory (high maturing temp) among all glazes. The minimum maturing temperature is about 1250°C . The raw materials used in these glazes are alkaline earth (calcium and magnesium carbonates), clay, quartz and feldspar . All materials are insoluble , so these can be used as such .

The glazes formed are

- 1) Insoluble in water acids and alkalis.
- 2) Resist the action of all acids (Except HF, H_2SO_4 , Phosphoric acid)
- 3) These are hard (scratch resistant) and mechanically strong
- 4) Increase the tensile strength of body
- 5) If properly applied they increase the tensile strength of ware.
- 6) They interact better with body because of same composition as that of body.
- 7) Because of low volatilisations these can be fired in kilns without any protection like muffles or saggars

Uses:- These are used in chemical and cooking wares, electrical porcelain insulators.

Formula:- The standard formula for porcelain glaze is



To give colours following oxides are used

Blue : Co_3O_4

Green : Cr_2O_3

Brown MnO_2

1.9.2 Raw lead Glazes: These glazes are an important type of ceramic glaze which contain lead oxide (PbO) as a major constituent. These glazes are brilliant, cheap and suited to a wide variety of wares fired at widely different temperatures.

The use of raw lead glazes is limited because

- 1) These are less resistant to abrasion and weathering than other glazes.
- 2) These can be easily attacked by weak acids present in fruit juice and beverages. This creates health hazards to users of glazed wares.
- 3) The handling of lead compounds and raw glaze batch mix can create health problems for workers.
- 4) These are more prone to crazing defects.

These glazes can be applied on bodies in a leather hard condition, bone dry and biscuit condition. These are mostly used for art wares, wall tiles and sometimes on sanitary ware. The basic formula of this glaze is $1 \text{PbO} \cdot 0.1 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and mature at about 650°C .

Raw materials :- used are white lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), Litharge (PbO), red lead (Pb_3O_4) and artificial lead silicates

Firing:- The lead compounds have high vapour pressure, so wares coated with raw lead glaze must be enclosed in suitable containers during firing to prevent volatilisation and hence loss of gloss.

1.9.3 Leadless Glaze :- Leadless glaze was developed because of the problems associated with lead glaze. These problems are

- i) lead poisoning
- (ii) mechanical softness
- iii) Tendency to dull in sulphurous atmosphere conditions
- iv) Sensitive to reducing gases and yellowish tinge

Due to the above problems, a variety of leadless earthenware glazes were developed. In these glazes, low melting is achieved by using a combination of alkalis, alkaline earth, Magnesia and zinc oxide and boric oxide.

Parmelee and Lyon give the following limits for frits containing Na_2O , CaO , B_2O_3 , Al_2O_3 and SiO_2

Na_2O	0.3 to 0.7 equivalents.
CaO	0.7 to 0.3 equivalents.
B_2O_3	not more than 0.5 equivalents.
Al_2O_3	upto 0.1 equivalents
SiO_2	upto 3.0 equivalents

1.9.4 Vapour Glaze :- Salt glazing is one type of vapour glaze. It is different from slip glazing. In this raw or biscuit ware is not coated with glaze slip. The salt glaze is formed in the kiln by salt vapours, water and other substances on the hot fired body.

Uses :- Salt glazing is used in stone ware sewer pipes, chemical stoneware, glazed bricks tiles artware

Salt glazing depends on 1) composition of body 2) firing schedule 3) Composition of salting mixture.

Composition of body :- The sodium ions from glazing vapours react mainly with silica in the body surface. For good salt glazing, SiO_2 : Al_2O_3 ratio should be 4.6-12.5.

The clays on which good salt glaze is not achieved due to silica deficiency, finely ground sand or sandstone is added.

Generally white burning (iron free) clays may be salt glazed. But iron present in clays helps information of salt glaze in two ways

- (a) By reacting with salt vapours during glaze formation
- (b) By acting as flux to vitrify body which can then better take the glaze.

Clays with 0-2% iron oxide = white to tan glaze.

3.5 - 4.75 % iron oxide = brown

4.75-8.2% iron oxide = mahogany

Firing schedule :- The vaporisation of salt and its interaction with steam takes place at 1160°C . Normal salt glazing cannot be done under 1160°C . But in bodies which mature early and have high alkali and iron oxide content can be salt glaze at 1050°

Other low temp. bodies can be salt glazed by mixing borax with salt.

The salting mixture: During salt glazing sodium chloride is vaporised and react with hot steam in presence of silica. This give hydrogen chloride and sodium oxide. Water is added with sodium chloride. The sodium oxide immediately reacts with silica to form sodium silicate.

Other vapour glazing :- It include zinc salts.

1.9.5 Opaque Glaze : A vitreous (glassy) phase can be made opaque if path of light is suitably broken up and made to diffuse. This is brought about by fine particles index .

There are three ways by which we dispersed phases are produced

- 1) Crystal formed by crystallisation of the melt.
- 2) Introduction of crystals insoluble In the melt into the batch
- 3) Two(vitreous) phase formed by immiscibility.

The first method is not suitable commercially. The second method is most widely used and is the cause of opacity obtained by ceric and magnesium oxide. In the case of fluorides the mill addition may be cryolite ($(\text{Na}_3 \text{AlF}_6)$, Sodium silico fluosper.

If the reaction is complete than final opacifying agent will be thing crystals of alkali or alkaline earth fluorides and silicate glasses, which although are miscible at high temp, but separate on cooling. The phosphate forms ting particles of dispense phase and may crystallise.

1.9.6 Crystalline Glazes

Crystalline glazes are used for artistic purposes. In these glazes crystals(microscopic or macroscopic) grow within the body or in the glazes. These can be of different colours. By careful work these can be made to look beautiful.

Crystals particles are those materials which remain undissolved in glaze.

Crystalline glazes are of two types

Micro Crystalline Glaze In these glazes crystals are big enough to be visible by naked eye. These crystals are large, separate and suspended below the surface of glaze. Sometimes the crystals may cover the surface of glaze.

Micro crystalline In these glazes crystals are not visible by naked eye.

In these glazes iron oxide and chromium oxide is commonly used. Apart from this magnesia (MgO) and Zinc oxide (ZnO) are also used to produce variety of crystals. Zinc oxide give large crystals in certain areas. Titania produce small and evenly distributed crystals.

These glazes have low maturing temperature which ranges from 1200 to 1300 deg C.

1.9.7 Matt Glaze The surface of matt glaze is lustreless. It has silky appearance due to refraction and diffusion of light by micro crystalline. The matt glaze can be opaque or translucent. In this glaze crystals are distributed throughout the body of glaze. For these micro crystals excess alumina is required. These micro crystals can be of anorthite ($\text{CaOAl}_2\text{O}_3\text{SiO}_2$), mullite ($3\text{Al}_2\text{O}_3\text{SiO}_2$), wollastonite (CaO SiO_2), tridymite (SiO_2) etc.

The crystals in matt glaze break up the light rays making glaze opaque or translucent. The crystals will be fine if lime is present in glaze. In this case crystals be formed in matt glaze if lime is present as anorthite ($\text{CaO Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and wollastonite (CaO SiO_2).

Formation of matt glaze depends upon rate of cooling after firing. Rapid cooling produces glossy glaze. Slow cooling produce dull glaze.

Higher the silica content in the glaze slower must be the cooling for crystallisation to take place.

Certain matt glazes are more resistant to crazing than glossy glaze. The ware has good mechanical properties.

Composition

Raw Materials	Percentage
Chalk	8.8 %
BaSO ₄	27.5%
Feldspar	49.1%
China Clay	8.3%
Quartz	6.3%

UNIT-2

RAW MATERIALS

Raw Materials:

- Clay: china clay, bentonite, ball clay,
- Silica: quartz, flint, sand stone, silica sand,
- Fluxes: Soda feldspar, Potash feldspar, nepheline syanite, cullet,
- Amphoteric Oxide: Alumina,
- Alkaline materials: Sodium Carbonate, Sodium Chloride, Sodium Nitride, Sodium Hydroxide, Sodium Silicate fluoride Potassium Carbonate, red lead,
- Alkaline earth materials: Barium Carbonate, Calcium Carbonate, Borax, Boric oxide,
- Opacifiers: Tin oxide, Zirconia, Zircon, Antimony oxide, Calcium fluoride

Explain the role of each raw material in glaze.

2.1 Clay China clay, Bentonite, Ball clay

2.1.1 Clay These are hydrated alumino-silicate minerals having fine particle size usually below 2 micron. Clay minerals have layered structure and are formed by weathering of igneous rocks.

The physical and chemical properties of clays depend on composition, structure of clay mineral, particle size and shape.

2.2 Clay Minerals

2.2.1 Kaolinite Group

KAOLINITE (Al₂O₃.2SiO₂.2H₂O) It crystallises as hexagonal plates. It has

	medium plasticity.
HALLOSITE ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$)	It has high plasticity due to finer size and have two layered structure .
2.2.2 Montmorillonite Group	It has size less than 1 (micron). It has high plasticity, dispersion and swelling property.
2.2.3 Micaceous Group (Illite)	This mineral have Al, Mg ,K ,Si ,O and H.

2.3 Types Of Clays

2.3.1 China Clay It is formed by weathering of granite. It consists of kaolin mineral. Two types of kaolin are recognised namely.

Residual Or Primary Kaolin

These clays are found near the parent rock bed.

Sedimentary Or Secondary Kaolin

These clays are found distance away from parent rock. It has fine size. China clay is white burning clay due to low impurities. It has less plasticity.

2.3.2 Ball Clay It is secondary clay. It is highly plastic kaolinitic clay. It has very fine size. It has softening point of (1675°C) lower than pure kaolin mineral.

The colour of ball clay is dark in unfired state because of organic impurities. On burning its colour is white or cream. It has large proportion of kaolinite and have variety of impurities.

Uses It is mainly used in white ware industry to improve plasticity workability and green strength of finished products.

2.3.3 Bentonite This clay is derived from volcanic ash. It is widely distributed and occurs in beds.

The main clay mineral is montmorillonite, due to this it easily takes water and swells 4-5 times its dry volume. It is very plastic, has low fusion point and gives coloured product.

Uses It is mainly used to increase plasticity. It is around 10 times more plastic than ball clay. It is therefore used for making moulds of sands.

Role of clay in glazes

- Keeps the glaze in suspension
- Act as adhesion agent of unfired glaze slip to body.

- It controls shrinkage of unfired glaze coating on body.
- It controls shrinkage of unfired glaze coating on body.
- It give Al_2O_3 and silica to glaze. Amount of clay added depends on absorption or porosity of green or biscuit body.

2.4 Silica : Quartz, Flint, Sandstone, Silica Sand.

Silica After oxygen, silicon is most abundant element in earth's crust. It occurs as silicon dioxide (SiO_2) in free state or with metallic oxides as silicates.

Free silica is purest of naturally occurring minerals. Silica crystallize into different forms at different temperature .The most stable form is -quartz at room temp.



2.4.1 Raw Materials Of Silica

Quartz Quartz crystals occur in primary rocks, granite, gneiss etc.

Quartz crystals occurs

- Sometime alone
- Sometimes with other minerals

Quartz is not affected by weathering. When rock containing quartz weather and disintegrate, quartz washed away with weathered product.

Quartz crystal sometimes deposited separately or sometimes remain intermixed with weathered product.



Quartz mineral

Sandstone, Ganister, Quartzite, Sand

There are made from secondary quartz

Sandstone

Sand grains are cemented together by silica, lime, clay, iron oxide, mica etc. and its use depends on impurities



SANDSTONE

Ganister It is fine grained sandstone that contain some clay.

Quartzite It is metamorphised silica bonded sandstone with deposition of secondary silica cementing the quartz grains together so strongly that breakage occurs across grains.

Flint It is found in form of pebbles. It consists of quartz with water and carbonaceous matter. These are coated with calcareous matter. It gets fractured with conchoidal fracture.



2.4.2 Role Of Silica In Glazes

Silica is main constituent of vitreous (Glazes and glasses) composition.

- It gets vitrified under effect of fluxes with in very broad temp. range. These fluxes are PbO , B_2O_3 , K_2O , Na_2O and Li_2O .
- Glazes having high silica content have
 - High resistance to chemical attack.
 - High hardness.
 - Higher the silica content in a glaze the higher will be its firing temperature.

2.5 Flux

Definition : Flux are the material which lowers the fusion point or temperature of glazes or enamels or bodies.

2.5.1 Types Of Flux

- Soda feldspar
- Potash feldspar
- Nepheline syenite
- Cullet

Feldspar It is the most important flux used in ceramic bodies and glazes.

- Feldspar covers a number of alkaline or earth alumina silicate.

- Natural feldspar is mixture of varying proportion of alumina silicate of Na, K, Ca, Li, Ba & Cs.
- Feldspar have 3 dimensional network of Si-Al-O except spodumene which has chain of SiO₂ ions.
- Feldspar are not generally found in pure state. These are made pure by froth flotation process.



Feldspars are following type

- Soda feldspar – Na₂O.Al₂O₃.6SiO₂
- Potash feldspar - K₂O. Al₂O₃.6SiO₂
- Lithia feldspar - Li₂O. Al₂O₃.6SiO₂

Properties Properties of feldspar are found in range. Even pure feldspar have range of properties.

Melting point	1110-1532°C
Specific gravity	2.56 - 2.63
Hardness	6 - 6.5
Colour	White, green, pink, buff brown.
Lusture	Vitreous to pearly.

Uses: i) Potash feldspar is used in ceramic bodies.
 ii) Soda feldspar (low fusing) is used in glazes.
 iii) These are used as fluxes. It is used to lower melting point of glazes. Lithium feldspar is most powerful flux, but they are very costly.

Nepheline Syanite (K₂O.3Na₂O.4Al₂O₃.9SiO₂)

- It is igneous rock.
- It contains nepheline, potash feldspar and soda feldspar.
- It is used in place of feldspar in certain bodies.



NEPHELINE SYANITE

Properties

Specific gravity	2.56
Hardness	5.5—6.0
Color	Colourless, white, dark, green, brownish and yellow.

Cullet It the name given to broken glass, which contain the major materials required for glaze preparation.

Glaze is different. It is special type of glass which have lower thermal expansion and higher alumina (as compared to window glass ware glass).

Cullet

- Cullet increase the viscosity of glaze and help to other better with clay bodies.
- Mostly cullet contain SiO_2 , Na_2O , CaO , Al_2O_3 and MgO in minor proportion.
- Cullet is also used as flux. Sometime flux used to make glazes are costly and are not easily available. Since glasses also uses some fluxes as used in glaze, So cullet is used as flux in flux in glazes.
- It will also help to reduce environment pollution.



CULLET

Role of flux in glazes

Fluxes are material used in glasses and glazes, which lower the high melting point of main glass forming material usually silica and alumina.

- Flux help complete melting or promote melting.
- Common fluxes are PbO , Na₂O, K₂O, Li₂O, CaO, MgO, Ba₂O₃, ZnO, Si₂O₃, Mn₂O₃.
- The fluxes are added in batch material.
- Some material show fluxing action at higher temperature like CaO.
- Some material show fluxing power at low temperature like pbO, B₂O₃, and ZnO.

2.6 Amphoteric oxide –(Al₂O₃)

Alumina is added in glazes inform of feldspar, Kaolin, corundum (- Al₂O₃), calcined alumina or alumina hydrate. It is added as 4-8%.

Role of alumina

In low temp. Glazes

- i) It increase viscosity.
- ii) It reduces tendency of de- vitrification(crystallization).
- iii) Increases bending strength.
- iv) Reduce thermal expansion coefficient.
- v) Increase resistance to acids.
- vi) Improve opacity.

Role of Al₂O₃ in Glaze

It play's important role in glazes but in glasses it is present in very less amount. It increase viscosity of melted glass and reduce crystal growth. So it is present in low % in macro crystalline glazes or aventurine type, but in high % in micro-crystalline glaze of malt type.

Quantity (%age) of Al₂O₃

It depends on

- Firing temp. (higher in matt glaze and lower in high-glass glazes).
- Particle size (if finer size Al_2O_3 is less, if Al_2O_3 is in coarser size % is high).

2.7 Alkalies materials used in glazes.—($\text{Na}_2\text{CO}_3, \text{NaCl}, \text{Na}_2\text{NO}_3$)

A) Na_2CO_3 (Sodium carbonate)

It is added in glazes to add Na_2CO_3 .



SODIUM
CARBONATE

Composition of Na_2CO_3 .

Na_2O --58.48% , CO_2 —41.52 %

Properties:

Molecular weight—106.00

Specific gravity--2.5

Melting point—851°C

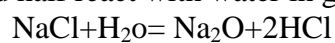
Uses It is used in glazes along with Soda feldspar.

B) Sodium chloride (NaCl)

Melting point (1160°C)

Sodium Chloride is used in glazes.

- It is used in small amounts in borosilicate glazes.
- It is used as main constituents in vapour glaze. During glazing half salt is lost by evaporation and half react with water in glaze and gets converted to Na_2O .



C) Sodium Nitrate (NaNO_3)

It has lowest melting point (306.8°C) of all glazes materials. During melting in glaze it is converted into soda. It helps in melting of glass batch. In glass it acts as a decolourising agent along with As_2O_3 and Sb_2O_3 .



SODIUM NITRATE

D) Sodium Hydroxide (Caustic Soda NaOH)

It acts as a fluxing agent. It is mainly used in soda lime glass glaze. It is added in form of concentrated solution to prevent dusting of glaze raw materials.

E) Sodium Silicate ($Na_2O \cdot SiO_2$)

It is made by fusing a mixture of sodium carbonate and silica powder.

Uses

It is mainly used in slips as deflocculants.

F) Sodium Silica-Fluoride (Na_2SiF_6)

It is a by-product and obtained during the manufacture of phosphate fertiliser.

Uses It is used as

- i) Opacifier
- ii) Refining agent to remove gas bubbles
- iii) It is used to develop some colours.

G) Potassium Carbonate (K_2CO_3)

- It is calcined K_2CO_3
- It takes up water rapidly in humid air.
- It is easy to handle and mixed with other batch ingredients.

Role It is used in glazes, enamels and glass to add K_2O

H) Red Lead (Pb_3O_4) OR ($2PbO \cdot PbO_2$)

It is used in glazes to make raw red glaze.

Role of red lead

- It is used as low temp. Flux.
- It can be used to produce glaze of good flow quantities without pin holes or other defects.
- It helps to make different coloured glazes.
- It is not used much because of poisonous nature.

Alkaline earth materials—(BaCO₃, CaCO₃, Borax, Boric Oxide)

A) Barium carbonate (BaCO₃)

- It is used to introduce BaO(Barium oxide).
- It increases density and refraction thus giving the glaze shine.
- It is excellent flux. It can be used in place of lead oxide.
- It present in high percentage (greater than 0.3 %) it harden glaze and introduce devitrification.

B) Calcium carbonate (CaCO₃)

- It is used to add CaO in glaze.
- It is used to improve durability of glaze.
- It is not added more than 3-5 % as it leads to devitrification.
- It improves bending strength of glaze and body
- It improves glaze and body glaze adhesion.
- It high temperature glazes it lowers viscosity.

C) Boron Oxide (B₂O₃)

- It is used in many glazes.
- In fritted glaze can be used in long temp. ranges.
- It has same effect on glaze as that of lead oxide but without toxicity.

Role of Boron Oxide

- i) Increases fusibility of silicate melts flux
- ii) Increases glass or brilliance of glaze. It do so by increasing refractive index.
- iii) Lowers the thermal expansion to some extent.
- iv) Have strong solvent action on colouring oxides.
- v) Do not promote devitrification.
- vi) Form melt(glazes) viscous at low temp. but fluid at high temp.

Raw materials of boron oxide

- i) Borax —(Na₂ B₄O₇.10H₂O)
- ii) Razorite
- iii) Dehydrated borax —(Na₂ B₄O₇)
- iv) Boric acid.

Borax (Na₂ B₂O₇.10H₂O)--It is one of the purest raw materials. It contain 36.6 % B₂O₇ and 16.3 % Na₂O. It is used in powder form.

Opacifiers

These are materials which are used to introduce opacity in glazes or glassy.

Opacity Means glazes/glasses which do not have transparency. It is due to

- a) Absorption or other interference with light when it passes through medium. It is done by solution or suspension of some glaze particles. For example SnO_2 , Sb_2O_3 , ZrO_2 , Cr_2O_3 etc.
- b) Diffusion of light by particles at the surface or inside the glaze medium. Diffusion or scattering is due to reflection of light at surface and also its refraction and diffraction inside by matrix and the suspended particles. Materials used in glaze to introduce opacity are insoluble or very little soluble in glaze melt. Examples Tin oxide (SnO_2), zirconia (ZrO_2), Zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$), Antimony oxide, calcium fluoride.

A) Tin oxide or stannic oxide – (SnO_2)

- At low percentage (6-10) % it is excellent opacifier.
- It is very costly.
- Opacity occurs due to suspension of oxide in viscous glassy phase.

B) Zirconium Oxide –(ZrO_2) or Zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$)

- It is used in form of zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$)
- It is also excellent opacifier and is preferred in industry.
- High % increase melting temp. of glaze.
- It increase crazing resistance of glaze.
- It stabilise the colour.

UNIT-3

Preparation of glaze: Selection of raw materials, composition, batch preparation, mixing, grinding. Definition of frit, preparation of frit & importance of fritting.

Application of glaze: Dipping, brushing, pouring & Spraying

3.1 Glaze Preparation

Glaze is applied after shaping or after biscuit firing. There are two methods for preparation of glaze.

- Raw glaze preparation
- Fritted glaze preparation

3.1.1 Raw Glaze Preparation In this method raw materials are directly used to make glaze slip.

3.1.2 Fritted Glaze Preparation In this method raw materials are first converted into frit, Then frit alone or with raw materials is used to make glaze slip.

3.2 Selection of Glaze Type Before preparation of glaze first step is to select type of glaze and its composition.

The glaze type is selected based on

- i) Type of body to be covered
- ii) Desired maturing temp.
- iii) Raw material availability and cost.
- iv) Composition and type (raw or fritted) is decided based on point 1 and 3.
- v) The compatibility of glaze with body in regard to thermal expansion.

3.3 Selection of Raw Materials of Glaze

The raw material are selected based on following points.

- 1) The raw materials must be insoluble in water. If these are soluble then, raw materials must be fritted before use.
- 2) Glaze is dried after application on the body. Glaze composition should be such that it should adhere with body regularly, otherwise rolling will occur.
- 3) During firing glaze must fuse and become homogenous. But fluidity must not be much otherwise it will flow on inclined path.
- 4) When glaze is applied on raw ware, then glaze composition must mature under same condition of body.
- 5) When glaze is applied at biscuit body, then it can mature at low temp. with desired properties.
- 6) Glaze composition must be such that at during firing it must become homogenous without mechanical aids (stiring).
- 7) The glaze composition must interact (bonding) with body.
- 8) Co-efficient of thermal expansion of glaze and body must be compatible.
- 9) Raw materials must be cheap.
- 10) Raw materials must be sufficiently mature.
- 11) Raw materials behaviour during firing.
- 12) Raw materials behaviour during storage.
- 13) Health Hazards of raw materials during use.

3.4 Frit : It is a homogenous mixture of inorganic raw materials. This is used for enamelling iron and steel. This is also used for glazing white wares (porcelain, pottery, bone-china).

Fritted glaze is one of the important type of glaze. In these glaze raw materials are fritted and introduced in glaze.

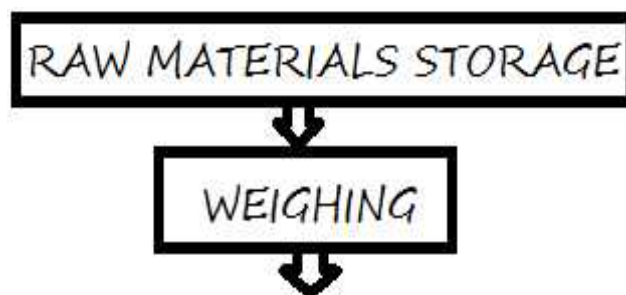
3.5 Purpose Of Fritting

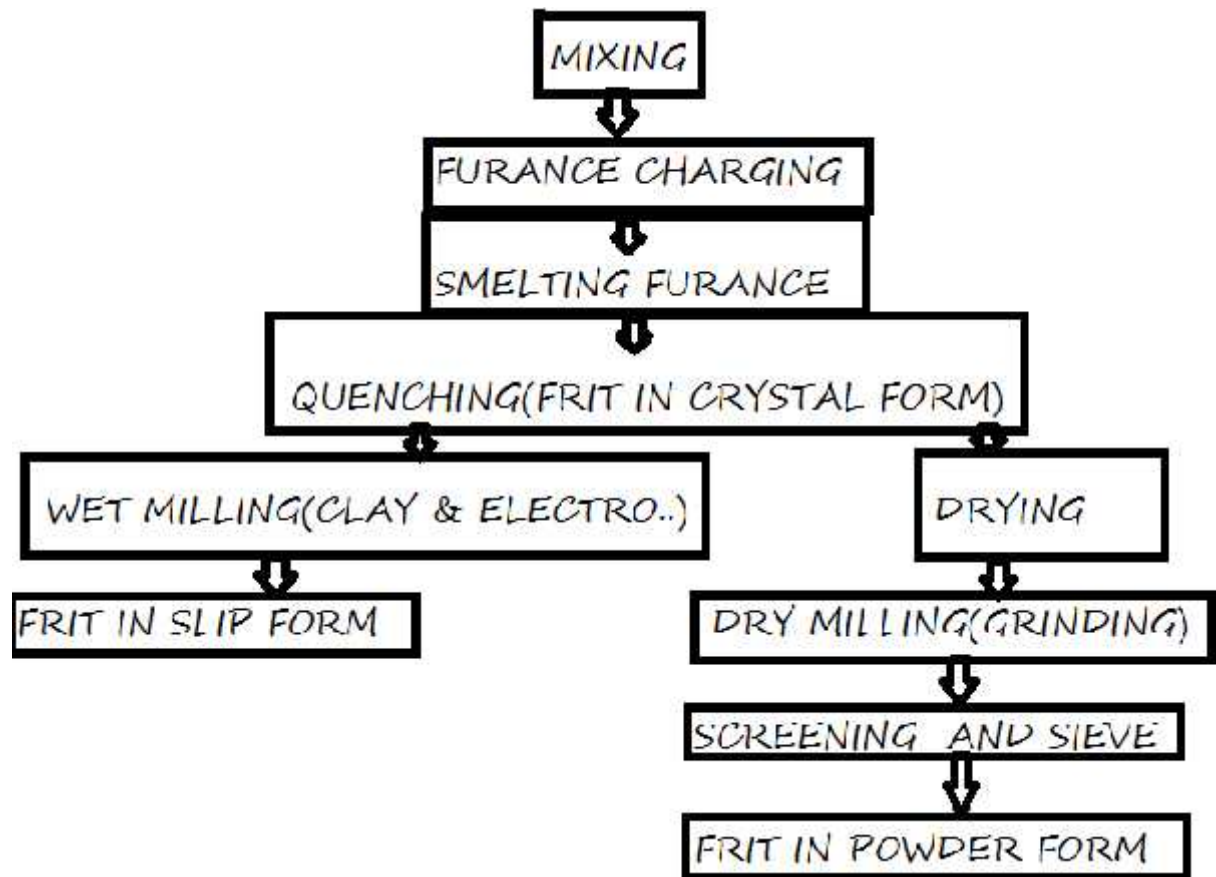
- a) To convert soluble material mostly fluxing materials into in soluble form Example--- Boron and Boric acid
- b) To convert toxic (poisonous) materials into less toxic and poisonous form. Example— Lead compounds.
- c) To convert dusty material (Fine particles like talcum powder or Talc) and bulk material, into heavy form. This helps to reduce shrinkage. Example—Precipitated $MgCO_3$ and Zinc Oxide (uncalcined)
- d) To get uniform colour when colour is introduced in frit.
- e) To complete some reaction between glaze ingredients (raw material) in advance to form smooth glaze.
- f) To convert slow to react raw material at high temp. into reactive oxide constituent members of frit. Example—Barium compounds.

3.6 Advantages of fritting

- 1) Good fluxing materials (like soda and potash) which are water soluble can used in glaze.
- 2) By fritting we can make different glazes which can mature at low to fairly high temp. So we can glaze wide range of wares.
- 3) The fritted glaze will react lesser with body and under glaze decorations. So we can make smooth glaze surface.
- 4) The fritted glaze can be applied more thinly on ware. So fine contours of wares are resulted.

3.6 Frit Making Process





Frit making process involve following steps

- 1) Raw material storage.
- 2) Weighing and mixing.
- 3) Charging in furnace.
- 4) Smelting in furnace.
- 5) Quenching
- 6) Dry milling or wet milling.
- 7) Frit storage.

1) Raw material storage

First of all different kind raw materials (Silica, feldspar alumina or aluminium oxide, lithium carbonate, magnesium carbonate etc.) are shipped to industry. Then these raw materials are dried passed through magnetic separator to remove iron particles. Then these raw materials are stored in different storage bins or hoppers.

2 Weighing and mixing

The different raw materials are weighed carefully as per batch composition. After that mixing is carried and raw materials are stored in hopper.

3 Furnace charging

From hopper the batch is charged fed into smelting furnace i.e pot furnace, hearth furnace, rotary furnace. These furnaces are generally continuous. These furnaces can be batch type like pot furnace. In batch furnaces feeding is done manually. If furnace is continuous then mixed batch charge is fed by screw conveyor directly into the furnace.

4 Smelting

Depending upon frit composition, frit smelting furnaces operate at 930°C to 1480°C. Continuous furnace operate at 1090°C-1430°C. During smelting homogenous melt is obtained.



5) Quenching

When smelting is complete the molten materials is passed between water cooled metal rollers to adjust the thickness of material. After this glass sheet is quenched with water spray. This will shatter (broke) the material into small glass particles called frit.



6) Milling After quenching the frit is shipped in crystal form or in slip form or in dry form.

- a) **Wet milling** When frit is wet milled, then after quenching it is directly fed into ball mill. During wet milling clay and other electrolytes are added with 30—40% addition of water . Separate balls are used for ground coat, white cover coat, coloured coat enamels/glazes. In case of hollow wares addition of 0.4% china clay and 0.07% to 0.08% boron is used . The frit slip is unloaded from ball mill, then it is passed through 200 mesh screen and magnetic separator.
- b) **Dry milling** If frit is to be dry milled (ground) then it is dried in either in stationary driers or in rotary driers. During drying hot air from furnace is used. After drying the frit is fed into ball mill with addition of china clay and other electrolytes. After ball milling the frit powder is screened (sieved) and passed through magnetic separator and stored. This is then shipped to ceramic industries for applications.

3.7 Preparation of glaze

First decide on type of glaze to be made i,e raw or fritted glaze. Then decide its formula. After this following steps are used.

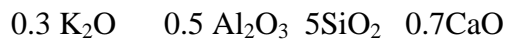
- a) Calculation of batch composition – from chemical composition
- b) Mixing and milling.

- c) Preparation and adjustment of glaze slip
- d) Application of glaze slip

a) Calculation of batch composition

Consider the porcelain glaze having formula

Empirical formula



To calculate batch composition following steps are used.

- 1) Selected the raw materials to supply required oxides. These raw materials should be insoluble in water. Usually the raw materials selected are feldspar, nepheline syenite, raw or calcined clay, magnesium carbonate, whiting, zinc oxide and quartz.
- 2) From the chemical analysis of raw material determine the molecular formula of raw material for example molecular formula of pure potash feldspar $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ and raw clay is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.
- 3) From the glaze formula (chemical composition) and molecular formula of raw materials, calculate weight of each raw material to be added to make required quantity of glaze batch.

b) Mixing and milling of glaze

- First of all individual raw material are crushed and ground. This is done for stony and lumpy raw material. These are then passed through 160 mesh.
- These are material are then fed into ball mill along with other raw material.
- In ball mill flint pebbles or during milling water is also added
- The milling helps to achieve required and uniform particle size. This also lead to uniform mixing.
- The speed of ball mill should be loss than critical speed of ball mill. In small ball mill quicker milling can be done as compare to bigger size ball mills. The ball charge should be 55% to 62.5% of batch charge volume.
- The batch charge may go up to maximum of 45% of mill volume.



C) Preparation and adjusting the glaze slip

In this step glaze is prepared to desired specific gravity and proper consistency. The specific gravity is measured by litre weight method. This is adjusted by dilution by adding water. The consistency of slip depend on physical properties of slip. The consistency of slip determine the suitability of application of glaze by dipping, spraying, brushing or other method.

- When glaze is a applied by dipping or spraying the consistency is measured by flow rate method. In such case consistency is controlled by adding deflocculants.
- When glaze is applied by painting, brushing or printing, then adhesive materials are added in glaze. Exp--- Dextrine, gums etc. Especially in fired bodies.
- Chemical composition is also adjusted.

D) Application of glaze

- 1) Painting and brushing
- 2) Pouring
- 3) Dipping
- 4) Spraying

Before glazing surface of ware must be free from adhering particle and dust. The glazing is done after biscuit firing. This can be done by hand or machine.

1) Painting and brushing This is the oldest method of glaze or enamel application. In this process glaze is applied by hand brush. Earlier this method was used for once fired and large pieces.

This is the best method for partial colour ware. Brushing is used to give more thickness. For brushing, glaze must be sufficiently viscous so that brush can pick required quantity of glaze. The clay is added in glaze to obtain required viscosity. If clay content does not give required viscosity then glue, gum, starch, cellulose can be added to get required viscosity.



2 Pouring

This method is also called water falling method. It is mainly used for wall floor tiles. This method is the improved and scientific version of “water fall method”. In this method tiles move on a belt conveyor under stream of glaze falling from pipe. The pipe is placed across width of conveyor. The excess slip is collected, cleaned and recirculated. The speed of belt is controlled to get desired thickness of glaze.



3 Dipping

In this method ware is dipped in pool of enamel or glaze. This method is used for wares which can be easily held in one hand or both hands. This method is very simple but for uniform and good glaze thickness, dipper must have must have following skills.

- To fix the time of dipping.
- To twist or jerk the glazed ware to evenly distribute the glaze and to throw of excess glaze.
- To finish the glazing without leaving hand marks.

Dipping can also be done by hand or automatic M/C . In dipping dipper picks the ware in such a way that minimum marks are left on ware. This can be done by using wires on fingers. After dipping the ware is twisted or given suitable jerk, So that glaze is evenly distributed on ware and extra glaze slip is thrown. Every shape needs to be handled in different way for applying uniform glaze.



Following faults can be found on dipped ware

- Uneven glaze layer on a single article.
- Short glaze edges.
- Over glaze at centres.
- Inequality of tint (shade of colour) on single piece.
- Wastage of glaze at time of jerk.

4 Spraying In this method glaze is applied by spraying on ware. In spraying process glaze slip is atomised (converted into small drop lets) and directed towards surface of wares. In this method many faults gets removed which appear during dipping.

Spraying can be by

- Hand Spraying
- Automatic Spraying



Hand spraying In this method spraying is done in spraying booth having ventilation (exhaust) and system for recovery over sprayed material. The worker must wear mask. The spraying is done by spraying gun held perpendicular to surface of ware and at correct from it. This method is much slower than dipping.



Automatic spraying The spraying can be done by machines designed for each job. The machine consists of conveyor with or without rotating spindles, oscillating or reciprocating.

Following points are important in spraying

- Spraying gun must be simple to use, easy to clean, easy to adjust and wear resistant.
- Air pressure for atomising must be able to regulate. The pressure must be between 2.1 to 2.8 g/cm².
- The gun must be held perpendicular to surface . It also must be held at correct distance to avoid splashing or bouncing of glaze.
- The glaze must be fed to spray gun from a constant head (level).

UNIT-4

FIRING OF GLAZE WARES

Firing of glazed ware: Drying, placing precautions of glazed ware before firing.

- Glaze defects & remedies : Crazeing, Crawling, Peeling, Pin hole discuss their causes and remedies

4.1 Drying

It is the process of removal of moisture/water after shaping. The amount of water removed from shaped ware depends on method of shaping and composition.

- However water removed during casting, filter pressing and spray drying will not cover under drying.
- During drying water is removed by evaporation. So drying involve
 - 1) Transfer of heat from surrounding to shaped ware (solid water system).
 - 2) Removal of water through air.

Removal of water depends on

- Whether water is present on surface or inside.
- Movement of water from inside of body to surface.

4.2 Factors affecting drying rate

A) External factors

- 1) Temperature of surrounding of ware
- 2) Humidity of surrounding of ware
- 3) Flow of air in surrounding

B) Internal factors

- 1) Loss of water in vapour from article.
- 2) Movement of water/moisture in the article.
- 3) Shrinkage during drying.
- 4) Crocking or warping of articles.

4.3 Placing of (setting) of ware in kilns

Placing of ware in kiln depend on

1) Ware

- Biscuit or glost.
- Load bearing capacity when hot i.e, more or less liable to ware- page.
- Whether ware is unharmed by flame or it require protection.

2) Kiln

- Whether kiln is open flame or muffle or electric.
- Fuel dirty (coal) or clean (gas fuel).
- Kiln batch or continuous or tunnel kiln.

4.4 Precaution while placing ware in kiln

Following point to be kept in mind while placing ware in kiln.

- i) Unglazed wares can be kept in contact with each other. However glazed ware must be carefully kept apart (separate) from each other. Other- wise they will stick together.
- ii) Low grade (quality) wares like bricks roofing tiles etc, may be fired in open contact with kiln gases flames. High quality wares particularly white wares, must be protected from direct contact with flames, smoke, ash etc. These should be placed in sagger or muffle kiln should be used.
- iii) Wares are placed (individual or in sagger) in such a way that optimum (desired) circulation of hot gases takes place. This will help in achieving maximum uniformity of (equal) temp. of all wares. If more gap, gases will pass easily and get waste. If wares are placed very close hot gases will not reach all wares. The gap should be uniform.
- iv) In case of large uneven wares (sanitary ware) smaller pieces can be placed in between other- wise large pieces may become over fired.
- v) Table wares cannot be directly placed in kiln. It requires both support and protection. Sagger provide both support and protection for tableware. They are of oval shaped or round, for tiles sagger are square or rectangular.
- vi) In biscuit firing hard porcelain and earthenware do not require sagger. So these can be placed directly. Large pieces and special pieces are supported, so that they should not sag or deform.

4.5 Glaze and glaze defects

4.5.1 Defects caused by glaze

a) Excessive or insufficient grinding

- Over grinding has negative effects on glazes with very high surface tension. Example— zircon white.
- This causes cuts or cracks during shrinkage before melting.

Remedy This problem can be avoided by screening and checking percentage of residue.

b) Lack of plasticity (adhering problem of glaze with body)

- This problem cannot be detected at green stage.
- It appears during initial stages of firing, when glaze first shrink and then melt. In this defect glaze does not stick properly with glaze and tends to 'crawl' away from body.

Remedy

- In single firing CMC adhesive is used in glaze.
- Plasticity can be improved by adding ball clay, kaolin (8-10 %) and bentonite (max 2%)

c) Poor firing stability

Some glazes are highly unstable and sensitive to very small temp. changes. This results in tiles of different shades.

d) Excessive fusibility

This is related to glaze composition. It results in surface bubbles (pin holes) at sides or at place where glaze is thin.

e) Incomplete frit melting

This result i) Surface bubbles due to escape of gases which are not removed during fritting (melting). ii) Partial solubility of material which are not completely chemically reacted during fritting.

4.5.2 Application defects

a) Glaze detachment

If glaze slip is not proper glaze may 'crawl' and gets detached from surface.

b) Glaze shrinkage

Tensions between glaze and body may generate small fracture.

4.5.3 Poor glaze body match

a) Crazeing and peeling (flaking)

b) Glaze body interaction.

4.5.4 Glaze surface defects (Pin Holes)

4.6 DEFECTS OF GLAZES

4.6.1 Crazeing and Peeling

Crazeing is a network of lines or cracks at the fired glazed surface.

Causes :

- When body and glaze expansion co-efficient are not compatible (matched), It leads to serious defects.
- During cooling (in glost firing) molten glaze interacts with body. If Coefficient of thermal expansion (CTE) of glaze is considerably higher than that of body, then glaze contracts more than that of body, and hence glaze stretches. If this tension is more than modulus of elasticity of glaze, breakage occurs. This is known as crazeing. It result hairline fracture.

The crazeing occurs when

- 1) Coefficient of thermal expansion/ contraction (CTE) of glaze is more than that of body.
- 2) It also occurs due to moisture expansion (due to pores) in body.
- 3) It also depends on elasticity and mechanical strength of glaze.

Prevention of crazeing/remedies Crazeing can be prevented by

- A) Changes in body to increase CTE.
- B) Changes in glaze to decrease CTE.

A) CHANGES IN BODY TO INCREASES CTE.

- i) Increase plastic clay content and decrease quartz contents.
- ii) Partial substitution (replacing) china clay by plastic clay.
- iii) Finer grinding of silica materials examples--- quartz, flint, sand etc.
- iv) Firing of body at high temp.
- v) Increase the feldspar contents (flux).

B) CHANGES IN GLAZES TO REDUCE CTE

- i) Increase the amount of silica or decrease the amount of flux.
- ii) Increase boric oxide content in place of silica.
- iii) Substitution (replacing) flux of higher molecular weight (Na_2O) by that of lower molecular weight. Replacing soda (Na_2O) by Lithia (Li_2O)

C) **CHANGES IN GLAZES TO INCREASE ITS MODULUS OF ELASTICITY** Replacing soda (Na_2O) by Lithia (Li_2O)

Peeling is the fracture of glaze into number of flakes. This results detaching of glazes flakes from surface of glaze. This is known as peeling.

Causes The peeling occurs during cooling when CTE of glaze is less than that of body. This results in compression in glaze, which in turn results flaking of glaze. This occurs due to fracture of glaze of circular shapes mainly at sides of tiles. Peeling is less common than crazing because resistance to compression is 10 times greater than resistance to tension.

PREVENTION OF PEELING/REMEDIES Peeling can be prevented by

A) **CHANGES IN BODY TO DECREASE CTE**

- i) Decrease plastic clay content and increase quartz content.
- ii) Partial substitution (replacing) plastic clay by china clay.
- iii) Firing of body at low temp.
- iv) Decrease the feldspar content (flux)

B) **CHANGES IN GLAZES TO INCREASE CTE**

- i) Decrease the amount of silica
- ii) increase the amount of flux by that of by higher molecular weight.

4.6.2 Crawling This defect occurs in glazes due to irregular contraction of glaze into thick lumps and islands leaving behind un-glaze patches is known as crawling of glazes.

Causes of crawling

A) **Crawling arising from composition, preparation and application of unfired glaze.**

- 1) **Bad adherence of glaze to ware** A glaze adhere better to porous surface than dense surface. Also glaze do not adhere better on oily or greasy surface and surface having sharp curvature. In this case crawling can be best prevented by adding material to the glaze to reduce surface tension.
- 2) **Excessive shrinkage of glaze leading to crawling of raw glazing**

This can be due to following reason

- a) Over fine grinding
- b) Thick glaze layer.

- c) Due to presence of constituent having large drying shrinkage. Example—plastic clay, un-calcined zinc oxide, organic binder.
 - d) Fast pre-heating of moist ware.
 - e) Re-absorption of moisture before setting in kiln.
- 3) **Lack of internal cohesion** If cohesion among raw glaze particle it less. It leads to dusting off when dry or it leads to crawling. It is due to presence of large quantity of very fine ground material. This can be prevented by less fine grinding, by adding, binding materials etc.
- B) **Crawling arising from composition of fired glaze** If surface tension of fused glaze is more, than it draws the glaze together and hence result crawling. The surface tension of glaze depends upon glaze composition. Some constituents have more influence on surface tension, so these can be replaced with other constituent having low surface tension.

4.6.3 Pin holes on the glaze surface

- Pin holes are small holes present on surface of glaze after firing.
- This is most general problem and is difficult to eliminate.
- The pin holes are minute holes, hollows or craters found on surface of ware.
- Pin holes do not affect working, but it affects appearance. These are created during firing by gaseous bubbles escaping through surface of molten glaze.
- Formation of pin holes depends on viscosity of glaze at its maturing temperature. If the glaze is more fluid (less viscosity), then gases can escape easily and holes created by escaping gases are filled by molten glaze. But if the glaze viscosity is high at maturing temperature, then these holes are not filled and large pin holes are created.

Causes and remedies

- 1) **Defective fritting** During glaze frit preparation some glaze materials (constituent) do not react perfectly. These materials again interact with other materials during firing and release gases.

Such frit glazes during rapid (fast) firing cycles give rise to pin holes. Because during firing less time available for release of gases.

Prevention This type of pin holes can be removed by preparing frit properly.

2) **Additions during glaze milling** In case of rapid (fast) firing cycles and when certain materials are added in mill, then in such cases raw materials added in mill must not give gas.

Also such materials should not release gas by reacting with other materials otherwise dot like pin holes will be formed.

Prevention Such raw materials should be added in mill, which should not release gas during firing of ware.

3) **Over firing** Over firing (firing at higher temp.) can result pin hole. Glaze having high alkaline of boron oxides, become volatile. This leads to pin holes.

Prevention This can be avoided (prevented) by maintaining correct temperature. During firing

4) **Salts** Salts such as sulphates and carbonates (soluble) can enter in glaze from

i) Body ii) Grinding water iii) pigment iv) Additives in ball mill

Such salts results in pin holes, as they release gas during firing of ware.

Prevention Such pin holes can be prevented by using water, pigments, additives free from such salts.

Unit V

Branch : Ceramics Engineering

Semester = Fourth

Subject : Ceramics Coating Technology

Faculty: Faculty: Ashwani Kumar, Sr Lecturer, Govt. Polytechnic .Jhajjar (Haryana)

Syllabus Covered:

Decorations: Under glaze, in glaze & on glaze decorations, Decoration methods like painting, stamping, stenciling, screen printing, & chromolithography

5.1 Decorations: are designs on surface of ware to give aesthetic(good) look. There are seven main types of colouring / decoration of ceramic wares.

Types of Decorations Three types of decorations are concerned with the body and four with glaze.

A) Body Decorations

i) Coloured bodies and body stains

Many ceramic raw materials contain colouring agents, which give products made with them of particular colours. e.g. red building bricks and tiles where the colouring agent is iron and in yellow bricks colouring agent is iron with calcium. Sometimes coloured clays are used for fine wares, crockery and art work.

Coloured wares are left unglazed or covered with colourless transparent glaze.

ii) Engobes Coloured or stained body raw materials can be used to decorate the piece.

e.g. Thick ware may be made up from body of undesired colours . Such wares are covered with engobes or body slip of higher quality and good colour.

iii) Relief work and inlaying

These are also body decorations in which body surface is worked (designed) in leather hard condition by scratching, modeling and piercing. Then colours are inlaid.

B) Glaze decorations

i) Under Glaze Decorations

In this method, the ware is first decorated by colouring agents (paints, inks,oils etc) by spraying, dusting, stamping, transfer or screen printing etc. The glaze is then applied on the decorated piece and then piece is glost fired. This is the most durable(more life) method of decorations. But in this method less numbers of colours range can be used due to reactions of colouring agents with bodies and glazes. Also at high temperatures less colours can be used.

ii) On glaze decorations

This decorations is applied on ware after glost/glaze firing. In this method of decoration, colouring agents are mixed with low melting glassy flux and are applied on ware. After this ware is again fired at low temperature. (Third firing)

In this method decorations (colour designs) can be applied by spraying, brushing, dusting, stamping, transfer and screen printing. The decoration firing temperature (Third firing) is less than that of glost firing temperature. So in this case more range of colours can be used, than glost firing. The durability of decoration is less than that of underglaze decorations. It depends on temperature difference between glost firing and decorating firing. Less is the difference more is the durability e.g. In bone china bodies the temperature difference between glost firing and decorating firing is 350 deg C, so considerable interaction takes place between glaze and decorations . So durability is more. In hard porcelain the temperature difference is 700 deg C so little interactions takes place between glaze and decorations. So durability of decorations is less so it can be easily scratched.

iii) In glaze decorations

This is not the common method of decorations. In this method ware is glazed and when it become dry glaze is decorated by hand painting.

iv) Coloured, opaque and crystalline glazes (In glaze colouring)

In this method surface of piece is uniformly coloured by using a glaze having colouring agent. If the body is coloured then opaque glaze is used. An allover, but not uniform colour is done by using crystalline glaze.

5.2 Decorations Mehods

5.2.1 Painting or Brushing

In this method free hand design is sketched on ware by pencil before painting. If the design is to be made on more pieces, than design outline is transferred on ware by perforated stencil .

For under glaze and on glaze decorations colourants are mixed with suitable oily media for application with brush. Under glaze decorations are also mixed with glycerine to avoid hardening on firing.

5.2.2 Stamping

Monochrome decorations (single colour) can be applied by rubber stamp. The rubber used should be soft for better impression. In this method colour is first spread on glass plate and then stamp is pressed on it. Then the stamp is pressed on ware to transfer the design. In this method a very thin line is transferred. To obtain thick design fatty oil is first transferred by rubber stamp and then the dry colour powder is sprinkle which gets sticks with fatty oil.

5.2.3 Stencilling

In this method design are made by using stencils. Three types of stencils are used paper or tissue stencil, tinfoil stencils, zinc sheet stencils

i) Paper Stencil

In this method flat ware is decorated. First of all required design is made/ traced on the paper. Then it is placed on felt and holes are made on lines after 5mm. Then this stencil is held between ware and linen bag. Linen bag contain talcum powder if ware is coloured or charcoal powder if ware is white.

The bag is pressed gently against stencil, in this way design is obtained. The design can be painted in by engobe or in glaze or on glaze or under glaze colourant.

ii) Tin foil stencil These can be prepared by two methods

Hand cutting i) Coat the tinfoil with thin layer of kaolin mixed gum Arabic solution

ii) Dry the coating

iii) Draw the required design

iv) Place the coated tin plate on matt glass plate, cut the design with knife. Steel ruler can be used to draw straight line. The portion which is removed, colour will be applied at that portion

Etching Method i) First coat the tinfoil with heated mixture of 41% beeswax, 40% stearine candle wax and 19% machine oil.

ii) It is then cooled and dried

iii) Then place the plate on matt glass

iv) Place ready cut stencil on it

v) Remove the wax in exposed parts with brush

vi) Then immerse the foil in to nitric acid bath(50%), till the unwanted parts are dissolved

vii) Wash the acid with water

ix) Remove the wax with turpentine.

The prepared tin foil is used for brushing and spraying underglaze decorations. The bottom portion of stencil is coated with Vaseline and placed on ware with left hand. With right hand the colour is brushed or sprayed.

iii) Zinc sheet stencil It is prepared by applying kaolin gum mixture and design is made with frit-saw.

5.2.4 Screen Printing

It is used to make mono chrome or poly chrome decorations. Decorations can be made directly on ware or design transfers can be made.

Screen is made up of silk, nylon or metal. The design on screen is made by direct cutting or stencil, or photochemical method.

The screen is then stretched on wooden or metal frame. The colour is prepared by mixing colour powder with oily substance. The screen is then placed on ware or transfer. The colour is then pressed through screen by rubber blade.

5.2.5 Chromolithography

Polychrome transfer sheets can be prepared by lithography printing on lithography stones. The lithography stones are absorbent stones which can be cleaned off and re-used. Now a days zinc plates are used whose surface is grained by sand and porcelain balls so that it can retain moisture. The design is drawn on moist stones or plates in a special lithographic ink. This ink contain an oily substance which do not mix with water. Plates are prepared for each colour to be printed.

Now a days hand designs are replaced by photolithography. The zinc plates are coated with gum solution containing potassium dichromate. It is then dried. The coating is light sensitive and plates are kept in dark room. The colour separation negatives (design) is placed on plates and exposed to powerful light of a carbon arc. Due to this potassium dichromate reacts with gum and

make it water insoluble. The whole plate is inked with greasy lithographic ink and then placed in warm water. By doing so unexposed portions are washed out. The plate is dried and inked gum-bichromate design is dusted powdered resin and chalk which act as a resist. The remaining portion is etched. Finally the plate is gummed over with gum Arabic solution and dried. This plate is then used for printing.

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Unit 6

Branch : Ceramics Engineering

Semester = Fourth

Subject : Ceramics Coating Technology

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Syllabus Covered: Introduction & Classification of Enamels: Definition of Enamel.
Types of enamels.

- Base Metal preparation : Cleaning by organic detergent, chemical method, de greasing by heating method & pickling
- Preparation & Application:- Composition, batching, grinding, & milling additives. Ground coat and cover coat, application of enamel by dipping and spraying.
- Defects in Enamel: Under fired, rolling, scaling, chipping, pinholes, crazing, & their causes (16 hrs)

6.1 INTRODUCTION

DEFINITION Enamels are the thin glassy protective coatings applied on metal surface. These are also called vitreous enamels. These are made by fusing powdered glass to a surface by firing at low temperature (750 – 850 °C).

Enamels are applied on metal surface to improve its surface properties. When vitreous or glassy enamel is applied on metal surface and it is fired it gives mirror like surface and make it resistant up to 1000 deg C.

Enamel is a form of glass. Its constituent parts are of the combination of glass flux with silica, flint, soda or potash, and borax, each element effecting the composition and fluidity of the enamel. The addition of metal oxides gives the substance its colours. Other compounds are notably present in some enamel, lead for example is used in clear fluxes and a number of colours for brilliance, and tin is added to enamel to give it its opaque properties

6.2 TYPES OF ENAMELS There are different types of enamel, namely

6.2.1 OPAQUE ENAMELS These enamels are totally solid in colour. They can be used over silver & gold but are more typically used over copper, as the metal base does not need to be interactive with the colour of the enamel.

6.2.2 OPALESCENT ENAMELS These enamels have a beautiful milky sparkling quality. In opalescent enamels colour range is limited. For best results they are fired over an engraved surface. This helps the enamel to catch the light through the metal surface, allowing the gloss

of the colour to show through it. Firing of opalescent colours require practice. The first firing should be high while the second firing requires a lower rate of heat to reduce the finish to its required opalescence.

6.2.3 TRANSPARENT ENAMELS

This enamel allow light to pass through it and we can see the metal surface. These enamels should be fired over engraved or textured metal surfaces. Transparent glazes (coloured) show best effect ground coarsely. They are mostly used over silver and gold as these metals have good reflective qualities.

6.2.4 PAINTED ENAMELS

These enamel are very finely ground powdered oxide. In these enamels a wide range of effects can be produced. Painted enamels can be used over opaque, opalescent or transparent enamels. It is applied with a fine brush, over a previously enamelled base coat of enamel. Images are built up in layers over several firings. Painted enamels colours can be applied as under glaze or over glaze colours. Under glaze colours need an additional layer of clear flux to finish and protect the image.

6.2.5 LIQUID ENAMELS

These enamels are finely ground enamel . It is suspended in an aqueous solution combined with special additives. Liquid enamel can be applied by dipping, spraying, pouring or painting onto the metal surface.

6.3 BASE METAL PREPARATION

The preparation of the metal surface is very important. The metal surface area where enamel is to be applied, must be free from any dirt, grease and oxide / fire stain. Otherwise it will affect the colours of enamels. Even small amount of grease contaminate the enamel. After preparation of metal surface it must not be touched . Apply the enamel as soon as surface is cleaned, or wrap in paper. . The cleaning of metal surface can be done thermally, mechanically or chemically & pickling

6.3.1 Cleaning by organic detergent and Chemicals

This step is carried out to remove oil, grease and other organic impurities by using organic solvents or chemicals (Generally) alkaline solutions. The animal and vegetable fats are converted into soap bubbles by alkalis and the soap formed is washed off. However mineral oils are removed as emulsion.

This process can be speeded up by mixing/stirring of the solution and heating to 80–100°C. Control of solution composition and temperature is necessary to ensure proper cleaning.

After cleaning, the ware is rinsed with overflowing water for complete removal of traces of adherent cleaning solution

6.3.2 Thermal degreasing (de greasing by heating method)

It is a heating operation used to remove organic impurities (grease) and strain in the metal. The temperature and duration (time) of the process depend upon quality and size of the metallic article. Scale (layer) is formed during the operation. This scale is removed during pickling. Heating schedule must be closely controlled to avoid (prevent) excessive scaling.

6.3.3 Mechanical cleaning

It is used for large shapes or heavy stocks. It is done by blasting the metal surface by a jet of an abrasive material such as quartz, alumina or steel shots to remove scale, rust and dirt. The surface becomes clean and slightly pitted which helps good bonding of enamel.

The material removed from the surface should not be much (excess). It is controlled by adjusting the air pressure and time of blasting.

6.3.4 Pickling

After chemical or thermal degreasing, the rust and scales are removed from the metal surface by dipping the articles in an acid solution. Pickling (cleaning by chemicals) in HPO_4 improves the quality of the surface. But it is very costly acid. So it is not used much. Generally, pickling is done either in H_2SO_4 or HCl .

During pickling the strength, iron content in solution, sludge and pickling time is controlled. The pickling time should be minimum to avoid hydrogen absorption.

6.4 PREPARATION OF ENAMEL

6.4.1 Composition First of all glass and glass-ceramic coating suitable for desired end properties is selected. Depending on type of enamel coating chemical composition is decided. The main raw materials include Silica, soda feldspar, boron oxide, Arsenic oxide, Titania, zirconia, alumina, Lime, Berillia etc.

The raw materials are converted into frit. Frit is used to make enamel slip. It can be bought in lump or powdered form. Lump form of frit is preferred for long life.. It does not deteriorate over time. However for convenience powdered enamel frit can also be used.

6.4.2 Batching

Required frit is taken and it is mixed with other raw materials. The frit can be used from 80% to 100% to make enamel batch.

6.4.3 Grinding and mill additions

Lump(frit) enamel are ground to form it into a granular powdered state. The grinding of enamel from lump is done largely to determine particle size. These frits (glass) are ground in a mill in dry or wet condition.

6.4.4 Mill additives

During wet milling certain mill additives, usually Plastic clays, various types of natural or synthetic gums and electrolytes (BaCl_2 , MgSO_4 , K_2CO) are incorporated. A thick creamy suspension (slip) is produced for application over clean metal surface. Some refractory materials such as quartz, feldspar etc are incorporated (normally in ground coat) to increase the maturing range and workability. Opacifier and colours are often added along with other mill additions in some cover coats..

The glass frits, in the form of powder (60 mesh BS sieve) is mixed with mill additives (as mentioned above) and milled to form a slip (- 200 mesh BS sieve) which is allowed to age. Finally, flowability, spreadability, setting characteristics and pH of the slip are measured to effectively control the slip of coating material before application.

6.4.5 Application:- The common application techniques are dipping, brushing and spraying. Before enamelling surface of ware must be free from adhering particle and dust. The enamelling is done after cover coat firing. This can be done by hand or machine.

1) Painting and brushing This is the oldest method of glaze or enamel application. In this process glaze is applied by hand brush. Earlier this method was used for once fired and large pieces.

This is the best method for partial colour ware. Brushing is used to give more thickness. For brushing, glaze must be sufficiently viscous so that brush can pick required quantity of glaze. The clay is added in glaze to obtain required viscosity. If clay content does not give required viscosity then glue, gum, starch, cellulose can be added to get required viscosity.



2 Dipping

In this method ware is dipped in pool of enamel or glaze. This method is used for wares which can be easily held in one hand or both hands. This method is very simple but for uniform and good glaze thickness, dipper must have must have following skills.

- To fix the time of dipping.
- To twist or jerk the glazed ware to evenly distribute the glaze and to throw of excess glaze.
- To finish the glazing without leaving hand marks.

Dipping can also be done by hand or automatic M/C . In dipping dipper picks the ware in such a way that minimum marks are left on ware. This can be done by using wires on fingers. After dipping the ware is twisted or given suitable jerk, So that glaze is evenly distributed on ware and extra glaze slip is thrown. Every shape needs to be handled in different way for applying uniform glaze.



Following faults can be found on dipped ware

- Uneven glaze layer on a single article.
- Short glaze edges.
- Over glaze at centres.
- Inequality of tint (shade of colour) on single piece.
- Wastage of glaze at time of jerk.

3 Spraying In this method glaze/enamel is applied by spraying on ware. In spraying process enamel slip is atomised (converted into small drop lets) and directed towards surface of wares. In this method many faults gets removed which appear during dipping.

Spraying can be by

- Hand Spraying
- Automatic Spraying



Hand spraying In this method spraying is done in spraying booth having ventilation (exhaust) and system for recovery over sprayed material. The worker must wear mask. The spraying is done by spraying gun held perpendicular to surface of ware and at correct from it. This method is much slower than dipping.



Automatic spraying The spraying can be done by machines designed for each job. The machine consists of conveyor with or without rotating spindles, oscillating or reciprocating.

Following points are important in spraying

- Spraying gun must be simple to use, easy to clean, easy to adjust and wear resistant.
- Air pressure for atomising must be able to regulate. The pressure must be between 2.1 to 2.8 g/cm².
- The gun must be held perpendicular to surface . It also must be held at correct distance to avoid splashing or bouncing of glaze.
- The glaze must be fed to spray gun from a constant head (level).

6.5 Ground (Under) Coat Enameling

Ground coat cover enamelling is a very thin coating on a steel surface. The purpose of ground coat enamel is that

- 1) It provides the bonding of cover coat enamel and iron sheet. A glassy coat was thought to be necessary to provide adherence of the cover coat to the metals.
- 2) It eliminates reactions that would otherwise occur between the cover coat and the base metal.
- 3) The glassy coatings would tend to flow and result in defects in the surface of the base metal.
- 4) It also protects iron from oxidation (rusting) while being heated to the temperature at which cover coat enamel fuses. If the ground coat enamel is not used then maximum number of pieces found can not be used.

A ground coat enamel is a very refractory coating material is generally sintered on iron sheet. The purpose of this coating is to produce porcelain like coating on metal. On this coating cover coat enamel layer acts as glaze.

These ground coat enamel is made from frit. This frit is made from flint and borax or from flint, feldspar and borax. While preparing enamel from frit clay and flint or clay and feldspar are added in sufficient quantity so that enamel gets sintered (forms bond) with metal surface without fusing on it.

Magnesium oxide or sulphates are added as deflocculants. The firing of ground coat is carried out until the ground coating is not rubbed with fingers and grains become round.

To obtain satisfactory adherence between these ground coats and the metal, it is necessary to make additions of costly metallic oxides of cobalt, nickel, and manganese. These ground coats also had the disadvantage of requiring surface preparation, such as pickling, and sometimes nickel plating the metallic basis material prior to coating, in order to promote adherence.

It has been discovered that, by means of the present invention, satisfactory ground coats may be obtained without the use of expensive metal oxides and without the necessity of surface preparation prior to applying the ground coat.

Composition A flint-feldspar-borax frit comprising 110-160 parts by Weight of flint, 290-390 parts feldspar, 300-340 parts dehydrated borax, 1575 parts soda ash, 15-80 parts sodium nitrate, 60-90 parts fluorspar, 9-15 parts calcspare, and up to 5 parts red iron oxide.

The slip or enameling composition, which is applied to a metallic surface to a weight of about 8 grams per square foot, dry Weight. This is then fired for 3 to 8 minutes at a temperature of from 1300° F. to 1700° F.

6.6 COVER COAT ENAMEL

It is applied on ground coat. For cover coats the frit is composed to both bind to the ground-coat and produce the desired external properties. The chemical composition depends on required properties of coatings. The cover coat enamels must have decorative properties. Gloss, opacity and colour stability are most important properties.

There are basically three types of coatings used for cover coat

- 1) Clear frits which gives no opacity. It produces dark translucent colours.
- 2) Semi opacified frits
- 3) Opaque frit used for white colour

6.7 Defects in Enamel:

6.6.1 Under fired: Under-firing means not firing the enamel at desired temperature or not holding the enamel at maximum temperature for desired time.

It results to rough(gritty) appearance, a roughness in surface and aesthetic look is not achieved So enamels must be fired at desired temperature to avoid such defects.

6.6.2 Rolling (Crawling) Crawling is also called retraction or pulling back enamel layer from surface of metal. It is caused due high surface tension of enamel slip covering the metal surface. The resulting effect is that the liquid adhesive does not fully wet the substrate but it retracts and forms droplets, leaving part of the substrate naked.

In crawling,

- i) The enamel parts during melting leaves bare spots of metal exposed. The crawl may expose only few tiny places, or it may leave a pattern of exposed areas like cracks in dried mud.
- ii) In some 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

Causes : The crawling is due to the higher viscosity imparted by excessive boric oxide. It occurred when coat is applied in a sufficiently heavy coat to give the desired opacity

Prevention Substitutions of lead oxide for flint proved very satisfactory, for they improved the adherence to the castings without causing crawling.

6.6.3 Cracking

Cracking in coating is smooth surface fractures into sections. This results the cracks in the coating. The area of metal which is exposed leads to contaminants.

6.6.4 Scaling The defect of scaling is one of the commonest in steel enamelling. It consists of flaking on the enamel coating in the form of semicircles. This defect is clearly visible. It is deep transverse crack, cutting into the local zone of the enamel coat. It do not usually penetre to the metal.

Sometimes the scaling is present over the entire circumference, and then its center does penetrate to the metal.

The defect is of two types: fine flakes with a high density (about 10 cm⁻²), and large with a low density (about 1 cm⁻²), although these may be mixed.

Cause Scaling is not formed when the bond between enamel and metal is weak, or when the coating is porous.

Formation of this defects depends on

- 1) The capacity of the metal to absorb water during enamelling
- 2) Diffusion mobility after the enamel has cooled
- 3) The structure of the intermediate layer and the strength of the bond on the steel
- 4) The continuity of the coating; and the mechanical and physical properties of the enamel and metal.

The steel absorb more than 10 ml of hydrogen during pickling, and when the ground coat it absorbs iron. This leads to rapid flow of excess hydrogen to the steel-enamel interface. If the intermediate layer is continuous, then a high local pressure is set up which tends to form scales

6.6.5 Chipping-off - A spalling or breaking off of enameled surface in flakes of various sizes. Chipping phenomena probably are caused chiefly by hydrogen effusion (release).

6.6.6 Black specks These results due to due to the longer time required in melting down the cover enamels by the wet process, whereby the ground coat became overfired, and small particles of it were dissolved by the cover enamel, resulting in dark specks.

6.6.7 Open pinholes - Pitting and pin holes are most difficult enamel defect to remove. The enamel which may come from the kiln is covered with minute pits or pinholes. These pinholes may be small, or they may be larger, resembling miniature volcano craters.

Refiring is sometimes used to remove the defect . But it sometimes make make the pinholes larger or more frequent on the surface of the enamels could in most cases be closed over by increasing the length of firing. There still remained, however, small incipient pinholes in the covers which could not be entirely eliminated.

Causes of Pin h oles Experiments show that when hydrogen is absent, regardless of the depth or nature of the surface chill, no pinholing or blistering results during firing at 725°C

6.7.8 Lack of opacity This means gloss is absent in glaze surface. This defect occurs in enamels due to volatilization of the opacifying agents and of the fluorides. This is generally observed when length of time of firing required is more to obtain the desired texture.

6.8 Raw materials

Glass formers of the frit composition of this invention are silicon oxide (SiO_2) and boron oxide (B_2O_3). If percentage in frit is not proper then cover coat will not provide smooth, adherent or consistent coatings.

Flux It is essential to include sodium oxide (Na_2O) or potassium oxide (K_2O) to provide the necessary flux addition to the preferred frit composition. Either sodium or potassium oxides or mixtures of both may be used..

Calcium Oxide (CaO) is a flux material that is essential to the preferred frit composition. It is used to improve chemical stability.

Aluminum Oxide (Al_2O_3) is essential for best results, and serves two purposes.

- 1) First it is necessary to provide a wider firing range;
- 2) When the frit is applied as a slip, aluminum oxide produces a composition that is more easily maintained in suspension.

Zinc Oxide (ZnO) imparts properties to the frit that are similar to those provided by aluminum oxide in many respects, but it does not increase the refractoriness of the frit nearly so much as aluminum oxide.

Iron Oxide (Fe_3O_4) It has been found that black iron oxide (F6304) is the most essential addition to the frit composition . It promotes uniform adherence and smooth coatings. Also, it increases the ranges of time and temperature over which satisfactory coatings can be produced

Lithia (Li_2O_3) is a flux material that acts to lower the firing temperature of the resulting frit much farther than the additions of sodium and/or potassium oxide.

Barium oxide (BaO) is another flux material.. It may be used to partially replace the sodium oxide and/or potassium oxide..

Calcium fluoride (CaF_2) is also generally considered to be merely a flux, but it improves the texture of the resulting coat.

Zirconium oxide (ZrO_2) may be used to replace some of the silicon