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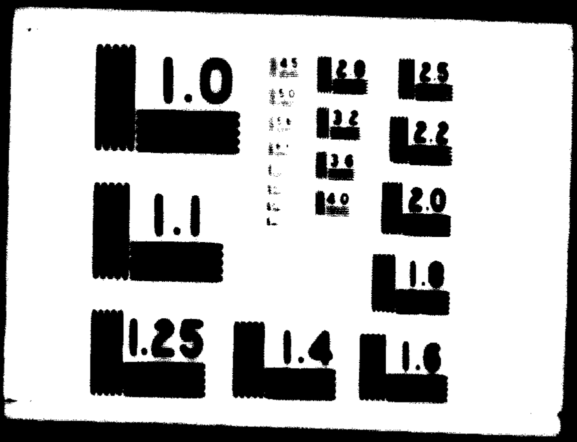

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SANITARY WARE FROM COMMON CLAYS[1]

by

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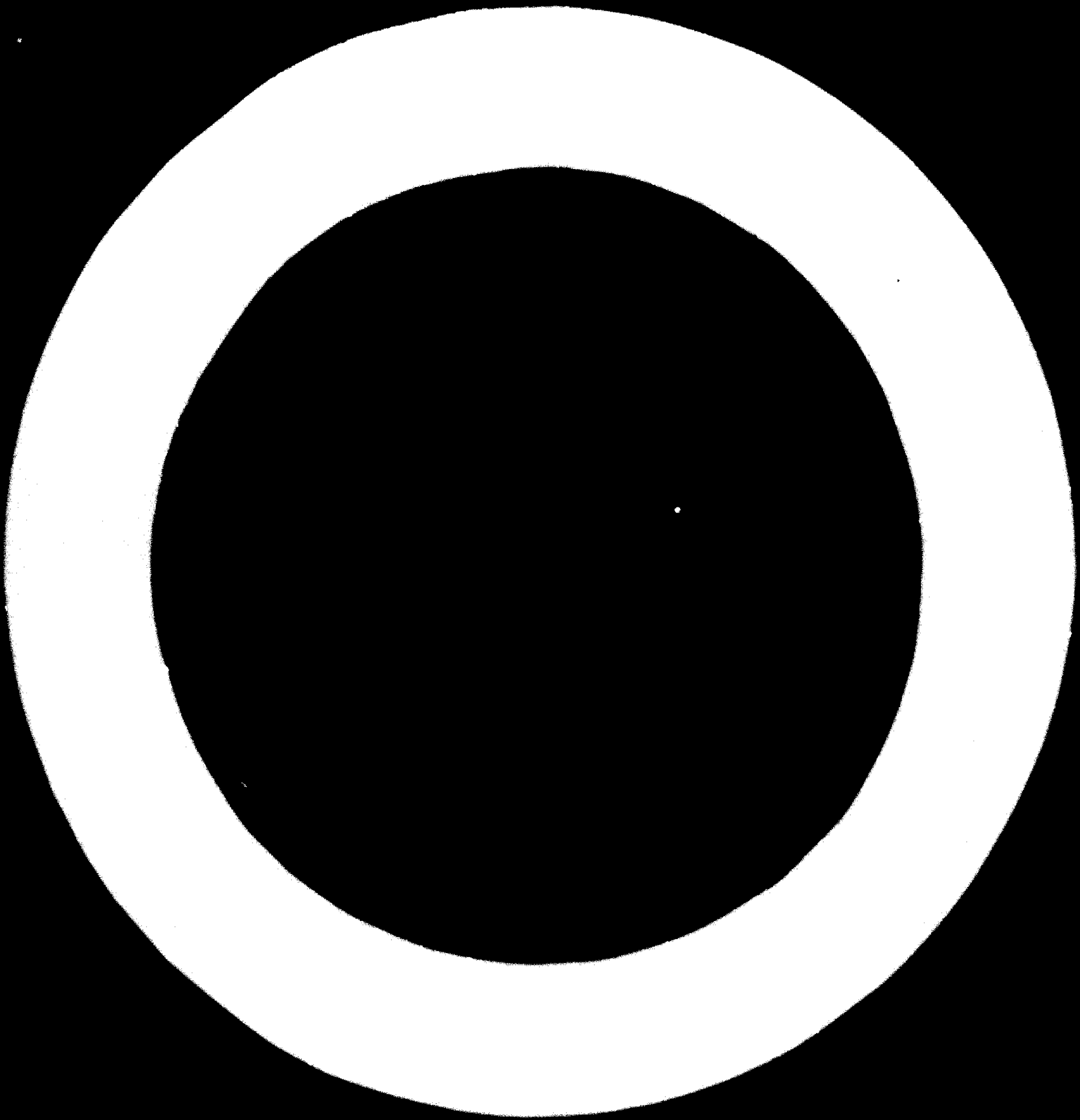


Contents

Contents (contd.)

ANNEX

Tables

Figures

PREFACE

This paper is written with the intention of helping ceramists in developing countries in solving problems related to the production of sanitary ware articles.

In the field of ceramics progress is being made at a high rate and this paper does not make any pretentions to have covered such points. It is intended to give the basic information to an engineer on the factory floor.

The paper does not cover drying, firing and mould making as such information is quite general and is easily available in text books on the subject, but such parts could be incorporated in subsequent editions.

It is hoped that this paper serves its purpose.

C. Castelli

Bergamo
Italy
1968

1. FOREWORD

The history of ceramics does not permit the fixing of a definite date for the start of this industry. Because of the diversity of the products it is difficult to ascertain which country has given this industry the greatest impetus. It is without doubt that the Chinese have done a great deal of work in this field and have obtained very good results. The Japanese, besides others, have also made enormous progress in this field.

The requirements of new and sophisticated ceramic articles call for new techniques for their production.

For a long period the manufacture of ceramic articles was practised as a cottage industry and the jealously guarded trade secrets were handed down from father to son, and the quality of the product depended only on the long attained experience of individuals.

Eventually the developments of science, resulting in analytical and mathematical scientific methods, and the quest of scientists to know the composition of the raw products and finished products, brought it a systematic approach and the manufacture and production of such articles was undertaken on a larger scale.

Chemical analysis, physical methods of testing and calculation techniques are of much help to ceramic engineers in gaining a better understanding of the complexities of this field but they do not lay down definite rules.

The technology of ceramics is a field where much has to be learnt and a great deal of knowledge is required; because of the diversity of the raw materials and the finished products this can only be attained by experience.

This information is not always to be easily found in one book and it is the purpose of this paper to bring together such information as is necessary for the production of sanitary ware, keeping in mind the everyday practices and experiences in such industries.

Just as sulphuric acid is the index for the industrialization in a country, so is the growth of the sanitary ware industry an index of the improvement of the living conditions in the country. Both developing as well as developed countries are facing the same difficulties with their increasing housing schemes tied up with the population explosion. Modern concepts require the installation of suitable sanitary equipment to enable man to live in hygienic conditions. Increasing demands of the community lead to the promotion of the Ceramic Industry.

Houses, public places, resorts, gardens, etc. have to be equipped with sanitary articles of one type or another. An important aspect of sanitary goods is the necessity for sewage and drainage systems. It is a fact that sanitary ware occupies an important place in the life of man, and it is necessary in all spheres of life to give him a comfortable and luxurious life. Thus, the Ceramic Sanitary Ware Industry has a great impetus for manufacturing, creating new products and improving their quality.

2. DESCRIPTION AND TYPES OF SANITARY WARE ARTICLES

Sanitary ware articles are classified into the following five groups:

a) Semi vitreous china articles
b) Vitreous china articles
c) Fire clay articles
d) Stone ware articles
e) Cast iron articles

Semi vitreous and vitreous china articles. These goups include water closets, wash basins, soap and sponge trays, kitchen sinks, plate racks, pedestals, shelves, shower plates, urinals, etc.

Fire clay sanitary ware articles. The following are included in this group - kitchen sinks, plate racks, basins, shower plates, bath tubs, Turkish closets, urinals.

Stone ware articles. sewage pipes.

Cast iron articles. These include bath tubs and basins.

2.1. Vitreous China is a body (ceramic composition) developed at the beginning of the century by the ceramists of the United States. This body was found suitable for sanitary ware articles and some years after, it was discovered that it could also be used for table ware manufacture. The term 'vitreous china' does not define an exact body distinguishable by physical and chemical characteristics. It is to be considered similar to the porcelain body.

In fact its hardness, white colour, vitrification, low porosity, ability to withstand mechenical stresses, and its resistance to corrosion, is such that it is commercially called porcelain.

In the beginning sanitary ware articles in vitreous china were biscuited with glaze and eventually were fired with a suitable glaze. Actually single firing gives quite satisfactory results and now there are only a few factories where two firings are carried out.

The composition of vitreous china body for sanitary ware articles fired at Seger Cone 10 is given below:

Ball Clay	26%	China Clay	26%
Nepheline Syenite	22%	Quartz	26%

In order to make proper use of available raw material and at the same time to reduce the firing temperature from Seger Cone 10 to Seger Cone 9 or 8 or 7, variations of the above composition can be and generally are undertaken. As is well known the reduction of the firing temperature is an important factor for economic production, but the lowering of this firing temperature has to be introduced with care, so that the properties of the body detailed below do not undergo a change with the drop in firing temperature.

Porosity (water absorption)	from 0.2 to 1%
Compressive strength	from 4000 to 7000 kg/sq.cm
Colour	Whitish
Hardness (Mohs scale)	from 7 to 8 kg/sq.cm
Thermal coefficient of expansion	from 2.8 to 4 x 10^{-6}

With the discovery of vitreous china the manufacturers of sanitary ware abandoned the old hand moulding methods for the new casting system which presented many advantages, insured a better quality and a higher production rate.

The glaze used for sanitary ware articles in vitreous china subjected to double firing is general to the lead calcium and alkalis type. The composition of such a glaze is as follows:

Feldspar	17.9%	White Lead Oxide	6.4%
Red Lead Oxide	51.3%	Fired Kaolin	16.4%
Clay	4.2%	Quartz	3.8%

When single firing was applied to sanitary ware the glaze composition was changed considerably. To suit its thermal expansion to the new type of glaze applied the body composition also had to be changed. In glazes for single firing lead oxides were replaced by Calcium Carbonate, the Feldspar percentage in the mixture and the Quartz content had to be proportionally increased.

The recent composition of a vitreous china body for Seger Cone 8½ is as follows:

Ball Clays	20.5%	China Clays	27.0%
Quartz	23.5%	Feldspars	29.0%

A suitable glaze for the above composition is as follows:

Quartz	31.0%	Feldspar	32.5%
China Clay	7.0%	Zinc Oxide	4.0%
Zirconium Silicate	8.0%	Calcium Carbonate	14.5%
Tin Oxide	1.5%	Magnesium Carbonate	1.5%

2.2. Fire Clay Bodies. It is difficult to ascertain the origin of this type of body which has been used for centuries in the manufacture of different types of articles and has been applied to a great extent in the manufacture of sanitary ware articles produced by hand moulding methods. At present large sized fire clay sanitary ware articles are mainly cast.

Fire clay body composition include clays which after firing present a reddish colour and have as a component also grog or grit (fire clay). This plays an important role in the mixture and permits to produce articles with greater wall thickness. The presence of Feldspar gives better resistance to firing, a higher rigidity and lowers the porosity. The introduction of Feldspar has compelled the ceramist to make a restudy of the firing clay body with respect to the Engobe and Glaze accord. After firing, the fire clay body acquires a reddish colour and it is necessary to coat it with a covering mass to give it the appearance of white ware articles. Such a covering mass is called an Engobe, over which a glaze is applied. Preparation of fire clay composition is the most difficult of all the types of bodies existing and it is only the modern manufacturing techniques that give fire clay sanitary ware articles their good looks and make their manufacture economical.

The composition of fire clay body is given below together with a suitable Engobe and Glaze:

Body Composition		Engobe Composition	
Clays	40.0%	Quartz	26.0%
Quartz	5.0%	Kaolin	14.0%
Feldspar	3.0%	Fired Kaolin	20.0%
Grog (Chamotte)	52.0%	Feldspar	40.0%

Glaze Composition

Quartz	23.0%
Calcium Carbonate	16.0%
Zinc Oxide	13.0%
Kaolin	3.0%
Feldspar	45.0%

Fire clay used for such a purpose has to show the following characteristics:

a) In the raw state - good castability; reasonable strength in the dry state to enable the handling of heavy and large articles.

b) In the fired state - should fire straight and not warp; have high brilliancy of glaze; its surface smoothness should be high; its appearance should be comparable to white ware.

2.3 Stone Ware Body. These bodies are the basics for the production of sewage pipes. The stone ware body is composed of clays, quarts, and grog (or chamotte). Pipes are produced by extrusion using special mixing and extruding equipment. The following different types of glazing procedures are used: Salt Glazing; Slip Coat Salt Glazing; Dipped Glazing.

Salt Glazing. This is done when the body has been heated to the highest necessary temperature. Sodium Chloride is sprinkled on to the fire and the salt vapourises. These vapours react with the body to give a glaze type silicate.

Slip Coat Salt Glazing. The glaze composition also containing salt is sprayed on to the body in the raw state which is then fired.

Dipped Glazing. The article to be glazed is simply dipped in a glaze suspension.

One of the most important branches in clay working is stone ware production. Although sanitary ware and stone ware pipes (sewage pipes) belong to the same field they are not produced in the same factories. The two branches - sanitary ware articles, and sewage pipes, are considered as two different types of products and therefore are manufactured in two different plants.

2.4 **Enamelled, Cast Iron, and Steel Sanitary Products.** The skeleton of baths and basins are generally produced from steel or cast iron; a glaze called enamel is applied and then fired in special kilns. Here only the enamel is of interest as it is basically a ceramic and has reactions similar to those of ceramic glazes. The only difference lies in the method of production.

3. INTRODUCTION TO CERAMIC TECHNOLOGY

At this point the author would like to emphasise some aspects, and eliminate prejudices of raw material usage for the production of ceramic goods. In the countries where suitable materials are not available one should encourage the use of any other material for the production of ceramic goods.

Ceramics cover a wide range of products and one has to give equal attention to a number of useful products using suitable technologies for their production. It is necessary to classify them according to standard specifications, working and health regulations in existence in individual countries. It is an acknowledged fact that the most simple methods of production are the most economical. One should therefore strive to keep the shapes and forms of the articles as simple as possible, to adopt simple and effective flow sheets and the usage of simple equipment. This enables the ceramic expert to transfer the skills to the layman at the plant in a short time. This should be borne in mind especially in countries where limited skilled labour is available.

The field of ceramics is not an easy one. This is quite obvious from the large number of defects that show up in finished ceramic goods. Raw materials used in the manufacture of ceramic articles often contain salts and these influence the ceramic reactions to a great extent and one's attention has constantly to be drawn to them. A thorough examination, physical as well as chemical is therefore absolutely essential, and a well equipped laboratory is therefore a necessity. To get the best finished product one has to pay proper attention to the selection of raw materials, and in the absence of suitable materials a suitable available material should be used.

The economics of such a venture is an important factor in the planning and lay-out of such an industry. The availability of national raw materials such as Kaolin, Quartz, Feldspar, etc. does not mean that the greater part of the production cost is covered, as these constitute only about 10 - 15% of the total cost. The most expensive raw materials are the components that make up the glaze Engobes, colours and decorations. In some countries these are not available and have to be imported at high prices. In these cases proper research has to be done to find suitable substitutes at competitive prices. The import of such raw materials which are absolutely essential will have to be done on a planned basis. It is not economical to have large stocks of such materials as kaolin, oxides, opacifiers and glaze materials. Such raw materials are produced by a large number of firms. Comparison of prices is necessary as each firm has a varied price range.

In a country where a new ceramic industry is being set up the products are subject to considerable criticism. They are compared with imported products which are well designed, have a high quality, and good finish, and a pleasant colour. In this case the ceramic technologist and the designer will have to introduce an article which not only meets the demands and tastes of the modern market, but at the same time introduces new trends. An important factor for the sale of sanitary ware is colour. It is therefore necessary to be able to produce good colours and especially a white colour. This is not an easy job when the necessary raw materials are not available. In this case a suitable combination of colours or masking by decoration could be a solution.

In the production of ceramic goods it is not easy to point out the cause of a definite defect as there are so many factors which combine to produce the reaction. When defects appear they have to be analysed and by a process of elimination the most probable influencing factor has to be traced. The most troublesome defects are the ones which appear and disappear without one being able to ascertain their causes. In this respect ceramics are still an empirical science requiring constant control and expert attention during their production.

4. SANITARY WARE TECHNOLOGY

4.1. Raw materials

4.1.1. Clays. The term clay materials includes all hydro-silicates of alumina whose chemical formula conforms to the one given below:

$$n\,Al_2O_3 \cdot m\,SiO_2 \cdot y\,H_2O$$

They are available in nature in large quantities and constitute a major proportion of the earth's crust. Clay materials are so numerous that it is difficult to classify them systematically. With the help of molecular structural analysis considerable progress has been made during the past 30 years. With the aid of new discoveries between the relation of structure and characteristics of clay minerals it was possible to solve many problems which chemical analysis alone could not achieve.

Clays which are found along with the rock from which they are derived (mother rock) are called residual clays; these are generally found mixed with fragments of the mother rock, and therefore a washing is necessary, to separate them from such fragments. Such clays are called Primary Clays. Secondary clays are to be found as sediments or deposits in lakes and swamps; they are produced by the action of errosive forces on the rocks and are transferred by river or rain water. These waters on entering lakes or swamps become slow and sedimentation takes place. During transportation the clay particles undergo considerable chemical and physical alteration.

The following table, suggested by W. Stout, gives a picture of the process of Clays Formation:

Table 1

Classification of Clays as to Origin

Residual matter	No movement during formation	Products of ordinary weathering	From crystalline rocks	Impure Residual Clay Primary Kaolin
			From sedimentary rocks	Impure Residual Clay Kaolinitic Clay
		Same as above with additional chemical action	From crystalline rocks	Bauxite
			From sedimentary rocks	Bauxite - Diaspore
	Deposited in still water, little or no current action, seas, lakes, bogs etc.		Products of ordinary weathering Same as above with additional intensive chemical action	Argillaceous shale Argillaceous silt Sedimentary Kaolin Ball Clay Some bauxites Coal formation clay Diaspore
Transport matter	Deposited by slowly moving waters, streams estuaries, etc.		Products of ordinary grinding with some weathering	Siliceous shale Siliceous silt
	Deposited by glacial action		Products of abrasion with slight weathering	Glacial Clay or till
	Deposited by winds		Products of abrasion with slight weathering	Loess

Table 2

The clay minerals

KAOLINITE GROUP

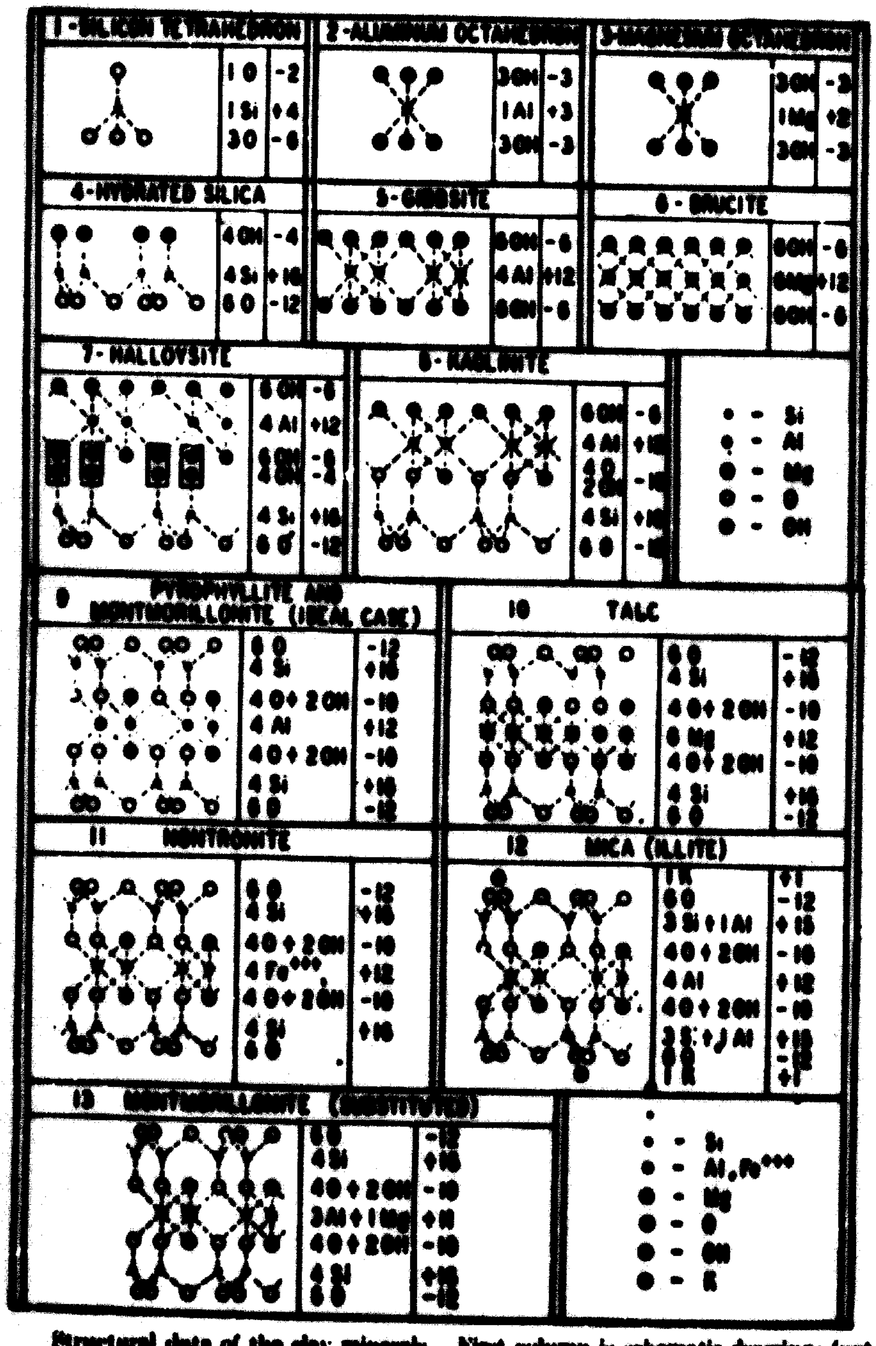
Kaolinite	$Al_2O_3 \quad 2SiO_2 \quad 2H_2O$
Dickite	$Al_2O_3 \quad 2SiO_2 \quad 2H_2O$
Nacrite	$Al_2O_3 \quad 2SiO_2 \quad 2H_2O$
Anauxite	$Al_{2-n} (Si_{2+n}O_5) (OH)_4$
Endellite	$Al_2 (Si_2O_5) (OH)_4 \; 2H_2O$
Halloysite	$Al_2 (Si_2O_5) (OH)_4$
Allophane	Amorphous

MONTMORILLONITE GROUP

Pyrophillite	$Al_2Si_4O_{IO} (OH)_2$
Talc	$Mg_3Si_4O_{IO} (OH)_2$
Montmorillonite	$(Al_{I.67}Mg_{0.33}) Si_4O_{IO} (OH)_2$ $Na_{0.33}$
Beidellite	$Al_{2.17} (Al_{0.83} Si_{3.17}) O_{IO} (OH)_2$ $Na_{0.33}$
Nontronite	$(Fe_{2.00}) Al_{0.33} Si_{3.62}) O_{IO} (OH)_2$ $Na_{0.33}$
Saponite	$Mg_3 (Al_{0.33} Si_{3.62}) O_{IO} (OH)_2$ $Na_{0.33}$
Hectorite	$(Mg_{2.67} Li_{0.33}) Si_4O_{IO} (F,OH)_2$ $Na_{0.33}$
Sauconite	$Zn_3 (Al_{0.33} Si_{3.67}) O_{IO} (OH)_2$

Figure 1

Refractory raw materials



Structural data of the clay minerals. First column is schematic drawings (not to scale) of the atoms in a unit cell projected into one plane. Second column gives number and type of atoms in each lattice plane and third column gives the corresponding valence charges. Where (+) and (−) charges are equal, lattice is neutral; where unequal, the charge is equal to the algebraic difference. (*From E. A. Hauser, J. Am. Ceram. Soc.*)

To a ceramic technologist the following groups are important and are most suitable for his purposes: Kaolinite, Halloysite, Montmorillonite and Illite.

1	**Kaolinite**	is a constituent of ceramic and refractory clays. China clays, ball clays, and fire clays belong to this group.
2	**Dickite and Nackrite**	are of hydrothermal origin and resemble Kaolinite in all their characteristics but differ only from it in the disposition of their layers.
3	**Fire Clays**	clays which fuse above 1600°C (2900°F) and are not white burning are called Fire Clays.
4	**Halloysite**	clays belonging to this group are fine grained white in colour and soapy. The amount of water obtained in halloysites is twice that of Kaolinite. By heating Halloysite, Metahalloysite is produced which cannot be hydrated. Both Halloysite and Metahalloysite are found in many ceramic clays. Owing to the fineness they act as amorphous bodies.
5	**Anauxites**	could be considered as mixtures of Kaolinite and Amorphous silica. They contain large amounts of silica.
6	**Allophanes**	the general opinion is that allophanes are natural mixtures of Kaolinic clays and colloidal silica with hydrates of alumina. They are Amorphous or without molecular structure.
7	**Montmorillonite**	its particles are mostly smaller than a micron in diameter and many of them lesser than 0.1 micron in diameter. Bentonite belongs to the montmorillonite group and is sometimes used to increase the plasticity of ceramic body mixes. This particular use of bentonite is justified by its property of gel formation.
8	**Illites**	are found in brick clays; it is believed that their formation takes place under sea-water conditions. Muscovite and Biotite belong to this group. Vermiculite is an altered illite. It is important for insulating purposes.

Both Kaolin and Ball Clay belong to the Kaolinite group and are the most frequently used clays for the production of ceramic articles.

4.1.1.1. Kaolin and China Clays. Kaoline and china clays could be of primary or sedimentary origin, and are characterised by the presence of impurities. Kaolins of primary origin are very often mixed with fragments of the mother rock which are removed by refining. Kaolins are produced by the action of one or more of the following effects alone or together on feldspatic rocks.

1. Dis-segregation under atmospheric and humid conditions.
2. Action of waters containing carbon dioxide.
3. By the action of lava from volcanoes.

Dis-segregation could be explained as a washing out action of the alkalis, (K_2O or Na_2O) and the hydration of the material as shown in the following examples:

$$\begin{array}{lll} \text{Potassium Feldspar} & K_2O\ .\ Al_2O_3\ .\ 6\ SiO_2 & \\ & \text{less}\ \ K_2O & 4\ SiO_2 + 2H_2O \\ \hline & & Al_2O_3\ .\ 2\ SiO_2\ .\ 2H_2O \end{array}$$

A pure Kaolin has a melting point of 1785°C (3245°F) but the presence of small quantities of impurities could reduce this fusion temperature slightly. Kaolin has the following chemical composition:

Silica SiO_2	from 45 to 50%
Alumina Al_2O_3	from 33 to 39%
Titanium oxide TiO_2	traces to 1%
Ferric Oxide Fe_2O_3	from 0.5 to 1%
Calcium oxide CaO	from 0.1 to 0.5%
Magnesium oxide MgO	from 0.1 to 0.5%
Alkalis K_2O - Na_2O	from 0.5 to 2.0%
Combined water	from 10.0 to 13.0%

The introduction of Kaolin in the raw mix formula of ceramics is essential as it introduces Kaolinite which under firing conditions leads to the formation of Mullite. The formation of Mullite is considered as the last stage of the ceramic reactions and is responsible for giving the finished fire good its maximum strength. Under the heating conditions that exist in furnaces Kaolin undergoes various changes, before reaching the final stage at which the physical properties of the clay are radically transformed.

At a drying temperature of 100°C (212°F) only part of the water is removed and a considerable amount of it still remains adherent to the particles. As the temperature is raised to 450°C (840°F) the chemically combined water (the OH groups) are driven off from the Kaolinite molecule, but some amount of water still remains up till a temperature of 700 - 800°C (1290°F - 1470°F) is reached. At about 980°C (1800°F) Alumina crystallizes into the γ - from and the direct formation of Mullite, takes place. When the ratio of Alumina to Silica is 1:2 the heat effect reaches its maximum efficiency. After the formation of the γ- Alumina, the same starts dissolving in the glass and the Mullite crystallizes out.

The first crystals of Mullite are very small and difficult to see under a microscope, and for this reason an X-ray system is used. At higher temperatures, however, it is possible to detect the Mullite crystals with the help of a microscope as they have now grown in size. Kaolin is introduced into the ceramic composition also because of its white burning colour, its plasticity - although low, its good castability when in a water system and its rheological properties.

4.1.1.2. **Ball Clays.** Ball clays are finely sub-divided, and contain a good amount of lignite or organic matters, present a high plasticity or workability, have a fusion point around 1670°C (about 3050°F) and contain various impurities.

They are not white after firing except the special clays which contain such a high amount of organic matter that, under firing conditions, reducing reactions favour the formation of white burning compounds. Ball Clays are widely used in the Sanitary Ware Industry because of their ability to cast, exchange ions, to endow plasticity to the raw mixture and together with Kaolins form the mullite.

Ball clays have very fine particles and have the following characteristics:

a) absence of mother rock fragments

b) presence of impurities like organic matter, carbonates, sulphates

c) metallic oxides and hydrates - the hydrates impart the different colours to the clays

d) high plasticity.

4.1.2. Characteristics of Clays. Clays differ among themselves in the following physical properties:

a) Particle size
b) Ability to exchange bases
c) Reactions of clay minerals with some organic cations
d) Plasticity
e) Zeta Potenzial
f) Influence of soluble salts
g) Castability
h) Viscosity and pH value
i) Tixotropy
j) Drying
k) Firing

These properties, although influenced by exterior factors and phenomena, find their source in the reticular structure of the clays.

a) Particle size. Clays differ from one another in their particle size. The particle size distribution depends upon the size of the Kaolinic particles, upon the size of the particles coming from the mother rock as well as upon the size of the particles of foreign materials, the clay transport and sedimentation. The size of the clay particles is generally less than a micron in diameter. The knowledge of the particle size is important in determining the surface of the mass reactions and has influence on the plasticity and fluidity of clay-water suspension.

b) Ability to exchange basis. Microscopic examination shows that the colloidal particles are crystallized and have a negative charge of electrostatic nature. The charge is due to absorption of cations as well as to a breakdown of the molecular reticulum, leaving unsaturated valencies. When a clay is suspended in water its particles are surrounded and covered by a film of water. The Hydroxyl ions are fixed firmly to the particles. Of the different ions present in a water suspension of clays, a part is inside the water film and the rest are in the water outside the particles. Under certain conditions the cations change their place; Hydrogen ions can be more easily replaced by other ions. The nature of the cations contained in the system, influences the thickness of the ionic sphere around the particles. When the cation is more hydrated the thickness is greater.

Hoffmeister gives the following series showing the increasing order of hydration:

Cations: H, Al, Ba, Sr, Ca, Mg, NH_4, Na, Li
Anions: SO_4, F, NO_3, Cl, Br, I, CNS, OH

The ion dimension also has influence. In fact the Potassium ion is too big to be easily replaced by another ion.

When the absorbed ion stands too high in the Hoffmeister series, the clay could be completely dispersed in the water.

Clays saturated with H^+ and Ca^{++} ions, do not dissociate completely in water and with the same amount of water they give a higher viscosity but are generally more plastic. The viscosity of a clay is a rough indication of its ability to exchange ions.

There are a number of methods for determining the ion exchange ability of clays. These are as follows:

i. Saturation of the clay with NH_4 ions and titration.
ii. By means of a spectroscopic analysis.
iii. By determination of the pH-value of 100 grammes of clay to which increasing quantities of electrolytes are added.
iv. By determination of the viscosity of a water suspension and plotting a viscosity curve in relation to increasing quantities of electrolytes.
v. The determination of the electrical conductivity.

c) <u>Reactions of clay minerals with some organic cations</u>.

Clays react with some amines to give a floculated mass. This is due to the modification of the surface of the clay particles produced by absorption of large organic cations. This effect, especially with the Montmorillonite, permits the manufacture of porous articles.

d) <u>Plasticity</u>. It would be useful to have some method of determining the plasticity of the ceramic clays quickly and exactly. Little is known about the causes and the factors which influence the plasticity. Plasticity can be defined as the property of a material to maintain the shape given to it when the shaping forces are removed. According to H. A. Seger plasticity is "the property of a solid to take up and retain liquid in its pores. The resulting mass can be pressed and shaped to assume any form which it retains after the pressure is released and any liquids which it contains are removed".

One could say that the workability of a solid, has to be related to the treatment which the material has to undergo during the process of manufacture. Not all plastic solids are plastic enough for all manufacturing processes.

A material is considered elastic when it offers resistance to forces which tend to deform it on removing these deforming forces the material assumes its original shape. Clays are considered elasto-plastic solids which means that when force is applied they obey the laws of plasticity up to a point where these forces are lower than certain critical values. When these critical values are surpassed they deform.

Many factors related with the structure of clay need plasticity, in particular the size, shape and structure of the particles, the amount of foreign matters, colloidal particles present, and specifically the ratio of clay to water. Plasticity, is an important property which can be easily repeated and checked. In order to maintain the workability of clays and consequently the properties of the body mixture within certain required characteristics the property of plasticity is used as a controlling characteristic. Its determination is useful also when the apparatus used for the determination is not a standard one. What is important is that the results should be capable of reproduction, and desired standards although not absolute should be developed for this particular plastimeter.

e) **Zeta Potential**. A clay particle in water is covered by a film of negative charges made of hydroxyl ions and this is further surrounded by a cloud of positive charges (cations) which are in the surrounding water and could diffuse into the liquid film. This cloud of cations forms the ionic atmosphere. The Zeta Potential can be calculated with the help of the Helmholts equation:

$$\zeta = \frac{4 \Pi e d}{D}$$

e = Electric charge
d = Thickness of the double layer
D = Dielectric constant of the liquid

The Zeta potential enables one to determine the stability of a suspension.

When the forces of molecular attraction are greater than the forces of repulsion the suspension is not stable and floculation takes place; on the other hand when the forces of repulsion are greater than those of attraction the suspension is stable and is defloculated or peptized.

f) Soluble Salts. Clays generally contain a certain amount of salts soluble in water and when a suspension of clays is made in water the salt dissolves. It is possible to modify the characteristics of the liquid phase of the suspension.

The following examples illustrate such a modification: The addition of a strong base like Sodium Silicate to a water suspension; if the liquid contains a weak acid we have the following equation:

$$\underset{\text{Sodium Silicate}}{Na_2SiO_3 + 2\,(\text{Clay OH-H})} = \underset{\text{Silicic Acid}}{2\,(\text{OH-Na}) + H_2SiO_3}$$

From the above equation we observe that the hydrogen ions of the clay are replaced by sodium ions and there is a formation of acid. If we add more sodium silicate the sodium ions hydrate and give sodium hydroxide which supplies the liquid with hydroxyl ions causing a defloculation. If a neutral salt or a strong base is present an acid results. The equation is as follows:

$$\text{Clay OH-H} + NaCl = \text{Clay OH - Na} + HCl$$

and similarly

$$\text{Clay OH-H} + NH_4Cl = \text{Clay OH-}NH_4 + HCl$$

In these cases pH-value decreases and the clay floculates. When sulphates are present in the clay it is not possible to convert them into insoluble salts by the additions of Sodium Silicates or Carbonate.

$$(\text{Clay OH})_2 - Ca + H_2SO_4 + Na_2SiO_3 = 2(\text{Clay OH-Na}) + CaSiO_3 + Na_2SO_4 + H_2SiO_3$$

In this case before adding the electrolyte it is necessary to add Barium Hydroxide or better Barium Carbonate. The reactions are as follows:

$$(\text{Clay OH-})_2Ca + H_2SO_4 - Ba(OH)_2 + Na_2SiO_3 = 2(\text{Clay OH-Na}) + BaSO_4 + CaSiO_3 + 2HO_2$$

If the additions of Sodium Carbonate and Silicate permit the precipitation of the Ca^{++} and Ba^{++} ions, the Sodium Hydroxide does not produce the same effect, because (Clay OH)$_2$ Ca does not decompose. In fact in the presence of Barium Hydroxide we have the following reactions:

$$(\text{Clay OH})_2\,\text{Ca} + H_2SO_4 + \text{Ba}(OH)_2 + 2\,\text{NaOH} =$$

$$= \underline{(\text{Clay OH})}_2\,\text{Ca} + BaSO_4 + 2\,\underline{\text{NaOH}} + 2\,H_2O$$

If Barium Carbonate is added the electrolytes Sodium Silicate as well as Sodium hydrate permit the decomposition of the Clay:

$$(\text{Clay OH})_2\,\text{Ca} + H_2SO_4 + BaCO_3 + NaSiO_3 =$$

$$= 2(\text{Clay OH} - \text{Na}) + BaSO_4 + CaSiO_3 + H_2CO_3$$

and

$$(\text{Clay OH})_2\,\text{Ca} + H_2SO_4 + BaCO_3 + 2\,\text{NaOH} =$$

$$= 2(\text{Clay OH} - \text{Na}) + BaSO_4 + CaCO_3 + 2\,H_2O$$

Sodium Silicate is the best **defloculant** in presence of Calcium.

As a result of the reaction, Sodium Carbonate gives Calcium Carbonate which is slightly soluble in water. When the Mg^{++} ions are present as soluble salts, both Sodium Silicate and Sodium Carbonate permit the complete precipitation of Magnesiums.

The production of a good casting slip depends to a great extent on the choice of the right electrolyte with respect to the soluble salts present in the raw material. According to G. Bieler the following points are indispensable to produce a good casting slip:

i. The defloculating electrolyte to be added should be a salt of monovalent cation which hydrates strongly i.e. Lithium and Sodim.

ii. The electrolyte has to give hydroxyl ions by ionisation as well as by hydrolises.

iii. The cations which have a greater tendency to be absorbed have to be eliminated as insoluble salts.

iv. Anions having less tendency to absorption have also to be elminated as insoluble salts.

To be able to take proper action one has to ascertain which soluble salts present in the raw materials interfere with the **electrolytic effect.** This can be easily realised by simple chemical analysis as follows:

100 grams raw material are boiled in distilled water, filtered appropriately so that the colloidal particles of clay do not escape into the filtrate. The salts present are chemically analysed. On the other hand quantities present are determined. At this point it is not out of place to give attention to the use of suitable waters. Often water contains soluble salts. A careful and thorough analyses of the water used will have to be made.

Feldspars and Quartz also contain salts and they have to be tested and selected to ensure good casting.

Often castability tests are done by adding an electrolyte, without taking into account which salts are present in the raw materials. Independent of the castability it is always useful to determine the salts present as it is only then possible to add the proper electrolyte.

g) Castability. Not only deflocculating conditions affect the castability. Other factors that play a role and influence the slip properties are:

Particle size distribution, the ratio of plastic clays to hard materials, the presence of organic matter.

By modifying these properties it is possible to obtain a better castability. It is not always advisable to maintain the maximum density or to use a minimum of electrolyte and only one electrolyte. Tests have to be done to establish the best castability in relation to electrolytes of different types which suit the chemical reactions mentioned above in order to decompose the clay completely.

The layer formation tests conducted in a standard mould will show that a high amount of fine particles speed up formation and the rate of formation is proportional to the amount of fine particles present but drying is slow and this causes shrinkage. Temperature and the humidity of the mould influence such tests and therefore if the results are to be used for comparison purposes the conditions will have to be the same. Other factors affecting the castability are the preparation system used for the slip. The blunging system does not alter the particle size of the clay. On the other hand a ball mill preparation tends to increase the fineness of the particles and consequently the casting properties are affected. A reaction between ions and the gypsum mould and those of the slip could also interfere with the casting and favour fluculation.

Such a theory is based on the fact that calcium sulphate is soluble in water to a slight extent. This does not take place in reality, as the absorption of water by the mould is only a physical phenomena.

h) pH-Value and Viscosity. The pH-value gives the acidity or basicity of a solution or suspension. The isoelectric point is that value of pH at which clays are equally dissociated into cations and anions without the addition of electrolytes. A water suspension of clay should theoretically have a pH-value of 7 as the charge of the particles is zero. In practice the suspension is acid the pH being 3.5. An addition of sodium oxide increases the pH-value as the hydrogen ions are replaced by sodium ions. When the base exchangability is saturated an extra addition of sodium hydroxide makes the suspension alkaline, the pH-value increases rapidly and the viscosity drops. This lowering in viscosity is due to the setting free of water around the particles.

i) Viscosity is resistance to flow exhibited by an article resulting from the combined facts of coalition and adhesion. Clays can be considered as viscoelastic fluids because they exhibit elastic recovery from deformation which increases during flow. Viscosity, thixotropy and plasticity are effects of shear force. Water suspension of clays are not real fluids i.e. the flow is not proportional to the applied force. An apparent viscosity at a fixed temperature is characterised by an elastic limit without yield value or yield point. The viscosity is important to determine the rate of flow, most convenient for use in the casting of sanitary ware articles. It is essential to know the viscosity curve of the various clay components of the slip as well as the viscosity curve of the slip itself. A low viscosity indicates a high deflocculation point. At the saturation point the drop in the viscosity curve presents a means of determining the exchange capacity of a clay.

j) Thixotropy is the property of certain colloidal gels to liquify when agitated and to return to the gel state when at rest. According to Norton Thixotropy is that property of a body which causes a decrease in shearing stress with time, at a constant rate of shear. When a water suspension of clays is agitated water is displaced, the orientation is disrupted and a Sol is formed with the release of water. When in a colloidal system the dispersed phase is solid (clay) and the dispersing medium is liquid (water) a suspension is formed with a tendency to form colloidal solution. Colloidal solutions are called "Sols" which when coagulated become gels. When the dispersion medium used is water the colloid is called a hydro-sol and when coagulated hydrogel. A coagulation of a Sol is done by addition of an electrolyte. By agitation gels can be reconverted into sols. Thixotropy is a property which is only possible when the dispersed particles are present in a very fine divided state. The particles should retain a large amount of water and should not be spherical.

Under shear stresses the particles crowd in layers which slide freely over one another. With increasing shear stresses, the distance between the layers increases and as a result the viscosity is lowered. During rest such layers disappear and the particles assume a position suitable to the clay charge. This phenomena is called Thixotropy. The time required for gel formation depends upon the ratio between the ions of electrolytes in solution with ions absorbed. The Thixotropy increases with the increase of acidity i.e. the pH-value decreases. In order to increase the Thixotropic time it is necessary to increase the amount of electrolyte in relation to the viscosity curve of the clays. The phenomena of Thixotropy is important in sanitary ware casting because the slip remains in the mould for a certain time until the desired thickness is reached. The longer the time the clay suspension remains in the Sol state in the mould the quicker it thickens. In the case of vitreous bodies the surface is kept clean and uniform, due to drainage. During the period the slip remains in the mould it could be converted to the gel state and at this moment water does not pass through the particles and is not absorbed by the capillaries in the plaster. When this happens the formed piece remains soft, drainage is no longer possible and it is difficult to remove the piece from the mould.

4.2. The Hard Materials

4.2.1. Quartz. Quarts or Silica is very widely spread in nature and is found in different forms, e.g. quarts-sand-crystals.

There are also many crystalline forms of the quartz itself and the presence of foreign materials in the quartz contributes to variations in its physical characteristics. It is therefore necessary for the **Ceramist** to know the phenomena which affects the quality of the products. Silica (SiO_2) is found in nature in the following forms:

Name	**Crystal System**	**Spec. Gravity**	**Fusion Point**	**Refract. Index**
Quartz	Hexagonal	2.65	1600°C(2912°F)	1,553
Trydimite	Rhombic	2.31	1670°C(3038°F)	1,473
Cristobalite	Pseudo Regular	2.31	1710°C(3110°F)	1,487
Amorphous	Amorphous	2,21	- -	1,460

The most common form is Quartz. It is crystalline and very brilliant in appearance.

Trydimite has often a needle-like and sometimes triangular form. Cristobalite is found as small crystals which are difficult to distinguish from one another.

Eight forms of the SiO_2 are known:

1. α Quartz
2. β Quartz
3. α Trydimite
4. β Trydimite
5. γ Trydimite
6. α Cristobalite
7. β Cristobalite
8. Amorphous Silica

These forms of silica change from one to the other. The transformation depends on the temperature and follows the Oswald Law.

The following forms are to be found:

α Quartz until 575°C (1067°F)
β Quartz from 575°C (1067°F) to 870°C (1598°F)
α Trydimite from 0°C (32°F) to 117°C (242°F)
β Trydimite from 117°C (242°F) to 163°C (326°F)
γ Trydimite from 870°C (1598°F) to 1470°C (2678°F)
α Cristobalite up to 265°C (509°F)
β Cristobalite from 1470°C (2678°F) to 1655°C (3011°F)

The above mentioned forms are influenced by the presence of catalysts like Barium Carbonate, Ferric Oxide, etc.

Quartz is used as a component of practically all ceramic mixtures for the following reasons:

a) it reduces the shrinkage during firing

b) it reduces the plasticity of the mixture

c) it gives the mix a white colour

d) increases the thermal coefficient of expansion of porous products

e) decreases the thermal coefficient of expansion of vitrified products

f) in porous products a structure of Free Silica is formed around which clay substances and the fluxes build up

g) in vitrified products quartz is useful for the formation of mullite as well as silliminite and various other silicates formed with the fluxes.

The knowledge of the expansion curve of quartz is important; from these expansion curves one can see that the type most suitable for use is Trydimite because its expansion is more regular and its coefficient is lower.

A dangerous type of silica to be used is the Cristobalite form. Sudden changes in its expansion could cause breakages also the selection of a suitable glaze for use on a body containing Cristobalite would be difficult.

In ceramic products, fired at low temperature the quarts remains practically unaltered and produces an increase in volume of about 0.3% during heating, and undergoes contraction on cooling. In products fired at high temperature (vitrified) there is a formation of cristobalite with a considerable increase in volume.

If the cristobalite formed is in considerable amount the volume could increase up to 17% with consequent cracks and low resistance to thermal shocks.

Silica is introduced into the ceramic mixture finely ground and porosity as well as shrinkage depends upon the fineness of the silica. Geller, Evans and Creamer demonstrated that at different temperatures 1150°C - 1250°C - 1350°C (respectively at 2102°F - 2282°F - 2462°F) a ceramic mixture, composed of 50% clay, 35% silica, and 15% Feldspar, presented different porosity and shrinkage with the Quartz and Feldspar of fineness 10 and 75 microns. There is also an influence on the mechanical stress and thermal expansion.

	Fineness	Shrinkage %	Porosity %
Quartz	75 microns	6.4	18.5
	10 microns	10.0	2.8
Feldspar	75 microns	5.9	18.4
	10 microns	7.5	13.0

The finer the Quartz the lower is the porosity; the expansion of the body being directly connected with the continuity of the constituting particles, an increase of the porosity is related to a decrease in expansion.

4.2.2. The Feldspars. The fundamental reasons for using Feldspar in a ceramic body are connected with the melting points of the components. Clays, china clays and Quartz melt at high temperatures. To promote the necessary reactions, which give mechanical strength to the finished goods, feldspars or fluxes are indispensable. Besides acting as a flux the feldspar also lowers the firing temperature. This reduction in the firing temperature contributes to the economics of the process. By the introduction of Feldspar into the mix, combination of Silica with Alumina is facilitated and leads to formation of the required compounds. Vitreous feldspar is able to dissolve remarkable amounts of silica, alumina and mullite. Between 1300°C and 1400°C (2372°F and 2552°F) the vitreous mass produced is a solution of practically all the silica saturated mainly with crystallized mullite.

Feldspars are found in nature in different forms. The most common are:

Orthose $KAlSi_3O_8$	or $K_2O\ Al_2O_3\ 6\ SiO_2$
Sodium Orthose	$(K\text{-}Na)\ Al\ Si_3O_8$
Albite	$Na_2O.Al_2O_3.6\ SiO_2$
Anorthite	$CaO.Al_2O_3.2\ SiO_2$

The most commonly used and important types of Feldspar are Orthose, Albite, Anorthite. Feldspars being formed by solidification of magmas are rarely pure. They generally contain minerals. In ceramics the Feldspars mostly used are:

Potassic Feldspars: Pegmatities, aggregates of Potassium and Sodium Feldspar with Quartz.

Sodic Feldspars: Albite, frequently associated with magnesium and iron minerals.

4.2.2.1. Fusion of Feldspar. The mechanism of Feldspar fusion is important in order to know the possible and probable reactions with the other components constituting a ceramic body.

Some studies were undertaken on mixtures of Feldspars and to understand these studies it has to be kept in mind that the melting point of Potassium Orthose is at 1180°C (2156°F). Gradually the Feldspar dissolves to form Leucite and a liquid mass of great viscosity results. As the temperature increases the liquid also increases and at 1530°C (2786°F) the whole mixture is in the liquid state.

A mixture of Orthose plus Albite has an eutectic point in proportion of one third Orthose and two thirds Albite at a temperature of 1070°C (1958°F).

The above mixture is of interest to the Ceramic Technologist from the two following aspects:

1) When the quantity of Albite in a mixture is greater than 50% there is no formation of Leucite and the formation of the liquid phase does not take place.
2) When the Orthose present in the mixture is less than 50% there is practically no viscous fusion and during melting there is no plastic state.

More recently a ternary eutectic was studied with the composition: 25.02% Potassic Feldspar, 71.21% of Sodic Feldspar and 3.77% of Calcium Feldspar. It was found that this mixture gives the bodies a high degree of vitrification, a high mechanical strength and a good translucency at a relatively low temperature.

The facts enlisted below are of special interest:

a) The Potassium Feldspar viscosity diminishes slowly as the temperature increases.

b) The viscosity increases rapidly when increasing additions of silica are made.

c) The viscosity decreases on increasing the temperature; this decrease in viscosity is inversely proportional to the amount of silica added.

d) In figures plotted with temperatures as one axis and with the logarithm of viscosity as the other it is possible to see that the lines are not parallel for different proportions of silica.

e) Alumina added in small amounts decreases, whereas added in large amounts, increases the viscosity of Feldspar.

f) Additions of 2% Calcium Oxide lowers the viscosity to a greater extent than the same amount of Barium Oxide, Zinc Oxide, or Magnesium Oxide.

g) With Magnesium Oxide the viscosity decreases slowly on increasing the temperature.

h) At 1100°C (2012°F) the viscosity of Sodium Feldspar is greater than that of Potassium Feldspar. By raising the temperature the viscosity of Sodium Feldspar decreases rapidly, so that at 1200°C (1200°F) it is lower.

i) Additions of 2% of each of Calcium Oxide, Barium Oxide, Magnesium Oxide, or Zinc Oxide increases the viscosity of Sodium Feldspar at 1100°C possibly due to crystallisation.

j) Potassium glass is more viscous than sodium glass.

k) The rapid softening of Albite, which could cause a deformation of vitrified bodies is slackened to a great extent by the presence of silica.

4.2.3 Nepheline Syenite. Recently the use of Nepheline Syenite has become more wide. Nepheline Syenite is an igneous rock similar to granite. It contains a large percentage of mineral Nephelite Na_2O . Al_2O . $2SiO_2$ along with Potassium and Sodium Feldspar, Muscovite, Biotite, Magnetite, etc. Free Quartz can be present in small quantities or may be completely absent. Nepheline Syenites because of their relatively low content of Quartz and high content of Alumina give a mixture a wide range of vitrification and are in this respect different from Feldspars. They melt at lower temperatures; vitrification starts at Seger Cone 08 (945°C or 1733°F) and the pyroscopic resistance is approximately Seger Cone 6 (1190°C or 2174°F).

The eutectic for 75% Albite and 25% of Nepheline melts at 1050°C. In the vitreous state the co-efficient of thermal expansion of Nepheline Syenite is less than that of Feldspars. Nepheline Syenites are used with advantage in ceramic applications as they lower the firing temperature and at the same time give a wider range of vitrification; the tendency to deform decreases without affecting the mechanical strength.

4.3 Selection and pre-treatment of Raw Materials for the preparation of the body mix

The production of sanitary ware articles by using a casting process compels the ceramist to select proper raw materials to get the best casting slip and at the same time to maintain the characteristics for good castability, viscosity and also the suitable (approximate) litre weight.

The casting slip is a deflocculated suspension of clays and hard materials with a definite amount of water, electrolyte and additional salts. This suspension has to be poured into the mould at a definite and fixed (for the same slip) flow rate to fill up all the spaces in the mould. The casting slip should remain in a Sol state as long as possible. After removing from the mould the formed pieces should be rigid enough to stand by themselves and at the same time be plastic enough to allow repairs, finishing, and lastly it should be strong enough to be handled and transported within the factory.

Clays give the casting slip plasticity, rigidity, and strength in the dry and semi-dry state. Clays have a certain amount of impurities such as occluded minerals and oxides which affect the colour, viscosity and shrinkage as well as the firing cycle of the article. Apart from the laboratory analysis selection during mining and before transportation is indispensable. In nature clays are found as lumps or layers. Between these layers iron is frequently found, and quartz grains and Feldspar are often in a more or less intimate aggregation with clays. Excavation has therefore to be carefully done in order to avoid contamination. Washing is not always possible and economical for some types of clay but good selection in a mine is essential for good quality. Separation from the mother rock is generally done by means of refination, based on the difference in specific gravities of the clays and foreign matters. The clay is separated from organic and foreign matters by sieving. In the case of sanitary ware the separation is done by sieving a water suspension through 120 - 140 Mesh Sieve. Laboratory tests are conducted to indicate which material should be removed. When Quartz is present in such large amounts that it affects the fusion characteristics, porosity, and shrinkage or alters the workability of the clay it is separated by a sieve of appropriate fineness.

4.3.1 Hard Material Preparation - Crushing. Before use Feldspar and Quartz have to be ground finely in order to increase their reacting surface and to allow their suspension in water. The increase in the reacting surface implies a consistent, complete and easy participation in the formation of ceramic compounds.

The fineness of Feldspar and Quartz determines the quality of the final product. There is no fixed rule for the fineness of hard materials as a different fineness is appropriate for a different body mix and its covering glaze, and may not be suitable for another body.

Feldspar and Quartz supplied to the factory in rock form have to be crushed. This is generally done with Jaw Crushers, Gyratory or Cone Crushers.

Jaw Crusher: This is the most widely used machine. It consists of a cast iron or steel frame in which the driving mechanism and two jaws are housed. One jaw is stationary and the other is movable about a pivot joint. The movable jaw is actuated in a backward and forward direction so that the V-shaped hopper is broadened and narrowed alternately. Such movement allows the material to fall gradually downwards until the crushed particles pass through the exit opening. Modern jaw crushers have mechanisms which allow adjustments thus giving any desired particle size.

Gyratory Crusher: This is formed by two cones, an upper and a lower, a spider and a hopper, the lower cone also forms the base of the machine and supports the upper one to which it is bolted. The lower cone is fitted with a movable bottom which can be lifted for inspection. The suspended shaft which carries a crushing head hangs suspended from the spider at a pivoted point while the lower end of the shaft is made to gyrate with the help of an eccentric.

Cone Crusher: This is similar to the gyratory crusher. The crusher consists of a conical head gyrated by an eccentric which is driven by a gear and a counter shaft. The distributor and regulating plate is mounted on the top of the shaft with a vertical, adjustable feed spout. With the help of one of the described crushers the rocks are reduced in size and are passed on to the pulverizer where they are reduced to small crystals.

Pulverizers: Dry Pan Pulverizer consists of two heavy end frames between which a revolving pan is placed. A pair of heavy Mullers are mounted in the pan on the periphery and are placed parallel to each other. The pan bottom is fitted with a renewable grinding plate. Scrapers are placed in such a way so that the crushed material is carried to the screens. With primary crushing and regular feeding the grinding efficiency increases considerably. The crushed material is collected in the pan frame.

Hammer Mills: A horizontal shaft is fitted with pivoted hammers. In this type of mill crushing takes place by impact between the hammerheads and breaker plates. This type of grinding is efficient and rapid.

After the hard material has been reduced in size it is subjected to fine grinding and for such purposes a Ball Mill or a Pebble Mill are the most suitable.

Ball Mills: In the ceramic industry hard materials like Quartz, Feldspar, Dolomite, etc. are to be reduced to very fine particles. The size reduction is done for the following two purposes:

a) Body preparation;
b) Glaze and Engobe Preparation.

It is a good practice to use special grinding equipment for these two purposes in order to avoid contamination and to omit careful cleaning of grinding equipment when the mill is used to crush two or more materials.

To get the product to a high fineness and to maintain a high mill capacity it is essential to follow the rules detailed below:

a) maximum grinding efficiency
b) minimum heating of the media and the material
c) minimum wear of grinding media
d) minimum wear of mill lining
e) the practice of grinding with ball mills

i. Mills and Equipment: The number of mills required will depend upon the size of the factory and range of the products produced. There should be one mill each for:

a) Engobes
b) Raw glazes
c) Fritted glazes
d) Hard materials
e) Colour glazes
f) Coloured engobes

The reason for using a special mill for the above is contamination. In addition it must be borne in mind that Engobes, Glazes, and hard materials for body mix and the glazes have different requirements in respect of particle size distribution and it is difficult to obtain constant fineness by using one mill for different materials.

ii. Grinding Media: Ball mills are classified according to the capacity of the materials used. The grinding media or pebbles, whichever are used, have to have the following characteristics:

Regular shape and as round as possible
Resistance to impact
Resistance to wear
Free from holes and cracks
No porosity

The most common type of grinding material used in ball mills is flint pebbles. Porcelain balls are also used and wear less and grind more accurately.

Two sizes of balls are generally used: big balls - the size varying from 50-75 mm and small balls from 15-30 mm. The grinding efficiency of a mill is dependant and effected by the ball size. The exact choice of ball size is not easy on considering the fact that after a period of grinding the ball size decreases. For this reason a portion of big and small balls are used. To get a constant grinding efficiency one must maintain the same porportion and same size of the grinding media.

Experiments have shown that the efficiency of pebbles of 50 mm is as high as that of 75 mm. Friction plays an effective part in grinding. It is obvious that smaller balls on account of their larger surface are better suited. Round balls have a better grinding action.

Silica or flint pebbles are better suited because of their higher specific gravity of 2.6 compared to porcelain balls with a specific gravity of 2.4. The smoother the surface of the pebbles and the lining the higher is the sliding action and thus a greater grinding efficiency.

Experience has shown that when the load of pebbles is 55-62% of the mill volume grinding is most effective. The grinding media can be distributed in the following two proportions and sizes:

60% - 55 mm
40% - 35 mm

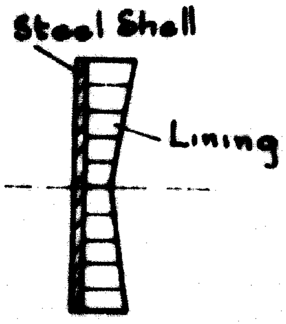
The volume of material to be ground:

The higher grade of fineness can be achieved with the Flumary and the volume of the material being equal to the grinding media voidage. Such a volume corresponds to 35-37% of the total volume of balls or about 20-22% of the mill volume.

Amount of Water:

Very dense mixtures are to be avoided because they hinder the proper movement of the balls. It is difficult to fix the exact amount of water required as this varies with the components in the mixture to be ground. When Feldspar or Quartz are to be ground the water amount should not exceed 25% of the total mill volume.

iii. Mill Lining: The Lining as well as the Grinding Media are very important factors for the grinding efficiency. Lining is done with porcelain blocks as well as with silica blocks. It is a good practice to use blocks of not less than 36 mm thickness when porcelain is used and 70-75 mm when silica blocks are used for lining purposes. Nevertheless, the thickness of the lining will depend on the mill size. The internal surface of the lining, that is the surface which comes into contact with the grinding media and the material to be ground has to be smooth. For cost reasons most suppliers of silica blocks do not place much importance on the smoothness of the surface. It is therefore necessary that the mason chooses the blocks properly so as to get minimum gaps between joints. The most effective system of lining mills is to start from the sides. The thickness of blocks used for the lining of the sides has to be some millimetres less in thickness than those of the blocks used for lining of the cylindrical part. The reason for that is that during grinding both the grinding media as well as the material to be ground abrades the side walls along a peripheral radius, whereas the centre of the side walls remains practically not attacked. The side walls are generally lined with blocks which decrease in thickness on approaching the centre giving them the necessary concave appearance. See diagram below.



Section of Millwall

After the lining of the side walls is completed the cement is allowed to harden and shrink. This is then followed by the lining of the cylindrical part. The lining of the cylindrical part of the mill is done in steps. In small ball mills one half of the lining is done in one day and the other half the following day.

In case quick setting cement is used for lining purposes one has to wait 36-72 hours, and longer if a normal cement is used, before the mill can be taken into operation.

Gaps between joint of blocks should be reduced to a minimum and the surfaces of the joints have to be equalised.

iv. Cleaning of Mills: A thorough cleaning of the mill has to be undertaken before using it. For such purposes generally sand or hard grit with 6-7% clay and 50% water is run through. After thorough washing the interior of the mill is inspected for cement or foreign matters.

v. Milling Operation: When the material to be ground consists of part of a fritted glaze and other materials have to be added it is better to load the mill with about 50% of the total frit at first, followed by the additions to be made, and last of all adding the remaining 50% of the frit. In following this procedure a better distribution of components results.

The material to be found is loaded into the mill already containing the grinding media. Water is added last and has to be carefully measured to get the proper density. Grinding media or pebbles should occupy 50-55% of the mill volume. Recent experiments have shown that 50 mm diameter pebbles are sufficiently large to enable good grinding of the largest particles. Small pebbles are more effective when the material particles are reduced in size. The minimum diameter of small pebbles should not be less than 15 mm. Small pebbles increase the discharge time. Approximately it has been found that the following cycles are suitable:

60% pebbles - 35 mm diameter
40% pebbles - 50 mm diameter

Small mills used for laboratory purposes need:

80% pebbles - 15 mm diameter
20% pebbles - 35 mm diameter

The rate at which the mill should rotate (r.p.m.) depends on the interna diameter of the mill. In summer time in hot countries it is necessary to coo the mill down during operation. Some modern mills have water jackets to maint a low temperature. Heating of raw materials such as glaze can be detrimental. When the ball mill has been in operation for a long period an increase in its volume takes place owing to the wear of lining. For example, in a mill of inner dimensions - 1020 cm x 1520 cm, with a wear of 2.5 cm, an increase in volume of 104 litres takes place. On account of this increase in volume a regulation in the quantity of grinding media, water, and the material to be ground has to be taken into consideration. During grinding the pebbles themselves also abrade and their grinding efficiency is decreased. An addition of bigger pebbles which compensate the wear and balance the milling efficiency is necessary. An average decrease in weight of 2.25-4.5 kg in pebble weight was found for grinding 450 kg of material. This loss in weight was periodically replaced with pebbles of larger size.

The unloading of mills is generally done by gravity, and in some cases compressed air is used to speed up the discharge operation. To avoid damages it is advisable not to overstep the pressure limit of 0.7 atmospheres.

Cleaning operations have to be repeated until water leaving the mill is clear. Such an operation is necessary especially when the mill is used successively for grinding of different type of materials.

vi. Ball Mill Practice: The power consumption of a mill depends upon the size, speed, its pebble and material load. When the load is not proportional to the mill size a longer time will be required to reach the required fineness and greater wear of the grinding media will result. A load lower than the lay out capacity lowers the grinding efficiency. On the other hand an excessive charge does not allow the grinding media to reach the highest point and fall onto the material to be ground. The material itself will not slide on the mill wall thus lowering the grinding produced by friction. Eventually the motor will itself become too hot, absorb greater energy, and sometimes burn out. Control of the power consumption and the fineness tests on the material are essential to predict whether the mill is operating efficiently. When the replacement of the grinding media lost by wear, is not done at the proper time a decrease in grinding efficiency will be noticed. Fineness tests show a larger amount of oversized grains in these cases.

4.3.2 <u>Fineness Test for Ground Materials.</u> Test on ground materials is necessary. The grinding efficiency of mills and the particles size distribution of hard materials are controlled by tests conducted on each batch. The samples to be tested are taken before the mill is unloaded. The equipment necessary for carrying out such a test is:

1 - sieve
1 - scale 500 grs. capacity able to measure 1/10 of a gram
1 - container of 150 grs. capacity
1 - dryer
1 - glass cylinder of 1 lt. capacity.

<u>Procedure</u>. The sample taken from the mill is passed through a 14 mesh sieve. 100 grams of material are placed in the 100 mesh sieve and carefully washed using running water. Care has to be taken to avoid the expulsion of material from the sieve. Washing is carried out till the water leaving the sieve is clear. The residue remaining on the sieve is dried and sieved again in the dry state. The weighed residue represents the percentage relative to 100 grams of wet ground material. In order to express the percentage in relation to dry material it is necessary to know the litre weight of the material taken as sample.

Table 3

Recommended loads and operational data for ball mills

Size of the Mill				Grinding Media*		
External ø x length mm.	Internal lining ø x length mm	Volume in litres	Speed R.p.m.	Porcelain Balls in litres	Flint Pebbles in litres	Frit Load kgs.
305 x 457	229 x 381	16	70	12	13.5	6.5
381 x 483	305 x 406	30	67	23.5	26	11
381 x 533	305 x 457	33	67	27	30	14
457 x 610	381 x 533	60	60	50	55	23
533 x 711	457 x 635	105	54	82	90	34
610 x 610	533 x 533	120	50	96	105	45
610 x 914	533 x 838	187	50	145	165	68
762 x 914	686 x 838	308	44	250	270	115
762 x 1066	686 x 991	365	44	295	315	135
ø 800 x 750	610 x 580	170	50		150	60
813 x 635	737 x 559	240	43	195	215	90
813 x 940	737 x 864	368	43	295	315	135
914 x 1219	787 x 1092	532	42	430	475	180
1066 x 1219	940 x 1092	758	37	610	680	270

Recommended loads and operational data for ball mills

Size of the Mill				Grinding Media*		
External ø x length mm.	Internal lining ø x length mm.	Volume in litres	Speed R.p.m	Porcelain Balls in litres	Flint Pebbles in litres	Frit Load kgs.
1371 x 1524	1244 x 1397	1703	29	1362	1498	500
1500 x 1450	1290 x 1270	1650	28		1450	550
1524 x 1066	1397 x 863	1422	26	1135	1271	499
1524 x 1219	1397 x 1092	1750	26	1362	1544	636
1524 x 1829	1397 x 1702	2605	26	2043	2315	908
1574 x 1829	1448 x 1702	2803	25	2225	2497	999
1829 x 1524	1702 x 1397	3180	21	2542	2815	1135
1829 x 1829	1702 x 1702	3860	21	3087	3450	1362
1829 x 2134	1702 x 2007	4565	21	3632	4086	1634
1829 x 2438	1702 x 2311	5261	21	4177	4676	1816
1829 x 3048	1702 x 2921	6661	21	5448	5902	2452
2184 x 2438	2057 x 2311	7790	19	6129	6901	2724
2438 x 2438	2311 x 2311	9697	18	7718	8626	3405
2438 x 3048	2311 x 2921	12278	18	9761	10669	4313
2438 x 3658	2311 x 3531	14785	18	11804	13166	4994
1143 x 1244	1016 x 1117	908	35	725	795	320
1219 x 1219	1092 x 1092	1020	33	820	910	360
1219 x 1524	1092 x 1397	1310	33	1045	1135	450
1371 x 1066	1244 x 940	1150	29	910	1000	410

Size of the Mill				Grinding Media*		Frit Load kgs.
External ø x length mm.	Internal lining ø x length mm.	Volume in litres	Speed R.p.m.	Porcelain Balls in litres	Flint Pebbles in litres	
1371 x 1219	1244 x 1092	1330	29	1045	1180	450
1371 x 1371	1244 x 1244	1520	29	1225	1360	540

* Attention has to be given to the size and proportion of the grinding media.

4.3.3 Clay Stirring: Stirring breaks down the clay lumps and brings about a water suspension. Stirring is needed when the clay suspension has to be uniformly mixed with other components present in the mix before casting and filter pressing can be undertaken. The most common kind of stirrer used in the clay industry is the propeller type of stirrer. The propeller stirrer is operated at about 200-300 revolutions per minute. A good deal of research work has been done with the purpose of reducing the stirring time and at the same time to increase the capacity or the stirring ability.

At the Annual Convention of the Canadian Ceramic Society in 1960, Mr. K. G. Timm of Struthers Wells Corporation - Warren, Pennsylvania, presented a paper on "A High Speed Preparation of Clay Slip" (The British Clay Worker, August 1962, Page 235-241). The paper describes the Use of Radial Propeller Mixer. Such type of propellers show a marked improvement in stirring. The author personally has used such a propeller with satisfactory results. Stirring in itself is a very simple operation. Nevertheless connected with such an operation are the important steps of weighing, selecting and loading of the material to the stirrer container. Weighing has to be done accurately. Selecting of the material is an important factor, the main purpose of which is to avoid the contamination of the raw materials with parts of paper, jute, plastic bags etc. Care has to be taken that iron nails or iron wire used for packing purposes do not get into the mix. Lumps of raw material often contain heterogeneous materials and are to be selected, inspected and rejected, if necessary.

5. BODY PREPARATION

A sanitary ware body is composed of plastic clays, china clays or Kaolins, Quartz, and Feldspar. The other additions are:

a) Barium Carbonate to precipitate sulphates as insoluble salts

b) Cobalt Sulphate to colour the body blue in order to mask the yellow colour of iron oxides present

c) Electrolytes such as Sodium Silicate, Sodium Carbonate, Sodium Hydroxide, etc. to make the slip fluid

d) Water to suspend the components of the body.

Plastic Clays. These clays confer on the plasticity or workability which means that they allow water to be retained thus keeping the piece in a plastic state for some time during which the sticking of accessory parts, repairs and finishing of the piece can be done. During drying of the body these clays help in the gradual release of water.

China Clays or Kaolins. These give a white colour to the body, plasticise it to a certain extent and like other clays take part in the ceramic reactions to form Mullite. They also raise the melting point of the mix.

Quartz. Reduce the plasticity conferred by the clays. Give a white colour and take part in the reaction to form Mullite.

Feldspars. Act as fluxes, i.e. they lower the melting point of clays and Quartz thus allowing the formation of Mullite to take place at a lower temperature.

Water. Acts as a suspending medium for the components, dissolves the salt.

From the characteristics, methods and systems already described one could now be in a position to prepare a body mix but before this can be undertaken one has to prepare the right mix formula. One has to determine how much water, barium carbonate, electrolytes, cobalt oxide, or sulphate will have to be added. The state of fineness of the hard material and the right plasticity of the finished mix have all to be determined before production starts. Another question to be considered is the availability of gypsum for mould production.

The author is of the opinion that as far as possible vitreous china, or at least semi-vitreous sanitary ware body should be laid stress upon. In case a factory already exists one should try to change over to vitreous ware. According to the author vitreous goods show many advantages and at the same time are not too difficult to manufacture.

Some years ago ceramics were still an art based on experience, but with the help of science one is able to calculate and thus find out the required composition of bodies and other mixes. The following chapter deals with such computational methods.

6. CERAMIC SANITARY WARE IN VITREOUS CHINA

Each type of body requires a different firing temperature, depending upon its characteristics. It is possible to determine these time-temperature curves by complicated calculations but they are only of theoretical value.

As already stated it is possible to vary the firing temperature and cycle (within limits) by varying the components of the mix and their quantities present.

The body mix with the following composition has a firing temperature corresponding to Seger Cone 9 (1250°C) (2282°F). This is called the Seger Formula and is useful to study and compare body compositions:

CaO = 0.092
MgO = 0.078
K_2O = 0.157
Na_2O = $\underline{0.673}$
= 1.000

Al_2O_3 = 3.625
Fe_2O_3 = 0.045

SiO_2 = 18.53
TiO_2 = 0.0498

This formula shows the ratios of the different oxides present in the raw material in a combined or free state which participates in the physical and chemical reactions indispensable to the formation of resistance and finished ceramic body. The first group of this formula represents the oxides of the type RO which have only one oxygen atom. The second group ø the oxides of the type R_2O_3 and the third group represents the oxides with two oxygen atoms and the formula RO_2. This empirical formula is used mainly for glass composition. The Seger Formula for bodies is expressed with R_2O_3 as unity but for comparison purposes it would be advisable to use the same system.

By multiplying the equivalents of the various oxides by the molecular weights, the weight ratio is obtained and from this the percentage composition of the body:

Results for Seger Cone Formula

Oxides	Equivalent	Molecular Weight	Ratio Weight
CaO	0.092	56.1	5.161
MgO	0.078	40.3	3.143
K_2O	0.157	94.2	14.789
Na_2O	0.673	62.0	41.726
Al_2O_3	3.625	101.9	369.387
Fe_2O_3	0.045	159.7	7.186
SiO_2	18.53	60.1	1113.653
TiO_2	0.050	80.1	4.005
			1559.050

From the proportion of the oxides to the total:

$$5.161 : 1559.05 = X : 100 \qquad X = \frac{5.161 \times 100}{1559.05}$$

The percentage composition of the oxides in the mixture are obtained:

CaO = 0.33% Al_2O_3 = 23.69%
MgO = 0.20% Fe_2O_3 = 0.45%
K_2O = 0.95% SiO_2 = 71.43%
Na_2O = 2.66% TiO_2 = 0.25%

To convert the empirical formula into the raw composition weight we consider the different materials to be pure and on this basis have an approximate result near enough to that in practice.

Sanitary ware mix contains:

Kaolinite $2H_2O$ Al_2O_3 $2SiO_2$ having a molecular weight = 258
Sodium Feldspar Na_2O Al_2O_3 $6SiO_2$ " " " " = 525
Potassium Feldspar K_2O Al_2O_3 $6SiO_2$ " " " " = 558
Quartz SiO_2 " " " " = 60

Having the correspondent equivalents of the oxides we may calculate as follows:

0.673 Na_2O	0.157 K_2O	3.625 Al_2O_3	18.530 SiO_2	Materials	Mol. Weight	Mol. Equiv.	Ratio Weight
-0.673		-0.673	- 4.038	Na-Feldspar	525	x 0.673	= 353.3
	-0.157	-0.157	- 0.942	K-Feldspar	558	x 0.157	= 86.6
		2.795	- 5.590	Kaolin	258	x 2.795	= 721.1
			7.960	Quarts	60	x 7.960	= 477.60
			Total parts in weight or ratio weight				1638.6

Represented as a percentage:

Kaolinite (Clays)	44.00%		
Feldspars (Na + K)	26.82%	≈	27%
Quartz	29.18%	≈	29%
	100.00%		

Normally the ratio of Plastic Clay to Kaolin is around 1:1. We therefore have the following composition:

Plastic Clays	22%
China Clays	22%
Feldspar	27%
Quartz	29%
	100%

The above composition is not by any means a final one. Tests have to be done in order to determine the different characteristics of the mix with respect to variations of its components and for such purpose the six bodies given below are used as examples:

Components	Body 1	Body 2	Body 3	Body 4	Body 5	Body 6
Plastic Clays	22%	24%	26%	25%	24%	25%
China Clays	22	20	16	18	16	24
Feldspar	27	27	29	27	26	25
Quartz	29	29	29	30	30	26
	100	100	100	100	96*	100

Method of preparation:

a) the Feldspar is to be ground until it passes through a 120 Mesh Screen, leaving no residues.

b) Quartz is to be ground until it passes 140 Mesh Screen completely.

To prepare 100 kg. of a body mix the proportion of the components detailed below should be added stepwise to the blungers and mixed.

1. The blungers are filled in with 27 litres of water and kept running.
2. An addition of Cobalt Solution ($CoSO_4 . 7\ H_2O$) corresponding to 16 gr.
3. Addition of Barium Carbonate ($BaCO_3$) 16 gr.

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* See page 54, Body no. 5.

4. Sodium Carbonate (Na_2CO_3) 32 gr.
5. The blungers are kept running until all the materials are dissolved.
6. Preparation of sodium silicate solution by adding 460 gr. Sodium Silicate to 460 cm^3 water (total 920 cm^3).
7. Additions of 460 cm^3 of the silicate solution to the blungers.
8. Gradual additions of plastic clays to allow a good dispersion.
9. The china clay is now added and the blungers kept running until all the added materials are in suspension.
10. Feldspar and Quartz powders are now added and thoroughly mixed.
11. The litre weight and viscosity are now determined.

The litre weight is determined by filling up a container of exactly one litre capacity and weighing it. This gives the litre weight of the slip.

The viscosity is determined with the help of a tube type viscometer or a torsion viscometer. The tube type is the simpler and is recommended for use. Its dimensions are:

Length of the tube	330 mm
Inner diameter	33 mm
Diameter of the exit nozzle	3 mm

The viscosity is determined by measuring the time required to fill up a glass container of 200 cm^3 capacity by the slip flowing from the viscometer nozzle.

The viscosity and litre weight of the six bodies is shown in the table below:

Determination	Body 1	Body 2	Body 3	Body 4	Body 5	Body 6
Litre weight grs/Litre	1792	1789	1806	1796	1789	1804
Viscosity seconds/200 cm^3	96"	108"	110"	98"	105"	110"

The first step to take is to bring all the slips to the same litre weight. This correction is possible by the addition of the amounts of water calculated by the formula given below to the slips of a higher litre weight:

$$\text{Water to be added cm}^3\text{/litre of slip} = \frac{(D - d) ; 1000}{d - 1000}$$

where D = the higher litre weight

d = the required litre weight

Example: D = grs/litre 1806
d = " " 1789

$$W = \frac{(1806 - 1789) \cdot 1000}{1789 - 1000} = \frac{17000}{789} = 21.5 \text{ cm}^3$$ of water to be added to each litre of water

Once the litre weight is adjusted the viscosity of all the bodies are again checked.

At this stage an addition of silicate to the slips will give different values of viscosity for the same amount of electrolyte (silicate) added. By measuring the viscosity of the slips the viscosity curve can be plotted which determines the maximum fluidity of the slip and the amount of electrolyte that can be added to the suspension. It is seen that there is a point in the curve at which a further addition of sodium silicate causes coagulation of the mix. Obviously this point should not be reached.

The amount of electrolyte which allows the slip its maximum fluidity without causing a settling of the material is that point of the curve at which the slip has the lowest rate of flow and can be taken as the highest viscosity for that slip.

Now it is necessary to add the amount of electrolyte to the water suspension. The amount of electrolyte to be added to the slip can be taken from its viscosity curve taking into account the amount of electrolyte already added during the body mix preparation. After addition the mixture is homogenised.

The container is emptied over a vibrating screen of 120 - 140 mesh and the suspension is now subjected to magnetic separation. The slip is now collected in an agitator and kept in an agitated state until casting in a gypsum mould. The litre weight and viscosity determination is once again repeated before the casting process. The slip is well stirred and then cast into standard gypsum moulds which give the samples for the various tests to follow:

Shrinkage; modulus of rupture and mechanical strength; porosity; rate of layer formation in gypsum mould; water content of the slip; colour after firing - with and without glaze; glaze - body accord.

6.1. Tests

6.1.1 Shrinkage test: The slab cast with the slip to be tested is formed by hand pressing and is left to dry for some time on a gypsum slab. As soon as this slab is formed two marks are made on the surface either with the help of a compass point or a sharp knife. The marking is done as shown in figure I Appendix and the distance between the two marks has to be exactly either 5 cm or 10 cm, the thickness of the slab should be about 1.5 cm. The first measurements are taken when the slab is dry. The difference between these two measurements reported in percentages gives the wet to dry shrinkage. The slab is then fired at Seger Cone 9 and the difference between the value now measured and compared to that in the dry state gives the dry to fired shrinkage. The sum total of these two percentages gives the total shrinkage e.g. suppose we have marked two points at a distance of 5 cm. and on drying it measures 4.5 cm. the difference of 0.5 cm. = 10%, is the shrinkage from wet to dry, and after firing it measures 4.3 a difference of 0.2 cm. = 4% is the shrinkage from dry to fired, and 10% + 4% = 14% the total shrinkage.

6.1.2 Modulus of Rupture and Mechanical Strength

This is the resistance of a piece to an applied force. The test is conducted on a test piece placed on two supports 10 cm. apart. At the centre a force is applied and gradually increased until the test piece is broken. The force required to break the piece is calculated as follows:

$$\text{kg/cm}^2 = \frac{3}{2} \frac{P \cdot l}{(a \cdot b)^2}$$

where: P = total weight applied in kgs. at breaking point
l = distance between supports
a = width of the test piece at the broken point
b = thickness of the test piece at the broken point

For vitrified bodies this is generally between 400 - 800 kg/cm^2. The resistance of the material can also be tested by means of an apparatus based on compression tests and traction tests. Traction tests are conducted by means of a dynamometer. Traction values for vitrified products can be as high as 250 kg/cm^2.

Compression tests are conducted on cylindrical or cubic pieces. A force is applied by means of presses. One condition which must be fulfilled in order that the tests be correct is that the two parallel surfaces have to be exactly parallel to one another. For porous products fired at low temperatures compression values are around 100 kg/cm^2. For vitrified products fired at high temperatures values can reach 5000 kg/cm^2.

6.1.3 Apparent Porosity - as measured by water absorption. For this test pieces are generally used on which the tests for mechanical strength have already been carried out. The absolute porosity is given by the following:

$$P_A = \frac{V - v}{V} = (1 - \frac{1}{\pi}) 100$$

where V = apparent volume - total external volume

v = actual volume occupied by solid particles

d = apparent density

π = absolute density

The determination of apparent porosity is done according to the following procedure: The piece is fired at a Seger Cone corresponding to the firing temperature required (in this case Seger Cone 9). A piece is broken off and is weighed accurately. This is then left in distilled water and boiled for at least 3 hours. After cooling it is removed from the water and carefully run over with a damp cloth in order to remove any water film that may be adhering to its surface. This piece is then again weighed. The difference in the weight represents the amount of water absorbed. The apparent porosity can be calculated as follows:

$$\text{Apparent porosity } \% = \frac{\text{water absorbed} \times 100}{\text{dry weight of the piece}}$$

6.1.4 Rate of layer formation: The slip ready for casting is poured into a gypsum mould with special dimensions and left inside for at least three hours. After one hour the quantity of the slip corresponding to about 3 - 4 cm. in depth is drained off by means of a draining hole at the bottom of the mould. An equal quantity is removed after the second and third hour. During the presence in the mould the slip in contact with the gypsum will lose a certain amount of water, removed by the capillarity forces of gypsum. When drainage is done a layer of body mix remains attached to the mould surface. The three layers corresponding to the 3 drainages made at intervals of an hour each

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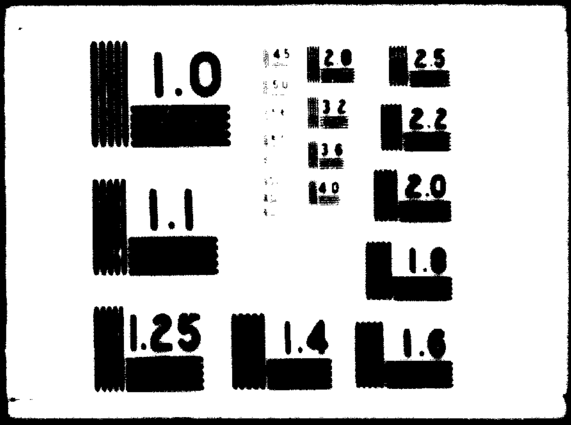


present difference thicknesses. By measuring the layer thickness one can know the thickness of the layer formed in one, two and three hours by the presence of the slip in the mould. This is useful to determine the residence time of the slip in the mould to obtain the right thickness required for the piece and at the same time to allow the drainage of the surplus slip. By determining the viscosity of the slip drained out of the mould after three hours residence time, it is possible to compare the time of flow with the viscosity determination made previous to the casting operation. Such a difference is taken as a value of the thixotropy of the slip at the measured residence time. If this value is too high it means that the slip when drained off the mould is dense and does not flow well. The change in voscosity is such that the layer formed and in contact with the mould does not have the right consistency and separation from the mould could occur, so affecting the properties of standing and drying of the piece. In such a case it will be necessary to correct the viscosity of the slip before casting it.

6.1.5 Determination of the amount of water present in the slip: A weighed quantity of the slip is dried to remove the water present. This determination of the water content of the slip allows easy reproduction of other similar slips. With the help of this determination it is also possible to vary the litre weight with regard to the Thixotropic value when required.

6.1.6 Colour after firing: The colour of the formed piece after firing is important. The amount of Cobalt Oxide will have to be adjusted in relation to the colour obtained in order to get the whitest colour possible. Adjustments of Cobalt Oxide can be done both in the slip as well as in the glaze.

6.1.7 Accord between body and glaze: Crazing is the most common defect of glazed ceramic articles. Crazing appears to a greater extent on porous bodies although the opinion is that vitrified ceramic pieces craze with difficulty although it is possible to see such a defect when a new body is being developed or when the adjustments are not yet just right. The origin of crazing can be traced back to a disagreement between the body and its glaze.

Tensions existing in the body after firing cause it to expand. This expansion is not followed by the glaze whose elasticity coefficient is low and as a result of such tensions the glaze is criss-crossed by very fine lines easily seen when the article is held under a light source at a proper angle of incidence. Crazing sometimes takes place a long time after firing of the body. The reason for this being the hydration of the Kaolinitic compounds with consequent increase in volume of the body. Even when crazing occurs only in a few cases proper investigations have to be done to establish the causes. In any case attention has to be given to the following general rules:

a) Increasing of the firing temperature or an extension of the soaking time (period at which the glaze is at highest temperature) decreases or eliminates crazing defects.

b) The fineness of Quartz and Feldspar have an influence on the accord between body and glaze. On increasing the fineness of hard materials the thermal coefficient of expansion adjusts itself.

c) When the thermal coefficient of expansion of the glaze is too high it is necessary to increase the amount of Quartz.

d) The amount of Feldspar when increased raises the coefficient of thermal expansion i.e. the glaze is in compression over the body.

e) When using fritted glaze it is necessary to replace a part of Quartz with B_2O_3 (Boron anhydrate).

f) Replacement of a flux by one of a higher molecular weight increases the compression of the glaze.

g) By reversing the conditions in c), d), and e) in the body composition it is also possible to remove crazing defects.

The tests to establish thermal expansion of bodies and glaze are conducted by means of dilatometers. These are generally expensive and the testing requires considerable time. In order to speed up the testing the Ring System is used (described in 9.8.1).

6.1.8 <u>The Warping Test</u>: Warping is a defect common to many ceramic articles especially vitrified ones. The test piece made to dimensions is cast from the slip. When the piece is dried it is placed in a kiln and fired at the same temperature at which other tests are carried out. The piece is set in the kiln in such a position as to allow a free deformation. The deformation is then measured. Deformation is expressed in mm. Attention is drawn to the fact that the tests outlined above have to be carried out not only on bodies but as well as on each of the raw materials to be used in order to know their characteristics before using them. The samples of the raw materials as well as samples of bodies under test are to be preserved with indications on them for comparison purposes.

The table 4 gives supposed values for the various tests on the six previously mentioned bodies.

From this table the following conclusions can be derived. The bodies 1 and 5 are of special interest and are specially discussed below:

Body No. 1. In this body the rate of layer formation is high enough. Viscosity value at 160 seconds is reached with a low amount of silicate. Porosity is low. Deformation is the lowest. Its colour after firing is white. Its mechanical strength is the second in the series. This type of body should be given preference over the other five.

Body No. 5. The composition of this body has been prepared deliberately with an error. In fact the sum total of the components is 96 and not 100. This error has to be corrected and this can be done by altering the composition. In this case instead of 100 the components have to be calculated proportional to 96 and converted to the base 100. The procedure is as follows:

$$96 : 24 \text{ (Plastic Clay)} = 100 : X \qquad X = \frac{24 \times 100}{96} = 25$$

On this basis the composition is:

25.0 % Plastic Clay
16.6 % China Clay
27.08% Feldspar
31.25% Quartz
100.00%

This body mix is sufficiently plastic, has a good time of flow in relation to the amount of silicate present, deformation is not considerable, but the mechanical strength is the lowest of the series of bodies. The flowing time of the surplus slip is the lowest.

The body mix chosen is now tested again in a sanitary ware mould. For this purpose a water closet has been chosen.

The mould is made of gypsum or plaster and can be divided into one foot (base of the mould), two side walls, and one piston with its cover (together one piece.) Before the slip can be poured into the mould it has to be cleaned and wet slightly (humid sponging) this operation removes any gypsum powder clinging to the surface of the mould and at the same time reduces to a slight extent the absorption power of the gypsum at the initial stages especially when the mould is dry.

Table 4

Test results

Denomination	Body 1	Body 2	Body 3	Body 4	Body 5	Body 6
Litre Weight	1789	1789	1789	1789	1789	1789
Viscosity (25°C)	160 sec.	150 sec.	128 sec.	140 sec.	118 sec.	174 sec.
Shrinkage (wet to dry) %	2.68	2.90	2.40	2.30	2.25	3.10
Shrinkage (dry to fired) %	8.92	8.50	8.70	8.32	8.64	8.05
Shrinkage (total) %	11.60	11.40	11.10	10.62	10.89	11.15
Firing °C	1250	1250	1250	1250	1250	1250
Firing °F	2282	2282	2282	2282	2282	2282
Layers after						
1 hour (mm)	7.5	7.0	7.5	8.0	7.0	8.5
2 hours "	10.5	11.0	11.5	11.5	10.5	11.5
3 hours "	13.5	13.5	13.0	13.5	14.5	12.0
Mech. strength (kg/cm^2)	10.7	9.8	9.5	9.9	9.0	11.5
Deform. (mm)	23	27	35	30	25	40
Porosity %	0.24	0.[illegible]2	0.33	0.27	0.29	0.35
Thyxotropy (25°C)	234 sec.	220 sec.	200 sec.	210 sec.	189 sec.	300 sec.
Colour after firing	White	Whitish	White	White	White	Creme
% Water	27	28	26.5	28.2	26.0	29.0
Silicate %	0.26	0.34	0.40	0.40	0.30	0.46
Cobalt Sulphate %	0.016	0.016	0.016	0.016	0.016	0.016
Barium Carbon. %	0.016	0.016	0.016	0.016	0.016	0.016
Sodium Carbon. %	0.032	0.032	0.032	0.032	0.032	0.032
Plasticity (mm of deformation)	10.-	12.0	14.0	15.0	15.5	10.-

The parts of the mould like the piston and the base which are to be removed and due to their complicated shape and also due to the slip sticking to them they have to be dusted with Quartz or talc powder to ease removal. The parts of the mould are now brought together and set properly. The completed mould is held together with tension bolts to prevent the mould parts falling apart under the pressure of the slip.

The drain holes are stopped with aluminium rods coated with leather hard clay. Funnels (preferably rubber ones) are set over the casting holes. The mould is now ready to receive the casting slip which is poured into it at a regular and continuous rate avoiding interruptions. Continuous filling prevents air getting into the mould. When a mould is of the closed type it is necessary to have one or more small holes at the highest point to permit the escape of air during casting. Such holes are stopped when the slip rises up to the surface.

The residence time was measured already by means of an open casting mould, whereas in the case of closed mould the layer formation takes place between the gypsum walls. The residence time in a two-walled mould is shorter and this has to be kept in mind. The table below shows the time at which different operations are to be carried out:

Type of Article	Casting Time at	Drainage Time at	Piston Removal at	Piece Removal at
Water Closet	6 h 30 min	9 h	10 h 15 min	11 h
Wash Basin	6 h 30 min	9 h	11 h	13 h
Bidet	6 h 30 min	9 h	11 h	14 h

Water closet articles can be of the open casting type having an upper rim open (obtained by drainage) or the upper rim closed. The closed rim is cast in a proper mould and stuck on to the bowl of the closet after removal of the piston. The intervals given in the above table are only indicative, depending on the temperature and relative humidity of the casting room. The condition of the mould (dry or slightly wet, new or used) is the controlling factor for the variations in time. Complex assemblies or stick-up pieces mean additional operations such as casting the parts separately, sticking the pieces together and finishing off the exposed joints. Bad finish in stick-up pieces and badly done finishing operations are visible on application of the glaze and lead to more rejects. Internal joints are a great danger and give rise to leaks. The sticking of parts is done by applying a layer of coagulated slip on the surfaces to be stuck together. Coagulation is done by adding a few drops of acid to the slip. The parts are placed together and pressed until the surplus slip flows out of the joint. This extra slip is removed with a thin steel plate. The first finishing is done by a rubber plate and eventually the blurs are removed with a wet sponge. During sticking one has to avoid air pockets being enclosed between joints because during drying and firing an increase in the volume of the air causes cracking. After the repairs have been done the formed piece is left on a base. Repairs of superficial cracks are done by introducing slip into the cracks by means of a brush. Finishing is done when the piece is still leather hard. The piece is then inspected for defects. At this stage repairs are no longer possible in most cases. A careful use of a thin steel and rubber plate removes unevennesses and smooths off the edges. A wet sponge is passed over the surface to remove a thin layer of very fine particles of clay which migrate to the surface under the capillary action of gypsum and to open up the pores in which tiny particles are accumulated. When the sponge is well applied it removes scratches left behind by the scraping operation of the steel plate and contributes to the evenness of the surface in general.

The finished piece is now set on a wood base dusted with very fine Quartz or talc powder (to allow the body to move freely - shrinkage movements during drying). A plastic cover is generally put on to the piece and keeps the drying rate low and protects the body from air currents.

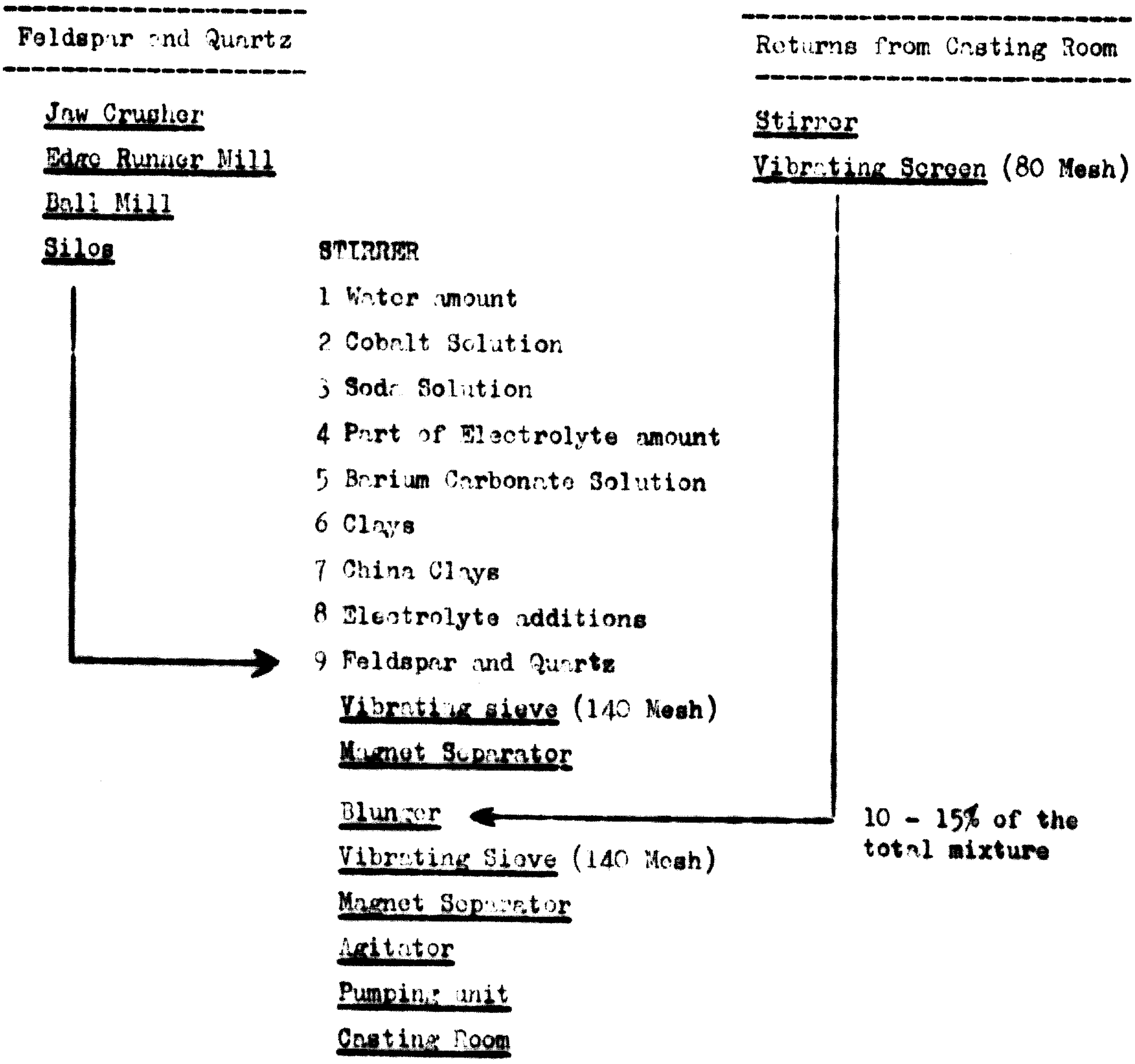
6.2 Summary of the casting operations:

a) Mould Preparation:	Wet sponging with clean water. Dusting of the movable parts with very fine powder of Quartz or talc. Assembling of the mould parts, and tightening. Fixing on funnels to mould. Closing up of drainage holes.
b) Casting:	Filling up of the mould is done beginning with the funnel at the lowest level until the rising slip fills up the other funnels. Closing of air escape holes.

c) **Drainage:**	Removal of the rods closing the drain holes after tilting of the piece toward the side of the draining holes.
d) **Piston removal:**	Careful removal of the piston after cleaning the casting holes and air escaping holes.
e) **Sticking:**	Application of coagulated slip over the surface of the stick-up pieces. Assembling of the stick-up parts and pressing. Removal of the surplus slip from the joint surfaces.
f) **Removal of the piece:**	Careful removal of the covers and side walls. The piece is left on its base until the following day. Repairs of the cracks.
g) **Finishing:**	Scraping by means of a thin steel plate, rubber scraper and wet sponge. Covering of the piece with a plastic sheet after it has been set on a wooden base. Setting in the drying place.

Figure 2

Steps in the preparation of vitreous and semi-vitreous bodies



Controls on casting slip:

a) Litre Weight b) Viscosity c) Rate of Layers formation d) Thyxotropy test e) Water content %

Controls on cast specimens:

a) Shrinkage wet to dry b) shrinkage dry to fired c) Mechanical strength d) Plasticity e) Deformation

Controls on fired specimens:

a) Porosity b) Mechanical strength c) Deformation d) Colour e) Accord
f) with glaze

7. FIRECLAY SANITARY WARE

The Fireclay type of body is used in making sanitary ware articles of large size. For the manufacture of Fireclay, sanitary clays which after firing are not white are used. The reason for this is purely economical. In fact the use of more expensive raw materials as clays would raise the cost of production to prohibitive levels.

Feldspar content in a fireclay body is low: between 3 to 10%. Quartz content is also low, lying between 5 to 15%. An important raw material is Grog (fired clay or rejected ceramic articles, crushed and sieved). This is introduced into the mix in a size varying up to 2.5 mm diameter.

The function of the Grog is to increase the water absorbing capacity of the gypsum mould, thus allowing the thickness of pieces to be increased. By introducing Grog into the body, they become more porous and thus allow the formation of thicker layers than Vitreous bodies. The porous nature of the body in the raw state permits water to travel to the gypsum mould more easily.

Depending on the size of particles, the Grog occupies different volumes. In other words, Grog of grain size 2.5 mm has a different volume than the same weight of Grog of size 2 mm or less. Different volumes cause the body to behave differently in terms of thermal expansion. Thus a variation in the Grog grain size has to be done carefully taking into account the consequent change in volume. The grain size has considerable importance in preserving the slip characteristics.

The introduction of Grog is done in relation to the thickness required and to produce a body which is as compact as possible a uniform distribution of grain size is essential. A simple method of finding out the best Grog size distribution is to mix varying percentages of different grain sizes and to examine these mixtures in a graduated glass cylinder. It is possible to observe the grain orientation and to measure the total volume occupied by a given quantity of the Grog. The choice will fall on the more compact mixture.

A variation of the percentage of the grain sizes of the Grog in the mixture could alter the coefficient of thermal expansion of the body either favourably or not. Preferably one should use more types of Grog. Grogs of different fired characteristics, for example porous, non-porous, vitrified, compensate water absorption and consequently lower the wet to dry shrinkage.

A very high content of vitrified Grog will decrease the final strength of the finished article as it is difficult for the required reactions to occur between this type of Grog and the surrounding clay particles. When the Grog is too porous it will absorb an undue amount of water.

In general, plants producing semi-vitreous or vitreous sanitary ware reuse their rejected articles in this branch as Grog for fireclay bodies. There are also factories that manufacture Grog but it is quite normal for a factory to crush a prepared fireclay. This is done by extruding clay bricks and firing them in kiln of most varied types. Firebricks coming from the dismantled kilns are sometimes also used as Grog. The bricks are crushed in a jaw crusher and then in an edge runner mill and the ground product is then passed through a rotary sieve and separated into different grain sizes and stored separately.

The following diagram shows the steps in the preparation of a fireclay body.

Comments on the results of Fireclay bodies

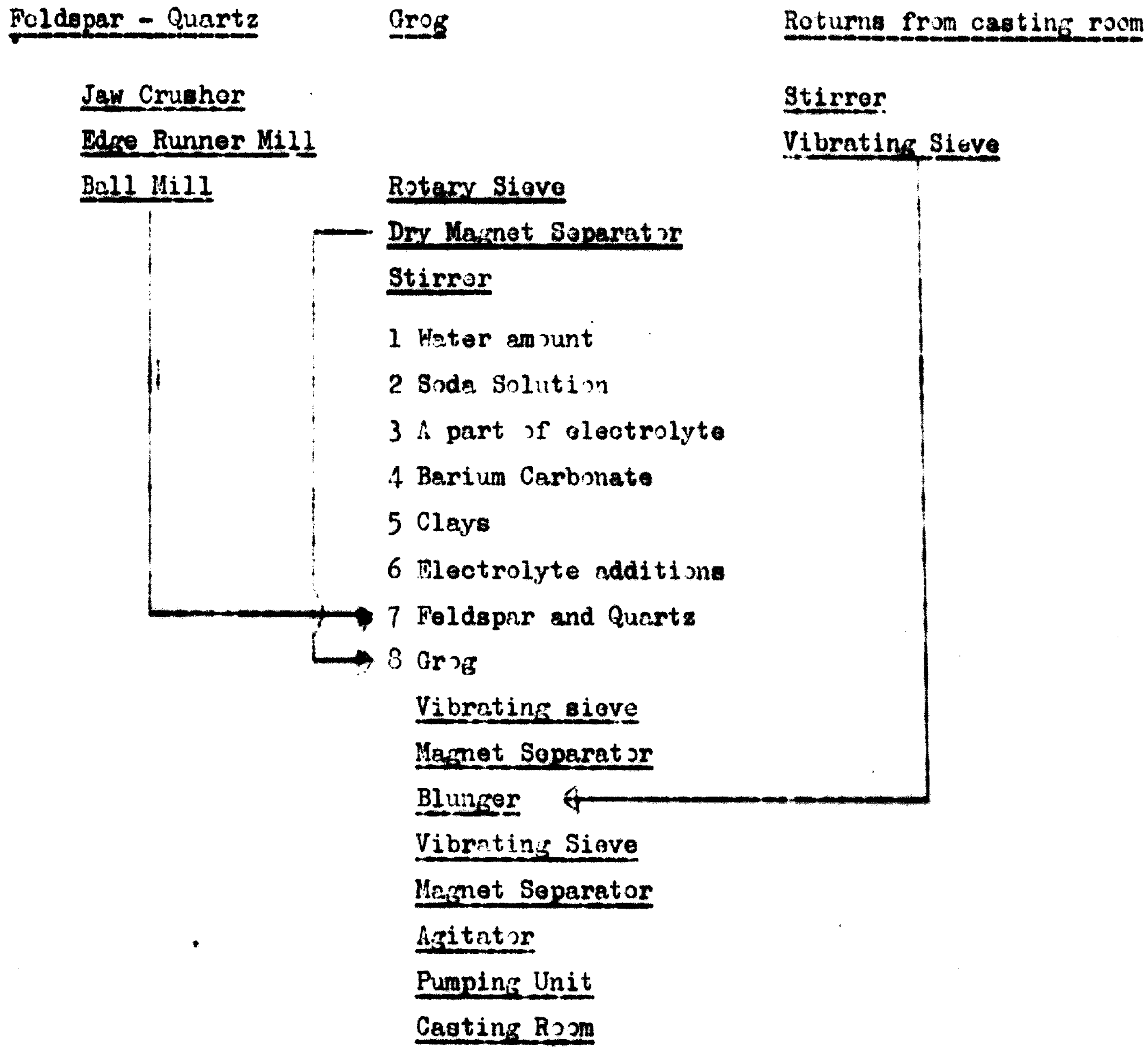
Thermal shock resistance tests on the fireclay specimen (after firing) either with an engobe alone or with both engobe and glaze are very important for Fireclay articles as they have greater thickness and when under test, tensions develop between the body and the covering matter (engobe and glaze). In use these articles are subjected to sudden changes in temperature and in such case a temperature gradient exists between the inner and outer surfaces. When the resistance to temperature shocks is not sufficiently high, the tension that builds up in the article is greater than the forces of cohesion of the material and the body breaks or cracks. These very fine lines are called Dunting.

The litre weight of the above body is about 2 kgs. and the shrinkage is very low. Those two facts are related to one another. A higher shrinkage in a larger and heavy article causes cracks during drying and firing. The amount of electrolyte added is high and the viscosity of the body is lower than that of the vitreous one.

The possibility of soluble salts present is higher as less valuable clays have been used for the purpose (unwashed clays).

Figure 3

Steps in the preparation of fireclay body



Controls on Casting Slip:

a) Litre weight b) Viscosity c) Rate of layers formation d) Thyxotropy e) Percentage water content.

Controls on cast specimens:

a) Shrinkage wet to dry b) Mechanical strength c) Plasticity

Controls on fired specimens:

a) Porosity b) Mechanical strength c) Deformation d) Colour e) Accord with glazes

The following gives the composition and characteristics of a Fireclay body. The Seger or empirical formula of the body is as follows:

CaO	0.26	Al_2O_3	3.80	SiO_2	22.39
MgO	0.28	Fe_2O_3	0.23	TiO_2	0.28
K_2O	0.18				
Na_2O	0.28				

$$\text{Ratio of Silica to Alumina} = \frac{SiO_2}{Al_2O_3} = 5.89$$

The chemical composition is as follows:

SiO_2	72.54%
Al_2O_3	20.95
Fe_2O_3	2.03
CaO	0.77
MgO	0.64
K_2O	0.96
Na_2O	0.92
TiO_2	1.18

Body mix composition

Plastic Clays	35.75%	
Clays	21 25	
Quartz	3.50	
Grog 2 mm porous type	3.26	
" 1 " "	1.00	
Less than 1 mm porous type	1.00	
" " 0.1 " "	1.00	
" " 0.2 " "	1.26	
Less than 0.2 mm vitrif.	5.48	
" " 0.1 mm "	3.00	
" " 0.1 mm rejects	7.00	(wash basins)
" " 0.2 mm "	13.00	(WB-WC etc.)
" " 0.2 mm bricks	3.50	
	100.00	

Test characteristics

Litre weight	1940 grs.
Viscosity (25°C)	108 sec.
Shrinkage (wet to dry)	2.14%
Dry to fired	2.78%
Total shrinkage	4.92%
Firing °C	1225
Firing °F	2237
Layer formation after 1 hour	9 mm
" " " 2 "	12 mm
" " " 3 "	14.5 mm

Test characteristics (cont.)	
Mechanical strength	11.3 kg/cm^2
Deformation	5.5 mm
Porosity %	8.93
Colour after firing	Reddish
Water amount %	20.90
Electrolyte (silicate)	0.55%
Barium Carbonate	0.15%
Sodium Carbonate	0.10%
Plasticity (mm of deformation)	6.00
Thermal shock	after 5 shocks on the engobed specimen: Crazing
Resistance from 110°C to 15°C	After 7 shocks on an engobed and glazed specimen : Dunting

The flow rate of the Fireclay slip is higher. Because of the larger particle size (2.5 mm) 6 mm diameter nozzles are used for viscosity measurements.

7.1 **Fireclay Casting Slip:** The casting process is as follows:

The Fireclay slip ready to be cast is transferred to the mould. The casting system used in the previous chapter is closely followed. For the purpose of description a kitchen sink consisting of a basin with plate-rack and a stick-up overflow incorporated is considered.

With Fireclay slip there is no possibility of having hollow rims and for this reason there are no drainage holes in the mould. The piece is obtained by solid casting. Only in exceptional cases where the articles are large, the drainage of surplus slip is possible (big bath-tubs, large urinals, etc.).

The kitchen sink mould consists of two pistons and a case. A separate mould is used for the production of the overflow part which is then stuck on to the piece. Both are in a raw state when they are stuck together.

The piston constitutes the base on which the mould stands. The upper part of the case has 4 or more casting holes. Casting funnels of 2 to 3 litres capacity are set onto these holes and the casting slip is poured into the funnel at the lowest level at regular rate continuously till the slip rises up and fills the other funnels. The air escape holes are closed as the slip rises to the surface.

A little water is added to the funnels so that the slip here is covered with a film of water to prevent the formation of a coagulated slip film, thus making easy the feeding of slip during the period of time the body remains in the mould. Due to water absorption by the mould, the level of the slip falls. Slip has therefore to be added during the time of residence of the slip in the mould which is 15 to 20 hours.

The casting process is as follows:

a) Mould preparation
  - The piston is wet with a humid sponge followed by dusting with talc or quartz powder.
  - The interior surface of the case is wetted.
  - Mould is assembled and set up-side-down on the casting bench.
  - Tightening up of mould.

b) Casting
  - Filling up of the mould with slip. Slip is poured in at the funnel at the lowest level till the slip rises and fills up all the other funnels.
  - Closing air escape holes.

c) Mould removal
  - Cleaning up of casting holes.
  - Loosening of the mould.
  - Removal of case.
  - Closing up of the casting holes with leather hard slip.
  - Fixing on of the stick-up over-flow.
  - Placing of a wooden plate on the piece bottom.
  - Turning over of the mould to its normal position.
  - Removal of piston.
  - Repair of cracks using slip.
  - Cutting out of the over-flow window in the position indicated.
  - Covering up of piece with a plastic sheet.

d) Finishing
  - Transfer of piece to a rotating pedestal, scraping to remove blurs and asperites using a thin steel plate.
  - Washing with humid sponge. This operation is repeated till the surface of the piece is slightly rough.
  - Transfer of piece to the racks.
  - Covering up with a plastic sheet.

Observations. The scraping and washing operations are necessary to remove the thin layer of fine clay particles which migrate to the surface of the piece during the absorption of water. Such a layer, if not removed, will have a greater shrinkage than the successive layers. Thus the shrinkage of the applied engobe will follow the shrinkage course of the first film and cause cracking. The result will be a cut engobe. The defect is more marked in the interior corners of the piece from where it is difficult to remove the film and where the accumulation of the engobe, during application, takes place. Washing and scraping operations are long and difficult. If scraping is done by applying too much pressure, the surface becomes too rough and the engobe will not cover up the asperities. When scraping is only superficial, the fine particles remaining behind will cause a defective engobe.

Washing has to be done by means of a sponge dipped in clean water to remove clay particles collected in the sponge pores.

In order to allow a complete and uniform engobe covering, the edges of the piece have to be rounded.

In Fireclay articles, repair of cracks is possible, also when the pieces are leather hard.

The particular areas of the surfaces of the articles on to which stick-up parts are to be attached have to be scraped well to make them rough to increase adhesivity. Generally the moulds are so formed that there are grooves in the articles surface to ease the positioning and fixing of stick-up parts.

On drying, the piece is once again scraped before applying the engobe.

7.2 The Engobe: An Engobe is a type of porcelain or vitreous body, the application of which is done with the express purpose of covering up the rough surface of the fireclay and to mask its reddish colour. It is applied with a brush (old method) or by spraying.

The preparation of Engobes is complicated and their application is difficult and costly.

An engobe suitable for the fireclay body considered can be prepared from the formula given below.

Seger or empirical formula

CaO	0.11					
MgO	0.06	Al_2O_3	2.44	SiO_2	13.73	$SiO_2/Al_2O_3 = 5.63$
K_2O	0.09	Fe_2O_3	0.02	TiO_2	0.01	
Na_2O	0.74					

Chemical composition:

SiO_2	72.23%
Al_2O_3	21.86
Fe_2O_3	0.29
CaO	0.54
MgO	0.20
K_2O	0.75
Na_2O	4.04
TiO_2	0.07

Batch composition:

Quartz	26.00%		
China Clays	27.00%	Fired	20.00%
		Raw	7.00%
Plastic Clay	7.00		
Feldspar	40.00		

Engobe preparation for a fireclay body: Quartz and feldspar are ground to a very fine powder so that it passes through a 180 mesh sieve.

The engobe is prepared in a Ball mill and the following components are put into the mill in the order:
1) Water, 2) Cobalt Solution, 3) Clays, 4) China Clays, 5) Feldspar, 6) Quartz.
The Ball mill is kept running until a fineness corresponding to a 180-200 mesh is reached.

The prepared engobe is then transferred to a container and kept agitated for some time. The litre weight and viscosity are then adjusted and controlled. The engobe is now passed through a vibrating screen and a magnet separator and depending on production requirements stored in small container of 100 litres capacity.

Due to the fact that the thickness of the engobe layer is to be 0.8 - 1 mm as also to increase the adhesive property of engobe, it is necessary to add an organic adhesive to the engobe. Adhesives of animal origin are the most suitable. When using such an adhesive, care has to be exercised in their preparation and addition. The water temperature should not exceed 60°C, otherwise decomposion of the adhesive takes place. The solution is added in amounts determined previously and homogenized by high speed stirring. The homogenized water suspension is sieved to remove coagulated particles of the adhesive. The engobe is now stored in a cool room at a temperature of 10°C till it turns to a gel. The gelified engobe is stirred and transferred to the pressure containers and is sprayed onto the fireclay articles.

Determination of the gelyfying power of glues (Piekarski):

This test is done to establish the minimum concentration at which a glue gelifies. The lower the concentration at which the glue gelifies the higher is its adhesivity.

Test procedure

5 grams. of powdered dry glue are put into 95 cm³ of cool water; after about an hour the glue particles increase in volume. The solution is now heated to a maximum temperature of 60°C. 25 cm³ of the solution are cooled to 25°C, of which 20 cm³ are placed in one test tube and the remaining 5 cm³ in a second. To the first test tube containing 20 cm³ solution 5 cm³ water are added.

5 cm³ of the solution are taken out and put into a third test tube. This procedure of adding 5 cm³ water and then removing 5 cm³ of solution is repeated a number of times. The following decreasing concentrations of solution are obtained:

Solution	1	5%	Glue	in	Water
"	2	4%	"	"	"
"	3	3.20%	"	"	"
Solution	4	2.56%	"	"	"
"	5	1.64%	"	"	"
"	6	1.31%	"	"	"
Solution	7	1.048%	"	"	"
"	8	0.837%	"	"	"
"	9	0.6707%	"	"	"
Solution	10	0.5364%	"	"	"

These solutions are a period of 1 hour at 15°C. The test tube in which gelification takes place is noted and gives the necessary minimum concentration.

Characteristics of the Engobe:

Litre weight	1,486 g/litre
Viscosity	38 secs.
Cobalt Sulphate	0.017%
Gelatine solution	80 g/kg. (corresponds to 25 g. dry glue per kg. of engobe in water suspension).

Note: Gelifying glues are affected adversely by humidity and temperature. In hot season the amount of glue to be added to engobe increases up to 30 g/kg.

Phases and Operations in applying the Engobe:

1. The pieces coming from the dryers are carefully unloaded from the cars and placed on tables. The support is removed from the piece.

2. Glazing of the overflow tank: The discharge hole of the overflow tank is stopped with a rubber cork. The tank is filled up with the glaze. The glaze is emptied through the discharge hole again.

3. Inspection: The articles are now placed on cars and sent for inspection. It is here decided whether such defects are repairable or not.

4. The selected pieces are inspected further for eventual cracks at crucial points (corners, joints, edges, rims, stuck-up lines). This is done by brushing such points first with kerosine and reinspecting. The piece is then washed with a wet sponge and rinsed at least 3 times. Compressed air is used to remove dust and foreign matter.

5. The article is then numbered as follows:

   Date - Shift Number - Line Number - Ball Mill Number.

6. The piece is now conveyed to the engobe and glaze cabins stepwise. The operations are generally carried out in cabins as described:

I Cabin:

Three layers of engobe are applied by spraying.

The sprayer uses his hands to make the engobe layer uniform. This operation also improves the adhesion of the engobe to the articles and prevents the formation of patches on the surface.

Drops of engobe hanging on the rim, discharge hole, overflow window and in corners are removed.

After a general inspection a thin layer of engobe is applied on the rim edges.

II Cabin:

Two layers of engobe are applied here.

The distance between the I and II cabins should be at least 4 metres, i.e. the article should have enough time between these two cabins to allow the first layer to dry.

III Cabin: (4 metres from II cabin)

Here again two more layers are applied. The surface is made even by running over with the hands.

IV Cabin: (6 metres from III cabin)

The pieces have to be dried before application of another two layers of engobe. While applying the engobe, care has to be taken that the engobe does not accumulate in corners. In any case, corners have to be cleaned with a moist sponge. After application of the two layers, blurs and drops of engobe are removed and the surface is made even by running a very soft sponge over the articles.

V Cabin: (6 metres from IV cabin)

When the piece is dry, glaze is applied. Three layers of glaze are applied by spraying.

Glaze accumulated in corners is removed with a wet sponge.

The glazed piece is conveyed to intermediate lines and is not set on the kiln cars before the surface has dried - in the particular case we have selected, not before 30 mins.

7.3 <u>A new method for the application of engobe to fireclay bodies</u>: Owing to various complications involved in the application of the engobe by spraying, the author (C. Castelli) developed a new system of engoving. This new system has advantages and is economical as well.

<u>Method</u>: Vitreous China slip of a litre weight of 1,789 g. and viscosity of 160 sec. at 25°C is poured at a regular rate into the mould. The casting operation is stopped when the funnels are quarter full. The slip is allowed to remain in the mould for about 12 mins. The surplus slip is then drained off through two drainage holes made previously at some hidden point in the mould. When draining, the mould is tilted towards the drainage holes.

The drain hole diameter should not exceed 2/3 (maximum) of the inlet hole diameter. The reason for this is that when the slip drains out at a high rate and air cannot flow into the mould cavity at this rate, a vacuum is created, resulting in a pulling in of the walls, thus separating them from the mould. This gives rise to such defects as warping, cracks, etc. in the green and dry stages.

When the vitreous slip has been completely drained off, the drain holes are stopped with rubber corks. Now fireclay slip is poured into the same mould using the same funnels and the slip is left in the mould for the same time as for normal fireclay slip.

The operation of case, piston and piece removal is just the same and normal. The stick-up parts are produced by the same method described above. The sticking is also exactly the same, the only difference is that the sticking is done using Vitreous china slip and vitreous china instead of fireclay.

Tests carried out show that with an interval of 5 mins., 10 mins., 15 mins., 30 mins. between the draining of the surplus slip and the casting of the fireclay slip does not affect the adhesion of the fireclay and the Vitreous china slip.

The drying of the pieces has to be done slighly slower than that in the normal process with spray application and hand finishing. The piece now removed from the mould is complete, i.e. it does not require any engobing. Articles engobed by using such a method have to be glazed not as fireclay articles but as Vitreous china. Firing cycle and firing temperature are the same as in the traditional method.

Gypsum moulds used for such a method require careful preparation; joints require special attention and have to be perfect.

A section through the cast piece shows a regular and uniform distribution of the two layers of Vitreous China and fireclay. The finished articles are similar to vitreous ones.

The system can also be used for articles requiring a coloured engobe. In such a case the vitreous slip has to be coloured and this is done by simply mixing in a colour into the slip.

Table 5

Results of tests on traditional and plated fireclay bodies

Vitreous China Slip

Litre weight	1.789 grs.
Viscosity (25°C)	160 secs.
Residence time in mould	12 mins.
Thickness obtained	1.5 mm to 2 mm.

Fireclay slip

Litre weight	1.940 grs.
Viscosity (25°C)	108 secs.
Residence time in mould	18 hours

	Plated Fireclay	Traditional Fireclay
Shrinkage wet to dry:	2.54%	2.63%
" dry to fired:	3.02%	2.49%
" total:	5.56%	5.12%
Porosity:	0.50%	8.93%
Thermal shock resistance:	After 5 shocks dunting cracks observed.	After 5 shocks dunting cracks observed.
Accord between glaze and body:	As in the Vitreous China Body.	In accord

Table 6

Comparative times of casting and finishing

Operations	Sink Length 90 cm.				Sink Length 100 cm.			
	Fireclay				Fireclay			
	Traditional		Plated		Traditional		Plated	
	min	secs	min	secs	min	secs	min	secs
Mould and Funnels cleaning	2	30	2	80	1	80	1	80
Mould tightening	2	15	2	15	1	45	1	45
Casting	0	30	2	0	0	57	1	20
Piece removal	3	90	3	80	2	45	2	45
Exterior finishing	6	50	6	50	2	90	2	90
Upsetting the mould	2	30	2	80	1	83	1	83
Interior finishing	11	0	11	0	6	85	6	85
Outside finishing	8	30	8	30	4	50	4	50
Sponge washing	7	0	7	0	3	75	3	75
Transfer to dryer cars	0	95	0	95	0	60	0	60
Total times	46	20	47	30	26	70	27	33

Table 7

Comparison between Fireclays with respect to times and consumption of raw material

Plated Fireclay			Traditional Fireclay		
Sink 100 cm.		Sink 90 cm.	Sink 100 cm.		Sink 90 cm.
1.449	Kgs. of Glaze	2.777	7.940	Engobe kgs.	5.730
1 min. 60 secs.	Time reqd. to apply	2 mins.98 secs.	7 min.49 sec.	Time reqd. to apply	5 min.40 secs.
6 mins. 9 secs.	Total Time	7 mins.70 secs.	21min.80 sec.	Total time	17min.35 secs.
			2.183	Glaze kgs.	1.827
			3 min. 5 sec.	Time reqd. to apply	2 min.25 secs.
			5 min.30 sec.	Total time	4 min.50 secs.

Table 8

Comparative costs of two types of Fireclay Sinks

Operations	Sink 100 cm.		Sink 90 cm.	
	Tradit.	Plated	Tradit.	Plated
Slip preparation	817	1005	1109	1375
Moulds making	143	143	195	197
Casting	598	608	844	862
Drying	88	88	120	118
Engobe preparation	198	-	244	-
Engobage	388	-	477	-
Glaze preparation	60	161	72	309
Glazing	94	184	113	231
Loading on cars	58	58	58	58
Firing	663	663	750	750
Classifying and dispatch	62	62	85	86
	3169	2971	4067	3986

In the described Plated Fireclay the tendency to craze found in traditional fireclay is decreased. In fact, traditional fireclay is engobed and glazed only on the front, bottom and interior of the article. On the other hand, plated fireclay articles are practically totally covered by the vitreous engobe and therefore do not offer a porous surface capable of water absorption.

8. GLAZE

8.1 The necessity of glazing ceramic articles

At present there are a few ceramic articles which are not glazed. At the beginning of the pottery making epoch glazes were unknown and perhaps also not wanted.

According to a legend, glazing is supposed to have been discovered by accident when salt fell into the fire. Salting of pots was repeated till man finally did achieve a glazed surface. Other salts and metals were tried out, leading to the development of more complicated and beautiful glazes.

The application of a glaze has a number of advantages.

(a) The articles have a better appearance.

(b) The porous surface of articles is covered up and no absorption takes place. Thus cleaning is easier.

(c) Resistance to acids and alkalies is a characteristic of glazed ceramic products.

(d) Glaze on insulators increases resistivity. Glazed sewage pipes resist corrosion against waste waters.

(e) Glazed articles are hygienic.

(f) Glazed wall and floor tiles give better living conditions.

8.2 The glazes and their calculation

Glazes are expressed by most ceramists by a molecular or an empirical formula which gives the molecular fractions of the oxides present in the glaze. From the molecular formula it is easy to derive the percentage of oxides present in a glaze.

For example the following gives the molecular formula of a partial fritted glaze:

	RO	R_2O	RO_2
CaO	0,380		
K_2O	0,076	0.260 Al_2O_3	2,900 SiO_2
Na_2O	0,210		0,370 B_2O_3
PbO	0,334		

To get the weight ratio the equivalents of the oxides given in the molecular formula are multiplied by their molecular weights as shown below.

Oxide	Equivalent		Molecular weight		Weight ratio
CaO	0,380	x	56,1	=	21,318
K_2O	0,076	x	94,2	=	7,159
Na_2O	0,210	x	62,0	=	13,020
PbO	0,334	x	223,2	=	74,548
Al_2O_3	0,260	x	101,9	=	26,494
SiO_2	2,900	x	60,1	=	174,290
B_2O_3	0,370	x	69,6	=	25,752
			Total weight of the batch		342,581

The oxides present in the molecular formula are in a definite ratio and to obtain the percentage composition, one has to divide the weight ratio of the oxides by the total batch and multiply by 100.

CaO	21,320	:	342,580 x 100	=	6,22
K_2O	7,160	:	342,580 x 100	=	2,09
Na_2O	13,020	:	342,580 x 100	=	3,80
PbO	74,550	:	342,580 x 100	=	21,77
Al_2O_3	26,490	:	342,580 x 100	=	7,73
SiO_2	174,290	:	342,580 x 100	=	50,88
B_2O_3	25,750	:	342,580 x 100	=	7,51
					100,00

The above mentioned glaze contains oxides of lead and Boron and is therefore a partially Fritted glaze. A partially fritted glaze is one in which water soluble salts are converted to an insoluble form by fritting (fusing). This fritting process improves the colour, fusibility and maturity of the glaze.

From the empirical formula of a glaze, it is possible to calculate the batch weight. The following explain the derivation of a batch composition from a simple molecular formula of a blaze of the composition shown here:

RO		R_2O_3		RO_2	
0,3	K_2O				
0,5	CaO	0,40	Al_2O_3	3,85	SiO_2
0,1	MgO				
0,1	BaO				

Calculation:

Feldspar has the formula K_2O Al_2O_3 6 SiO_2 which means that for one equivalent of K_2O, one equivalent of alumina and 6 equivalents of silica would be required. Thus 0,3 of K_2O calls for 0,3 of Al_2O_3 and 0,3 x 6 = 1,80 of SiO_2.

Alumina is supplied by Kaolin with the formula: Al_2O_3 $2SiO_2$ $2H_2O$. Now calculate the amount of Kaolin present in the glaze using the quantity of alumina left over after Al_2O_2 required for the Feldspar has been deducted as a base. Silica is added as flint or Quartz to make up the Silica content required in the glaze.

Each molecular equivalent is then multiplied by its respective molecular weight to give the batch weight. See Table 9 for batch weight calculation.

<u>Calculation of the glaze formula from the molecular formula of the partially fritted glaze:</u> For convenience the formula has been repeated here.

RO		R_2O_3		RO_2	
CaO	0,380				
K_2O	0,076	0,260	Al_2O_3	2,900	SiO_2
Na_2O	0,210			0,370	B_2O_3
PbO	0,334				

A portion of this glaze is fritted. First of all it is to be decided which part of the glaze is fritted.

Silica, Alumina and the group RO combine to form the base of the insoluble silicates.

The oxides of sodium, potassium, lead and boron act as fluxes.

Table 9. Batch weight calculation

Equivalents of the Molecular Formula:

K_2O	CaO	MgO	BaO	Al_2O_3	SiO_2	Raw Materials	Molecular Equivalent	– –	Molecular Weight		Parts by Weight
0,3	0,5	0,1	0,1	0,4	3,85						
0,3				0,3	1,80	K-Feldspar	0,30	x	556	=	166,8
	0,5					Calcium Carbonate	0,50	x	100	=	50,0
		0,1				Magnesium Carbonate	0,10	x	84	=	8,4
			0,1			Barium Carbonate	0,10	x	197	=	19,7
				0,1	0,20	Kaolin	0,10	x	258	=	25,8
					1,85	Quartz	1,85	x	60	=	111,0
									Batch weight		381,7
0,3	0,5	0,1	0,1	0,4	3,85						

By dividing the parts by weight by the batch weight and multiplying by 100, the raw materials are converted to a percentage basis as shown below.

Potassium Feldspar	166,8	:	381,7	x	100	=	43,69%
Calcium Carbonate	50,0	:	381,7	x	100	=	13,09%
Magnesium Carbonate	8,4	:	381,7	x	100	=	2,20%
Barium Carbonate	19,7	:	381,7	x	100	=	5,16%
Kaolin	25,8	:	381,7	x	100	=	6,76%
Quartz	111,0	:	381,7	x	100	=	29,08%
							100,00

For fritting, the following rules exist and these govern the relative amounts of constituents:

1) Ratio of acid : base should be between 1 : 1 and 1 : 3
2) Ratio of alkalies : RO should not exceed 1 : 1
3) Ratio of silica : boric acid should be at the minimum 2 : 1
4) Alumina should be less than equivalents 0,2
5) All soluble alkalies and boric oxide have to be fritted
6) Oxygen ratio should be between 2 and 6 as calculated by the equation

$$\text{Oxygen ratio} = \frac{2 \text{ x equivalent of } SiO_2}{RO + (3 \text{ x equivalent of } Al_2O_3)} = \text{between 2 and 6}$$

7) Most of the lead oxide and toxic constituents have to be fritted to avoid danger.

On the basis of these rules we arbitrarily select the following amounts for fritting:

RO		R_2O_3		R_2O	
K_2O	0,076				
Na_2O	0,210	Al_2O_3	0,10	SiO_2	1,50
CaO	0,100	B_2O_3	0,3		
PbO	0,334				
	0,720				

These values give the portion of raw materials that are not to be fritted

CaO	0,28	Al_2O_3	0,16	SiO_2	1,90

To be able to calculate the batch weights of the frit it is necessary to convert the selected frit formula into a true molecular formula. This is done by summing up the values of the group RO and dividing the resp. value of the oxides by this RO sum (in our case 0.72).

					A	B	(Values from A rounded up)
K_2O	0.076	:	0.720	=	0.10	0.10	
Na_2O	0.210	:	0.720	=	0.29	0.03	
CaO	0.100	:	0.720	=	0.14	0.15	
PbO	0.334	:	0.720	=	0.46	0.50	
Al_2O_3	0.100	:	0.720	=	0.14	0.15	
B_2O_3	0.370	:	0.720	=	0.51	0.50	
SiO_2	1,500	:	0.720	=	2.08	2.10	

The values under A (exact values) are rewritten in the form shown below:

RO		R_2O_3		RO_2	
K_2O	0,10				
Na_2O	0,10	Al_2O_3	0,14	SiO_2	2,08
CaO	0,14	B_2O_3	0,51		
PbO	0,46				

The equivalent weight or combining weight of the frit is found by multiplying the equivalents of each oxide by its respective molecular weight and adding them.

Oxide	equivalent A		Molecular weight		Combining or equiv. weight (A values)
K_2O	0.10	x	94.2	=	9.42
Na_2O	0.29	x	62.0	=	17.98
CaO	0.14	x	56.1	=	7.85
PbO	0.46	x	223.2	=	102.67
Al_2O_3	0.14	x	101.9	=	14.27
B_2O_3	0.51	x	69.6	=	35.50
SiO_2	2.08	x	60.1	=	125.01
			Equiv. weight of the frit		312.70

The equivalent weights of the frit calculated as given by the column B are:

K_2O	0.10	x	94.2	=	9.40
Na_2O	0.30	x	62.0	=	18.60
CaO	0.15	x	56.1	=	8.40
PbO	0.50	x	223.2	=	111.60
Al_2O_3	0.15	x	101.9	=	15.30
B_2O_3	0.50	x	69.6	=	34.80
SiO_2	2.10	x	60.1	=	126.20
					324.30

8.3 The importance of fineness of glazes

Glazes are applied in the form of water suspensions. The fineness of the glaze components is important with regard to the formation of suspensions because the finer the particles, the easier it is to suspend them. Generally, zinc oxide, zirconium oxide or zirconium silicate tin oxide, borax, boric acid, lead oxides, calcium carbonate are available on the market in powder form. Materials like feldspar, quartz, dolomite are sold in stone form and have to be ground to powder.

The Batch weights of the frit are calculated as follows: (Values based on Column A)

Table 10

Batch weights
Based on exact values (A)

Equivalents of oxides

0.10	0.29	0.14	0.46	0.14	0.51	2.08	Raw	Molecular		Molecular		Parts by
K_2O	Na_2O	CaO	PbO	Al_2O_3	B_2O_3	SiO_2	Materials	Equivalent		Weight		Weight
0.10				0.10		0.60	K-Feldspar	0.10	x	556.7	=	55.67
	0.255				0.51		Borax	0.255	x	331.2	=	97.20
	0.035			0.035		0.21	Na Feldspar	0.035	x	524.5	=	18.36
		0.14					Calcium Carbon.	0.14	x	100.1	=	14.01
			0.46				Lead Carbonate	0.463	x	775.6	=	118.90
				0.005		0.01	Kaolin	0.005	x	258.1	=	1.29
						1.26	Silica	1.26	x	60.1	=	75.73
0.10	0.29	0.14	0.46	0.14	0.51	2.08		Batch Weight			=	381.16

Components of the frit by percentage:

		Formula
K-Feldspar	55.67 : 381.2 x 100 = 14.62 %	$K_2O\ Al_2O_3\ 6\ SiO_2$
Na-Feldspar	18.36 : 381.2 x 100 = 4.82 %	$Na_2O\ Al_2O_3\ 6SiO_2$
Borax	97.20 : 381.2 x 100 = 25.49 %	$Na_2O\ 2B_2O_3$
Calcium Carbonate	14.01 : 381.2 x 100 = 3.67 %	$CaO\ CO_2$
Lead carbonate	118.90 : 381.2 x 100 = 31.19 %	$3PbO\ 2CO_2\ H_2O$
Kaolin	1.29 : 381.2 x 100 = 0.33 %	$Al_2O_3\ 2SiO_2\ 2H_2O$
Quartz	75.73 : 381.2 x 100 = 19.88 %	SiO_2
	100.00 %	

Table 11

Batch weights

Based on values from column B (rounded up values)

Equivalent of oxides

0.10	0.30	0.10	0.50	0.15	0.50	2.10
K_2O	Na_2O	CaO	PbO	Al_2O_3	B_2O_3	SiO_2
0.10				0.10		0.60
	0.25				0.50	
	0.05			0.05		0.30
		0.10				
			0.50			
						1.20
0.10	0.30	0.10	0.50	0.15	0.50	2.10

Raw Materials	Molecular Equivalent		Molecular Weight		Parts by Weight
K-Feldspar	0.10	x	556	=	55.60
Borax	0.25	x	381	=	95.25
Na-Feldspar	0.05	x	524	=	26.20
Calcium Carbonate	0.10	x	100	=	10.00
Lead Carbonate	0.50	x	776	=	128.50
Silica	1.20	x	60	=	72.00
	Batch weight				387.55

The percentage composition of the frit is as follows:

K-Feldspar	55.60 : 387.55 x 100 =	14.34 %
Na-Feldspar	26.20 : 387.55 x 100 =	6.78 %
Borax	95.25 : 387.55 x 100 =	24.58 %
Calcium Carbonate	10.00 : 387.55 x 100 =	2.58 %
Lead Carbonate	128.50 : 387.55 x 100 =	33.15 %
Quartz	72.00 : 387.55 x 100 =	18.57 %
		100.00 %

Table 12

Original glass batch weight and percentage composition calculations of the glass

0.076	0.210	0.380	0.334	0.260	0.370	2.900
K_2O	Na_2O	CaO	PbO	Al_2O_3	B_2O_3	SiO_2
0.076	0.21	0.10	0.334	0.100	0.370	1.600
		0.28				
				0.160		0.320
						0.980

Raw Materials	Equivalent Weights		Molecular Weights		Parts by Weights
Frit	0.72	x	381.16	=	274.43
Calcium Carbon.	0.28	x	100	=	28.00
Kaolin	0.16	x	258	=	41.28
Quartz	0.98	x	60	=	58.80
Batch weight of glass					402.51

The percentage composition of the glass will thus be:

274.43 : 402.51 x 100 = Frit	68.18 %
28.00 : 402.51 x 100 = Calcium carbonate	6.95 %
41.28 : 402.51 x 100 = Kaolin	10.25 %
58.80 : 402.51 x 100 = Quartz	14.61 %
	99.99 %

The two batch weights calculated with exact figures and with round figures do not show an appreciable difference.

The batch weights of the glaze have now to be determined.

The amount of frit to be put into the glaze can be calculated as a simple ratio between the formulae of the glaze and the frit.

Calculated Frit Formula		Glaze Formula (Original glaze formula)	
0,10	K_2O	0,076	K_2O
0,29	Na_2O	0,21	Na_2O
0,14	CaO	0,38	CaO
0,46	PbO	0,334	PbO
0,14	Al_2O_3	0,200	Al_2O_3
0,51	B_2O_3	0,370	B_2O_3
2,08	SiO_2	2,900	SiO_2

The ratio between the two formulae is about 0.72 : 1 which means that 0.72 of frit equivalent could be put into the glaze thus furnishing the following equivalents:

K_2O	0,076
Na_2O	0,21
CaO	0,10
PbO	0,334
Al_2O_3	0,10
B_2O_3	0,370
SiO_2	1,60

These equivalent have to be subtracted from the equivalent of the original glaze.

The difference between the equivalents of raw materials and the frit composition is completed by calculating as shown in table 12.

The grinding of these materials is generally done stage-wise in

i Jaw crushers

ii Cone crusher

iii Edge runner mill

The powder obtained is then subjected to fine grinding in a ball mill. The fineness of hard materials has to be measured and controlled for the following two reasons:

a) constancy of the particle size distribution for different batches of the same glaze and constancy of glaze tests, done for comparison purposes.

b) In order to preserve the above constancy and to set the right reactions afoot, a definite fineness of the particles is essential.

These two points are important for the entire glaze preparation process and also for the glass formation step during firing. As a matter of fact, a glaze is a water suspension of the different glaze components which have to satisfy certain requirements:

1. All components of the glaze have to be in the same state of fineness as it is only then possible to attain a constant glaze density (litre weight) for the same water content. A constant litre weight for the same water content is important for glazes because the thickness of the glaze layer on the body as well as its shrinkage is a function of the proportion of water in the batch formula.
   The settling time of the glaze suspension should be high. This high settling time can only be achieved by increasing the fineness of the particles.

2. Surface reactions must be consistant and constant for different batches so that these melt at the same temperature or within a similar temperature range.
   Surface reactions are phenomena during which an aggregation or a breakdown of particles takes place under the influence of the chemical and physical changes of state. For example, a piece of feldspar, say 100 g. in weight, does not melt whereas 100 g. of powder of the same piece melts. This is due to the fact that grains offer a lower resistance to the firing action and start melting at a definite temperature. These grains influence the neighbouring ones during melting till the whole system turns to a glassy mass. On the other hand, heat transmission into a piece is on quite different basis and one observes that only the surface melts and an incomplete fusion of the interior of the piece has taken place. It is clear that the greater the fineness of the particles, the larger is the surface, thus the surface reactions are increased and melting is easier and complete.

The fineness of the glaze particles also influences the accord between glaze and body. The finer the particles, the lower is the tendency to crazing defects. The ability of the glazed surface to reflect light is also influenced by the particle fineness. By increasing the surface area per unit weight of certain glaze component and certain glazes, the ability to reflect light is decreased.

The fineness is therefore of considerable importance in glaze preparation and it is an absolute necessity to check the fineness and particle size distribution of the glaze and its components.

8.4. The glaze properties and their tests

One of the characteristics that a glaze must have is its adaptability to the body on which it is applied.

Adherence between glaze and body is necessary to keep them bound to one another till the firing process increases the adherence needed to transform body and glaze into one inseparable piece. This property is called accord between glaze and body and to get the best accord, able to resist the stresses and shocks which a glazed article is subjected to during its use.

Physical and chemical phenomena and reactions both for the glazes and bodies, have to be taken into account in order to understand them and their behaviour during different stages the article undergoes in the process of manufacture. Special consideration has therefore to be given to the raw materials to be used in glaze as well as in body preparation; their quality and purity have to be known and the required treatment has to be determined to be able to get the best results.

In order that a glaze be suitable and good, it must have the following characteristics:

a) Prior to application on the body:

1. Should be well ground and conform to the required specifications.
2. Must be homogenous.
3. Must have the specified density.
4. Must have the specified viscosity.

b) On the articles and before firing:

Sufficient adherence to the surface of the body to enable easy handling in the factory without damaging the glazed surface.

c) <u>On the finished product:</u>

1. A perfect accord with the body.
2. Smooth clean surface, free from dirt and spots.
3. A definite desired fusibility.
4. A covering ability.
5. Even thickness.

These properties can be obtained by following the process specifications exactly and following this up with proper testing and control.

In glaze preparation, grinding is done by means of the Jaw Crusher, Edge Runner Mill and Ball Mill. The use of machines like the Jaw Crusher and Edge Runner Mill is relatively simple. The Ball Mill requires greater attention because efficiency of grinding and the size of the particles depend on its proper use.

The finer the Feldspar and Quartz particles, the greater is their reaction surface and therefore the glaze batch will be more uniform and during firing, maturation is quicker and complete. The fineness of hard material particles has to be fixed by appropriate trials.

Consideration has to be given to the fact that very fine particles of the hard materials affect the thermal expansion of the glaze for the same firing cycle and temperature. One effective remedy for crazing is a finer grinding of the glaze or of the hard material (quartz).

Fineness has to be checked carefully once it is fixed. There are different methods of checking fineness. Comparative numbers help to control and maintain the required fineness within limits.

After proper grinding, a glaze suspension is prepared and this is then carefully screened to the specified fineness.

Magnetic separation is also necessary to remove metallic particles which cause coloured spots, pin holes, and interrupted glaze surface. The glaze suspension density is then adjusted to the specifications.

<u>Litre weight:</u> The litre weight of a glaze batch is important because it effects the sticking ability, the thickness, shrinkage as well as the homogeneity of the glaze. On considering the fact that each type of body requires a definite glaze

layer thickness, it is obvious that a careful control of the layer thickness is essential. The thickness can only be maintained constant by keeping a fixed litre weight and by applying the glaze uniformly.

Another point that requires consideration in connection with glaze density is that the glaze should remain a stable suspension. This is only possible when a certain density is reached. Any deviations from this density cause the heavier particles to settle, thus affecting the homogenity.

When a glaze is too light (i.e. too fluid) it has the tendency to flow off the body. The amount of glaze adhering to the body is proportional to the quantity of water present in the glaze batch.

The amount of water absorbed by the body and that evaporated both influence the wet to dry shrinkage of the glaze. When the shrinkage is too high, cracking takes place which cannot be removed even under melting action.

<u>Viscosity</u>: The viscosity of a glaze suspension is an important property and is used to control and maintain the spreading of the glaze in the raw state over the surface of the piece within the required limit. A glaze which is too fluid runs out over the edges of the piece leaving uncovered patches and will accumulate in the corners or at the bottom of the article. Fluidity is partially related to the litre weight of the glaze and can be adjusted by adding a floculant or a defloculant as the case may require. The viscosity of a glaze is of importance to the maturing period during firing. The viscosity is increased or decreased depending upon the glaze composition. Glazes with Silica and Potassium as components are more viscous than glazes with Silica and Sodium. A viscous glaze flows more evenly during melting.

<u>Adherence</u>: is the property of a glaze to remain attached to the body for a relative period of time. The adherence can be increased by the addition of organic adhesives. Sometimes adherence is improved by floculating materials. These agents increase the tendency of the glaze particles to come closer to one another. The addition of adhesives requires special attention to avoid such defects like <u>crawling</u> on the glazed surface caused by using excessive or insufficient amounts of the adhesive.

The thickness of the glaze layer is maintained constant by observing the following:

By maintaining a fixed and constant litre weight and viscosity of the glaze suspension.

By adding the right amount of adhesive.

Applying the right pressure when using a spray gun for the glaze application.

Right time of immersion when dipping.

By maintaining the porosity of the articles to be glazed constant.

There are no fixed rules for establishing the quantities or values for the points mentioned above. These can only be determined by a procedure of trial and error.

The ability of a glaze to cover: This property varies with the type of the glaze. If only the colour of the body has to be covered up, it is sufficient to apply an opaque glaze. If in addition also the asperities of the body have to be covered, then an opaque glaze would have to be used and the layer thickness must be increased.

In some articles the roughness of the article surface is considerable to be covered easily by a layer of glaze of reasonable thickness. The glaze layer would have to be very thick in order to cover up such roughness with consequent bad results. In such cases, for example fireclay bodies with considerable grit content, an engobe or covering porcelain has to be applied. The glaze is then applied to cover the engobe.

Fusibility: The temperature range within which a glaze attains maturity varies from glaze to glaze. As a matter of fact there is only one temperature at which a glaze matures best. There are also different glaze compositions for the same temperature but on closer examination one observes that each of these have a definite maturing period and maturing point.

The Seger cone firing temperature control is the most effective method. In order to make comparative tests between different firings, the temperature increments have to be constant. For example, a cone which is subjected to a firing cycle with an increment of 30°C per hour will melt or fall later than the same cone when subjected to a cycle with 60°C/hour increments. For comparison purposes and to maintain a constancy of results it is important to use only one type of cone. When it is necessary to change cones, it is essential to compare the two or more cones by firing all of them together and noting their comparative behaviour. A change of cone has to be brought to the notice of the operators in charge of the firing so that they can acquaint themselves with the new cones.

Smoothness of the glazed surface: The smoothness of the surface depends on the composition of the glaze, on the selection of the right firing temperature and on the evenness with which it is applied.

The glaze department should be kept clean. Unnecessary handling of the glazed article should be avoided and operators should keep their hands clean. The loading of the articles to the kilns should be done with care to avoid dust and dirt falling on to the glazed articles. Dirt should be removed by brushing or vacuum cleaners and not by blowing air or by pressurized air blowers unless some device is used later to clean by suction.

Accord between body and glaze: A good accord can be obtained by proper calculation, right preparation and application of the glaze. To be able to calculate the composition of the glaze, both the characteristics of the glaze components and body characteristics must be known. In glaze calculations one distinguishes between glazes for Vitreous bodies and those for porous bodies.

Vitrified bodies: From the molecular formula of these bodies one can calculate the ratio of Silica to Alumina and from this ratio it is possible to indicate whether or not certain glazes agree with the body. In the case of vitrified bodies it is possible to calculate the coefficient of thermal expansion with a greater surity and to compare it with that of the glaze. From this it is possible to say whether compression or tension will build up after firing.

Porous bodies: From the molecular formula alone one could derive some information but this is by no means sufficient to allow the forecasting of a proper glaze. For the purpose of finding out the accord between body and glaze, various empirical systems have been developed like the ring system (Chapter 8.8.1) or the autoclave test. Thermal expansion testing apparatus giving very accurate expansion curves as well as relative and absolute coefficients of expansion have also been designed and developed. Such apparatus could be used to measure and compare the expansion of body and glaze.

8.5 The Raw Materials for Glazes

The raw materials for glazes can be classified on the basis of their chemical formula as follows.

1. Raw materials supplying basic oxides. These flux with SiO_2 and B_2O_3 to form glasses.
2. Materials supplying Al_2O_3
3. Materials supplying SiO_2 - B_2O_3
4. Opacifiers
5. Crystalizers
6. Colouring agents.

Raw materials supplying **basic oxides:**

a) Na_2O (Sodium Oxide)

Borax crystals	$Na_2B_4O_7 \cdot 10H_2O$	Soluble in water
Borax anydrous	$Na_2B_4O_7$	
Sodium Carbonate	$Na_2CO_3 \cdot 10H_2O$	
Sodium Carbonate	Na_2CO_3	
Sodium Nitrate	$NaNO_3$	

Feldspar, Sodium Albite Na_2O Al_2O_3 6 SiO_2

b) For K_2O (Potassium oxide)

Potassium Carbonate	K_2CO_3	Soluble in water
Potassium Nitrate .	KNO_3	
Potassium Feldspar	$K_2O.Al_2O_3{}^{6}.SiO_2$	

Water soluble salts have to be fritted to convert them into insoluble compounds. Fritting is the melting of glaze components to form glasses which are not soluble in water. Fritting is also necessary to convert salts which evolve gases during decomposition. These salts are converted to stabilized compounds, thus avoiding evolution of gases during the maturing of the glaze. The following examples show the reactions that take place during fritting.

$Na_2B_4O_7$	Na_2O	+	$2B_2O_3$
Na_2CO_3	Na_2O	+	CO_2
$NaNO_3$	Na_2O	+	NO_2
K_2CO_3	K_2O	+	CO_2
KNO_3	K_2O	+	NO_2

Alkaline Earth Oxides are introduced into a glaze by adding:

Calcium Carbonates $CaCO_3$. This decomposes to give CaO and CO_2

Barium Carbonate gives Barium Oxide and Carbon Dioxide
$BaCO_3 \quad BaO + CO_2$

Lead Oxide (PbO) is supplied by one of these compounds.

PbO litharage Pb_3O_4 red lead 2 $PbCO_3$ $Pb(OH)_2$ white lead.

The oxides of lead are poisonous and their use is decreasing in commercial glazes.

Boric Oxide is supplied by one of the following compounds:

$Na_2B_4O_7$ Anydrous Borax $Na_2B_4O_7$ $10H_2O$ Borax Crystals H_2BO_3 Boric Acid

Silica (SiO_2) is introduced as Feldspar, Quartz or Flint, China Clay and clays.

Zinc Oxide (ZnO) is generally found as such in commerce.

Alumina (Al_2O_3) is supplied by Feldspar (K_2O or Na_2O $Al_2O_3.6SiO_2$) and China clay (Al_2O_3 $2SiO_2$ $2H_2O$)

Tin Oxide SnO_2 is found as such.

Zirconium silicate ($ZrSiO_4$) gives ZrO_2 and SiO_2 on decomposition.

ZrO_2 Zirconia is also found as such.

CaF_2 is also a supplier of CaO when introduced as Feldspar mineral.

8.6. Grinding characteristics of glaze raw materials

The resistance a material offers to a crushing force is a function of the following properties:

a) Hardness of the material. The values of hardness of some materials are listed below

Quartz	7	(Mohs Scale)
Feldspar	6	(" ")
Porcelain grit	8	
Earthware grit	6-7	

b) Tenacity of the material. This property depends on the compactness of the material. The higher the density the greater is the power consumption to crush the material.

c) Elasticity of the material. This is the tendency of a material to assume its original shape under the action of the forces of deformation.

Another factor to be considered is the condition of the material to be ground.

1) The moisture content of the material to be crushed should be kept low when using edge runner mills or crushing mills to avoid the formation of a plastic mass. This does not apply to Ball mills.

2) Factors of considerable importance are the size of the material to be crushed and also the required size of the crushed product. Crushing and grinding machines are not all capable of handling different material sizes and producing the required particle size and particle shape.

To produce a definite particle shape, a particular grinder has to be selected. Various shapes can also be produced by a proper regulation of the machine. In the ceramic industry particles of different shapes are required for different purposes. It is therefore essential to make the right selection of size reduction machinery.

The machines required for the crushing and grinding of glazes and glaze raw material are the same as those required for the preparation of hard materials (see chapter 4.2).

8.7 Glaze preparation

In the Ceramic industry glazes are as important as bodies themselves. Their use in most of the ceramic factories, is more and more extended and complex glazes are bringing a new touch of brilliancy and beauty to articles. The introduction of a new glaze which corresponds to the requirements and at the same time gives aesthetic appearance, resistance and durability to the article is a great achievement for a ceramic technician.

Glazes have to possess the following characteristics in order to serve the purpose of their application.

1. Insolubility in water
2. Resistance to attack by acids and alkalis
3. Resistance to scratching
4. Should not absorb liquids
5. Resistance to peeling and crazing
6. Suitability for decorative work
7. Fusibility at predetermined temperatures
8. Smoothness of surface

Glazes are practically glasses which may or may not be transparent and can have different colours. Glass makers almost always enter into the manufacture of glazes. Elements like Silica, Boron, Phosphorous, Arsenic, Germanium and a few others form glasses. These elements are linked with oxygen atoms and other components to form a glass of a definite structure. Both glasses and glazes contain other elements called stabilizer or modifier elements. The more common stabilizers are:

Sodium	Na	Lithium	Li
Potassium	K	Beryllium	Be
Magnesium	Mg	Calcium	Ca
Barium	Ba	Strontium	Sr
Lead	Pb	Titanium	Ti
Aluminium	Al	Zirconium	Zr
Zinc	Zn	Tin	Sn

Each of these elements have different chemical and physical characteristics and when present in a glaze they effect its characteristics, for example hardness etc. The composition of a glaze is normally expressed as a molecular formula; this expresses the molecular fraction of the oxides present in a glaze. The molecular formula is expressed as: Basic Oxides - Amphoteric Oxides - Acidic Oxides. From this molecular formula it is possible to calculate a batch composition, but the results obtained are not exact because different materials can be used in a glaze to produce, more or less similar characteristics.

The following give a classification of some of the available oxides:

<u>Basic oxides are:</u>

Potassium oxide	K_2O
Sodium oxide	Na_2O
Calcium oxide	CaO
Lead Oxide	PbO
Zinc oxide	ZnO
Magnesium oxide	MgO
Barium oxide	BaO

<u>Amphoteric oxide:</u>

Aluminium oxide	Al_2O_3

<u>Acidic oxides are:</u>

Silica oxide	SiO_2
Zirconium oxide	ZrO_2
Tin oxide	SnO_2
Titanium oxide	TiO_2
Boron oxide	B_2O_3

Glazes with high melting points have only Silica as an acidic oxide, but glazes with lower melting points have along with Silica also B_2O_3 as an acidic oxide.

Like most of the other ceramic mixtures glaze can also be prepared by making a compromise between different factors.

By giving due regard to the rules of glaze formation, one can get good results and at the same time the glaze is easily adaptable to the body to which it is to be applied. Glazes could be classified as follows:

Glazes containing lead
Leadless glazes
Majolica glazes for temperatures between 900°C and 1050°C
Earthenware glazes for temperatures between 1000°C and 1150°C
Sanitary ware glazes for temperatures between 1200°C and 1250°C
Porcelain glazes for temperatures of 1300°C and above
Matt glazes
Semi-matt glazes, satin glazes, opaque glazes.

8.8 Testing of glazes and glaze raw materials

Raw materials used for glaze preparation have to be of the best quality, must possess definite characteristics and have a minimum of impurities. All the components that go into a glaze have to be chemically analysed to determine their oxides content as also the ratios of these oxides to one another as these values are required for the purpose of glaze batch calculation.

A suitable laboratory should always be an integral part of a ceramic plant and should be equipped with apparatus to carry out tests detailed below:

Fineness tests
Hydrometric and sieving tests
Firing tests to establish the colour after firing
Shrinkage test
Thermal shock resistance test
Coefficient of thermal expansion
Specific gravity and litre weight
Viscosity
Glaze layer thickness determination

The laboratory should also be equipped with apparatus to carry out chemical analysis.

Chemical analysis would include the determination of:

Iron
Titanium
Calcium
Magnesium
Potassium
Sodium
Silica
Alumina

Ignition losses of raw materials as feldspar, quartz, grit, china clay and clays.

The chemical laboratory would also be required to determine the purity of the following material and others not included in this list:

Calcium carbonate
Zinc oxide
Tin oxide
Cobalt sulphate
Barium nitrate
Lead oxide
Zirconium silicate

Physical tests:

a) Fineness test:

Procedure: 100 grams of the clay material is suspended in water. The particles must be well dispersed to allow them to pass through the sieve. This suspension is passed through a 140 mesh screen. The over-size i.e. the residue left on the sieve is dried at 110°C and weighed.

It is advisable to examine the over-size particles in order to prescribe the right sieve to eliminate the greater part of over-size particles during the preparation process.

The fineness could also be determined by sieve analysis but this method gives approximate results which are not suitable for exact comparison purpose.

The fineness of ground materials should be always determined by reliable methods. A number of methods are available to determine the fineness but for practical work the Kootgen-Halton method is suggested; this is based on the rate of fall of particles through a liquid.

b) Hydrometric test:

This is a rapid and practical method to determine the grain size. The liquid containing the fine particles in suspension is placed in a graduated cylinder and a hydrometer is placed in this liquid. As the particles settle the density of the suspension decreases and as a result the hydrometer sinks deeper. The hydrometer should be small to avoid errors due to its volume and also due to the development of deposits on its surface. By reading the positions of the hydrometer on the graduations of the cylinder a curve is plotted and by applying the following equation grain size composition is found:

$$\text{Percentage of material} = \frac{100\ (H - X)\ S.100}{W\ (S - 1)}$$

H = Hydrometer reading
W = Specific gravity of material
S = Specific gravity of powder
X = Factor based on the deflocculant added

<u>Shrinkage test</u>: The shrinkage of clays and china clays can be determined by preparing a water suspension and casting this slip with a definite litre weight and viscosity in a mould. When the tile is taken out of the mould it is marked as shown in Fig. I Appendix. The test method is also applicable to bodies.

This tile on drying shrinks and the lengths marked on it become shorter. The difference between the initial length and the length after drying gives the shrinkage. This can be reported as a percentage and is called the wet-dry shrinkage.

The tile is now fired and it shrinks further due to the change of state. The decrease in distance between the two points after drying and after firing gives the shrinkage from dry - fired state.

The sum total of these two shrinkages is the total shrinkage.

Example: Let us assume that the distance between the two points A and B soon after moulding is 10 cm, after drying 0.4 cm and after firing is 9.2 cm. The wet to dry shrinkage is:

10 - 9.4 = 0.6 cm   or 0.6 x 10 = 6 %

and the total shrinkage is

10 - 9.2 = 0.8   or 0.8 x 10 = 8 %

The dry to fired shrinkage is 8 - 6 = 2 %

This test gives the linear shrinkage of the body.

<u>Volumetric shrinkage</u>:

The volumetric shrinkage is found by immersion of the test piece in Kerosene and noting the displaced volume. Immersions carried out in the dry and fired states give the difference in volumes in these two states and in reported as a volumetric shrinkage.

Example: Let us assume that the volume of the piece in the wet state is 5 cm^3 and after drying 4.9 cm^3

Volumetric shrinkage wet to dry state:

$$5 - 4.9 = 0.1\ cm^3 \times 20 = 2\ \%$$

If the volume measured after firing is 4.75 cm^3 then the volumetric shrinkage from wet to fired or total volumetric shrinkage is

$$5 - 4.5 = 0.25 \times 20 = 5\ \%$$

The volumetric shrinkage from dry to fired state is

$$5\ \% - 2\ \% = 3\ \%$$

Thermal shock resistance:

The test is carried out on finished products to find out their resistance to crazing. The pieces to be tested or immersed in water containing 10% calcium chloride and kept boiling for 1 hour. These hot pieces are then plunged into cold water and kept there till they are cooled. The pieces are then examined for any crazing cracks. If no defects are detected the test is repeated another five times.

Specific Gravity

The determination of the specific gravity of raw materials is of great importance as it is one way to test the purity of the materials. The specific gravity is generally determined with the help of a specific gravity bottle or a pycnometer. A deviation of the specific gravity from the actual value is a definite indication of impurities. Specific gravities of some raw material for glases are listed below.

SiO_2	2.65 (quartz)	Pb_3O_4	9.80
Al_2O_3	3.96	MnO	5.40
$CaCO_3$	2.71	PbO	9.50
ZnO	5.78	CuO	6.40
SnO_3	6.60 (amorphous)	$BaCO_3$	4.30
SnO_2	6.75 (crystalline)	$PbCO_3$	6.43

Thermal expansion:

The coefficient of linear expansion is the increase in length per unit length by an increase of temperature of 1° centigrade. This increase is a function of the increase in temperature and does reflect the changes of state of ceramic materials. When these changes are known, they permit the proper selection of the best possible glaze for bodies and also enable the technician to take proper steps during firing. The coefficient of thermal expansion is determined with the help of special apparatus. The specimens are fired in a kiln within definite temperature ranges and the coefficient of thermal expansion is measured. This test is also used to determine the changes in size of raw bodies and clays in order to estimate the amount of free silica in clays and the degree of calcination of flint.

8.8.1 Method of testing the compression and tension of glazes on ceramic bodies

The "Ring Method" is one of the simplest ways of determining whether a glaze is in tension or compression on a ceramic body. The importance of the test is all the more emphasized by the need to know the tendency of a glaze to "crazing" or "peeling".

The study of accord between a ceramic body and its glaze is done with the following fundamental purposes:

a) Accord between body and glaze after firing

b) Accord between body and glaze for an indefinite period of time

c) Resistance of the body and glaze to thermal shocks.

On cooling a glazed piece one of the following two conditions could be met with:

i. The ratio of the thermal coefficient of the body (B) to glaze (G) is greater than unity i.e. $\frac{B}{G} > 1$. This means that the body contracts more than its glaze. This calls for a condition in which the glaze resists the contraction of the body and has a tendency to peel off. This phenomenon is called "Peeling".

ii. The ratio of the thermal coefficient of the body to the glaze is less than unity i.e. $\frac{B}{G} < 1$. In this case the glaze contracts more than the body. Thus the glaze itself will be subjected to tensile forces and when certain limits are exceeded tiny cracks appear on the glaze surface. This phenomenon is called "crazing".

Peeling and crazing are the most common defects in glazed ceramic articles. Only when the thermal expansion of the glaze and the body have equal values can an ideal accord exist between the two, i.e. when the ratio $\frac{B}{G} = 1$.

During firing the body and glaze behave quite differently. It has been observed that for the same coefficient of thermal expansion the expansion curve of a ceramic body has a different inclination as that of the glaze. The silica present in the body plays an important role. In the temperature range of 200°C - 575°C sudden variations in expansion are caused by silica. When these changes are not followed by the glaze, tensile forces are developed causing fissures in the article.

Specially in porous ceramic articles cracks in the body or crazing in its glaze is observed after the lapse of a certain period of time. Such a defect could be caused by tension between body and glaze; thermal shocks or jerks accelerate such defects. Another reason for this defect could be the hydration of alumina present in the body, which leads to an increase in volume and as a result the glaze is subjected to tensile forces. To counter balance such forces it is necessary to maintain the ratio $\frac{B}{G}$ slightly greater than unity i.e. $\frac{B}{G} > 1$. This means that in such a case, the glaze should have a slight peeling tendency.

The "Ring Method" has no pretentions to be a scientific way of measuring crazing. But it is of great help to ceramists in adjusting the accord. It is a very simple test and can be used for testing the accord of all types of glazed articles.

<u>Test procedure</u>

Two rings of the dimension shown in Fig. IIa and IIb Appendix are prepared by casting.

Ring dimensions: Inner diameter = 14.3 cm
Outer diameter = 15.0 cm
Height of ring = 2.5 cm

These rings are prepared from the slip batch under test which is poured into the gypsum mould shown in Fig. IIc Appendix. The ring is removed carefully from the mould, dried and polished lightly with fine sand paper. Before glazing, the rings are moistened with a soft sponge.

The glaze is applied with a soft brush and one of the rings is glazed only on the outer sides whereas the other is glazed only on the inside surface. The glaze has to be uniformly distributed on the ring surface and blurs or drops should be carefully removed.

Attention is drawn to the fact that in the case of articles which are biscuited before glaze application the ring test is also to be carried out on a biscuited ring.

After firing the rings with a glaze layer, two holes are cut in each of the rings at a distance of about 3 cm (see Fig. III Appendix) and screws fixed firmly into these. The distance between the screws is measured and the rings are both cut between the screws using a cutting wheel. The rings are now supported as shown in Fig. V Appendix and the distance between the screws again measured.

The difference between the first and second reading gives a measure of the tension or compression of the glaze on the body.

The following illustrates practical conditions: (see Fig. III Appendix).

1. Ring glazed externally: opens up x mm
   Ring glazed internally: closes x mm
   Inference: the glaze has a tendency to contract more as compared to the body. It is therefore likely to show crazing defects. The glaze is in tension on the body.
2. Ring glazed externally: closes x mm
   Ring glazed internally: opens up x mm
   Inference: the glaze has a tendency to expand more than the body. The glaze is thus in compression on the body and tends to "peel off".

The tension or compression of glazes are expressed in millimeters of opening and/or closing of these rings. The results are only comparative and do not express absolute values. With a little experience the adjusting of the accord with the help of this method is not difficult.

To avoid crazing, the glaze has to have a slight compression value. In fact this compression value when it is properly selected, compensates the eventual tendency of crazing caused by the hydration of alumina. This value of compression of a glaze measured by the Ring system has to be determined by a process of trial and error. In general 0.8 - 1.5 mm is found to be suitable for "once fired" bodies and glazes (i.e. vitreous china, type of sanitary ware).

A slight difference between the readings of the externally and internally glazed ring is generally noted even though the glaze layer thickness and all dimensions of the ring are exactly the same. This is due to the difference in surface area of the inner and outsides of the ring. The external area is greater and the amount of glaze required to cover it too with the result that the forces of tension or compression are also greater. This explains the discrepancy.

Visual testing of Crazing and Peeling: This method is generally used together with the ring method. A visual examination of a piece that has been subjected to an impact could in many cases give an idea of the accord between glaze and body.

Procedure:

A flat tile is glazed and fired. It is then placed as shown in Fig. IV Appendix under a sharp pointed iron rod, the point of which is 30-40 cm above the tile. This distance should always be kept constant. The rod is allowed to fall on the test piece perpendicularly so that the pointed end makes an impact. The weight of the rod is generally 300 g.

The impact of the point cracks the glaze and leaves a mark on it. The tile is now moistened with diluted ink. On wiping away the ink, one is able to see the crack and lines clearer. The length of these lines around the impact mark and also their number gives an idea whether the glaze has crazing defects or not.

In case the glaze peels off, the indication is that the accord between glaze and body is likely to be correct. If the glaze as well as a part of the body peels off then it is likely that the body is under great compression.

This empirical method is generally used to give a rough idea of the glaze-body accord.

9. GLAZE DEFECTS - THEIR CAUSES AND REMEDIES

Glaze defects are numerous and it is often the case that one defect is mistaken for others that appear quite similar. For this reason it is always advisable to make a thorough enquiry and a proper examination of a defect when it appears. Generally these defects appear after a normal and, at times, flawless production course.

In order to examine a defect more thoroughly it is generally advisable to examine the piece in bright light. The light should fall on the glazed surface and should be reflected. If the article is held at the proper angle, the examination becomes much more easy. A magnifying glass or a lense is of considerable help.

The most important problem for a Ceramist is to get at the cause of a defect and sometimes this task is a very difficult one. Often there are defects which appear suddenly and again disappear of their own accord. Generally these defects are the most troublesome and one should keep on investigating these particular types of defects even though they have disappeared.

The various types of defects found on glazed surfaces are:

1(a)	Cut Glaze	1(b)	Knocked Glaze
2(a)	Crawling	2(b)	Shrinking
3.	Spitting out		
4(a)	Pin holes	4(b)	Dimples
5.	Egg shell		
6.	Blisters in the glaze		
7.	Bubbles		
8.	Spalling		
9.	Rough edges and rims		
10.	Running of the glaze		
11.	Absorption by the body		
12.	Mat spots		
13.	Cracks		
14.	Flaking		
15.	Decolouration		
16.	Changes in colour		
17.	Spots		
18.	Salts efflorescences		
19.	Undulated glaze		
20.	Overglazing and its defects		
21.	Specking		

Before entering into a discussion of defects it is necessary to draw the attention of the reader to the ways and methods of recognizing glazed defects. Too often technicians take only a superficial look at a defective piece and prescribe a remedy that may not be the exact one. Some of the glaze flaws are a real problem for a factory and their solution can only be achieved by very deep study followed by an accurate analysis of the entire manufacturing process. It is generally advisable to organize technical staff meetings to discuss and analyse the defects that occur in daily production and to decide and discuss the steps to be taken to remedy them.

1(a) <u>Cut Glaze</u>. This defect is generally due to the layer of glaze being too thin. In earthenware this defect appears when the porosity is low. The glaze does not remain in sufficient quantities on the article whether it is sprayed or the article is dipped into it. Dust, dirt, grease, finger marks, oil and water prevent the glaze from sticking on properly. Soluble salts accumulate and form a film over the article surface so that the glaze cannot stick on.

Remedy Articles to be glazed should be kept as clean as possible. Oil drops generally come from the filter of the spraying device. It is therefore necessary to clean the filter frequently. Soluble salts can be detected by chemical analysis and such salts can be avoided by making use of water free from salts. If such salts are present in clays or glaze raw materials, it is necessary to neutralize these by adding Barium Carbonate in the presence of sulphates. When the biscuited article is over-fired and its porosity is lower than that required, it is good practice to use a glaze of a higher litre weight. For biscuited earthenware glazed by dipping it is necessary to dip these into two glaze batches of different densities. A glaze of higher density should be used for over-fired pieces and a glaze of lower density for articles of normal porosity.

1(b) <u>Knocked Glaze</u>. The cause of this kind of defect could be improper handling and stacking of the articles. Very often pieces already glazed are set one over the other before being sent to the kiln.

Remedy. It is advised to set up proper shelves rather than stack pieces. To improve the strength of the glaze it is sometimes necessary to add binders like gum or derivatives of cellulose. Addition of carboxymethylcellulose is recommended for glazes for wall tiles and tableware.

2. <u>Crawling</u>. The factors causing crawling are many.

(a) <u>Over-grinding of the glaze</u>: When a glaze is over-ground it becomes very viscous after melting. The forces of surface tension are greater than those of adhesion and this causes the glaze to accumulate into heaps. Practically the glaze shrinks too much and its force of adhesion is lowered.

Remedy. The glaze should be ground to a lesser extent and a small amount of adhesive should be added.

(b) <u>Low Plasticity</u>: When the glaze is not sufficiently plastic it shrinks at a lower rate and thus detaches itself from the body. This applies more likely to raw glazes.

Remedy. Add China Clay or replace a part of it with a more plastic clay. On making such a replacement care should be taken so as not to alter the fusibility of the glaze.

(c) <u>Materials of low density</u>: Glazes could contain a large proportion of materials that have a low density, i.e. a higher volume per unit weight. Such materials are Magnesium Carbonate, Alumina Hydrate, Talc, Lime, Zinc Oxide, Tin Oxide.

Remedy. These components should be fritted but as it is not always possible to frit a glaze without altering its characteristics, it is therefore advisable to calculate the glaze beforehand and introduce only materials of a low volume. A good result is obtained by using calcined alumina, magnesite, dolomite and calcined zinc oxide. A heavier tin oxide and Calcium Feldspar could also be used to replace some of these low density components. Addition of adhesives and less grinding is also helpful.

(d) <u>Too thick layer of glaze</u>: When the glaze layer is too thick its melting is irregular and its adhesion forces are low. During the loss of chemically or superficially combined water the glaze becomes dusty. In addition a glaze layer of higher thickness has a tendency to crack during drying, thus causing crawling. Melting does not take place througnout the glaze layer depth and it separates itself from the body.

Remedy. Keep the thickness of the glaze layer within the prescribed limits. This can be done by adjusting the litre weight of the glaze batch and by selecting the biscuited article of the right porosity.

(e) Raw materials absorb too much water: The reason for this could be that an excessive amount of adhesive is present which retains too much water, thus enabling the dissolution of some constituents. During the loss of water in the process of drying, the glaze shrinks quicker than the body and detaches itself and crawls.

Remedy. The constituents which require excessive quantities of water and also adhesives should be reduced. The pH-value of the glaze should be checked and maintained at its optimum value.

(f) Too fast pre-heating: **Pre-heating at too quick a rate can also cause** crawling. The reason for this is that the chemical and superficially combined water is removed too quickly. The defect is emphasized when the ware is loaded into the kiln when not perfectly dry. When the quantity of water present is too great it is converted to steam during the pre-heating process and this steam accumulates and condenses on the ware so that the glaze creeps.

Remedy. In this case one should dry the article sufficiently before loading it into the kilns. Proper outlets should be made on the roof of the kiln to allow the escape of vapours. Pre-heating curves should be adjusted to avoid a too high pre-heating rate. Also, one should make proper arrangements to ensure a good driving off of vapours and fumes. It should be noted that a kiln is the worst dryer. Sufficient circulation of the air in the kiln must be provided for. Pieces which are glazed on both sides are likely to dry at a slower rate due to the great amount of water they absorb. A proper drying time for such articles should also be provided for.

(g) Fuel Humidity: Wet fuel produces unnecessary extra steam and could accelerate crawling.

Remedy. The fuel should be supplied to the firing zone sufficiently dry. This can be done by introducing a drying system and also by supplying a greater quantity of air to the kiln.

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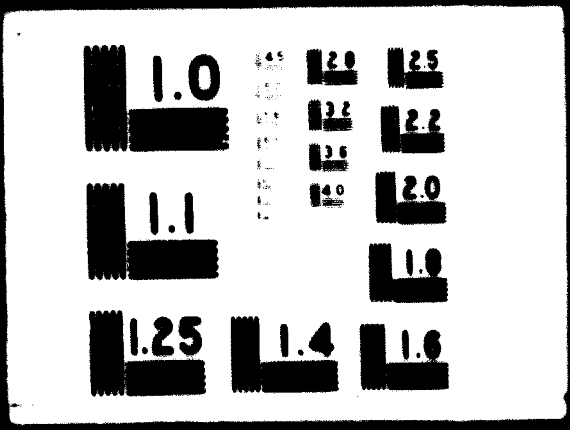


(h) Decoration: When a layer of under glaze is applied on the raw body and this layer is too "lean", a difference in drying rate between these two layers is obvious and they shrink differently.

Remedy. In such a case one should add plastic clays and Arabic Gum (0.5% maximum). In case the under glaze decoration contains too much grease and oily grinding media (Glycerine), one should reduce the Glycerine or fats used in grinding, to a minimum.

4 (a), 4 (b), 5 Occurrence of pin holes, dimples, egg shells. All these defects generally come from the same cause. Small air bubbles present in the body surface are only partially covered by the glaze during melting (pin hole). This can be found in bodies which are not properly de-aired. Foreign matter present in the body could also give rise to gas formation and consequently pin holes. Improper sieving of the slip, Silicon Carbide dust from grinding wheels and from Silicon Carbide slabs could also contaminate the glaze. It was sometimes experienced that dust falling from the tunnel kiln entrance often caused a lot of damage and egg shell surfaces could be caused by insufficient firing or by applying too hard a glaze for the selected firing temperature. The glaze does not melt properly and therefore does not fill up all the pores or pin holes present on the surface. On the other hand, a glaze that is too soft melts at an early stage and prevents the gases from escaping from the body as well as the glaze.

Remedy. The slip should be de-aired and the vacuum efficiency of the Pug Mill should be checked. The slip should be sieved and subjected to magnetic separation before casting or filtering. One should check the sieves. The necessary precautions should be taken against dust falling at the entrance of the tunnel kiln. Silicon Carbide slabs should be changed and a layer of paint of China Clay deflocculated with Sodium Silicate should be applied. The firing temperature should be adjusted when one suspects that the glaze does not reach its proper maturing point (egg shell). One should adjust the firing temperature and the pre-heating period to avoid early melting of the glaze.

6. Blistering of the Glaze. Blisters could be caused by using excessive wet moulds as well as when the under glaze decoration does not melt sufficiently.

Blisters are also produced when a fritted glaze is applied by spraying. Any enclosure of air which cannot escape from either body or glaze could provoke blistering.

Remedy. The melting point of the under glaze should be reduced. This is done by adding low melting frits. The glaze should be applied in thinner layers. The mould should be very dry. By enforcing such steps, one could avoid both blister formation and pin hole formation.

7. Bubble Formation. Bubbles and blisters are in principle caused by the same deficiencies in the material. The only difference between bubbles and blisters is that bubbles are blisters which have exploded leaving craters behind which are partially fused during firing. Bubbles are more often seen in raw glazed articles and especially in vitreous china bodies. Bubble formation could also be caused by:

(a) unsuitable glaze composition, e.g. when Boron or Carbonates are in excessive amounts. During firing, these compounds decompose to give gases which could cause blisters.

Remedy. In this case one should recheck the glaze formula and reduce the amount of Boron (replace partially with China Clay) and Carbonates. One should also check the pre-heating cycle so as to allow gases enough time to escape before the glaze melts.

(b) Too liquid glaze on a plastic body: In some cases the body contains excessive amounts of plastic materials. In such cases the glaze softens the body, causing swelling. The upper layer separates from the under layer and a pocket forms.

Remedy. One should reduce the plasticity of the body and/or increase the litre weight of the glaze (reduce water content).

8. Spalling. This defect is common to bodies not carefully prepared and is also seen in bodies for the preparation of which, clays containing lime are used. This defect is also caused by mould plaster, stones or metallic articles.

Remedy. The raw materials should be ground or washed to a greater extent, especially when an examination has shown the presence of materials like lime pieces, plaster of Paris granules. When re-using the rejected products coming from "fettling", one should make sure that they are properly ground, sieved and subjected to magnetic separation before they are added to the normal slip. When using Calespar, special attention has to be paid to its proper grinding as it is difficult to grind it on account of its elastic properties. Generally, Calespar grinding takes more time than any of the other raw materials.

9. Rough edges and rough rims. These defects are caused by a glaze which melts too early and combines with the upper layer of the body. When the edges of the article are too sharp, then one observes areas not covered by glaze. In this case the edges over-fire and the glaze is not properly absorbed. The result is an uncovered edge.

Remedy. The fusibility of the glaze should be re-adjusted. This can be done by adding, for example, China Clay. Another step to be taken would be to round up all edges of the article.

10. Running of the Glaze. The glaze runs off the article when its fusion temperature is too low, when the glaze temperature is too high or when the glaze layer is too thick. If underglase colours or decorations are used, then these will also separate and spoil the decoration.

Remedy.

(a) The glaze fusibility is to be corrected. This can be done by adding China Clay, finely ground glost or biscuited grog. For earthenware articles, the addition of quartz or zinc oxide is recommended when China Clay is increased.

(b) Either the glost firing temperature or the soaking time should be reduced.

(c) Underglaze stains used should be suited to the over glaze.

(d) The glaze layer thickness should be reduced.

11. Glaze absorption by the body. The glaze can be absorbed by the body when the glaze composition lacks in alumina and/or quartz. The glaze is also absorbed by the body when the body contains too much calcium. It will be observed that the glaze combines intimately with the upper layers of the body and thus the glaze surface will be less brilliant and porous.

Remedy. In this case one should recheck the glaze and increase its quartz and alumina contents. The composition of the body should also be altered and the calcium content reduced. The firing temperature should also be reduced.

12. Marked Spots. These appear as patches on the glaze or as an unglossy veil on its surface. This could be traced down to

(a) Easy fusing components in the glaze (too much alumina).

(b) Too high quantities of Calcspar, zinc oxide, or too low amounts of alumina or the presence of too much of titanium Oxide, Zirconium Oxide, Tin Oxide.

(c) Such glaze components as Lead Oxide, Zinc Oxide, Barium Oxide or Boron Oxide, etc. are attacked by sulphurous gases formed during firing.

(d) Sedimentation of the glaze.

Remedy.

a) The glaze composition has to be readjusted or the firing temperature has to be increased.

b) Large quantities of calcspar, zinc oxide, titanium oxide, zirconium oxide and tin oxide present make the glaze too mat. Their readjustment is necessary.

c) In this case the glaze should be recalculated and oxides which are not easily attacked by sulphurous gases (calcium carbonate and magnesium carbonate) should be incorporated. The fuel should be dried before firing. Air circulation in the kiln should be increased so as to remove the unwanted gases.

d) When sedimentation of the glaze takes place one should adjust the litre weight and stir thoroughly before using it.

13. Cracks. Cracks have to be examined very carefully to be in position to trace out their cause. In fact, cracks appear on account of a number of reasons. Cracks which cut the glaze and the body as sharp fine lines are most probably due to quick cooling during biscuit or glost firing. This type of crack could also appear after some time after the article is in use. Cracks that appear open, filled up with glaze or glaze interrupts the cracked edges are due to cracks already present in the body before firing. Cracks could also be caused by a big difference in the coefficients of thermal expansion of the body and glaze.

Remedy. The cooling rate should be lowered and attention is to be paid that air is not blown direct on the fired article during cooling. Pieces with such cracks cannot be repaired and must be rejected.

The coefficient of thermal expansion of the glaze and body should be checked and adjusted in case they are not the same. The raw materials should be checked for their coefficient of expansion and also chemically. A sudden change in the coefficient is possibly due to a change in the characteristics of the raw material. The laboratory should carry out tests on the raw materials periodically and recommend the necessary adjustments to be made in the glaze and body composition.

a) A network of Haircracks. These cracks generally appear just after firing. They could, at times, appear after some time. This defect is called crazing and is always due to tensions between body and glaze and to residual tensions which are increased by the rehydration of alumina due to water absorption. Alumina rehydration is a peculiarity of porous bodies.

This defect also appears when the glaze layer thickness exceeds certain limits.

Remedy. The thermal coefficient of the glaze and/or the body should be adjusted, leaving the glaze with a slight compression on the body. The ratio of the coefficients of the Body to glaze ($B/G > 1$) should be slightly greater than unity.

Care should be taken to keep the body porosity within limits.
Firing should be done at a higher temperature or for a longer time.
The glaze layer thickness should be kept within the prescribed limits.
Glaze should be applied both on the inside and outside of the article.
The interior of articles when they are within reach should be glazed.

The reduction of the coefficient of thermal expansion of the Glaze is done by reducing the amount of K_2O and Na_2O and replacing them with CaO, Al_2O_3 and MgO. It is also possible to lower the coefficient of expancion by firing the biscuit at a higher temperature. On the other hand, the expansion coefficient of the body can be varied by adding more quartz or by grinding the quartz more fine. In the case of earthenware, one should increase the lime content and reduce the clay content.

b) Compression Cracks. These are due to a high compression of the glaze on the body and the glaze spalls off and splits out together with a part of the body.

Remedy.

i) Reduce the thermal expansion of the body. In vitreous bodies this can be done by increasing the quartz or magnesium oxide content as they both lower the coefficient.

ii) Firing should be done at a lower temperature and/or for a shorter time.

14. Flaking of the Glaze. Flaking can be described as a coming off of the glaze like skin. When the coefficient of expansion of the glaze is far lower than that of the body or on the other hand the glaze coefficient of expansion is much greater than that of the body, flaking takes place.

A firing temperature that is too high accelerates flaking. When an underglaze decoration does not react with the body, and the glaze, it also causes flaking.

Remedy. The coefficient of thermal expansion of the glaze should be increased by adding for example K_2O and Na_2O and by lowering the contents of CaO, MgO, Al_2O_3. The glost firing temperature should be reduced. Reduce the thermal coefficient of expansion of the body by lowering the quartz content of the body or by grinding the slip to a lesser extent. In case it is an earthenware body, reduce the calcspar and $CaCO_3$ content. If the defect is due to the underglaze decoration, then increase its ability to flux by mixing it with a lower melting frit.

14 (a) Engobe Flaking. Engobe flaking occurs frequently in fire clay sanitary ware on which a thick layer of engobe has been applied. The engobe does not stick to the body if it is applied to surfaces which have already shrunk too much (Biscuited or dry bodies).

This defect is also caused when:

a. Insufficient adhesive is present in the engobe
b. Too much adhesive is present in the engobe
c. The adhesive decomposes
d. The adhesive is weak
e. Improper application of the engobe
f. A layer of dust or greasy materials is present between body and engobe
g. The engobe is too hard
h. Salts are present in the body

Remedy. To find out what the cause could be, all steps of the manufacturing process have to be examined giving the following points special consideration:

a) Bodies showing high shrinkage have to be engobed when still humid.

b) The adhesive has to be tested before use and should be stored in a dry place to avoid decomposition. Special emphasis has to be laid on tests like the adhesivity and gelification point of the adhesive.

c) An adhesive loses its adhesion properties after some time. It should therefore be made a point to fire glazed articles as soon as possible.

d) Too much adhesive in a glaze or engobe causes excessive tension when drying and it will often be noticed that the engobe separates from the body before firing. Special care should be taken when applying glaze and engobe to the edges and corners of articles. Corner lying in the interior of the body should receive less glaze and engobe as compared to exterior corner.

e) When the engobe and glaze is applied with long intervals between subsequent layers, drying takes place calling for a rewetting of the engobe and the piece, the adhesive loses its strength and movements due to alternating shrinkage and expansion cause tension development. This should be avoided by applying the engobe and glaze in the shortest possible time.

f) Clean the body to remove dust and dirt that could eventually form an insulating layer between body and engobe.

g) Lower the melting point of the engobe if the engobe is too hard and if it does not react with the body.

h) Roughen the surface of the body before applying the engobe.

i) One should check for the presence of salts in the body and neutralize them. (Sulphates: neutralize with $BaCO_3$)

15. <u>Changes in colour</u>.

a. It has to be kept in mind that white glazes containing SnO_2 change to pink in the presence of Chromium compounds even if these are present in small quantities. This could also take place in electrically heated kilns using Nickel-Chromium elements.

b. A yellow colour appears in glazes when they are applied in too thick a layer, especially when lead is present.

c. Presence of Vanadium causes a yellowish colour.

d. Carbonaceous matter if fired too high produces a dirty yellow colour.

e. Oxidation of Ferrous compounds also produces a yellow colour.

Remedy.

a. The reaction can be avoided if SnO_2 is replaced by ZrO_2.
b. The thickness of the glaze layer should be reduced. The action of Lead can be corrected by using a glaze containing SiO_2, Ka_2O, ZnO, B_2O_3.
c. Vanadium efflorescence can be counteracted by the presence of BaO and also by regulating the kiln atmosphere.
d. In this case, the kiln atmosphere has to be corrected.
e. The early stages of firing are to be done with a reducing atmosphere, followed by an oxidizing one and once again changed to a slightly reducing atmosphere until the end of the firing.

Other colours:

A brown colour is produced when Titanium compounds are mixed with Iron (Rutil). The best remedy to avoid this is not to use a glaze formula containing Iron and Titanium.

A green colour could be produced by chromium vapours. In this case the glaze should be fired before it is applied.

A black colour can be produced if a reducing atmosphere is maintained for too long a time. This black colour comes from carbonaceous matter. Sensitive oxides like Uranium are affected by smoke and high temperatures.

16. Spots. Spots seen in a glazed surface are due to impurities contained in the glaze as well as in the body.

Blue spots are generally seen on white or light coloured glazes and are due to cobalt impurities. It is necessary to avoid direct or indirect contact of two glazes. Mills, containers, spray gums, fillers and glazing tools should be well cleaned before use. Cobalt also gives rise to spots when badly ground or if not properly dissolved. Under certain condition Iron particles present could give rise to blue spots. In this case a careful magnetic separation and a proper sieving is necessary.

Green spots. When the spots are black in the centre and green around they are due to the presence of copper, brass or bronze impurities. On abrading the spot with a grinding wheel one can locate the impurity in the black zone in the centre of this spot. Such impurities generally come from injured sieve nets, worn or broken bronze bearings, machine parts or bronze tools. Special care should be taken when mechanics or electricians work in the body preparation and production rooms. Green spots are sometimes due to impurities present in clays. In such cases a fine sieving as well as good grinding will help a great deal to disperse such impurities uniformly thus avoiding such spots. Mills used for green or for that matter any coloured glaze should be thoroughly cleaned before they are used for other glazes.

Generally, nozzles and nipples of spray guns are made of bronze and their maintenance has to be done carefully.

White spots. On pink, red or reddish surfaces, white spots are easily seen. They are caused by the decomposition of pink colouring agents due to the interference of other oxides like zinc oxide (Zinc oxides, effect chromium stains). Some white spots when observed with a magnifying glass appear dark brown in the centre, surrounded by light green colour. These are due to the very fine particles of Iron, or Silicon particles falling from the silicon carbide slabs.

Brown spots. These spots are generally caused by iron particles present in the raw materials. They could have been introduced into the raw materials during mining, transport, grinding or sieving. They should be removed either by a proper sieving or by magnetic separation. Care should be exercised in handling of raw materials, in unpacking barrels etc. Nails and steel wire from packages have often caused much trouble.

17. **Salt efflorescence.** Salts specially $CaSO_4$ are always present in the raw materials. During drying and firing these salts rise to the surface and interfere with the application of the glaze as well as with firing. Salt efflorescence manifests itself as small spots on transparent glazed surfaces. These spots are produced when the article is exposed to high temperature flames and also when the quantity of alkalies present in the transparent glaze is too high. When this is the case, it is necessary to reduce the Soda content by replacing it with Lead, Potassium or Borax. Sulphate contamination can take place as a result of gypsum moulds used. Hence it is always advisable to sieve scraps when they are blunged.

18. Undulated glaze surface. Improper firing causes such a surface which is a result of an uneven spreading out of the glaze. This defect can be detected by simply running a hand over the glazed article. The brilliancy of such a surface is also weak.

Remedy. The firing temperature should be adjusted.

19. Defects of Overglazing. The defects that arise from applying a thick layer of glaze are outlined below:

a) Crazing
b) Articles sticking to its support
c) Accumulation of glaze in corners and bottom of articles
d) Glaze drops.

Remedy. Care should be taken that porous articles be dipped in the proper glaze batch with the right litre weight and viscosity. When dipping is being done, the immersion time should be short and shaking of the article should be done carefully. When the glaze is applied by spraying, the gun should not be held very close to the article. Spraying should be done uniformly. Corners and angles should always be glazed to a lesser extent as flat surfaces.

The underglaze also leads to such defects as Rough surfaces. A rough surface could be caused by a high percentage of Boric acid in the glaze.

20. Specking. This defect comes almost always from impurities falling into the glaze or over the glazed surface. Dust accumulated on beams and other structures always cause trouble. It is therefore advisable to keep the glase department absolutely clean.

Conclusion. It is quite clear that glazed ceramic articles have many defects and that these could be initiated in any part of the process. In most cases it is easy to see such a defect but not always so easy to locate and recognize the cause. Once a defect has been sighted, a systematic investigation should be started and all departments should collaborate to find the cause, otherwise it becomes a difficult and time consuming task to reinstate production on its proper lines which could effect the economics of the plant.

Figure I

Shrinkage test

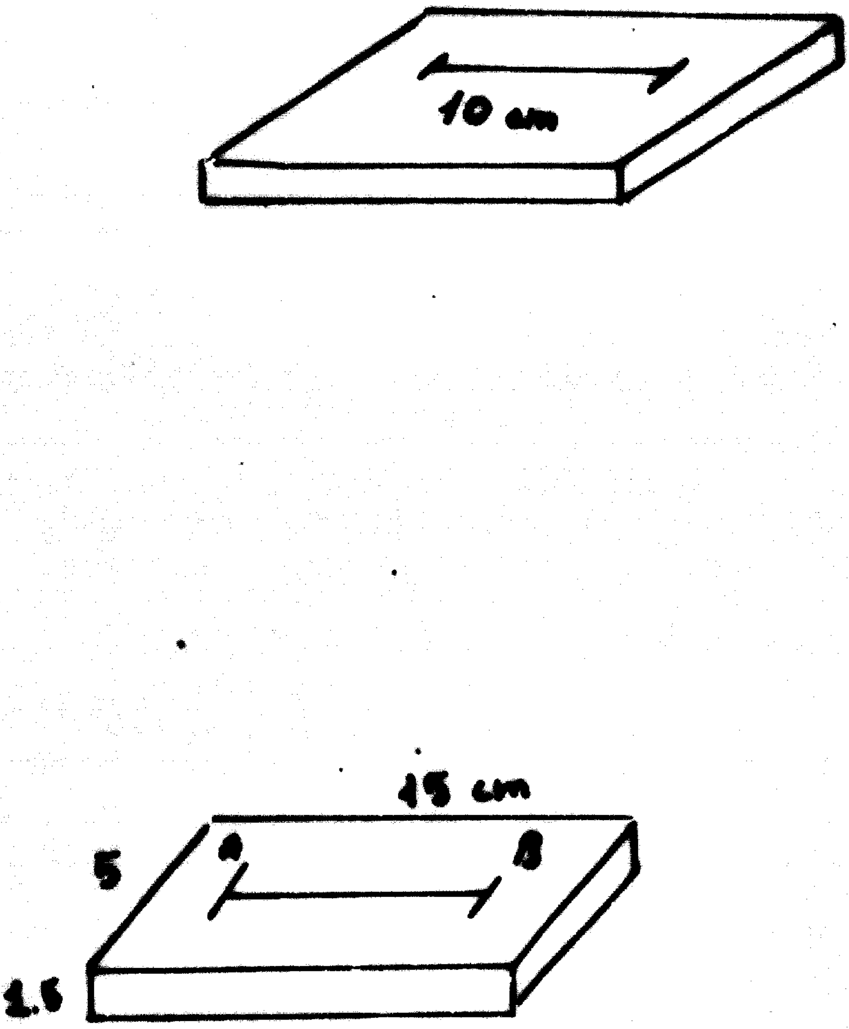
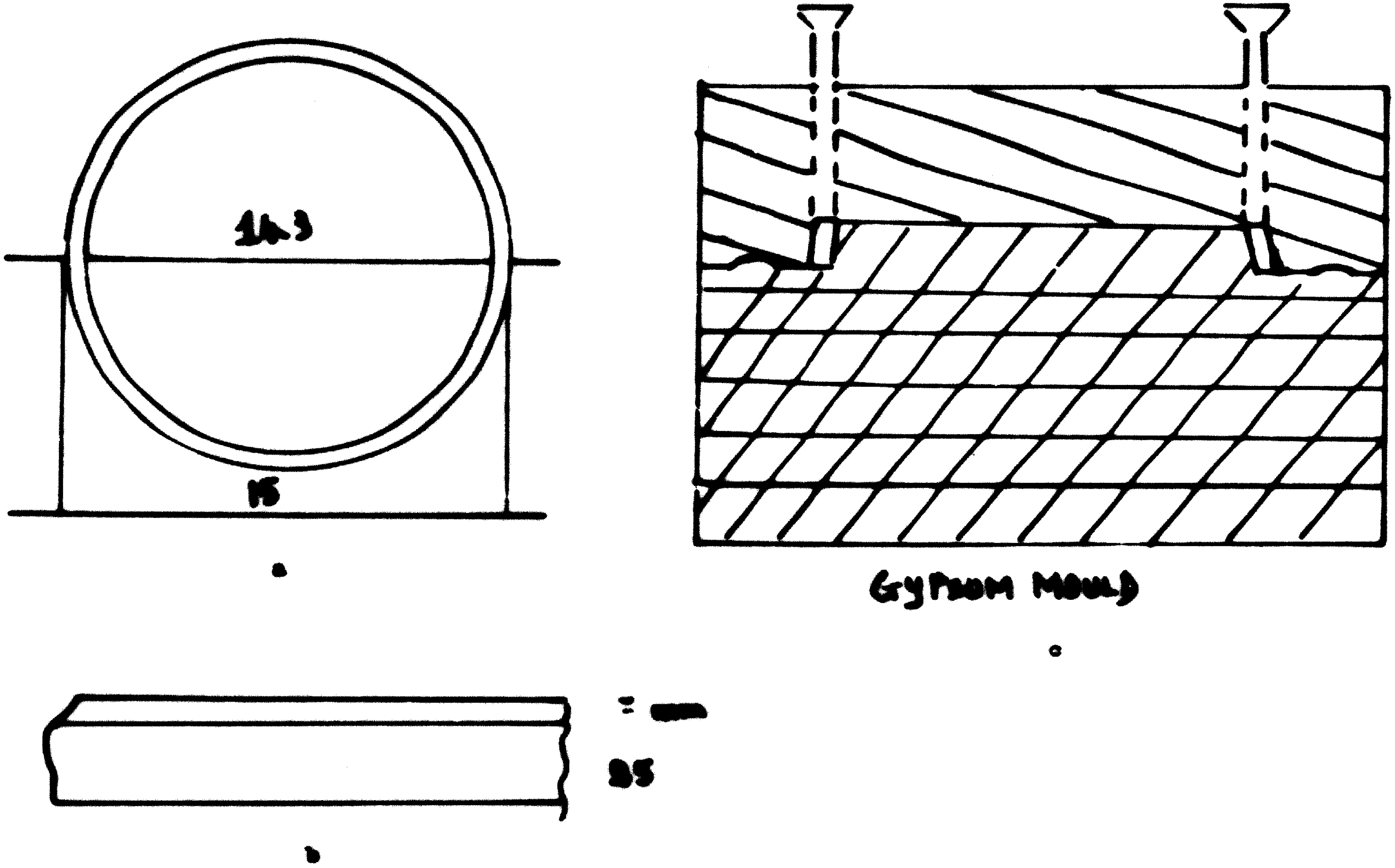


Figure II

Ring measurements and mould form



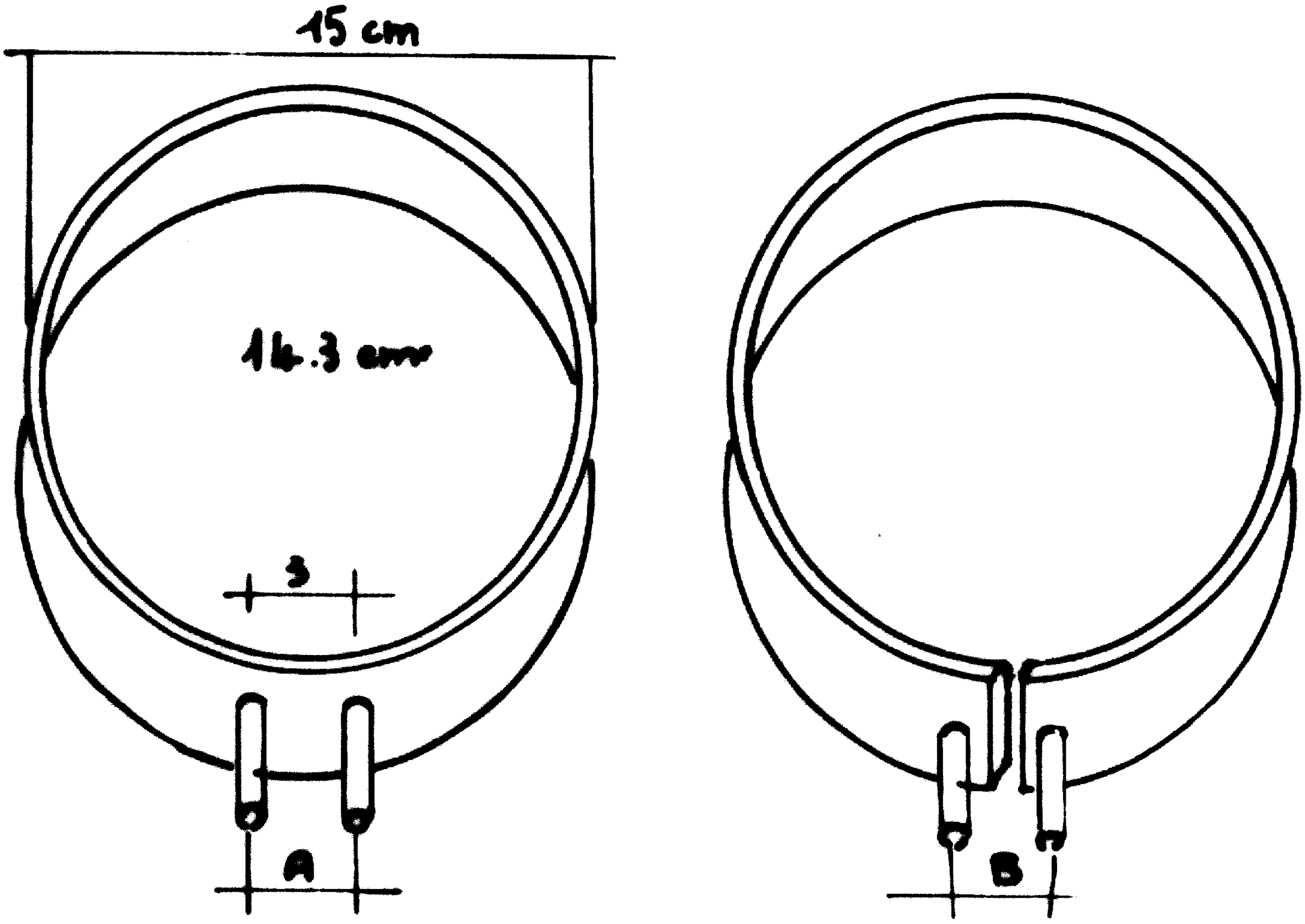
a

b

c

Figure III

Calculations based on the ring method



A = Distance measured after firing

Example 1: A = 30 mm B = 28 mm A-B = 2 mm
A = 30 mm B = 32 mm A-B = -2 mm

2: A = 30 mm B = 31 mm A-B = -1 mm
A = 30 mm B = 29 mm A-B = 1 mm

3: A = 30 mm B = 30 mm A-B = 0
A = 30 mm B = 30 mm A-B = 0

S = Distance measured after cutting

Example 1: Externally Glazed ring Closes 2 mm : Peeling Tendency
Internally Glazed ring Open 2 mm : Peeling Tendency

2: Externally Glazed ring Open 1 mm : Crazing Tendency
Internally Glazed ring Closes 1 mm : Crazing Tendency

3: Externally Glazed
Internally Glazed
Neither opening nor closing of rings

Note: When the body is not under compression, the glaze could craze due to expansion caused by Hydration of the body.

Figure IV

Impact test apparatus

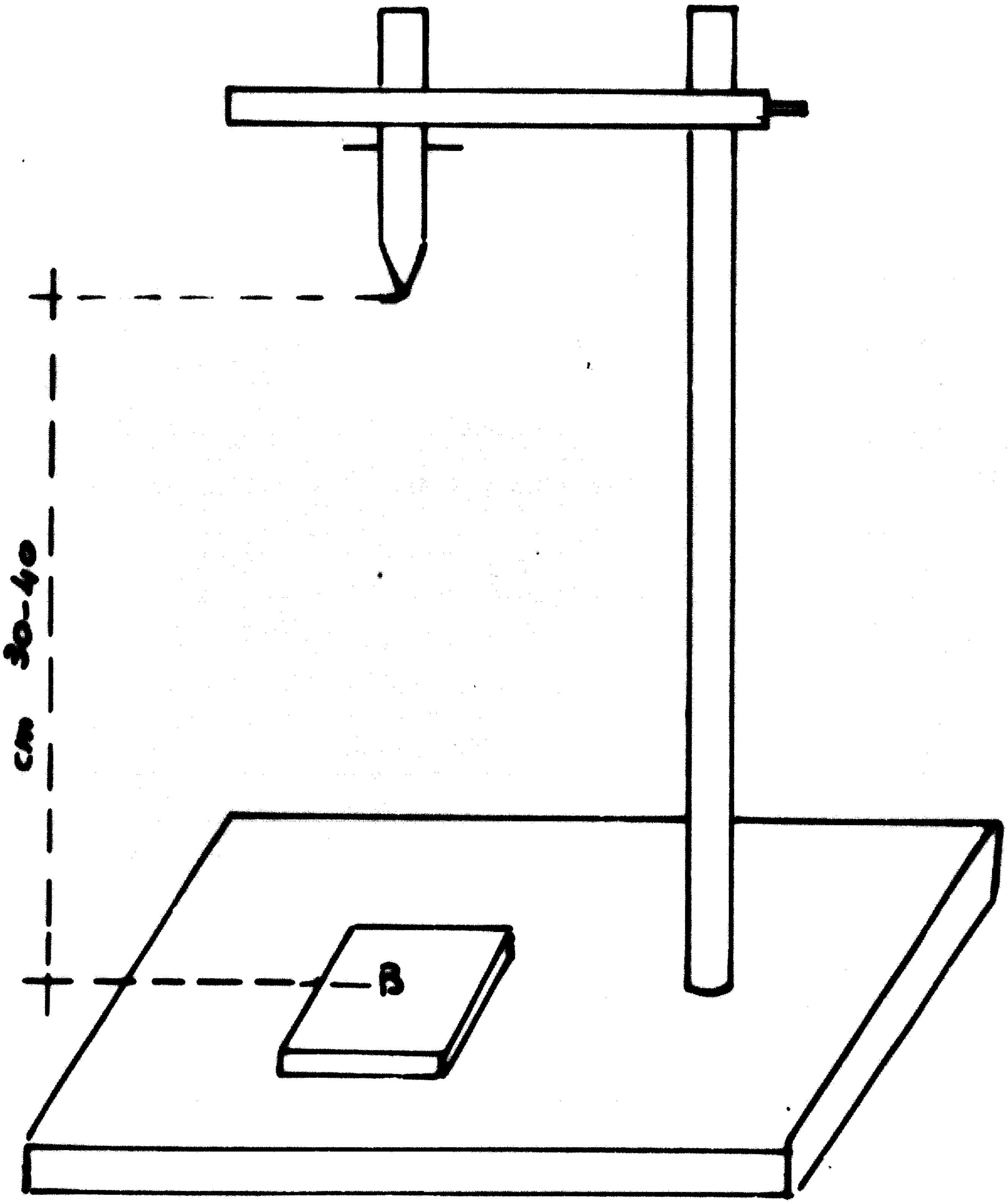
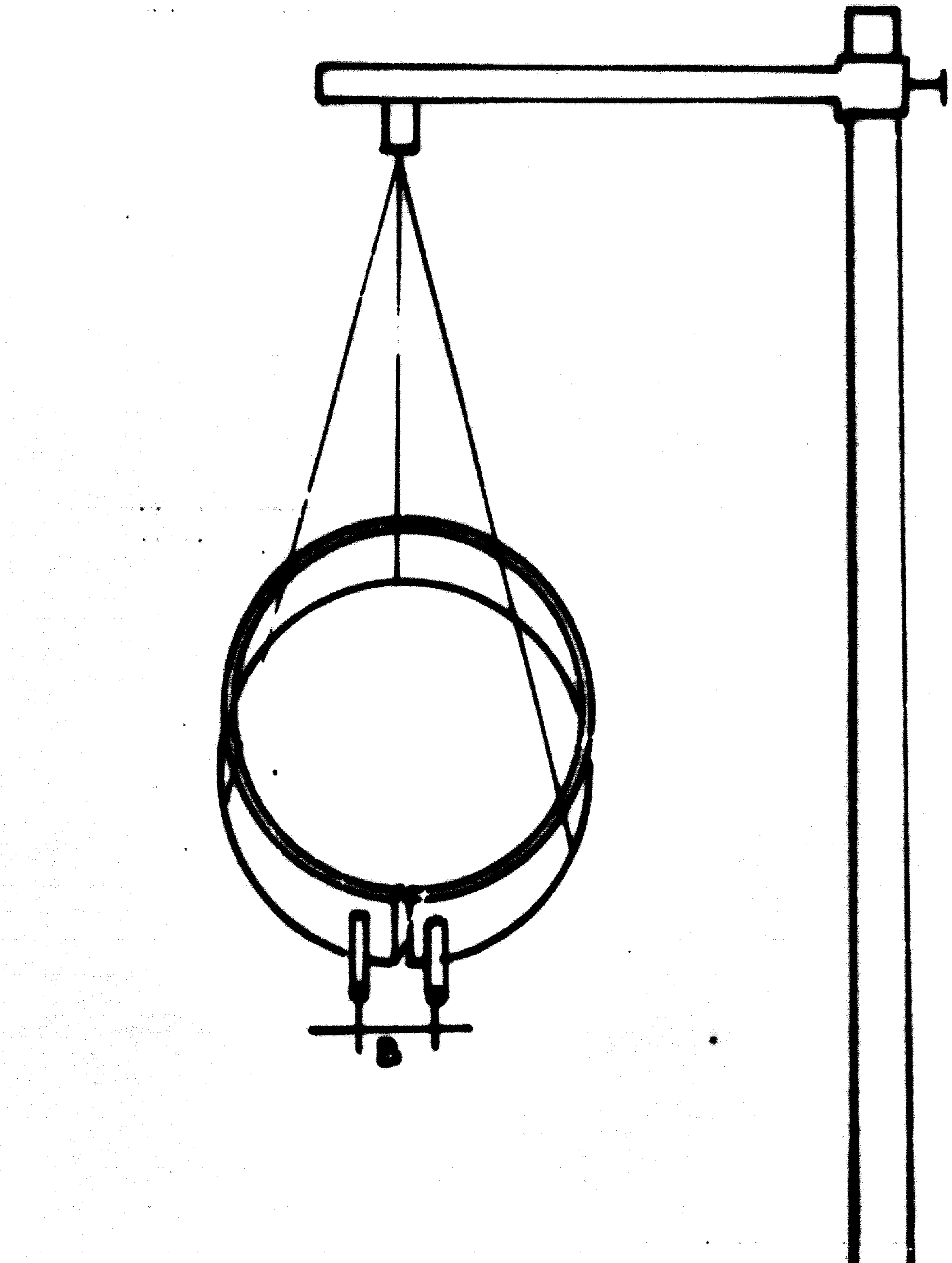


Figure V

Ring support



LABORATORY REPORT

Date ____________

RESULTS OF TESTS ON RAW MATERIALS ____________

____

A. GENERAL DATA

1. Supplier ____________
2. Locality ____________
3. Arrival date ____________
4. Store No. ____________

B. MATERIAL EXAMINATION

1. Colour ____________
2. Moisture % ____________

C. MATERIAL AND WATER

1. Residue on sieve
   No. ____ = Gr.% ____________
2. Residue on sieve
   No. ____ = Gr.% ____________

____

3. Litre Wt. kgs. ____________
4. Viscosity ____________
5. Sensitivity to electrolytes

____

____

6. Plasticity ____________
7. Modulus of rupture kg/cm^2 ____________
8. Shrinkage wet to dry % ____________

D. TESTS PIECES AT 1250°C SK

1. Shrinkage dry to wet % ____________
2. Shrinkage total % ____________
3. Porosity % ____________
4. Warping mm. ____________
5. Colour ____________
6. Accord with glaze (impact test) ____________

E. RAW MATERIAL PLUS 100% OF ____________

1. Shrinkage wet to dry % ____________
2. Shrinkage dry to fired % ____________
3. Shrinkage total % ____________
4. Modulus of rupture dry kg/cm^2 ____________
5. Modulus of rupture fired kg/cm^2 ____________
6. Porosity % ____________
7. Warping mm. ____________
8. Accord: Thermal shock from ____ °C to ____ °C
   With engobe ____________
   With engobe and glaze ____________
   With glaze ____________
9. Accord by impact test
   With engobe ____________
   With engobe and glaze ____________
   With glaze ____________
10. Accord by Ring method
   With ____________ ext. ____________
   int. ____________
   With ____________ ext. ____________
   int. ____________

Layer formations after:

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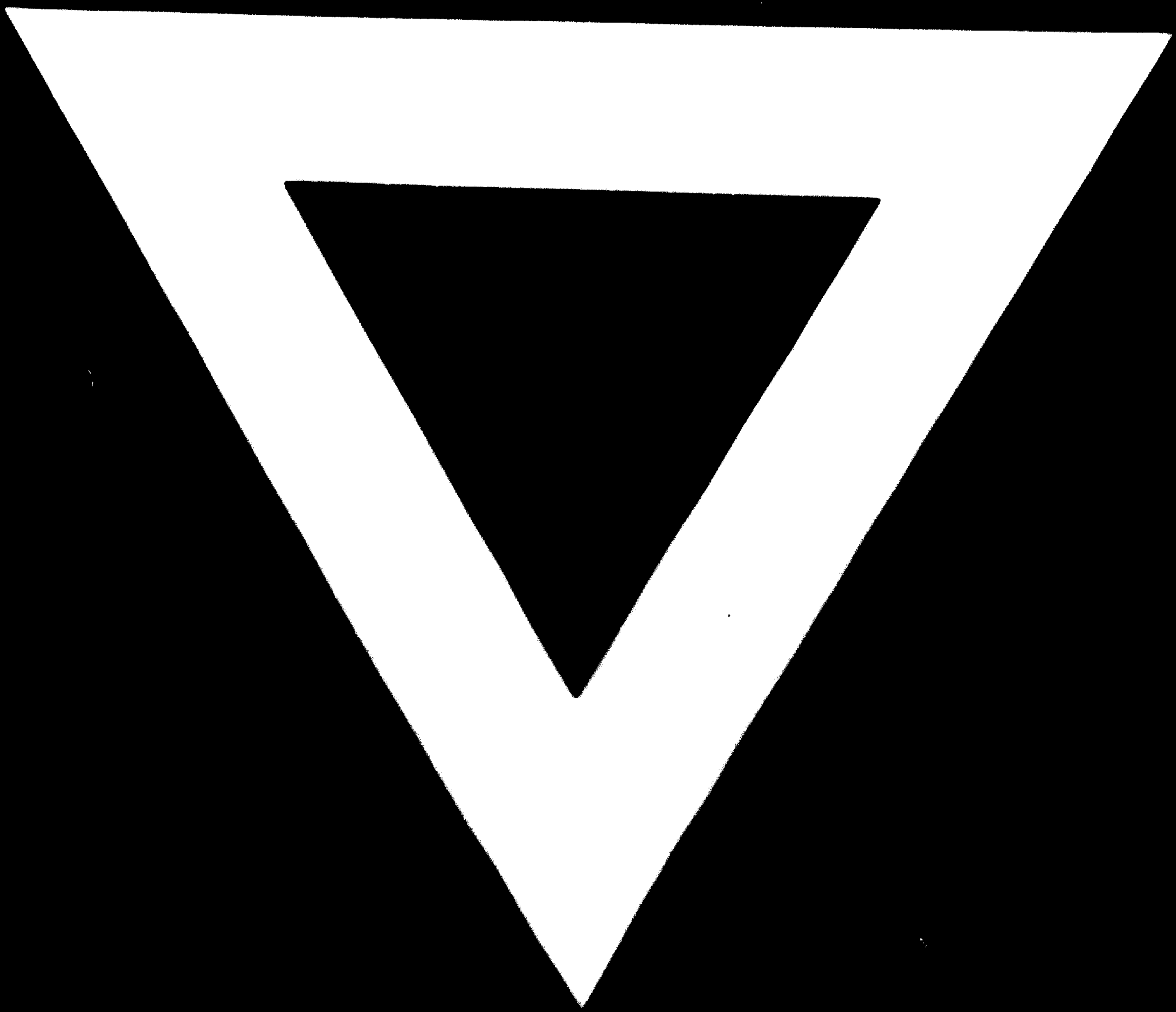

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