DRAFT Fine Ceramic Products

INTRODUCTION

Scope and Relationship to Traditional Ceramic Products

Fine ceramics are products that men and women encounter in their everyday lives. These products include ceramic dishes, toilets, tile, and related products. All of these products have in common the use of clay minerals in their composition, and the products have been processed at high temperatures to cause limited melting or fusion producing a "glass" phase creating a permanent bond within the articles. It is this glass phase, or "vitrification", that produces permanence and utility in the products.

Ceramic products are those composed of non-metallic and inorganic constituents. In other words, ceramics are composed of metal compounds such as oxides, and "traditional ceramics" have constituents that commonly occur in the earth's crust. This means that traditional ceramics contain oxides of aluminum, silicon, magnesium, calcium, iron, and alkali metals (sodium and potassium) along with trace quantities of other elements.

Fine ceramics are those that are essentially made from fine particles, with particle size essentially less than about 150 microns (μ) and typically less than 75 microns. After heating (also known as firing), such ceramics have a fine texture – meaning the solid material contains very small crystals and pores of small diameter with crystal size and pore size (diameter) less than the diameter of the starting particulate matter that comprised the ceramic mass.

By contrast, traditional ceramics made from large or coarse particles ranging in size up to about 6000 microns include such products as clay bricks, clay roofing tile, refractory bricks, and clay pipe. While coarse particulate ceramics are typically fired in kilns or furnaces to achieve permanence, they generally exhibit lower strength than fine ceramic products. Another important distinction is that many coarse particulate ceramics contain iron oxide in their composition in the range 2-8% by weight producing colors in the fired products ranging from pink to red to blue or black. Technologists apply the name "whitewares" to most fine ceramic products, and the term simply reflects the fact that most of the products are white (or near white) in color where "ware" is the technical name for a ceramic object that is sold in commerce. Under the name whiteware, three are many different functional products (Table 1). Whitewares are usually distinguished or classified in commerce according to these technical subgroups. The classifications usually are distinguished by the amount of void space in the fired ceramic called its "porosity". In the historical development of traditional ceramics, porosity was measured indirectly as "water absorption", i.e. the weight of water the ceramic would absorb on immersion in water compared to the dry weight of the ceramic object expressed as a percentage of the dry weight.

The general relationship in whitewares is that low porosities are associated with high mechanical strength, high resistance to chippage (or breakage), and excellent durability. Adjusting the composition or mineral constitution and increasing the amount or degree of vitrification in firing achieves low porosity in whitewares. With respect to composition, mixtures of clay, flint (ground silica), and feldspar minerals have been found to achieve the highest strengths of clay based-whitewares, and these products are called "triaxial whitewares: due to the three components in their composition. Further improvements in strength are noted when aluminum oxide (alumina) and/or other minerals, such as zircon, are added to the composition.

Vitrification is achieved in kilns as the ceramic composition melts as temperatures achieve "red heat", i.e. rise above about 950°C. As temperature is further increases, more melted phase is formed, and this glass is "distributed" by capillary forces throughout the ceramic. As temperatures generally increase above 1000°C, a new mineral named mullite appears. Simultaneously, the ceramic ware exhibits shrinkage effectively increasing density and reducing porosity. After cooling in the kiln, the fired product has mechanical properties reflecting the degree of vitrification and densification achieved in the firing process. The degree of vitrification is the percentage of melting of the original constituents that has occurred in manufacturing. In whiteware ceramics, the amount of melting may be as high as 40-60% while in glass products the

extent of melted phase approaches 100%. In manufacturing of whitewares, measurements of

firing shrinkage and porosity (water absorption) reflect the quality of the fired product.

Class	Description	Distinguishing Factor for this Class
Earthenware	Clay based ceramic ware of medium	Water absorption of 4-20%.
	porosity.	Earthenware is typically off-white to
		red in color due to its iron content.
Stoneware	Ceramics made form a single clay or	Water absorption 0-5%. Stoneware is
	clay blend with other minerals	typically off-white to gray in color
	(including silica) fired to produce a	due to its iron content and the
	harder and more durable product.	presence of non-clay minerals.
Vitreous China	Product classes include:	All product classes typically exhibit
	Hotel china	water absorption of less than 0.5%
	Bone china	except for cookware, which may
	Frit china	exhibit up to 5% absorption. The low
	Vitreous plumbing fixtures	water absorption creates high
	Cookware	strength and minimal water
		transmission in use.
Porcelain	Product classes include:	The products may be compositions
	Hard porcelain	of flint (quartz), clay, and feldspar (a
	Vitreous porcelain	vitrification enhancer), and they may
	Electrical porcelain	contain additional minerals to
	Dental porcelain	increase their strength (such as
		aluminum oxide).
Electrical	Product classes include:	Steatite ceramics contain the mineral
Porcelain	Steatite ceramics	talc to enhance the product
	Electrical ceramics	performance in high frequency
		electrical applications. Electrical
		ceramics usually are porcelains of
		high aluminum oxide content (such
		as spark plug insulators).
Technical	This general classification includes	Compositions are altered to include
Whiteware	many low absorption ceramics for	aluminum oxide, zircon, and other
Ceramics	structural and chemical applications.	minerals to obtain specific
		properties.

Table 1: Classification of Unglazed Ceramic Whiteware Products

Whiteware products are typically glazed in order to increase their utility and improve their appearance. A glaze is a glass coating over the ceramic surface formed by melting or fusing a coating that has been applied to all or part of the ceramic ware's surface. Glazes provide a smooth surface that can easily be cleaned. Glazes also prevent water to be absorbed by the product thereby promoting sanitation and/or improving performance. Glazes also can be colored using pigmenting oxides providing enhanced appearance.

One advantage of glazing over a white surface is that is it relatively easy to achieve light colors without "bleed through" of color from the substrate. This is a distinct advantage of whiteware products as compared to red clay (red body) ceramics. With red clay ceramics, it is frequently necessary to apply double layers of glaze (a white under glaze layer topped by a colored outer layer) to achieve a desired light color.

Raw Materials for Fine Ceramics and Reactions on Firing

Raw materials introduction. A variety of raw materials are used in the production of whiteware ceramics. These raw materials or minerals can generally be broken down into three categories, which are clay, flux and "fillers" (or non-plastics). Each material has a specific function, but in general, the clay is the component that provides plasticity or cohesion for forming, while the flux promotes vitrification. The filler is typically inert, but it also may serve to modify the glass viscosity during vitrification, which effectively extends the range of firing temperatures of the composition.

The component that receives the most attention in traditional ceramic compositions is the clay. Clay is a hydrous sheet silicate that is a product of the weathering of feldspathic parent rock. Clays are defined by their plasticity when mixed with water, and they exhibit an extremely small particle size in an unagglomerated state. A typical particle size distribution is given in Figure 1. This small particle size and the plate like morphology of the particles give rise to a large surface area. Thus, the particle surfaces tend to have an affinity for water. The clay's affinity for water gives rise to a monolayer of water around the particle. The water layer promotes cohesion and allows the particles to slip relative to one another during plastic forming.



Figure 1 – Typical Clay Particle Size Distribution

Since clays are the product of weathering of the parent feldspathic rock, they can exist as either primary (residual) deposits or secondary (sedimentary) deposits. Primary deposits are formed by geological processes in situ, and they typically have the largest particle size and lowest impurity level amongst clay sources. Secondary deposits of clay involved transportation of minerals by water with eventual deposition in the location where they are mined. Secondary deposits typically have smaller particle sizes and higher impurity levels when compared to primary deposits.

Being a product of weathering, clays are capable of a wide range of atomic substation in the silicate structure, which gives rise to the large variety of clay minerals. Clays, particularly secondary deposits, also contain non-clay impurities or accessory minerals.

The major accessory mineral found with clay deposits is crystalline silica (quartz). Sulfides, sulfates, carbonates and hydroxides can also be present as accessory minerals. Clays can also contain organic impurities. The organic impurity can play a role in the plasticity of the body, but must be controlled for some fast firing applications. A variety of processing and refining steps are available to remove the impurities, but the cost of these treatments versus the processing or quality benefit that is derived from them must be considered. Clays are usually available in lump or prill form, powderd (air-floated), and slurry form.

There are three main groups of clay minerals of kaolin, illite and montmorillonite. Kaolin clays are the most common group and they have the approximate composition of $Al_2(Si_2O_5)(OH)_4$. White colored clays of this composition are simply called "kaolins". Kaolin clay is also typically the major clay mineral in "ball clay" – a highly plastic and cohesive form of kaolin. Depending on the origin or geologic history, kaolins are used in several forming processes (product shaping) ranging from pressing for the extremely small particle size kaolins from Florida (secondary) to casting for the coarser kaolins from North Carolina (primary).

Kaolin. Some typical chemical analyses of kaolins are given in Table 2. Since fired color is typically a concern with kaolins, the iron content (reported at Fe_2O_3) and titanium (reported as TiO_2) content are very important. As the iron content increases, the fired color has more of a red shade, while increasing titanium content imparts a buff or tan color. For products where extreme whiteness is desired, the clay must be selected that has the minimum level of these impurities.

Oxide	Georgia Kaolin (USA)	Florida Kaolin (USA)
SiO_2	44.4	45.7
Al_2O_3	39.6	37.4
Fe_2O_3	0.4	0.8
TiO ₂	1.7	0.4
P_2O_5	trace	0.3
CaO	trace	0.2
MgO	trace	0.1
Na ₂ O	0.1	0.06
K_2O	0.1	0.3
LOI	13.7	13.9

 Table 2 – Examples of Kaolin Chemistry

The kaolin mineral undergoes chemical reactions during firing. The first and most important of these reactions is the dehydroxylation. During dehydroxylation, the crystalline water is evolved from the clay mineral above 500°C. Evidence of deydroxylation is give in Figure 2, which is a simultaneous thermogravimetric (TG) and differential scanning calorimetery analysis (DSC) - with evolved gas analysis of a commercial kaolin. After dehydroxylation, the clay mineral is in a disordered form existing a residual material called "metakaolin".

A second reaction, around 1000°C, is apparent in Figure 2 and it is associated with mullite formation, as characterized by a large exothermic peak. In this regime, a portion of the clay mineral reorganizes to form mullite (3Al₂O₃.2SiO₂). Mullite is considered advantageous since it has a needle like crystal habit and mechanically reinforces the glassy matrix of the whiteware ceramic.



Figure 2 – Thermogravimetric Analysis of Kaolin in Air

On heating above about 950°C, some of the residual material from the clay dehydroxylation forms amorphous material as melted phase or glass. Impurities present and other minerals contribute to the overall quantity of vitrified material during firing. On cooling, additional mullite (called secondary mullite) can crystallize from the glass present. The process of forming secondary mullite involves expansion reactions, and it may help in preventing excessive shrinkage or slumpage of the ware at the elevated temperatures in the kiln.

Ball Clays and Other Clay Minerals. In addition to kaolin, there are other commercially important clay minerals. Ball clays are commonly used in whitewares where higher plasticity is required. Ball clays typically fire to a buff or tan color due to a their iron or titania content, Some typical ball clay chemistries are given in Table 3.

Montmorillonite clay is another variety of clay mineral. Montmorillonites (Al, Mg)Si₄O₁₀(OH)₂ are characterized by an extremely small particle size and very high level of

plasticity. As the chemical formula implies, montmorillonites are subject to a high degree of atomic substitution. Bentonite is one form of Montmorillonite, and it is used in limited quantities to improve plasticity. Due to fine particle size, montmorillonites experience high drying shrinkage and their presence can make drying more difficult. They fire to a darker color than kaolins or ball clays due to a higher impurity level.

The last clay mineral is illite which is sometimes known as "hydrous mica". Illites have the least defined structure, due to the wide variety of atomic substitution that can take place. Illites are desirable for "fast-fired" tile formulations, due to a lower weight loss and shrinkage on firing than the other clay minerals. Examples of illite and montmorillite chemistries are also given in Table 3.

Oxide	Ball Clay A	Ball Clay B	Montmorillonite	Illite
SiO ₂	61.2	55.2	64.3	49.3
Al ₂ O ₃	24.3	27.9	20.7	24.3
Fe ₂ O ₃	1.4	1.2	3.5	7.3
TiO ₂	1.0	1.1	0.1	0.6
CaO	0.3	0.3	0.5	0.4
MgO	0.4	0.4	2.26	2.5
Na ₂ O	0.2	0.3		
K ₂ O	1.3	1.0	2.9	7.8
LOI	9.9	12.6	5.2	8.0

 Table 3 – Selected Clay Chemistries

Fluxes Used in Whitewares. Fluxes promote the formation of a glassy bond during vitrification. Fluxes provide alkaline (Na₂O and K₂O) or alkaline earth (CaO or MgO) to the composition, which promote glass formation and reduce glass viscosity during firing which serves to enhance vitrification. The level of fluxing components must be optimized to achieve the desired fired property in the selected firing range. Feldspars and nepheline syenite are the traditional fluxes of choice, but recycled glass powders and other waste materials are gaining popularity for cost reasons. Other materials such as spodumene (Li,Al)SiO₃, calcined bone ash (Ca(PO₄)₂), limestone (CaCO₃), dolomitic limestone (Ca,Mg)CO₃, wollastonite (CaSiO₃) and talc (Mg₃Si₄O₁₀(OH)₂) are also used as fluxes.

There are several types of feldspar that are used commercially. These include soda feldspar (albite, NaAlSi₃O₈), potash feldspar (microcline or orthoclase, KAlSi₃O₈) and lime feldspar (anorthite, CaAl₂Si₂O₈). Feldspar typically does not exist as pure albite or pure anorthite, but it is founds as mixtures of these major feldspar types. It is possible to buy a soda feldspar, for example, but this simply means that albite is the predominant mineral. Some example chemistries for feldspars are given in Table 4. Particle sizes can range from granular to powders and the selection of particle size depends on the application. Felspars typically contain some quartz as an impurity.

Oxide	North Carolina Feldspar	Potash Feldspar	Nepheline Syenite
SiO ₂	68.3	67.6	60.7
Al ₂ O ₃	18.8	18	23.3
Fe ₂ O ₃	0.1	0.1	0.1
TiO ₂			
CaO	1.4	0.8	0.7
MgO			0.1
Na ₂ O	6.8	3.0	9.8
K ₂ O	4.1	10.4	4.6
LOI	0.1	0.2	0.7

Table 4 – Examples of Feldspar Chemistry

Another flux used in whitewares is nepheline syenite, which is higher in alkali and alumina and lower in silica than feldspar. Nepheline syenite is a naturally occurring mixture up of nepheline (K₂Na₆Al₈Si₉O₃₄), microcline and albite feldspars. Nepheline syenite is relatively expensive, but it provides greater fluxing power (effectiveness) and a wider firing range than feldspars in porcelain compositions. Additionally, nepheline syenite does not susally have significant quartz contamination, although it may contain trace impurities of mica.

Fillers for Whitewares. The non-plastic or filler portion of the whiteware composition usually consists of flint (ground quartz), but it may include alumina (Al_2O_3) , pyrophillite $Al_2Si_4O_{10}(OH)_2$ or sericite depending on desired function of the filler. Ground quartz used in whiteware compositions is frequently called "potter's flint".

In the case of quartz, the silica particles are partially melted at high temperatures (above red heat) and enter the glassy phase formed by the fluxing components. One result is that the viscosity of the glassy phase is increased allowing for a relatively "wide" firing range characteristic of porcelain compositions. The residual or "unmelted" quartz serves as a "skeleton" preventing the product from slumping under its own weight at elevated temperatures.

Quartz undergoes a reversible phase change requiring special care during cooling of the fired ware in the kiln. On heating, quartz inverts from the α quartz ploymorph to the β quartz polymorph at 573°C. The reverse reaction happens on cooling to any residual quartz grains. An example is shown in Figure 3 illustrating the heat associated with the quartz inversion on heating and cooling. On heating the reaction consumes heat (endothermic), but on cooling, the reaction releases heat (exothermic). The primary concern is the two percent volume expansion on heating and an equal contraction on cooling. Excessive cooling rates in the kiln can result in a defect known as "dunting" (cracking) for compositions with residual quartz



Figure 3 – Quartz Inversion by Differential Scanning Calorimetry

When alumina is substituted for all or part of the quartz, the strength of the fired ceramic is increased due to increased mullite formation. Alumina porcelains are commonly used when very high strength is required. When alumina is substituted for quartz as the filler, dunting becomes less of a concern as compared to compositions containing a high content of flint..

In steatite compositions, talc $(Mg_3Si_4O_{10}(OH)_2)$ is commonly used as a source of magnesium. Talc can also be used in the production of cordierite ceramics, which have a very low thermal expansion and are used as substrates for catalyst in catalytic reactor products.

Glazes. Raw materials used for glazes include primarily clay, finely ground silica, and fluxes. High alkali and alkaline earth contents and low silica contents are desired in glazes to achieve good flow (coverage) during firing. By changing the alumina content, for example, a glaze with a gloss finish can be made into a matte finish. In some cases, lithium silicates such as spodumene are added to glazes to modify their thermal expansion characteristics to achieve better thermal expansion match (fit) between the glaze and the ceramic body.

Since the use of lead as a flux has been curtailed, borates and zinc oxide are used extensively in small quantities as fluxes. Zinc oxide also promotes color development in the fired glaze. A common source of B_2O_3 is borax (sodium tetraborate decahydrate). The levels of both zinc oxide and borates must be limited to avoid glaze defects.

Glazes are now commonly prepared from frits (premelted glass compositions). Frits have the advantage of requiring less energy to melt (advantageous in fast fire glazes) and they require less batching and material handling effort. Frits are typically purchased to achieve a particular effect for which they were specifically prepared. Frits simply need milling and mixing with the remaining glaze components to prepare the glaze suspension prior to application.

Clays are used in glazes as suspending agents to prepare the glaze slurry. It is also possible to purchase premixed combinations of frit and clay (known as compostos). These formulations simply need water to form a suspension and the addition of coloring agents to achieve a particular fired visual effect.

Transition metal oxides such as hematite (Fe₂O₃) or cobalt oxide can be added directly to formulations to impart color. These oxides are dissolved by the glassy phase during firing. More recently ceramic pigments based on zircon have become very popular due to their stability and coloring power in glaze formulation. These colorants are usually zirconium silicate crystals with small additions of transition metal oxides to achieve a coloring effect. Pink colors that are based on chemically "doped" alumina.

Zircon ($ZrSiO_4$) is also commonly used as an opacifier for white glazes and engobes. On cooling of the molten glaze, the zircon that has been dissolved in the melt precipitates and forms discrete crystals in the glassy matrix. These crystals block the transmission of light and opacify the formulation.

Forming Methods for Whiteware Products

Whiteware products are shaped (formed) by the traditional processes of plastic forming (turning, jiggering, extrusion, or combinations thereof), slip casting, or compaction (wet or dry pressing). In a few products, isostatic compaction may be followed by "turning" in lathe-like machines to achieve a formed shape. Drying, firing, and quality inspection follow these processes. Glazes may be applied prior to firing (in single-fire processes) or post-firing (in double fire processes) with the latter fired a second time to melt the applied glaze to the surface.

The object of forming is to achieve near perfect particle packing in the formed mass. This means that entrained air has been eliminated to the extent practically possible. In addition, constituents of the mixture are uniformly dispersed in the mass prior to the use of the forming process. The wetting of materials to the extent required by the forming process is achieved in special mixers and is frequently aided by "ageing" of wetted raw material mixtures. There is considerable art and science in preparing raw materials for the forming process so as to achieve optimum properties in the formed ware.

Plastic Forming. As is implied by the name, plastic forming involved deformation of a plastic mass of raw materials into a desired shape prior to drying and firing of the product. By definition, plasticity (in ceramics) is the ability to deform a clay-containing mass without breaking the mass or causing it to form cracks. Plasticity is derived from the clay constituent of the mix, and it is increased through mineral additions and polymeric additives.

The simplest plastic forming process is hand forming as is practiced by potters. In high production manufacturing, use of jiggers to force the plastic mass into a consistent shape is commonly employed. In many cases, the plastic forming process forces the mass into a mold cavity under pressure in a process called plastic pressing. If the mold is permeable, air may be used to assist in ejecting the formed product from the mold in a process called ram pressing.

The most common plastic forming process is extrusion where the plastic mass is forced through an orifice (die), which forms two of the three dimensions of the desired product. Extrusion is carried out in piston-type or auger-type devices. In higher volume manufacturing, the auger extrusion device may be preferred due to high production output. The column of clay is then cut with wires to form the third dimension of the formed product. Some products, such as electrical insulators, may be formed by extrusion into "blanks", and the blank is subsequently "turned" in lathe-like processes to accomplish additional forming of surface features. To avoid slumpage of the wet clay mass after forming, some degree of drying may be required between extrusion and the subsequent forming operation. Formed ware is always greater in dimension than the fired product due to shrinkage in drying and shrinkage in firing. The drying and firing shrinkage may exceed five to eight percent linear shrinkage in plastic formed products. For this reason, the formed dimension is always adjusted so that the net dimension after firing is the required product size.

Slip Casting. Slip casting is a process where a suspension of ceramic particles is poured (cast) into a permeable or absorptive mold so as to draw a layer of particles to the surface of the mold thereby forming a product. Slip casting can make both solid and hollow objects. Drain casting is the process of timing the casting process until the desired wall thickness of cast product has formed and subsequently draining the mold this preserving a void or cavity in the cast object.

After completing the casting process or draining the mold, the cast object is typically left in the mold until the mass has been dewatered sufficiently to allow handling of the formed object without deforming it. Then the mold is opened and the cast object is withdrawn. The object is typically placed on a tray or other fixture and conveyed into a "conditioning room" prior to drying.

The slip casting process is preceeded by the production of a "batch" of the required proportions of minerals. This batch is mixed with water and "chemicals" in special mixers called "blungers". The mixed material is stored in tanks that are agitated to prevent settling of the constituents of the suspension. The suspension is typically called the "slurry".

The slurry contains "chemicals" that cause deflocculation or chemical "separation" of the fine mix constituents. Some chemicals assist in wetting of the particulate matter and stabilization of the slurries. The solids content of the slurry is carefully controlled by meeting goals for the specific gravity of the slurry, and the viscosity of the slurry is monitored. By controlling the solids conten6t of the slurry and its viscosity, the casting rate (rate of build up of solid on the mold surface) is controlled allowing for use of schedules for draining molds to form consistent products.

The traditional mold material in slip casting is plaster of paris. Such molds must be handled carefully to avoid breakage or wear, and consistent mold moisture content prior to reuse is important. Polymer molds have been introduced in pressure casting operations where applied pressure over the mold increases the casting rate.

Dry Pressing or Dust Pressing. Powdered mineral mixtures may be formed by compaction in molds using large presses. The process is called dry pressing or "dust pressing", and it is extensively employed in producing ceramic tile and certain electrical ceramics. The process begins with the preparation of the powdered material using a granulation process. Granulation is required so that the dry or near-dry powders will flow into mold cavities achieving even fill prior to compaction. In high-volume manufacturing, spray drying is used to form granules one millimeter or less in diameter, and these granules or "pellets" are stored prior to use in pressing. In lower volume manufacturing, mix-pelletizing may be employed to produce granules. Granules may have a small addition of moisture, binders, or plasticizers added prior to their use in the pressing operation.

Modern presses can employ "isostatic molds" that allow for even pressure application to both sides of the part during compaction. The rate of compaction is important to allow deairing during compaction, and the total pressure applied in compaction largely determines the as-pressed or "green" strength of the pressed part.

Drying and Firing of Whitewares

Drying. Drying is conducted primarily in continuous convection dryers containing zones to control evaporation rate. The initial drying may be accomplished in "predryers" where the rate of evaporation is held as low (suing low temperature and high relative humidity) to avoid high shrinkage rates and associated cracking. In the initial dryer zone, temperatures are kept just below the boiling point of water to avoid steam spallation in the product. In the final dryer zone, the temperature may reach 150-200°C.

Radio frequency and microwave dryers are used in processing of higher valued whiteware ceramics. Such dryers allow for greatly reduced processing time, and they are amenable to larger objects like electrical insulators. Convection dryers remain popular as most ceramic plants have excess waste heat available from the cooling section of their kilns.

Firing. Firing of ceramics involves heating of the dried ceramic to high temperature at a defined heating rate, holding (soaking) for a discrete time, and cooling back to room temperature under a defined schedule. Firing can be accomplished in batch kilns or continuous kilns. Batch kilns hold a defined quantity of product and go though a complete firing schedule before unloading of the fired product. In continuous kilns, the product is continuously charged to one end of the kiln, and it moves through the kiln at a uniform rate prior to discharge. Continuous kilns include tunnel kilns (where product is set on kiln cars) and ro9ller hearth kilns (where the product sits on and is propelled by ceramic rollers).

PHYSICAL PROPERTIES OF WHITEWARES

Key Physical Properties

The physical properties of fired whiteware ceramics are established by the product requirements, and they can vary widely depending on the specific formulation, additives, forming method, and firing. A list of key physical properties is given in Table 5.

Product Type	Important Physical Properties				
Tile	Water Adsorption (Porosity), Strength, Abrasion Resistance, Chemical Resistance, Dimensional Tolerance, Surface Finish and Color				
Sanitary Ware	Water Adsorption (Porosity), Strength, Thermal Shock Resistance, Resistance to Staining and Color				
Tableware	Impact Resistance, Abrasion Resistance, Chemical and Staining Resistance, Resistance to Metal Marking, Resistance to Lead and Cadmium Release and Color				
Electrical Porcelain	Mechanical Strength, Water Adsorption (Porosity), and Electrical Resistance				

Table 5 -	- Key	Physical	Properties
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One of the central physical properties for all types of whiteware ceramics is the water adsorption or porosity. Low values of water adsorption or porosity indicate a high degree of vitrification. Some product standards specify that a product must be impervious which is defined as having a water adsorption less than 0.5%. Many products such as sanitary ware and tableware are glazed on any surface that will be exposed to water during use to improve their resistance to water adsorption.

Methods for determining water adsorption and porosity for whiteware ceramics are described in ASTM C 373 (Standard Test Method for Water Adsorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products) or ISO 10545-3. In these methods, the ware is exposed to saturation for a specific period of time to determine the quantity of water that the ware can adsorb. Saturation can be achieved through boiling or vacuum, depending on the method.

Mechanical Properties

The mechanical strength of a whiteware product is important for several types of applications. For sanitary ware, the product must be able to resist the stresses applied during normal use, while for tile the product must be able to stand the compressive load applied to the floor. Strength test can either measure compressive strength or tensile strength depending on the application. ASTM C 733 describes a method for measuring the compressive strength of fired whitewares. The most common type of test for the mechanical strength of whitewares is a simple bending test. Bending tests, such as a Modulus of Rupture test, essentially measures the tensile strength of the ceramic in flexure. As with all ceramics, whitewares tend to fail more readily under a tensile stress than a compressive stress due to their brittle nature.

An example of this type of test is given in ASTM C 648, ASTM C 674 or ISO 10545-4. In these tests, a load is applied which flexes the ware, and this load is applied until failure occurs. For many intricately shaped products such as toilets or other sanitary ware, it is difficult to measure strength on the finished product due to the irregular geometry. In this case, samples can be cut from the product to measure mechanical properties. Mechanical properties of whiteware products are given in Table 6.

Property	Eaethenware	Hard Porcelain	Bone China	Hotel China	Normal Electrical Porcelain	Hard Electrical Porcelain
Water absorption, %	6-8	0.0-0.5	0.0-1.0	0.1-0.3	0.0	0.0
Bulk density, g/cm ³	2.20	2.40	2.70	2.60	2.40	2.77
Compressive strength, MPa		400			700	700
Modulus of rupture, MPa	55-72	39-69	97-111	82-96	105	175
Modulus of elasticity, GPa	55	69-79	96	82		
Thermal expansion coefficient, /°C, 20-500°C	7.3-8.3		8.4	7.3-8.3	5.7	6.7
Thermal expansion coefficient, /°C, 20-1000°C		3.5-4.5				

 Table 6: Typical Mechanical properties of Whiteware Ceramics (after Wood)

Another aspect of mechanical strength that is important to tableware as well as any brittle ceramic is impact resistance. For tableware, the product must have enough impact resistance to withstand dropped utensils or to resist impact stressed in handling. Impact resistance is not only a function of the mechanical properties of the fired ware, but also has to do with the physical design of the product. Methods for measuring impact resistance for tableware are given in ASTM C 368. Using a pendulum arrangement, this method determines the magnitude of impact that will initiate failure and the amount of energy required to produce complete failure. A similar method exists for ceramic tile and is described in ISO 10545-5.

For products subjected to wear such as tile in flooring applications, the resistance to abrasion is a key concern. For glazed ceramics, this test measures the resistance of the glaze and not of the underlying ceramic ware. Tableware must be able to resist degradation by abrasive cleaning agents.

The measurement of abrasion resistance of ceramic tile is described in ASTM C 1027 and ISO 10545-7. In this method, an abrasive load is agitated on the glazed surface of the tile for a preset number of cycles. The surface is inspected at specific intervals. The number of cycles that the product passes before surface degradation is observed determines the category of abrasion resistance. After exposure to the abrasive media, the surface is inspected under prescribed viewing conditions. Unfortunately, these methods are subjective since the operators judgment is required to determine when abrasion becomes visible.

For unglazed surfaces, the procedure for measuring abrasion resistance is slightly different. In these methods, a large wheel is rotated over the ceramic surface. The wheel can be made of abrasive material or abrasive grit can be introduced just above the surface of the ceramic. The loss of mass after a defined number of cycles is used to determine the abrasion resistance. Examples of this type of measurement are given in ASTM C 1243 and ISO 10545-6.

Chemical Resistance

Resistance to chemicals and stains are important for most types of whitewares. Chemical resistance is important for products that are in contact food or to determine the potential effect of harsh cleaning agents. Staining is important for similar reasons. Properly formulated and fired glaze compositions should be very resistant to both household chemical attack and easy to clean. Some unglazed surfaces such as mechanically polished porcelain tile can have some issues with regard to staining resistance since closed pores near the surface can be exposed during polishing.

Most chemical and staining resistance tests involve a controlled exposure to the chemical or staining agent followed by a specified cleaning procedure. After the cleaning procedure, the surface is inspected under defined viewing conditions and the results are qualitatively determined. Staining resistance gives an indication of how easy the surface will be to clean after use which is especially important for sanitary ware and tableware. Examples of methods for measuring chemical resistance are given in ASTM C 650 and ISO 10545-13 and examples of staining resistance are give in ASTM C 1378 and ISO 10545-14.

The resistance of tableware to metal marking is related to staining resistance. In this case, the glaze must resist staining when cutlery is passed across the surface. Resistance to metal marking is a function of both the condition of the glaze surface, but also the composition of the glaze. Typically glossy surfaces are more resistant than more matte surfaces.

Also related to chemical resistance is the leaching of toxic metals from tableware. Test methods have been developed specifically for cadmium and lead release from ceramic products. The concern here is that acidic components of food or beverage contained in glazed ceramic ware may leach or transfer small quantities of these toxic metal species. These metals would then be ingested by the user and over time accumulate to a potentially harmful level. Test methods such as ASTM C 738 detail an accelerated leaching test for glazed ceramic surfaces, which can be used to determine the potential risk of metal exposure from a particular glazed surface. The leaching takes place in an acetic acid medium and the quantity of metal leached from the surface is measured by atomic adsorption spectroscopy.

Thermal Shock

Resistance to thermal shock is important for products that may experience thermal cycling such as sanitary ware, which may be subjected to rapid switching between cold and hot water. A method for measuring thermal shock resistance is reported in ASTM C 484. In this method, the ware is soaked in water at 60°F and then immediately moved to an oven operated at 293°F for up to ten cycles.

Thermal Expansion

In some cases, it may be desired to measure the thermal expansion of the ware. This is often done in product development to match the thermal expansion of the glaze and the body. The coefficient of thermal expansion (CTE) is measured according to the following equation:

$$CTE = \frac{\left(\frac{(L_2 - L_1)}{L_1}\right)}{(T_2 - T_1)}$$

where L_1 is the length at temperature T_1 and L_2 is the length at temperature T_2 . Thermal expansion can also be useful for architects or engineers determining where to place expansion joints in large ceramic tile installations. Thermal expansion is most accurately measured with a dilatometer which uses a ceramic pushrod to follow the dimensional change of a sample as it is being heated. Test methods for measuring thermal expansion with a dilatometer are given in ASTM C 372 and an example measurement of the coefficient of thermal expansion on a glaze sample is show in Figure 4.



Figure 4 – Thermal Expansion of Fired Whiteware Body and Glaze

Color and Gloss

Measurements of color and gloss are also routinely measured on whiteware products. The first step in measuring color is to quantitatively describe color. The phenomenon that we perceive as color derived from the interaction between visible light and matter. This interaction can include adsorption, reflection, refraction, diffraction, scattering and fluorescence. Adding to this complicated subject is the fact that color perception is strongly influence by the illumination source. The science of describing color has received a great deal of attention in the last century. There are several color measurement systems, but the most common is based on L^{*}, a^{*}, b^{*} measurements although many other color space systems are in use. These measurements describe a three dimensional color space where the L^{*} value describes the whiteness or lightness of the article while a^{*} describes a red to green color axis and a^{*} defines a yellow to blue color axis.

Fortunately, a host of instruments designed for measuring color are available. These instruments will have a selection of standardized illumination sources and illumination angles. Two types of instruments are available. Colorimeters are the simplest color measuring instruments. These instruments do not measure spectral data but use a set of filters to approximate the color space measurements and relate them to the standard observer curves published by CIE (Commission Internationale de l'Éclairage). Spectrophotometers are more advanced color measurement tools and measure reflectance and transmission data versus wavelength in small steps to describe the color. Several standards such as ASTM C 609 and ISO 10545-16, exist to quantify small color differences between glazed surfaces. The color difference, ΔE , is defined as the magnitude of the difference between the vectors describing the color of each sample as is shown in the following equation.

$$\Delta E = \sqrt{\left(\Delta L\right)^2 + \left(\Delta a\right)^2 + \left(\Delta b\right)^2}$$

The measurement of gloss is related to color. Several parameters contribute to our overall perception of gloss. One common method for quantifying the perception of gloss is the

method for measuring specular gloss described in ASTM C 584. In essence, high gloss surfaces result in very little scattering of the incident light while more scattering occurs as the amount of surface texture increases. Opacity measurements can also be made on translucent fine china.

Electrical Properties

Finally, for electrical porcelain applications, the electrical properties of the whiteware ceramic must be measured. These methods are summarized in ASTM D 116 which describes methods for measuring dielectric strength, electrical resistively and a number of other performance measurements of ceramics intended for electrical insulating applications.

GLAZES FOR WHITEWARES

Introduction to Glazes

Glazes are thin glass coatings applied to the whiteware surface. Glazes may simply serve as a decorative layer or they may serve a mechanical purpose such as making the surface impervious so that it resists water penetration and staining. Glazes may also serve to increase the electrical resistance or the mechanical strength of a particular product. Glazes are generally applied as a suspension (slip) of ceramic particles in an aqueous matrix, but dry applications are also available for special applications. Functionally, the glaze formulation must readily bond to the ceramic surface and provide even surface coverage during the firing cycle. The glaze should also have a similar thermal expansion as the body to avoid defects on cooling.

A variety of materials are used in glaze formulations that may include the basic materials used in the body formulations such as clay, feldspar and silica, but other components such as coloring agents, zinc oxide, carbonates of barium and strontium and borates may also be present. The function of each component will be briefly described. Silica (SiO₂) is the backbone of the glass formulation since it provides the network structure of the glass. It should be noted that although a network structure is described in glass, it is actually an amorphous material. This implies that unlike a crystalline solid that has a relatively spatial relationship between the constituent atoms, a glass has a more random relationship between the constituent atoms. The silica used to form the silicate structure is derived from quartz (flint), clay, feldspar or any other silicates in the formulation. Borates are unique in that they serve as network formers and typically decrease the melting temperature of the melt. Excessive levels of borates can result in

durability problems with the glaze. Borax (Na₂B₄O₇*10H₂O) is the primary source of borates, but other minerals such as colemanite (Ca₂B₆O₁₁*5H₂O) are also available. The boron content of a glaze is generally reported as B₂O₃.

Traditionally lead (as PbO) was an integral part of any glaze formulation. The addition of lead to the glaze imparted the glaze with a lower firing temperature and improved coverage. Leaded glazes typically produced a superior fired finish, but due to health concerns retaled to the leaching of lead and environmental concerns with lead volatilization during firing, the use of lead in glazes has been severely curtailed. Increased use of zinc oxide and borates in glaze formulations have been used to offset the removal of lead from glaze formulations. Zinc oxide also acts as a flux and typically enhances the effect of other fluxes.

The silicate structure is modified by alkaline and alkaline earth components which act as fluxes (reduce the melting temperature). These components serve to disrupt the silicate structure which reduces the viscosity of the melt. The more alkaline (Li, Na, K) and alkaline earth (Mg, Ca, Sr and Ba) in the glaze, the lower the melting point, but care must be taken because excessive levels can result in durability or devitrification problems. Alkalines are usually introduced into the glaze from silicates such as feldspar, but may also come from soda ash or other carbonates and hydroxides. Care must be taken when dealing with soluble carbonates or hydroxides which may alter the rheology of the glaze. In general, higher levels of alkali and alkaline earth components increase the thermal expansion of the glaze. As the thermal expansion of the glaze increases, the likelihood of defects in the fired product increases.

Oxides such as alumina (Al_2O_3) are known as modifiers and help to improve the chemical durability of glasses. Alumina can also be added to glazes to produce matte or satin finishes. These textures are due to the presence of alumina crystals in the glaze. Similarly, when zirconia is added to glazes, usually in the form of zircon (ZrSiO₄), in sufficient quantities, it acts as an opacifier by precipitating zirconia crystals in the glaze which block light transmission. Opacifiers based on titania and tin oxide may also be required with certain pigments.

Glaze Application

Glazes are usually applied in liquid or paste form and therefore require that the ceramic components be suspended prior to application. Depending on the starting particle size of the raw materials, glazes can either be milled to achieve the proper particle size, or if the components are fine enough, there are simply mixed with water in a high intensity mixer to disperse the suspension. Frits which are premelted glaze compositions are commonly used in glaze formulations. Frits allow for the use of soluble components such as B_2O_3 which would be difficult to incorporate in a raw mineral form and also offer an energy savings since they are

premelted and typically require less batching when preparing the glaze application. In some cases, compostos are used which contain frit and clay and only need to be suspended prior to use.

Glaze formulations that require milling are usually ball milled which reduces the particle size and disperses the components to give a homogeneous suspension. Like slips for spray drying, the residue, solids content and viscosity are monitored during milling of glaze suspensions. The residue is simply the amount of material retained on a screen, usually 200 or 325 mesh, after a sample of the glaze has been washed through. The higher the amount of material retained on the screen, the coarser the glaze. Specific gravity can be measured with a pycnometer and viscosity can be measured with either Zahn or Ford cups which measure the time required for a sample of the suspension to drain through a specific orifice.

Depending on the application technique, the specific properties of the glaze, specific gravity or viscosity for example can vary widely with fluid glazes used for spraying and thick pastes used for screen applications. Additives such as binders or suspending agents are commonly added to glazes to achieve desired effects. Organic binders such as cellulose (CMC) are commonly used as well as bentonite or hectorite clay minerals which thicken the glaze and improve green strength. Suspending agents such as kaolin, bentonite or colloidal silica are used to avoid settling in the glaze before application.

The oldest methods of glaze application are either dipping the ware into a bath of the glaze composition. This simply leaves a uniform coating of the glaze on the surface of the ware and works well with intricate shapes such as toilets. Handling of the glazed ware, especially for large or heavy pieces, can be somewhat problematic. Brushing is another simple technique where glaze is applied with a brush to achieve a uniform coating.

A modern glaze line is simply a collection of modular glazing equipment that is assembled to achieve particular effects. A variety of common equipment will be described in the following section. The simplest application is the bell or waterfall. In this system, a continuous flow of glaze is allowed to flow across a curved metal surface. The glaze makes a continuous waterfall which the ware passes under. This type of application is used to apply uniform coatings such as engobes or glazes in wall tile. Spray booths are also used to apply uniform glaze coatings. Spray booths use a centrigal system to apply a continuous layer of glaze. For some very intricate shapes, the glaze may be sprayed on by atomizing the glaze in a moving air stream. The glaze adheres to the surface of the ware when the droplets impact the surface. This type of application requires a skilled operator to achieve a uniform coating.

Excess glaze from these systems are collected and recycled onto the glaze system. Usually some sort of screening is employed to remove contamination from the glaze. Brushes or fettling systems are often employed to remove excess glaze from the edges of the tile. In some systems, brushes are employed after an application to partially remove the applied glaze. This is done to achieve a particular visual effect.

For many types of applications, uniform coatings are not desired. Either patterns or random effects may be desired. Spray guns are used to apply mists of glaze which are sometimes called fumes. The guns can be stationary or move as the tile passes underneath. Timers are also employed to turn the gun on and off to achieve a more random effect. Patterns are usually applied with silk screens. A paste or thickened glaze composition is placed on the back of the screen and when a tile passes under the screen, a squeegee moves across the screen which pushes the glaze through the screen and applies the pattern to the tile. Modern systems producing highly decorated tile may use banks of screens that either apply multiple patterns to a single tile. Other systems are based on counting circuits that apply a particular pattern intermittently to give a more randomized decoration to the tile. In addition to flat screens, roller systems are becoming more popular. These systems use a cylindrical screen to apply the pattern to the ware instead of the traditional flat screen described previously. These systems can be operated in an asynchronous manner which allows for more randomization of the decoration.

For products where a granular texture is desired, dry glazes or crushed frits can be applied to the tile. In these systems, a liquid glaze is first applied to the surface of the ware and then the dry glaze is distributed on the surface of the ware. The liquid glaze is designed to help the granular glaze stick to the surface. This application technique can also be used to apply abrasive to the surface of the ware. This is done with floor tile to improve the slip resistance of the fired surface.

Hand painting and decals are often used to apply a final decoration. This is especially true for fine china where a ceramic decal may be applied to the fired glaze which is followed by a final firing to bond the pigments in the decal to the glazed surface. Decals made from ceramic pigments are available from a variety of sources.

The variety of glaze decoration techniques is very diverse. These techniques can be used individually or in combination to achieve an array of effects that may serve either an esthetic or functional purpose.

Firing of Glazed Ware

During the maturing of the glaze in the kiln, a number of processes take place which include, decompositions, solid state reactions, vitrification, fusion, and crystallization. While these processes tend to take place in the order listed, in fast firing processes this may not be the case. For example, decompositions may still be taking place as a glassy phase is developing

which would have the effect of retarding the rate of decompositions. Decompositions include the oxidation of organic binders, dehydroxylation of clays used as suspending agents, and the decomposition of hydroxides, carbonates or sulfates. These decompositions yield porous, high surface area components that react more readily.

Prior to the formation of a glassy phase, some solid constituents will react to form new compounds. These can generally be characterized as acid/base reactions. Generally, the acidic species is silica and the basic species are either alkali or alkaline earth constituents. New compounds such as $CaSiO_3$ can be formed from CaO and SiO_2 at relatively low temperatures. The extent of the formation of new compounds is somewhat limited due to the limited mobility (low diffusion rate) of oxides in the solid state.

Before the glaze composition melts, it undergoes vitrification like the ceramic ware. During vitirication, a glassy phase forms. The formation of this glassy phase is a kinetic process which means that it is a function of both temperature and time. Some authors refer to this temperature/time relationship as heat work. As the heat work increases, the quantity of glassy phase increases. This glassy phase tends to wet the ceramic particles. The glassy phase grows by dissolving residual ceramic particles. The liquid phase tends to pull the unmelted particles together which results in shrinkage and reduced water adsorption. Additionally, the presence of a glassy phase improves the mobility of the various oxides in the glaze. This improved mobility helps to homogenize the glass composition and enhances the rate of glass formation.

As the quantity of glassy phase increases due to heat work, the viscosity of the glaze decreases and eventually the glaze becomes molten. The surface tension of the glaze allows it to wet the surface of the ware, which promotes adherence of the glaze to the ceramic surface. Once the glass is molten, degassing must occur to achieve a defect free surface. Gases can be the result of incomplete decompositions in either the glaze constituents or from the body. Components of the ceramic body formulation such as talc and carbonates can be problematic since they only begin to decompose after the glaze has begun to vitrify. Gas trapped between glaze particles or adsorbed on surfaces also can contribute to bubble formation. An example of bubbles in a glaze is given in Figure 5.



Figure 5 – Backscatter SEM Image of Gas Bubbles in a Sanitary Ware Glaze

On cooling, some species are not soluble in the glaze composition and precipitate crystals that grow as the glaze cools. The most common crystallization process that takes place is the precipitation of zircon crystals from the glaze on cooling which serves to opacify the glaze. Precipitated opacifier crystals are apparent as bright spots in the sanitary ware glaze shown in Figure 1. Matte or satin glaze finishes are produced by crystallization of either alumina or other aluminates on cooling. Other unintentional crystallizations, referred to as devitrification, can occur. These are mainly due to a high level of alkaline or alkaline earth consitutents in the glaze.

To impart color to the glaze, pigments are added to the glaze composition. The array of pigments and their potential interactions are extensive. There are three methods of imparting color to a glaze. For body colors in porcelains, finely ground transition metal oxides, such as CoO, Cr_2O_3 , and Fe_2O_3 are added to the glaze formulation. These metals dissolve into the glaze during firing. This method is not used frequently in glazes due to problems with obtaining sufficient coloring strength. A second method for coloring glazes is similar to opacification where the glaze is formulated for colored crystals to precipitate from the melt on cooling. Again, this method is not frequently used since it is difficult to control.

Adding insoluble colorants to the glaze is the most common method for coloring glazes. This method does not rely on either precipitation of a specific compound from the melt on cooling or the incorporation of a compound into the glaze during melting. The most frequently used insoluble pigments are doped zircon compounds although a wide variety of synthetic spinels and other oxides are available. The doped zircon compounds tend to be the most stable over a wide temperature range. Some examples of these colorants include $(Zr,Pr)SiO_4$ (yellow), $(Zr,Fe)SiO_4$ (pink or corral), and $(Zr,V)SiO_4$ (blue). These synthetic crystals use small substitutions of transition metals into the Zr^{4+} sites in the crystal structure to achieve the desired colors.

Defects in Glazes

There are several types of defects that are common to glazing ceramic ware. These defects are related to gas evolution from the ceramic ware of the glaze constituents, thermal expansion mismatch, or the adhesion of the glaze to the ceramic substrate. Bubbles or pinholes in the glaze are the most common defect. These defects are more prevalent in leadless glazes since they do not flow as well as older leaded glazes. The gases that cause these defects can either come from decompositions taking place in the glaze components, from decompositions taking place in the body or from the air trapped between particles in the glaze. To avoid these defects, thinner applications are better since the path that the bubbles have to travel is shortened. More heat work on the glaze or more fluid glazes at the firing temperature help in bubble removal. Alternatively, materials that decompose once the glaze is molten should be removed from the glaze or body composition if possible. Examples of materials to avoid if gas evolution is a problem are limestone and talc. Another approach is to prefire the ceramic ware before glazing. Double firing of wall tile is relatively common. Other examples of uneven or poor surface texture can indicate that either better firing or a more fluid glaze at temperature are needed.

Thermal expansion mismatch between the glaze and the body can result in either crazing or peeling depending on the type of mismatch. It is more common for the glaze to have a higher thermal expansion than the ceramic ware. When the glaze has a higher thermal expansion than the ware, it shrinks faster on cooling which results in tensile stress in the glaze. These tensile stresses can literally pull the glaze apart. Crazing is characterized by a pattern of cracks that radiate outward from the center of the ware. The tendency to craze can be corrected by using thinner glaze applications which reduce stress accumulation or reducing the thermal expansion. In some cases, Li is used to replace some Na or K in the formulation to reduce thermal expansion. Excessive dimensional change during the quartz inversion on cooling the ware can also result in crazing. Reducing the quartz content or reducing the particle size of the quartz can help to minimize crazing due to dunting. Thermal expansion of a glaze can be measured using dilatometery.

When the glaze has a lower thermal expansion than the glaze, compressive stresses result. Excessive compressive stresses result in a defect known as peeling or shivering. These defects are characterized by a section of glaze separating from the edge of the ware. These defects can be corrected by using a thicker glaze application and increasing the thermal expansion of the glaze. Increased alkaline content of the glaze will typically increase the thermal expansion.

Adhesion defects which are known as crawling or tearing can result from several sources. Adhesion defects appear as irregular areas with poor glaze coverage. Drying problems with the glaze are a common source of adhesion defects. When the glaze has excessive shrinkage due to a very fine particle size or high clay content, tearing of the coating can occur. An organic binder can be added to improve the green strength of the glaze to reduce tearing. A minimum application thickness, clay content and grinding will help to improve the tendency to tear. When there are multiple glaze applications, drying problems can result if adequate drying does not take place between the application layers. Surface contamination can interfere with the adhesion of the glaze to the surface and result in crawling. Green or bisque ware should be handled as little as possible to avoid contamination by dust or oils for example. Finally excessive levels of opacifier in the glaze can result in poor wetting of the ceramic ware by the glaze.

Foreign matter in the glaze can also result in defects. Poorly ground frit or other granular contamination can result in surface irregularities. Metal contamination can result in discoloration. The source of the foreign matter should be identified and removed from the system. It is also possible for problems with the ceramic ware to show through the glaze. Large pyrite or marcasite (FeS₂) agglomerates in the clay can erupt through the glaze surface during firing. Typically, the source of the contamination can be identified by splitting the defect and observing the origin (body or glaze). Chemical analysis of the contamination may also help in identifying the source of the defect.

ECONOMIC TRENDS IN NORTH AMERICA WITH FINE CERAMICS

Globilization and changes in consumer preferences are factors causing rapid change in the fine ceramic economic sector in North America. The effect of globalization is to place pressures on manufacturing costs, with imported products growing rapidly in volume. This is, in part, based on new consumption patterns, with large quantities of products purchased through wholesale and retail outlets that are part of national chain stores. With enormous purchasing power for chain stores, price is the overriding consideration in their purchasing philosophy. For toilet bowls, non-clay refractory, and ceramic tile, the selling price is relatively high compared to the unit weight of the product making importation economically viable. By contrast, import penetration for lower valued brick products is limited to land shipment from Mexico.

	Brick	Flat	Toilet	Non-Clay	Ceramic Tile
		Glass	DOWIS	Kelfactory	
Annual	8.0	1.4	0.2	00	
Domestic					
Production					
Increase, %					
Current	< 0.25	8	8	18	50+
Import					
Percentage					
Growth in	≤1.4	-0.3	0 until 1998	2.2	2.7
Market					
Share by					
Imports,					
%/Year					

 Table 7: Estimated Production and Import Statistics for North America For 2004

Changes in consumer preference have affected sales for some whiteware sectors including fine china. As an example, young couples of previous generations preferred fine china for wedding gifts, but many people in today's generation prefer other consumer products early in their lives.

Quality improvements in imported whiteware products and product innovation have been factors in increased import growth. In sanitary ware, "one-piece" toilets and innovative glazes that reduce home maintenance and provide a measure of protection from mold and bacteria are available in some imported products. These products provide value added for the consumer and they provide the potential for additional profits for construction firms.

With sales of whiteware products linked to slow population growth and housing starts in developed countries, the prospects for rapid market expansion appear to be limited. Growth in import percentages are likely.

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