*Kirk-Othmer Encyclopedia of Chemical Technology.*

# ENAMELS, PORCELAIN OR VITREOUS

Porcelain enamel is a glassy coating applied to various metal substrates through a high (usually >425°C) temperature fusion process (see also Coatings) (1). The resultant chemically bonded glass–metal composite exhibits properties which reflect the chemical, physical, electrical, and aesthetic properties of the glass while combining the strength, ease of fabrication, and durability of the metal (see also Composite materials). Porcelain enamels are formulated to develop specific properties on metals or alloys.

The porcelain enamel is composed of various inorganic metal oxides fused between 1100 and 1400°C to form an alkali borosilicate glass (qv). The glass is rapidly quenched to produce either flakes by rapid chilling using water-cooled rollers, or glass granules by water quenching a narrow stream of molten glass. The resultant product is known as frit [65997-18-4]. An enameled article is produced by applying either wet or dry finely ground frit particles to the metal substrate. The enamel is fired to form one or more glassy layers to achieve a desired surface finish and property group for the article.

Porcelain enameling has been an important industrial process since the late nineteenth century in the United States. Modern appliances were developed utilizing the chemical and physical properties of the glass-on-metal coatings on cast iron (qv), sheet steel (qv), and, more recently, aluminum (see Aluminum and aluminum alloys). The wide variety of colors and textures and the long-term durability of porcelain enamel surfaces have been attractive to appliance producers as well as users. Enamels have been used on a wide array of kitchen utensils, cooking devices such as ovens and range tops, sanitary ware such as bathtubs and lavatories, water heater tanks, specially built industrial chemical vessels, cast-iron piping, storage silos for agricultural and industrial products, as well as architectural interior and exterior surfaces. Porcelain enamel surfaces on architectural panels for domestic and industrial buildings have provided evidence of the long-term environmental durability of the surface. Even buildings dating from the 1940s have required only a minimum of maintenance. Controlled exposure experiments involving enamels at different geographic locations in the United States have shown only minimal color and surface degradation after 30 years of exposure near ocean and industrial locations (2).

Porcelain enamels are used in modern mass transit facilities because of inherent fire resistance as well as ease of maintenance and durability in the face of highly corrosive atmospheres resulting from vehicular traffic. Newer applications of porcelain enamels include electronic substrates (see Electronic materials), pyrolytic self-cleaning oven interiors, microwave oven interiors, outdoor cookers, and fireplace liners as well as wood-stove exteriors, writing boards for erasable markers, institutional surfaces such as bathroom stalls and hospital operating room walls that need to be easily disinfected, and subway car interiors and elevator walls that are durable and easy to clean. Porcelain enamel surfaces are frequently used in food contact applications. The glassy nature of porcelain enamels has a significant effect on encapsulating and minimizing any solubility of constituents. Enamels can also be formulated to have specific acid, alkali, and abrasion-resistant properties.

The early history of enameling is associated with the craft of enameling art. Porcelain enamel provides a low cost, extremely pleasing, nonporous protective and corrosion-resistant surface, using mass production techniques. There are many excellent summaries of the history of porcelain enameling and artistic uses of enamels. Porcelain enameling art is a continuing form of expression for many artists. Although enameling has

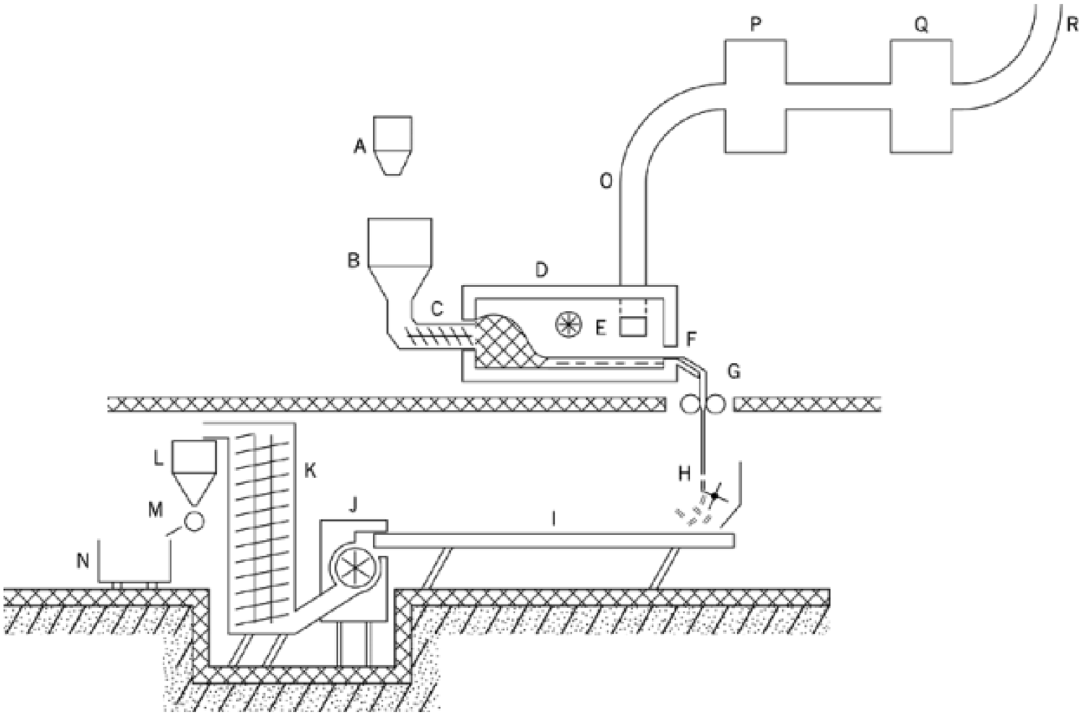

**Fig. 1.** Schematic of continuous smelter for porcelain enamel glass production where A is a raw batch hopper; B, batch hopper mixer; C, screw feeder; D, refractory furnace; E, burner for gas and air (oxygen); F, spout; G, water-cooled rollers for quenching glass; H, finger breakers to break glass ribbon; I, horizontal vibratory conveyer; J, hammer mill; K, vertical vibratory conveyer; L, surge bin; M, rotary magnetic separator; N, product container; O, exhaust gas flue; P, dry scrubber; Q, wet scrubber; and R, exhaust stack.

been known for at least four to five thousand years, only in the twentieth century has the widespread use of enamels on base metals such as cast iron, sheet steels, and aluminum alloys flourished.

## 1. The Enameling Process

### 1.1. Melting

The frit-making process involves all the technology ranging from proper selection of raw materials through mixing and smelting to uniform production of frit. Box smelters, predating continuous smelters, are used for small quantity production. Electric smelting of porcelain enamel glasses has been carried out in the United States and abroad. The most prevalent method of making porcelain enamel glass is in continuous smelters, as shown in Figure 1. Continuous smelters may produce from 700 to 1200 kilograms of frit per hour. First, the glass is smelted from raw materials such as those listed in Table 1. Typical ranges of formulations are listed in Table 2. In a continuous furnace the thoroughly mixed raw batch is fed in at one end and molten glass flows out at the other end. Decomposition, gas evolution, reaction, and dissolution occur during smelting. Modern smelters, which are fired by natural gas and often pure oxygen, are equipped with pollution control equipment on the smelter exhaust system (4) (see Air pollution control methods; Exhaust control, industrial).

**Table 1. Raw Materials for Frit Manufacture**

| Raw material | CAS Registry Number | Oxide content |
|---|---|---|
| alumina | [1344-28-1] | $Al_2O_3$ |
| antimony pentoxide | [1314-60-9] | $Sb_2O_5$ |
| antimony trioxide | [1309-64-4] | $Sb_3O_3$ |
| barium carbonate | [513-77-9] | BaO |
| borax decahydrate | [1303-96-4] | $B_2O_3$, $Na_2O$ |
| borax pentahydrate | [11130-12-4] | $B_2O_3$, $Na_2O$ |
| borax (anhydrous) | [1330-43-4] | $B_2O_3$, $Na_2O$ |
| boric acid | [10043-35-3] | $B_2O_3$ |
| cobalt oxide | [1308-06-1] | $Co_2O_3$ |
| copper oxide | [1317-38-0] | CuO |
| feldspar[a] | [68476-25-5] | $SiO_2$, $Al_2O_3$, $K_2O$, $Na_2O$ |
| litharge | [1317-36-8] | PbO |
| lithium carbonate | [554-13-2] | $Li_2O$ |
| magnesite[b] | [13717-00-5] | MgO |
| manganese dioxide[c] | [1313-13-9] | $MnO_2$ |
| nepheline syenite[d] | [37244-96-5] | $SiO_2$, $Al_2O_3$, $Na_2O$ |
| nickel oxide | [1313-99-1] | NiO |
| potassium carbonate | [584-08-7] | $K_2O$ |
| potassium silicofluoride | [16871-90-2] | $SiO_2$, $K_2O$, F |
| quartz | [14808-60-7] | $SiO_2$ |
| rutile[a,b] | [1317-80-2] | $TiO_2$ |
| soda ash | [497-19-8] | $Na_2O$ |
| sodium nitrate | [7631-99-4] | $Na_2O$, $NO_2$ |
| sodium silicofluoride | [16893-85-9] | $Na_2O$, $SiO_2$, F |
| sodium tripolyphosphate | [7758-29-4] | $P_2O_5$, $Na_2O$ |
| spodumene[e] | [1302-37-0] | $SiO_2$, $Al_2O_3$, $Li_2O$ |
| strontium carbonate[c] | [1633-05-2] | SrO |
| titanium dioxide | [13463-67-7] | $TiO_2$ |
| whiting[f] | [13397-26-7] | CaO |
| zinc oxide | [1314-13-2] | ZnO |
| monoammonium phosphate | [7722-76-1] | $P_2O_5$ |
| red iron oxide | [1309-37-1] | $Fe_2O_3$ |
| sodium fluoride | [7681-49-4] | $Na_2O$, F |
| vanadium pentoxide | [1314-62-1] | $V_2O_5$ |

[a] Also contains trace quantities of $Fe_2O_3$ and CaO.

[b] Also contains trace quantities of $SiO_2$, $Fe_2O_3$, and $Al_2O_3$.

[c] Also contains trace quantities of $SiO_2$ and $R_2O_3$ where R = an amphoteric oxide.

[d] Also contains trace quantities of $K_2O$.

[e] Also contains trace quantities of $Fe_2O_3$.

[f] Also contains traces of MgO.

After the molten glass has become a homogeneous liquid, it is poured in a thin stream into water or between closely spaced, water-cooled rotating metal rollers. This quenched glass, termed frit, is a friable material easily reduced to small-sized particles by a ball-milling operation. Ball-milling the glass frit into small-sized particles can be carried out whether the frit is to be used wet or dry (see Size reduction).

### 1.2. Grinding

Ball-mill grinding of the glass is accomplished using porcelain or high alumina balls 1.5–5.0 cm in diameter. Mill size, speed, and charge, and ball size and charge are important parameters for the determination of the milling time required for optimum size distribution in prepared slip. Ground-coat enamels are ball-milled to a

**Table 2. Porcelain Enamel Frit Compositions, wt %[a]**

| | Ground coats | | Cover coats | | | Aluminum enamels | |
|---|---|---|---|---|---|---|---|
| Oxides | Sheet steel[b] | Cast iron[c] | Titania | Cast iron (leadless) | Cast iron (Pb–Sb) | Leadless[d] | Lead-bearing |
| $SiO_2$ | 28–68 | 50–60 | 38–57 | 40–50 | 40–50 | 30–40 | 30–40 |
| $B_2O_3$ | 6–27 | 10–15 | 13–20 | 14–20 | 2–6 | 0–3 | 0–3 |
| $Na_2O$ | 6–24 | 5–10 | 6–13 | 6–10 | 15–20 | 15–20 | 10–18 |
| $K_2O$ | 0–8 | 3–8 | 2–11 | 6–10 | 0–2 | 7–12 | 5–10 |
| $Li_2O$ | 0–7 | | 0–2 | 0–2 | 0–2 | 2–5 | 2–5 |
| CaO | 0–15 | 0–3 | | | 3–8 | | |
| BaO | 0–16 | | | | 0–5 | 2–6 | 2–6 |
| $Al_2O_3$ | 0–12 | | 0–5 | 0–3 | 2–6 | | |
| $P_2O_5$ | 0–4 | | 0–4 | 0–2 | | 2–5 | 2–5 |
| $ZrO_2$ | 0–13 | 1–3 | 0–6 | 0–2 | 0–1 | | |
| MgO | 0–1 | | 0–2 | 0–2 | | | |
| $TiO_2$ | 0–10 | | 14–25 | 15–20 | 5–10 | 12–20 | 12–20 |
| ZnO | 0–4 | | 0–3 | 0–1 | | | |
| $Sb_2O_5$ | | | | | 5–10 | 2–5 | 2–5 |
| PbO | | 2–6 | | | 5–12 | | 10–20 |
| $F_2$ | 0–10 | | 0–10 | 3–8 | 2–6 | | |
| $NO_2$ | 0–7 | | 0–4 | 3–5 | 3–5 | 3–6 | 3–6 |

[a] Lead, Pb; nickel, Ni; and barium, Ba, may be restricted or absent in some formulations because of environmental regulations (3).

[b] Also contains 0–4 wt % $Co_2O_3$; 0–5, NiO; 0–4, $Fe_2O_3$; and 0–2, CuO.

[c] Light base coat.

[d] Also contains 3–8 wt % $V_2O_5$.

fineness of 95% of solids smaller than 74 $\mu$m (<200 mesh). Cover coats are ground more finely, to 98% of solids finer than 44 $\mu$m (325 mesh). Dry powders are used for dry process cast-iron enameling and for electrostatic application on sheet steel (see Coating processes, powder technology). Dry powders are also prepared and marketed for the subsequent preparation of slurries and slips used in wet-process application techniques.

For conventional wet processing of sheet steel, the porcelain enamel frit is ball-milled using clay, certain electrolytes, and water to form a stable suspension. This clay-supported slurry of small particles is called the slip and has the consistency of a heavy cream. The ingredients of the mill batch are carefully controlled. The amount and purity of all materials in the mill, including the clay and water, affect the rheological character of the slip as well as a number of the properties of the fired enamel such as chemical resistance, reflectance, gloss, color, and abrasion resistance.

### 1.3. Application

Ground coats are applied to metal by spraying, dipping, or draining as well as electrostatically. Large articles (washing machine tubs and stove chassis) may be coated only by spraying or flow coating the slip, whereas small articles may be dipped into a tank of ground-coat slip. Cover coats may be applied by similar methods, by electrostatic spraying (wet and dry powder), or by electrophoresis (qv) (see Coating processes).

Since 1975, one-coat or two-coat dry electrostatic application of dry frit particles has been a significant methodology in the appliance industry worldwide. Nearly all ranges in the United States are produced using this process technique. Dry ball-milled frit particles are coated with a silicone surface treatment, suspended in a fluidized bed, and delivered to spray guns that impart a negative electric charge to each particle. The metal article to be coated is at ground potential.

The glass particles without the coating may have a resistivity of $10^6$ ohm·cm; using the silicone coating, the glass particles can achieve a resistivity as great as $10^{15}$ ohm·cm (5). This greater resistivity is necessary to enable the charged particle to adhere to the metal substrate. The resistivity under ambient humidity conditions controls the rate of charge decay and therefore the adherence of the glass particles to the substrate. An overall resistivity of $10^{14}$ ohm·cm permits a coating thickness of 100 to 200 $\mu$m. The coating thickness is self-limiting and thickness uniformity is excellent even on curved surfaces. This dry process obviates the need for drying and intermediate firing for two-coat articles resulting in substantial savings in labor, materials usage, and energy costs (6), as compared to the conventional wet-process porcelain enameling of sheet steel. The dry system also eliminates the need for clay suspending agents that increase the refractoriness of the wet enamel systems.

The dry powder process has several additional advantages over the wet process. For example, much less waste of enamel occurs because the dry over-spray is airborne and recycled in a closed system. No-pickle ground coats have broadened the application of both wet-process and dry-process systems. These enamels are applied over cleaned-only metal. Thus the problems of disposing of pickling acid wastes containing iron sulfates and nickel wastes are eliminated (see Metal surface treatments) (7).

Prior to the development of the dry electrostatic process for sheet-steel enameling, the one-coat, direct-on wet process for cover coats had been adapted by a large sector of the industrial sheet-steel enamelers. This process requires the use of extra low carbon (decarburized) steel so that carbon oxide gas defects are eliminated. Also, a special pickling process is required to assure good adherence of the enamel. This process involves an accelerated etching of the metal by the addition of ferric sulfate in the sulfuric acid pickling solution, as well as subsequent heavy nickel flash deposits. Cover enamels are applied by flow-coating, spraying, dip-draining, or electrophoresis. A process flow diagram for sheet-steel enameling is shown in Figure 2.

Electrostatic wet enamel application, developed in the 1960s, is a minor commercial process in the United States. However, the technology is undergoing continuing development and improvement in process equipment. Disks, bells, and spray guns having high (100 kV) intensity d-c fields may be used to atomize and charge the enamel slip as it leaves the application apparatus. The negatively charged enamel particles are attracted to the surface of the metal article, which is at ground potential. This method of coating, which is usually automated, produces a uniform coating thickness and good coverage around corners (wrap-around) (8).

Electrophoretic application, also employed commercially on a limited basis, provides a dense uniform coating and excellent edge coverage. In this process the sheet-metal article is the positive electrode. Both the positive and negative electrodes are located in the enamel bath. The metal article, when subjected to a potential of 50 V and 50–300 A/$m^2$ in the enamel slip, attracts the charged frit particles which then pack into a tightly adhering coating layer (9). This process has been automated in Europe for appliances. In the United States it has been adapted for electronic substrates (see Electronic coatings).

Dry-process cast-iron enameling involves the application of the cover coat by dusting or dredging the dry glass powder (using a long-handled vibrating sifter) onto the heated cast-iron article. The cast iron, which has been previously ground coated, is removed from the furnace (870°C and higher) for the dusting operation and then is returned to the furnace to complete the fusion and maturation of the glass. Generally, two or more dusting and heating cycles are required for the development of an adequately thick and uniform coating (10).

Process flow diagrams for cast-iron and aluminum enameling are shown in Figures 3 and 4.

### 1.4. Metals for Enameling

#### *1.4.1. Steel*

Sheet steel is usually bought in precut sheets or coils for subsequent stamping and pressing into shapes. The steels are chemically formulated to make them suitable for the fabrication and porcelain enameling operations. The ASTM (12) has classified enameling-grade steels into Type I and Type II (A or B) as well as specifying various qualities such as commercial, drawing, and drawing quality special killed. Type I has an extremely low carbon level, commonly produced by decarburizing in an open-coil process. This material is suitable for direct

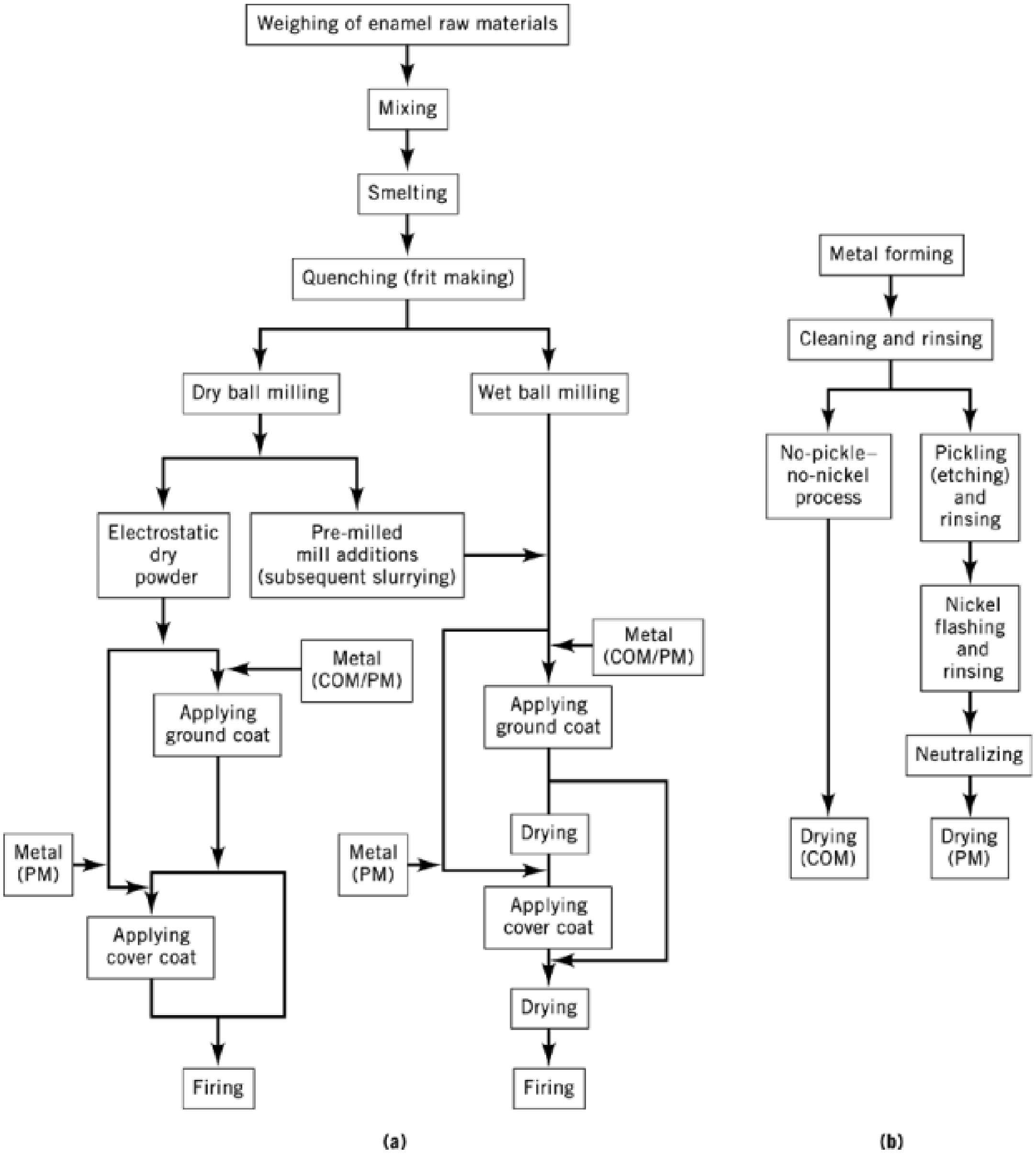

**Fig. 2.** Process flow diagram for sheet-steel enameling where COM indicates clean-only metal and PM, pickled metal, for (**a**) enamel preparation and application and (**b**) metal preparation.

cover coat enameling practice. The less expensive Type II has moderately low carbon and is suitable for ground coat enameling operations. Steels having a II-A designation are intended for use where sag resistance during firing is of prime importance. The designation of II-B is for steels requiring good formability. Table 3 (13) lists the general chemical requirements for the three classes of steels.

The basic steel types are undergoing gradual modifications to adapt the steels to the continuous casting process. This has led to changes in the minor constituents of steel such as boron, nitrogen, titanium, and other

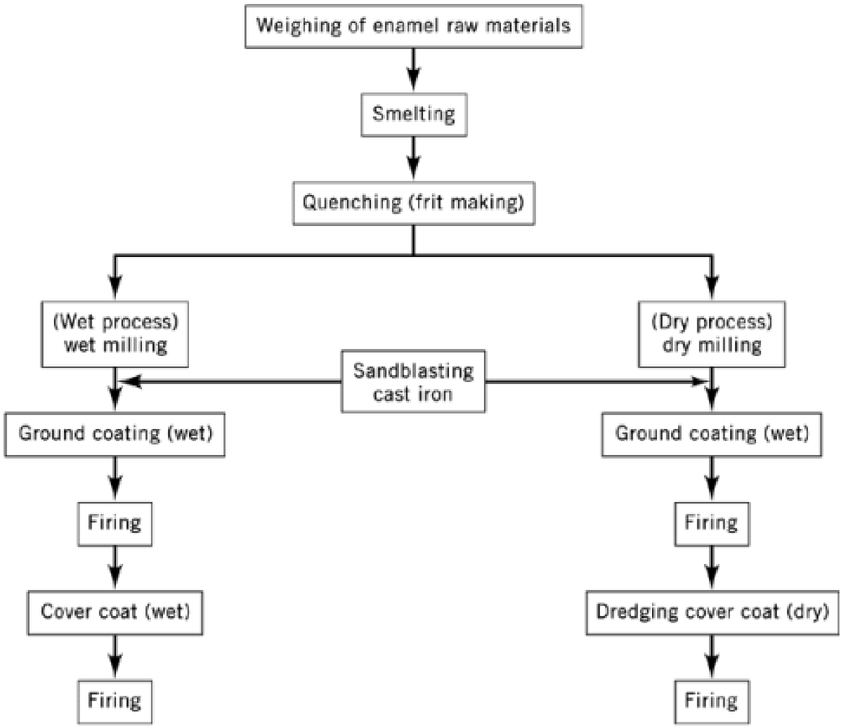

**Fig. 3.** Flow diagram of cast-iron enameling.

**Table 3. Sheet-Steel Chemical Composition,**[a, b]

| | | Type II | |
|---|---|---|---|
| Element | Type I | A | B |
| carbon | 0.008[c] | 0.04 | 0.08 |
| manganese | 0.60 | 0.15 | 0.50 |
| phosphorus | | 0.015 | 0.015 |
| sulfur[d] | 0.040 | 0.040 | 0.040 |

[a] Ref. 13.

[b] Values given are maximum.

[c] Cast analysis of carbon is not appropriate for Type I. Sheet products analysis is appropriate for checking proper type of material. Extremely low carbon levels can be checked accurately using carbon-combustion chromatographic-type analyzers.

[d] Drawing quality has 0.035 wt % max.

alloying elements. Titanium is used to tie up the carbon as titanium carbide [12070-08-5], TiC, and the boron nitride [10043-11-5], BN, and titanium nitride [25583-20-4], TiN, provide void sites for hydrogen accumulation after firing (see Carbides, nitrides) (14).

### *1.4.2. Cast Iron*

Cast irons for enameling contain between 2.8 and 3.7 wt % carbon; the more usual content is between 3.25 and 3.6 wt % (15). The carbon is usually found in two forms: graphitic carbon and combined carbon. Some

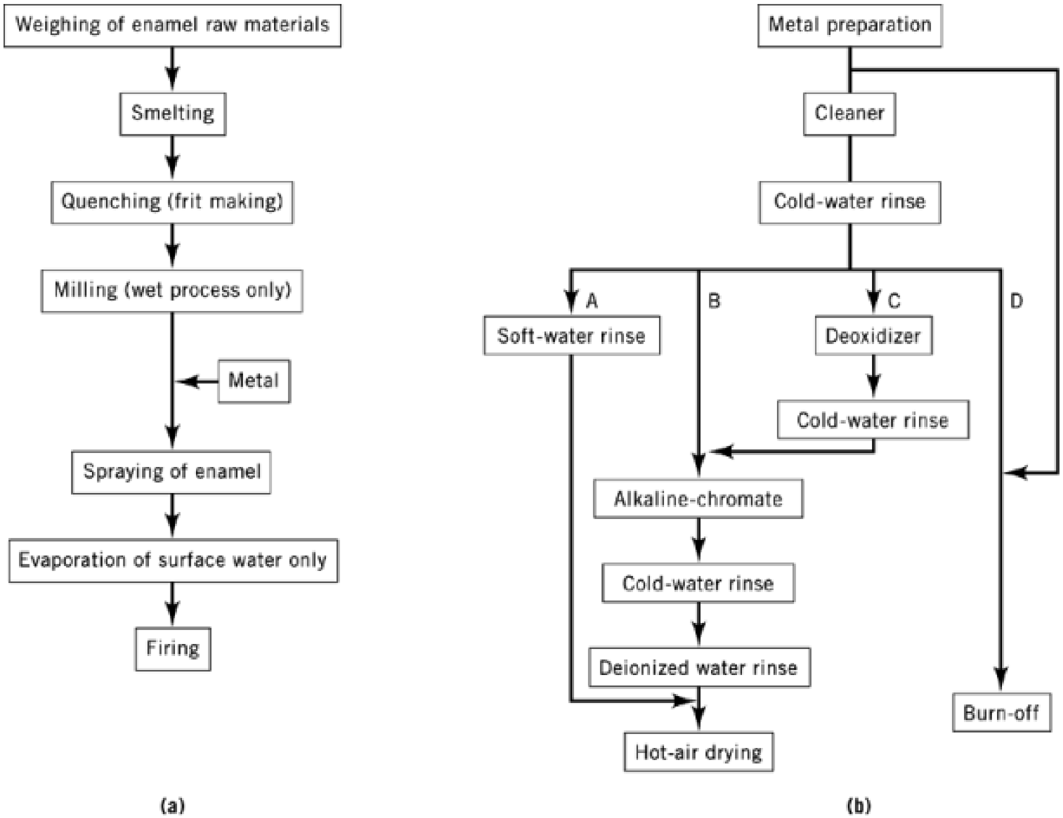

**Fig. 4.** Process flow diagram for aluminum enameling showing (**a**) enamel preparation and application, and (**b**) metal preparation, where the cleaning processes A, B, and C represent primarily sheet; D, primarily castings; and E, aluminized steel (11).

additional elements in the cast iron are silicon, manganese, sulfur, and phosphorus. The cast iron known as gray cast iron is the most widely used for enameling purposes. Before enameling, a casting must be cleaned, usually by abrasively blasting the surface with sand or steel shot.

### *1.4.3. Aluminum*

The most commonly used aluminum alloys for enameling are 3003 P.E. grade and 6061 P.E. grade. Other alloys are 1100 (commercially pure aluminum) 7104 (C74S) heat treatable, 43 casting alloy, and 344 and 356 casting alloys. It is important that the magnesium and copper contents of the alloys be kept to a minimum; otherwise, spalling of the enamel can occur (16).

### *1.4.4. Other Metals*

Metals such as the austenitic series, Types 301–347, and the ferritic series, Types 409–446, of stainless steels may be enameled, as well as a number of other alloys (17). The metal preparation usually consists of degreasing and grit blasting. Copper, gold, and silver are also enameled. These metals are usually prepared for application by degreasing. Copper is pickled using either a nitric acid [7697-37-2] or a sulfuric acid [7664-93-9] solution, followed by a dilute nitric acid dip. Silver may be pickled in hot dilute sulfuric acid followed by a dip in a nitric acid solution (18).

### 1.5. Metal Preparation

Sheet-steel parts are formed by stamping, bending, and shearing. Many parts require welding (qv), which needs to be carried out in a uniform, smooth manner so that the welded joint can be enameled without defects. Cast-iron parts are formed by the usual cast-iron foundry methods; however, additional care is given to prevent contamination of the surface. Surface contamination causes defects in the enamel, particularly blisters and bubbles. Aluminum metal can be formed in sheets, extrusions, and as castings.

Enameling cannot be successful unless the metal is thoroughly cleaned and kept clean until the final coat is fired. Simply touching the surface with a hand can cause defects. Cast iron, thick steel parts, and aluminum castings may be sandblasted. The thickness precludes the danger of deformation resulting from metal loss. Sand, silicon carbide, and steel grit are satisfactory abrasives (qv). Products made from thin sheet material are most satisfactorily and most economically cleaned by chemical methods that require alkali and soap solutions to remove grease and dirt, and acid solutions to remove oxidized metal.

#### *1.5.1. Steel*

Commercial enameling metal pretreatment for sheet steel has undergone significant changes since the 1970s. The introduction of the no-pickle enamels for a variety of ground-coat applications has significantly reduced the use of acid etching and nickel flashing. Clean-only systems for grease and grime removal are widely used by appliance manufacturers, reducing costs of in-plant processing and the problems of waste disposal. Two-coat–one-fire enameling processes have also reduced the need for heavy-metal etching and nickel flashing (nickel replacement) for direct-on enamel application to decarburized steels.

Chemical treatment in industrial metal preparation can be carried out with continuous cleaning and pickling equipment in either an automated or a manual batch operation. The latter is used for smaller sized substrates. The fabricated sheet-steel articles are supported on continuously moving racks or hangers which first pass through cleaning stages. For the clean-only systems, this is all that is required. For the processes needing pickled steel, the substrate is then subjected to pickling acids, nickel flashing, and neutralizing treatments. Spray-pickling equipment is designed for rapid and easy treatment of large substrates and lends itself to continuous drying and transfer of ware.

Compositions of the cleaning solutions are dependent on the type of oil, grease, and grime to be removed, including the type and amount of drawing compounds used in the metal-forming operations. Vegetable oils (qv) may be saponified and removed by alkalies alone, but mineral oils must be removed using soap (qv). A well-balanced cleaning compound contains an alkali, an alkali salt (which acts as a buffer material to maintain an approximately constant pH), and a soap. Commercial cleaning products are available and are usually used at a strength of ca 45 g/L (6 oz/gal) of water at or near boiling temperatures.

After being cleaned, ware that is to be pickled is immersed successively in one or more tanks of water at 80–95°C and then transferred to the acid pickling solution. The pickling solution of 6–8% sulfuric acid is contained in a stainless steel tank or, alternatively, a lead-lined wooden tank at 60–65°C. The metal remains in the tank until all oxide scale is removed, usually 5–15 minutes. Rinse water, which removes acid salts, is maintained at 80–90°C and rinsing time is usually 3 minutes. Plating galvanically or flashing a thin film of nickel on the iron after rinsing retards oxidation and enhances the enamel bond. The flashing solution contains 7.5 g/L (1 oz/gal) of nickel salt, such as nickel sulfate [7786-81-4], $NiSO_4{\cdot}6H_2O$, or the equivalent. The pH is maintained between 3.0 and 3.6 and the temperature at 75°C. The average time of immersion is 4–6 minutes and the deposit is usually 0.45–1.30 $g/m^2$ (0.04–0.12 $g/ft^2$). A stainless steel tank is usually employed as the container.

For the cover-coat direct-on process, a ferric sulfate [10028-22-5], $Fe_2(SO_4)_3$, etch is included in the metal pretreatment for rapid metal removal. It is designed to remove ca 20 $g/m^2$ (2 $g/ft^2$) of iron from the sheet metal surface. Hydrogen peroxide [7722-84-1], $H_2O_2$, is added intermittently to a 1% ferric sulfate solution to reoxidize ferrous sulfate [7720-78-7], $FeSO_4$, to ferric sulfate.

After being removed from the nickel bath, the ware is dipped into a hot or cold water rinse, quickly removed, and then transferred to a neutralizing bath where the last traces of acid are removed. Neutralizing using a solution of sodium carbonate (soda ash) and borax is common.

After being removed from the neutralizing solution, the ware is transferred to a dryer maintained at about 110–120°C that has good air circulation. This ensures quick and complete drying without rusting of the metal. After being dried, the sheet ware is ready for application of enamel.

#### *1.5.2. Cast Iron*

Cast iron is prepared for enameling by sand and steel shot blasting. The surface of the cast iron as it comes from the foundry has a thin hard skin which must be removed to achieve good enameled surface quality. The blasting operation also smoothes the surface, edges, and gates, and removes residual molding sand. Blasting is an operation that causes the abrasive grains to impact on the metal surface. Air-pressure blasting and centrifugally throwing the abrasive are common processes.

#### *1.5.3. Aluminum*

For aluminum alloys such as 1100 and 3003 only a cleaning operation is necessary before application of enamel. For alloy 6061, deoxidation and alkaline-chromate pretreatment processes may also be used to improve both the cleanliness of the surface and the development of enamel adherence. The spent chromium-containing solutions can present disposal problems and should be handled in accordance with existing regulations (19).

### 1.6. Firing of Enamels

Firing can be carried out in intermittent box-type furnaces or continuous furnaces (see Furnaces, electric; Furnaces, fuel-fired). The dryer and the furnace form one continuous unit or function as separate units in the continuous firing process. Most industrial furnaces are fiber-lined (low thermal mass), which lowers cost and downtime between firing schedules. In a continuous tunnel-type furnace, each piece progresses through the furnace on a conveyer supported on alloy firing racks designed to withstand the repeated thermal cycles. Very efficient U-type furnaces, in which the outgoing ware preheats the incoming ware, have been built (20). Gas-fired furnaces have alloy muffles to separate the combustion gases from the furnace atmosphere. Electrically fired furnaces have special alloy resistance-heating elements on the surface of the refractory lining (see Refractories). Gradual heating and cooling of the ware is more easily achieved using continuous firing than by using intermittent firing. In the latter process, a batch of ware is loaded on a large rack of special support tools and is introduced into the box furnace.

Enamels are fired to mature coatings in a matter of minutes. The firing time in the hot zone of a continuous furnace is about 3–6 minutes at 750–850°C. Cover-coat firing is generally carried out at similar temperatures, especially when two-coat–one-fire application processes are used. For two-coat enameling, it is preferable to fire the ground coat about 30°C higher than the subsequent cover-coating, in order to minimize hairlining in the cover coat and pull-through of the ground coat.

Enamel firing temperature is dictated by the coating composition, metal thickness, and the type of metal used. Enamels for aluminum are fired at 510–540°C, whereas those for high temperature alloys (qv) are fired up to 930°C.

The industrial porcelain enameling process can be automated to a great degree, from metal pretreatment (pickling) through the firing process. Flow-coating, electrostatic dry powder spraying, or electrophoretic deposition can be machine programmed. Robot sprayers controlled by a computerized sensing mechanism can coat complex shapes, and flow-coaters can be programmed to uniformly coat complicated shapes such as dishwasher cavities and washing machine baskets. Automated coating and firing of cast iron has also been achieved.

The level of moisture in the furnace atmosphere is also of importance in the development of good fired surface appearance. The range of moisture normally associated with good enameling practice is 1–2 vol %

of moisture (21). Levels below 1 vol % may result in reduced gloss of the glass surface; levels above 2 vol % may result in blistering or a scummy surface. Winter conditions usually cause dry furnace atmospheres, and summer conditions may result in excessive moisture if the furnace is not properly vented.

### 1.7. Energy Requirements

The energy needed to heat 0.45 kg of enamel ware and tooling to the firing temperature ranges from 400–1000 kJ/kg (300–450 Btu/lb) and depends on such factors as furnace loading, tool weight, and, in gas-fired furnaces, flue-gas losses. Advances in furnace design, firing systems, and low thermal mass insulating materials have reduced the total energy needed over the years. Thus overall energy requirements for enameling have dropped as much as 50% since the 1970s. Technologies such as electrostatic frit powder application, various two-coat–one-fire processes (eg, dry-over-dry, dry-over-wet, and wet-over-wet), as well as reductions in the metal pretreatment requirements have also contributed (22).

## 2. Composition

Porcelain enamels are basically alkali borosilicate glasses. These enamels are complex, however, because of the large number and types of oxides which are needed to develop proper adherence and functional properties (23, 24). Network-forming ingredients and modifiers are used as in normal glass (qv) making practice. The principal network formers are $SiO_2$, $B_2O_3$, and $P_2O_5$. Modifiers include the alkali metal oxides ($Na_2O$, $K_2O$, and $Li_2O$) and alkaline-earth metal oxides (CaO, BaO, and SrO). Other common oxides include $Al_2O_3$, MgO, $ZrO_2$, ZnO, $TiO_2$, $Sb_2O_3$, and the halide $F^-$. Transition-metal oxides such as $Fe_2O_3$, CoO, NiO, CuO, and $MnO_2$ are used for adherence to the sheet-steel substrate and color development in ground coats. Continuous-cleaning (catalytic) oven enamels have high percentages of the transition-metal oxides to achieve cleaning effectiveness. Less frequently used oxides of cerium, cadmium, lead, and tin are used in sheet-steel, cast-iron, and aluminum enamels.

Enamels used on cast iron and aluminum have traditionally been composed of $SiO_2$, $B_2O_3$, $P_2O_5$, and PbO. The lead oxide produces good surface quality, fusibility, and acid resistance when properly formulated with other oxides. More recently some nonlead-bearing compositions have been developed for both cast-iron and aluminum metals. Glasses containing lead oxide are not recommended for food contact surfaces.

Typical ranges of enamel compositions are listed in Table 2. Raw materials (Table 1) for the glass batch include minerals, such as feldspars and quartz, because these are inexpensive sources of $SiO_2$ and $Al_2O_3$ (see CLAYS). The batch composition for cover coats is comprised primarily of manufactured chemicals of known, controlled levels of purity to maintain reproducible, clean colors.

The silica content of a glass has a significant effect on the chemical and mechanical properties of the porcelain enamel. Increasing silica content is generally associated with increasing acid resistance and lowered thermal expansion. Increasing alkali content, particularly $Na_2O$, reduces acid resistance and increases the thermal expansion. Various modifiers such as $Al_2O_3$ (minor amounts) and $ZrO_2$ increase the alkali resistance, whereas $TiO_2$, generally an opacifier if in crystal form, improves the acid resistance. Self-opacified cover coats usually have titania as the crystalline phase; however, zirconia and antimony oxide are still used for some nonsheet-steel applications.

Porcelain enamels meet a variety of performance characteristics required for different applications. The common characteristics of all enamels include good adherence to the substrate and good thermal expansion fit to the metal. Specific properties depend on usage; for example, acid and alkali resistance, hot water resistance, abrasion resistance, thermal shock resistance, high gloss, high reflectance, specific color, heat resistance, and cleanability.

### 2.1. Titanium Dioxide

The recrystallization of titanium dioxide in a cover-coat glass is very important to the development of thin, highly opaque finish coats. Titania, $TiO_2$, is the primary opacifying agent for white finish coats. Two polymorphic forms of titania, anatase and rutile, may be present in the enamel (see Titanium compounds, inorganic). Anatase is preferred because anatase crystals are present in the size range (0.1–0.2 $\mu$m) for maximum reflectance, and therefore generate the most desirable bluish white color. Smaller pigment particles provide too much light scattering and give a more undesirable bluish color; larger particles give a more cream-white color. Moreover, in contrast to rutile particles, anatase crystals do not grow or change size depending on the firing temperature.

When the porcelain enamel glass is smelted, the titanium dioxide is dissolved completely in the glass and exhibits a complete transparency. Upon subsequent reheating of the glass, nucleation sites within the glass matrix and at the surface of the glass particle initiate recrystallization of the titanium dioxide. Control of the thermal history of the glass reheating affects the subsequent crystal growth and size development. Color stability of titania enamels can be obtained by adjusting the composition of the glass so that anatase crystallizes predominantly over a wide temperature range. The effect of $P_2O_5$ content on the relative amounts of anatase and rutile crystallizing from a titania enamel has been shown to be important (25). Additionally, other oxides are known to have an effect on the anatase to rutile inversion. This inversion is thought to be an irreversible change from anatase to rutile crystal structure between 700 and 815°C (1300 and 1500°F). The anatase form of the titania crystal is preferred because of color and the general stability of the form which can be developed through the glass formulation. Figure 5 shows a typical cross-section of a titania-opacified direct-on enamel and metal interface.

## 3. Properties

### 3.1. Thermal Fit and Residual Stresses

Thermal expansion measurements are typically carried out on dilatometric equipment consisting of a fused quartz pusher rod inside a tube of the same material (26). A bar specimen of the frit is prepared from crushed material of about 2000 $\mu$m (10 mesh) by reheating in a refractory or metal boat, annealing, and removing from the mold. A small furnace having a programmed temperature rise heats the tube containing the frit bar sample to a preset temperature or automatically shuts off when the dilatometric softening point is reached. The displacement of the pusher rod is automatically recorded, allowing a direct calculation of percentage of linear thermal expansion. Appropriate reference standards are used to calibrate the testing unit.

The expansion coefficient of the metal is usually constant over the entire range of the expansion of the glass, but the linear thermal expansion coefficient of the glass gradually increases with increasing temperature, accompanied by a noticeable change at the transformation temperature ($T_g$). The expansion of the bar appears to reverse after the softening point is reached because of sag. On the thermal expansion curves this is known as the dilatometric softening point. The glass bar becomes sufficiently fluid so that it cannot resist the spring pressure of the push rod and rapidly deforms.

A porcelain enamel glass becomes less viscous as the temperature is increased during firing. Above the softening point, the enamel is relatively fluid and conforms to the metal surface. As the porcelain enamel is cooled from the firing temperature of 750–800°C to the softening point, the fluid glass does not retain stress. However, as cooling proceeds below the softening point, the expansion (or contraction) of the coating exceeds that of the steel, and tensile stresses begin to develop in the coating, as shown in Figure 6. On further cooling, the stress increases until the temperature at which the expansion of the glass equals that of the metal. With still further cooling, the coefficient of expansion of the glass is less than that of the metal, coating tensile stresses decrease, and compressive stresses develop and are retained at room temperature.

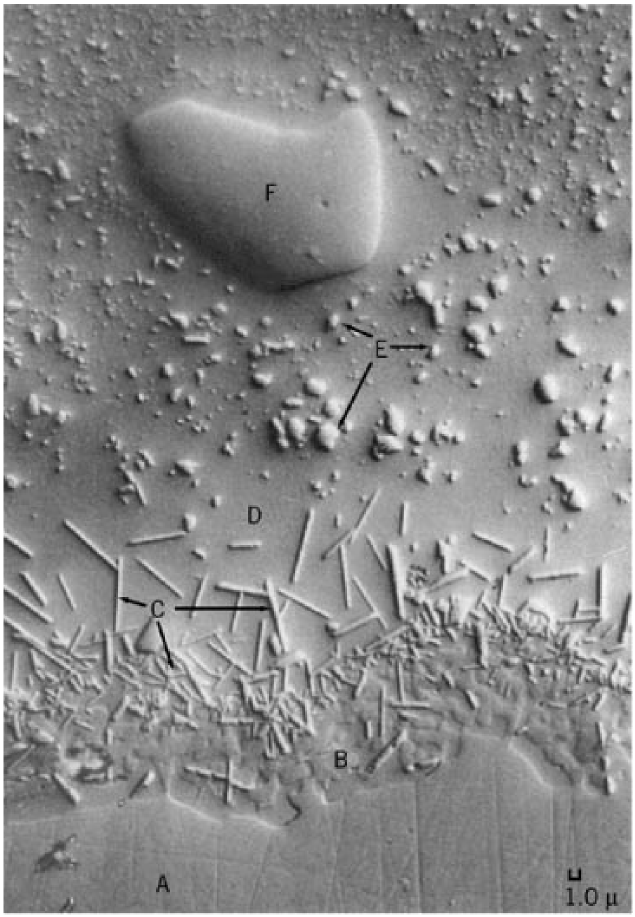

**Fig. 5.** A 90° polished cross section of a production white titania enamel, with the microstructure showing the interface between steel and direct-on enamel as observed by reflected light micrography at 3500×magnification using Nomarski Interface Contrast (oil immersion). A is a steel substrate; B, complex interface phases including an iron–nickel alloy; C, iron titanate crystals; D, glassy matrix; E, anatase, $TiO_2$, crystals; and F, quartz particle.(Courtesy of Ferro Corp.)

Thermal expansion comparisons of the coatings and metal have often been used to determine residual stresses in the coatings. The qualitative residual-stress analysis of Figure 7 shows how enamel A would develop high tensile stress and low residual compressive stress. Enamel B, having a higher softening point and lower expansion coefficient, develops less tensile stress and a much greater residual compressive stress.

Residual-stress analysis must take into account the cooling rates, the viscosity characteristics of the glass, the relative thickness of the metal and coating, and the modulus of elasticity of the coating and metal throughout the temperature range in which stress is developed. At high temperatures, glass behaves as a viscous material, exhibiting viscous–elastic and then primarily elastic properties as the temperature decreases.

Thermal expansion values can be calculated from measurements of thermal deflection of enamel–metal composites. The cubical thermal expansion coefficient in the temperature range of 0–300°C can also be calculated using the additive formula:

$$P = AX_A + BX_B + CX_C + \cdots$$

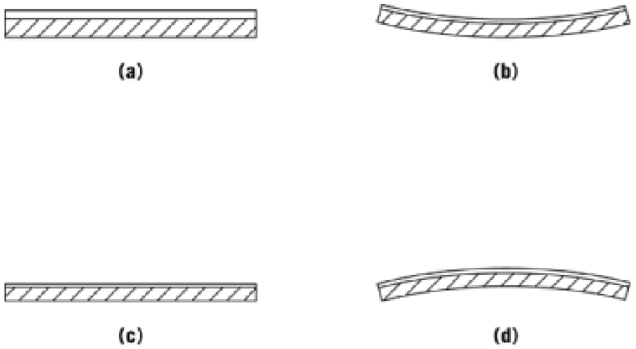

**Fig. 6.** Cooling cycle, where □ is the enamel layer and▨ is steel, at (**a**) the upper no-strain point, where the enamel is molten, with no stress; (**b**) after solidification of the enamel, where the porcelain is in tension; (**c**) the lower no-strain point, where no stress is evident; and (**d**) at room temperature, where the porcelain enamel is in compression (27).(Courtesy of Ferro Corp.)

**Table 4. Enamel Oxide Coefficient of Expansion Factors**[a, b]

| Oxide | Factor | Oxide | Factor | Oxide | Factor | Oxide | Factor |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 0.8 | CaO | 5.0 | $SnO_2$ | 2.0 | $Cr_2O_3$ | 5.1 |
| $Al_2O_3$ | 5.0 | MgO | 0.1 | $TiO_2$ | 4.1 | CoO | 4.4 |
| $B_2O_3$ | 0.1 | BaO | 3.0 | $ZrO_2$ | 2.1 | CuO | 2.2 |
| $Na_2O$ | 10.0 | $As_2O_3$ | 2.0 | $Na_3AlF_3$ | 7.4 | $Fe_2O_3$ | 4.0 |
| $K_2O$ | 8.5 | $P_2O_5$ | 2.0 | $AlF_3$ | 4.4 | NiO | 4.0 |
| PbO | 4.2 | $Sb_2O_3$ | 3.6 | $CaF_2$ | 2.5 | MnO | 2.2 |
| ZnO | 2.1 | | | NaF | 7.4 | | |

[a] Courtesy of Garrard Press (15).
[b] Summation of $(\text{factors} \times \text{wt\%}) \times 10^{-7}$ = cubical expansion coefficient in vol/$(\text{vol}\cdot{}^\circ\text{C})$.

where $P$ is the property, such as cubical thermal expansion coefficient; $A, B, C, \ldots$ are the property factors for each ingredient in the composition; and $X_A$, $X_B$, $X_C$, … are ingredient concentrations in wt %. Factors for calculating the cubical thermal expansion coefficient of glasses have been determined and are listed in Table 4 (28). Glass compositions high in $SiO_2$ content have low thermal expansion, whereas additional alkalies and alkaline-earth materials raise the thermal expansion coefficient. Frequently, thermal expansion is listed as linear thermal expansion, which is the cubical thermal expansion divided by three.

Residual compression in the coating is desirable because glass, as well as other ceramic materials, is much stronger in compression (about 2070 MPa (300,000 psi)) than in tension (about 69 MPa (10,000 psi)). If residual compression in the enamel layer is too great, the coating may fracture or spall where the radius of curvature of the article is too small. Failure of the coating occurs because the tensile-stress limit has been exceeded. High residual compressive stresses in the coating increase the tensile load-bearing ability by the amount of the residual compressive stress that must be overcome before tension can be induced. If the tensile stress developed during the cooling or reheating of the enamel is too high, the coating fractures. Crazing results when the damage occurs during cooling; a fine crack pattern called hairlining may be produced during reheating.

The calculated linear average thermal expansion coefficient in cm/$(\text{cm}\cdot{}^\circ\text{C})$ for the temperature range of 25–300°C for common materials in the porcelain enamel system is steel, $11.7 \times 10^{-6}$; ground coat, $10 - 12.5 \times 10^{-6}$; cover coat, $8 - 11 \times 10^{-6}$; aluminum, $23.5 \times 10^{-6}$; and cast iron, $10.5 \times 10^{-6}$.

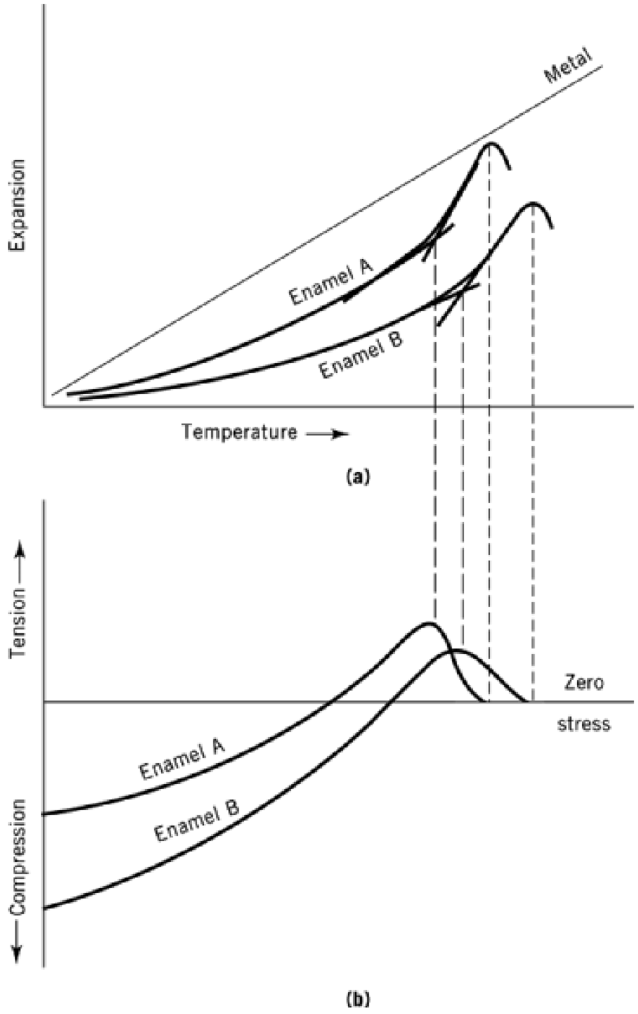

**Fig. 7.** (**a**) Relative thermal expansion of porcelain enamel on sheet steel. (**b**) Stress development in the enamel layer.

### 3.2. Composite Modulus of Elasticity

The modulus of elasticity of the enamel glass–steel composite system has been shown to lie between the modulus of the glass and that of the metal (29). The composite modulus can be calculated by

$$E_c = (E_m - E_e)\,Q^3 + E_e$$

where $E_c$, $E_m$, and $E_e$ are the modulus of elasticity of the composite, the metal, and the enamel, respectively; and $Q$ = thickness of the metal divided by total thickness of the composite.

### 3.3. Residual Compressive Stress

Residual compressive stress in commercial ground coat enamels varies with enamel thickness:

| Ratio of enamel thickness to metal thickness | Compressive stress, MPa (psi) |
|---|---|
| 0.8 | 69 (10,000) |
| 0.6 | 110 (16,000) |
| 0.4 | 138 (20,000) |
| 0.2 | 221 (32,000) |

Thinner coatings have higher compressive stresses, other factors being equal. Higher residual compressive stress in the coating also can be obtained by using enamel glass having a lower thermal expansion coefficient, or a metal having a higher expansion coefficient or a higher modulus of elasticity.

### 3.4. Maximum Strain

Strain in enamels that leads to failure is on the order of 0.002–0.003 cm/cm. Thinner enamels having higher residual compressive stresses are more flexible and can be strained to a greater degree.

Some other physical properties of enamel glass are density, from 2.5–3.5 g/mL; Mohs' hardness, 5–6; tensile strength, 34–103 MPa (4,900–15,000 psi); compressive strength, 1380–2760 MPa $(2 - 4 \times 10^5$ psi); modulus of elasticity, 55–83 GPa $(8 - 12 \times 10^6$ psi); and dielectric constant, 5–10.

### 3.5. Appearance and Color

Porcelain enamel allows the designer great variety with regard to color, texture, and aesthetic appeal. The enamels exhibit exceptional color stability whether used in domestic interiors or architectural exteriors. Colors should be grouped according to the type and the usage of enamel. Categories are (*1*) ground coats, which can generally be used by themselves as a finish coat or a base coat; (*2*) cover coats that are self-opacified; and (*3*) clear and semi-opaque enamels, used for developing a wide range of colors. Transition-metal oxides used principally to develop a bond between the glass and the substrate metal also produce specific colors. Those range in shades of grays from blue to yellow and red to green. Combinations of each are also possible. Cobalt oxide is the principal colorant for blue, nickel oxide, and iron oxide, $Fe_2O_3$, for green, manganese dioxide for red, and nickel oxide with other oxides for yellow.

Cover coats such as self-opacified titanium enamels derive their color (qv) from titanium dioxide crystals nucleated in the glass during firing of the coating. This method of opacification is of significant importance to the enamel industry. The titanium-opacified cover coats which exhibit a very high (80–85%) reflectance or Rd (reflectance which is a measure of brightness) are the most common type of white enamel in general use. Other types of opacified enamels are zirconia-opacified enamels $(\mathrm{Rd} = 75 - 80\%)$ and antimony-opacified enamels $(\mathrm{Rd} = 65 - 75\%)$. The difference in the refractive indexes between the base glass (1.50–1.55) and the crystal determine the covering power. The greater the covering power, the thinner the coating needed. The most effective opacifiers for enamels (30) are as follows:

| Opacifier | Index of refraction |
|---|---|
| NaF | 1.336 |
| $CaF_2$ | 1.434 |
| $Sb_2O_3$ | 2.087–2.35 |
| $SnO_2$ | 1.997–2.093 |
| $ZrO_2$ | 2.13–2.20 |
| $CeO_2$ | 2.33 |
| $TiO_2$ (anatase) | 2.493–2.554 |
| $TiO_2$ (rutile) | 2.616–2.903 |

As the level of opacifier is lowered in a glass system, the level of opacification drops. This yields semi-opaque glasses which allow the development of soft pastel colors. Strong colors result from clear glasses. The clarity allows the use of ceramic pigments (qv) (mixed-metal oxides) for the development of a wide variety of colors in almost any hue, saturation, and brightness.

Textures in enamels are developed by the use of semicrystalline glasses or by the addition of refractory materials such as quartz, alumina, zirconia and zircon, feldspar, various clays, and titania. More refractory glasses are also added to impart a lower gloss and a texture. Combinations of glasses such as ground coats and small amounts of self-opacifying cover coat are used to produce speckled finishes such as those found in some oven interiors and cookware utensils. A typical mill batch of colored enamels contains 100 parts by weight frit (clear alkali borosilicate-type glass); 4 parts clay for producing a stable suspension; $\frac{1}{4}$ part bentonite for supporting suspension; $\frac{1}{4}$ part sodium nitrite (to disperse flocs); 3 parts oxide pigment colorant; and 45 parts water.

Colored enamels are produced by tinting the titania enamels during the smelting operation through the addition of colorant oxides. Control of enamel color is most popularly done using computer-controlled color measuring systems consisting of spectrophotometric detectors (380–720 nm) and hardware to measure, integrate, evaluate, report, and store the color data. The most common systems in use are the Commission Internationale de l'Eclairage (CIE) $L^*a^*b^*$ and Rd,$a,b$ color scales and various illuminates (31).

### 3.6. Decorating

The decoration of enamels is primarily done by silk screening. Other methods include indirect printing such as use of decals (decalcomania), and indirect lithographic, thermoplastic, and total transfer printing. Photographic printing is also done as a specialty. The range of colors available is nearly unlimited. Textures can also be developed in the decorating materials (32). Older methods of decorating include stenciling, brushing of a second layer to expose an underlying coating, stamping with a rubber transfer device, and graining and marbelizing (33).

Screen printing is used in the highly specialized applications of graphics and circuit designs for electronic devices on a porcelain enameled surface (see Integrated circuits). Graphic design reproductions may entail between one and ten firings of overlapping prints to achieve a desired result. Halftone printing allows the development of a wider range of colors and effects than is usually achieved using solid colors. Screen printing of rounded surfaces has been developed for special application needs.

The paste used for decorating is typically a finely ground glass softer than the substrate glass, which is mixed with varying color pigments and suspended in an oil medium. The suspending medium is normally a pine oil commonly blended with resins, film formers, and surfactants. A hot oil can be used if the application screen is heated. The hot oil is composed of a variety of fatty alcohols and acrylic resins. Ultraviolet-sensitive vehicles, set by exposure to uv radiation, are composed of photosensitive multifunctional acrylates and resins which may be photoreactive. Some aqueous spray mediums are in use as are some roll-coating formulations which are pine oil based (34).

### 3.7. Microstructure and Thickness

The microstructure of enamels is of importance to understanding and thus being able to control the macroproperties of the enamel. The microstructure is also related to the thickness of the enamel and its firing history. Porcelain enamels typically have a bubble structure which is a result of gas evolution during firing. The gas is mainly a result of the decomposition of organic and inorganic materials. Other sources of gas are the moisture in wet enamel systems and carbon oxide gases from the carbon in the steel. The organics are mostly associated with the clays that are used for suspension of the glass slurry or slip. The inorganic carbonates produce $CO_2$ bubbles. These bubbles help to inhibit crack propagation in the glass and are reservoirs for the hydrogen gas which is gradually liberated from steels after firing. Figure 8 illustrates typical polished cross sections of various enamel systems.

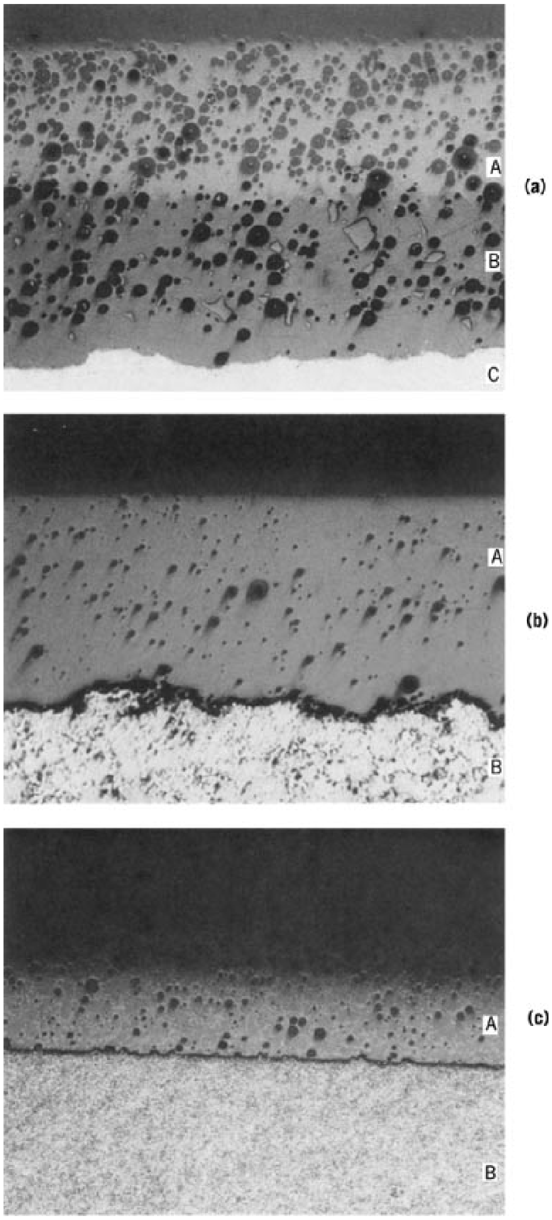

**Fig. 8.** Enamel cross sections, showing (**a**) two-coat–two-fire ground coat and cover coat on steel, 30° angle, reflected, polarized light, 100×magnification where A indicates the 125-$\mu$m titania cover coat; B, the 125-$\mu$m cobalt ground coat; and C, the steel substrate. (**b**) Dry-process white cast-iron enamel on gray casting, enamel thickness 755 $\mu$m, reflected, polarized light, 30° angle, 25×magnification where A is the titania cast-iron cover coat and B, the cast-iron substrate. (**c**) A 79-$\mu$m lead-bearing almond aluminum enamel, A, over aluminum alloy 3003, B; reflected light, 30° angle, 100×magnification.(Courtesy of Ferro Corp.)

The thickness of the enamel layer varies with the type of use and metal. However, typical thicknesses are from 75 to 150 $\mu$m (3 to 6 mils) for sheet steel, 175 to 359 $\mu$m (7 to 14 mils) for hot-rolled steel, 100 to 125 $\mu$m (4 to 5 mils) for each coat of wet process cast iron (760 to 788°C fire), 15 to 25 $\mu$m (0.5 to 1 mil) for dry process cast-iron base coats and 750 $\mu$m (average) to nearly 2250 $\mu$m (30 mils to 90 mils) for the dusted cover coats (898 to 955°C fires), and 25 to 50 $\mu$m (1 to 2 mils) for aluminum alloys. Stainless steel and copper may have enamel coatings from 40 $\mu$m to 175 $\mu$m (1.5 to 7 mils) thick.

The study of cross sections is extremely valuable as a way of tracking defects and determining sources of contaminant once the enameled article has been produced. Optical microscopy (qv) of about $10\times$ to $1000\times$ is useful for interpretation of metal grain structures, gas defect sources, and the morphology of the enamel metal interface. Electron micrography having up to hundreds of thousands magnification and the capability of energy dispersive analysis (edax) can be used to identify compositions of minute particles in a polished cross section.

## 4. Enamel Testing

### 4.1. Standards

The development of standards for porcelain enamel coatings is shared by several national and international organizations. The American Society for Testing and Materials (ASTM), the Porcelain Enamel Institute (PEI), and the American National Standards Institute (ANSI), as well as the Association of Home Appliance Manufacturers (AHAM) are active in developing, collecting, and disseminating information to interested organizations. Cooperation with the International Standards Organization (ISO) is also fostering the development of internationally unified standards for vitreous enamel coatings.

### 4.2. Abrasion Resistance

Porcelain enamel is the most scratch resistant and hardest of commercial coatings (see Hardness). This property is used to distinguish between porcelain enamel and organic enamel or painted coatings. The rate of abrasive wear in surface abrasion increases with time, and the subsurface abrasion which follows exhibits a higher, but constant rate of wear. Abrasion resistance can be evaluated by loss of gloss or weight (35).

### 4.3. Adherence

Tests for adherence of porcelain enamels include falling weight tests (36) and hydraulic deformation tests (37, 38). The hydraulic deformation test is used for heavy-gauge enameled panels and the drop test for light-gauge metals (18–22 ga). The drop weight test uses an impact energy of 0.9 cm·kg (80 in.·lb), with a 1.27 cm (0.50 in.) hemispherical indenter and a 1.9 cm (0.75 in.) diameter bottomless die. Evaluation of the adherence is typically done by a visual rating which assesses the amount of glass retained in the impact area, ranging from 1 (excellent adherence indicated by a nearly solid layer of glass shards) to 5 (poor adherence having little or no glass shards adhering to the metal).

### 4.4. Impact Resistance

Tests for impact resistance of porcelain enamels include falling weight tests such as a free-falling ball or a pendulum striking a rigidly held specimen. In such tests successively higher heights of fall are used until a visibly noticeable failure occurs. Factors affecting the impact resistance of porcelain enamels include: (*1*) lower modulus of elasticity of the metal contributes to higher impact resistance; (*2*) the larger radius of curvature of the article, the greater the impact resistance; (*3*) the thicker the metal and enamel, the greater the resistance to impact; and (*4*) the physical structure of the enamel, eg, excessive bubble content, large crystalline inclusions, and other discontinuities, often contribute to lower impact resistance. Weak bonding of the enamel to the metal also contributes to lower impact resistance.

### 4.5. Thermal Shock Resistance

Resistance of porcelain enamels to failure by thermal shock was developed for enamels for cooking utensils and other items subjected to high temperatures in service. Thermal shock is experienced by a heated enamel article on quenching with cold water. Thermal shock tests involve repeated cycles of heating and quenching with water; heating for each successive cycle is carried out at progressively higher temperatures. A visible fracturing, as evidenced by spalling, constitutes a failure.

Thermal shock failures using water result from the water vapor entering the enamel layer through small, submicroscopic cracks formed at the instant of shock. The water condenses in the cracks and in the bubbles of the enamel traversed by the cracks. On subsequent heating, the vapor from the entrapped water expands to cause spalling of the enamel layer. Other quenchant liquids, such as toluene, oils, and other organic liquids, also cause fine, almost invisible cracks, but thermal shock failures do not result with these quenchants on subsequent heating (39).

Thermal shock resistance is a direct function of enamel thickness. The greater the residual compressive stress in the porcelain enamel, the greater is the resistance to thermal shock failure. Thin coatings, such as one-coat enamels or the two-coat enamels having a low expansion titania cover coat, provide excellent thermal, shock resistance.

### 4.6. Resistance to Chemical Attack

The resistance to alkali and acid attack is evaluated on the basis of loss in weight, loss in gloss, or reduced cleanability of the surface.

A spot test employing 10% citric acidis used at room temperature for acid resistance of glossy, light-colored enamels. In the spot test, loss of gloss and cleanability are determined in a qualitative manner (40). Resistance to boiling 6% citric acid is determined by loss in weight (41). Lower alkali content of the glass yields higher acid resistance. Acid-resistant enamels for chemical service are compositions high in $SiO_2$ and $TiO_2$ content. Alkali resistance is improved with increasing $Al_2O_3$ and $ZrO_2$ content. Resistance of enamels to water attack is also introduced in coatings for domestic water heaters.

### 4.7. Other Properties and Tests

The other physical and chemical properties of porcelain enamels can be evaluated as shown below:

| ASTM test number | Property |
|---|---|
| C614-74 (1989) | alkali resistance |
| C538-83 | color retention of red, orange, and yellow enamels |
| C743-87 | continuity of porcelain enamel coatings |
| C374-70 (1982) | fusion flow of porcelain enamel frits (flow-button methods) |
| C346-87 | gloss of ceramic materials, 45° specular |
| C372-81 | linear thermal expansion by the dilatometer method |
| C285-88 | sieve analysis of wet-milled and dry-milled porcelain enamel |
| C703-72 (1983) | spalling resistance (enameled aluminum) |
| C385-58 (1983) | thermal shock resistance of porcelain enameled utensils |
| C448-88 | abrasion resistance |

### 4.8. Enamel Defects

Characterization of defects in porcelain enamel surfaces frequently requires detailed examination via microscopy to determine the sources of the defects. Defects are divided into processing and material defects. The greatest number of defects result from processing: blisters, pinholes, black specks, dimples, tool marks, and chipping. Defects often occur from unobserved sources at almost every stage of the enameling process, but they are not recognizable until the ware is fired. Conscientious process control helps to minimize the incidents of unacceptable finishes.

## 5. Economic Aspects

The porcelain enameling market has been gradually declining since 1974 in the United States in terms of tonnage. Self-smelters represent about half of the total production and specialty producers the remainder. The total U.S. market in 1990 was about 90,000 metric tons whereas the average selling price of porcelain enamel frit was about \$2.00–2.50/kg. Substitution of less expensive, and often less durable, organic coatings and plastics has been mainly responsible for the decline in the usage of porcelain enamel.

### 5.1. Shipment

The shipment of porcelain enamel is typically in 45-kg (100-lb) three-ply paper bags. More recently, 227-kg (500-lb) multi-ply cardboard barrels and bulk bags made of high strength woven polymers have been used. Porcelain enamel frit, powder, and premixed and premilled mill additions are shipped in these flexible containers.

### 5.2. Labeling

The typical labeling classification for frit may be followed by precautionary labeling for formulations containing lead oxide, free silica, or cadmium oxide. Special labeling for shipment to specific localities may also be necessary to meet local and state requirements.

## BIBLIOGRAPHY

“Enamels, Porcelain or Vitreous” in *ECT* 1st ed., Vol. 5, pp. 718–735, by R. M. King, The Ohio State University; in *ECT* 2nd ed., Vol. 8, pp. 155–173, by A. L. Friedberg, University of Illinois, in *ECT* 3rd ed., Vol. 9, pp. 1–20, by A. L. Friedberg, University of Illinois.

### Cited Publications

1. *1992 Book of ASTM Standards*, American Society for Testing and Materials, Philadelphia, Pa., 1992, p. 02.05.
2. M. A. Baker, *Proc. Porcelain Enamel Inst. Forum* **34**, 186–198 (1972).
3. J. E. Waggener, *Proc. Porcelain Enamel Inst. Forum* **52**, 861–863 (1990).
4. J. Wratil, *Vitreous Enamels*, Borax Holdings Limited, London, 1984, p. 13.
5. H. F. Evele and W. D. Faust, *Proc. Porcelain Enamel Inst. Forum* **47**, 643–650 (1985).
6. R. G. Rion and E. Smithberger, *Proc. Porcelain Enamel Inst. Forum* **38**, 69–74 (1976).
7. L. N. Smith, *Proc. Porcelain Enamel Inst. Forum* **52**, 661–663 (1990).
8. P. Vadeboncoeur and R. Hirt, *Proc. Porcelain Enamel Inst. Forum* **36**, 75–79 (1974).
9. F. W. Nelson and L. N. Beer, *Proc. Porcelain Enamel Inst. Forum* **33**, 111–115 (1971).
10. G. R. Prinzbach, *Proc. Porcelain Enamel Inst. Forum* **53**, (1991).

11. *Pretreatment of Alloys for Porcelain Enameling Aluminum*, PEI Bulletin P-403(70) and *Enamel Preparation, Application, and Firing for Porcelain Enameling Aluminum*, PEI Bulletin P-404(70), Porcelain Enamel Institute, Washington, D.C., 1970.
12. *1990 Book of ASTM Standards*, Publication A424-89, American Society for Testing and Materials, Philadelphia, Pa., 1990, 168–169.
13. Ref. 12, p. 169.
14. R. W. Nuske, T. A. Bloom, and T. L. Schiller, *Proc. Porcelain Enamel Inst. Forum* **52**, 836–846 (1990).
15. A. I. Andrews, *Porcelain Enamels*, 2nd ed., Garrard Press, Champaign, Ill., 1961, p. 111.
16. *Alloy Design and Fabrication Considerations for Porcelain Enameling Aluminum*, Bulletin P-402(69), Porcelain Enamel Institute, Washington, D.C., 1969.
17. Ref. 12, 136–137.
18. Ref. 12, p. 210.
19. *Pretreatment of Alloys for Porcelain Enameling Aluminum*, Porcelain Enamel Institute Bulletin P-403(70), 1970.
20. L. C. Kolar and co-workers, *Proc. Porcelain Enamel Inst. Forum* **49**, 420–424 (1987).
21. M. Bozin, *Chemical and Physical Determinations for Porcelain Enamel Plants*, Ferro Corp., Cleveland, Ohio, 1951, p. 12.
22. Ref. 20, p. 422.
23. B. W. King, H. P. Tripp, and W. H. Duckworth, *J. Am. Ceram. Soc.* **42**(11), 504–525 (1959).
24. A. L. Gugeler, *Proc. Porcelain Enamel Inst. Forum* **31**, 37–45 (1969).
25. Ref. 12, 96–97.
26. *1992 Book of ASTM Standards*, Publications C372-88 and C824-91, American Society for Testing and Materials, Philadelphia, Pa., 1992, p. 15.02.
27. E. E. Bryant, *Porcelain Enameling Operations*, Enamelist Publishing Co., Cleveland, Ohio, 1964.
28. Ref. 12, p. 53.
29. P. S. Wolford and G. E. Selby, *J. Am. Ceram. Soc.* **29**(6), 162 (1946).
30. Ref. 4, p. 39.
31. A. R. Robertson, *Color Res. Appl.* **15**(3), 167–170 (June 1990).
32. J. Tunnicliffe and M. Rose, *Vitreous Enameller* **40**(1), 1–5 (Spring 1989).
33. Ref. 12, 408–413.
34. J. VanNess, Ferro Corp., private communications, Nov. 1991.
35. Ref. 1, Publication C448-88, 1992.
36. *Adherence to Porcelain Enamel Cover Coats Direct to Steel*, PEI Bulletin T-29(72), Porcelain Enamel Institute, Washington, D.C., 1972.
37. *Adherence of Porcelain Enamel and Ceramic Coatings to Sheet Metal*, PEI Bulletin T-17(72), Porcelain Enamel Institute, Washington, D.C., 1972.
38. Ref. 12, Publication C313, 1990.
39. Ref. 1, Publication C385-58, 1992.
40. Ref. 1, Publication C282-89, 1992.
41. Ref. 1, Publication C283-54, 1992.

## General References

42. *United States*A. I. Andrews, *Porcelain Enamels*, 2nd ed., Garrard Press, Champaign, Ill., 1961.
43. J. F. Wright, C. G. Bergeron, and J. C. Oliver, "Porcelain Enamel," in S. J. Schneider, Jr., vol. chrmn., *Engineering Materials Handbook*, Vol. **4**, ASM International, Materials Park, Ohio, 1991, 937–942.
44. J. C. Oliver, "Porcelain Enamels-Review and Outlook," *Am. Ceram. Soc. Bull.* **62**(5), 562–563 (1983).
45. D. Balmer, *Proc. Porcelain Enamel Inst. Forum* **50**, 492–497 (1988).
46. L. Gypen, *Proc. Porcelain Enamel Inst. Forum* **52**, 885–897 (1990).
47. E. W. Hughes and D. F. Thomas, *Proc. Porcelain Enamel Inst. Forum* **49**, 391–393 (1987).
48. A. Bets and K. O. Helm, *Proc. Porcelain Enamel Inst. Forum* **49**, 380–385 (1987).
49. S. D. Brown, *Proc. Porcelain Enamel Inst.* **46**, 301–317 (1984).

50. D. B. Judd and G. Wyszecki, eds., *Color in Business, Science, and Industry*, 2nd ed., John Wiley & Sons, Inc., New York, 1967.

### International

51. J. Watril, *Vitreous Enamels*, Borax Holdings Ltd., London, 1984.
52. K. A. Maskall and D. W. White, *Vitreous Enamelling: A Guide to Modern Enamelling Practice*, Pergamon Press, Oxford, UK, 1986.
53. A. H. Dietzel, *Emaillierung: Wissenschaftliche Grundlagen und Grundzuge der Technologie*, Springer-Verlag, Berlin, 1981.

WILLIAM D. FAUST
Ferro Corporation

## Related Articles

Coatings; Coating processes; Metal surface treatments; Refractories; Electronic coatings