LEAD INDUSTRIES ASSOCIATION

60 EAST 42ND STREET

NEW YORK 17, N.Y.

July 11, 1958

SUBJECT: LEAD IN PORCELAIN ENAMELS

TO: INDUSTRY DEVELOPMENT COMMITTEE
TECHNICAL STEERING COMMITTEE
CERAMICS TECHNICAL COMMITTEE

I believe you will be interested in the enclosed reprint from the July, 1958, issue of "Materials in Design Engineering."

May I call your attention in particular to the references to lead bearing enamels for low temperature enamelling of steel and aluminum, starting at the bottom of the second column on page 108 and running to the top of the second column on page 109? Work on low temperature enamels is being conducted under two graduate research fellowships supported by us at the University of Illinois.

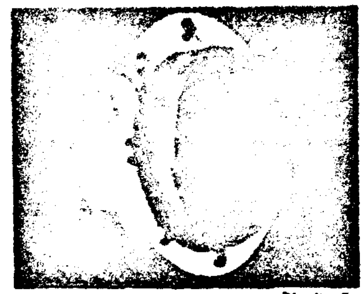
Sincerely yours,

Secretary

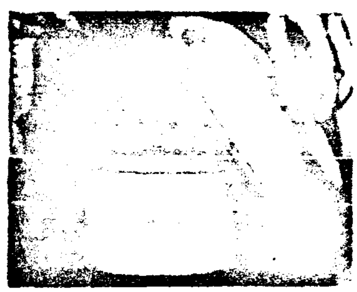
Sanitary ware

Electrical components

Engine parts



Processing equipment



Appliances

Materials
in Design Engineering

Manual No. 150
July 1958

Porcelain Enamels and Ceramic Coatings

by Robert J. Fabian,
Associate Editor, Materials in Design Engineering

Porcelain enamels and ceramic coatings are becoming increasingly popular as engineering materials. This article is an up-to-date survey for the engineer and designer on:

- *Major types of coatings available*
- *Their important engineering properties*
- *Principal metals that can be coated*
- *Coating selection and design factors*

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Porcelain enamels

Porcelain enamels have long been popular as engineering materials because of their combination of protective and decorative properties. Enamels can be formulated with a wide range of physical and mechanical properties, such as high hardness and excellent resistance to chemicals, corrosion, scratching, abrasion and high temperatures. In addition, they can be formulated in a limitless variety of colors and surface finishes to suit the requirements of any application.

What they are

A porcelain enamel is officially defined as "a substantially vitreous or glassy inorganic coating which is bonded to metal by fusion at a temperature above 800 F." The basic ingredient of all enamels is a glass or frit made up primarily of inorganic chemical compounds, minerals, or salts. To a considerable extent, these materials determine the physical and mechanical properties of the coating. Because of the large number of materials that can be used, the number of formulations that are available literally runs into the thousands.

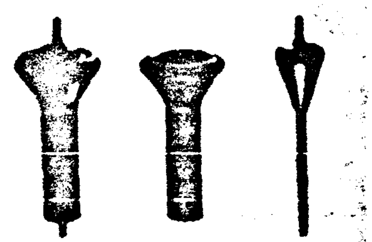
Once a frit has been selected it is charged into a mill, along with water, clay and electrolytes, and ground to form a water suspension (sometimes called enamel slip or milled enamel). The clay acts primarily as a binder and promotes suspension of the frit; the electrolytes (consisting of such materials as sodium nitrite, magnesium carbonate, borax or sodium aluminate) provide proper consistency and set of the slip.

Selecting an enamel

As mentioned, a very large number of enamel formulations (most of them proprietary) are available for different applications. Therefore, in order to narrow the choice down it is absolutely essential to prepare a list of operating requirements. The following points should be considered:

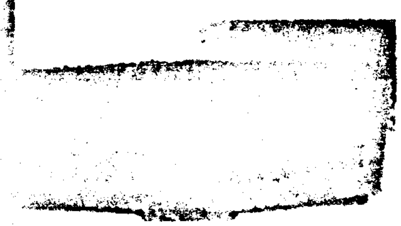
1. To what degree must the enamel resist abrasion, scratching or marring?

Porcelain enamel coatings:



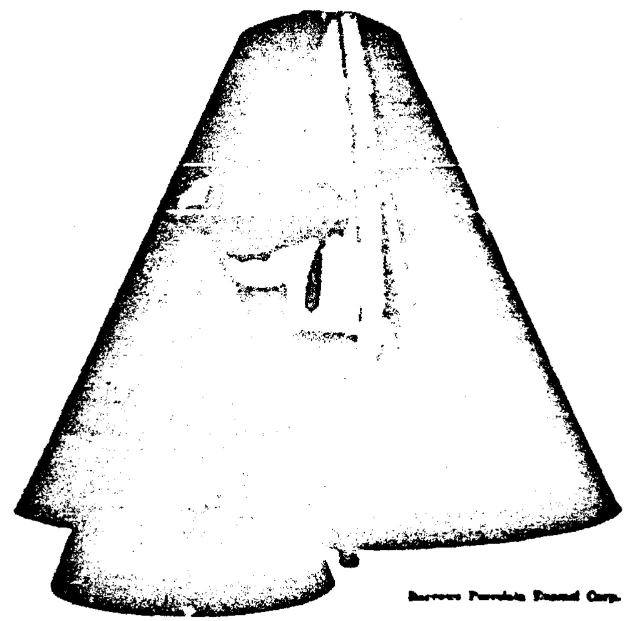
Porcelain Enamel Institute

***Rectifier components** are protected with porcelain enamels to provide a good combination of corrosion resistance and dielectric properties.*



Chicago Vitreous Corp

***Heat exchanger** is porcelain enameled to protect unalloyed steel from heat and vapor corrosion.*



[illegible] Porcelain Enamel Corp.

***Deflecting cones** for petroleum processing equipment use porcelain enamel over stainless steel for protection against heat and oxidation.*

2. Will the coating be subject to any impact?

3. Will the coating be exposed to acids or alkalis? If so, which ones, at what temperature, and to what extent—contact or immersion?

4. Will the enamel be subject to torsion or bending?

5. What is the maximum service temperature expected? Will temperature change be gradual or sudden?

6. Will the coating be subject to weathering or other corrosive conditions?

7. Is the product liable to distort or warp when the enamel is fired or fused? (In such cases a low temperature enamel may be required.)

8. What color and surface finish (matte, semi-matte, or gloss) will be required?

Once these operating requirements have been established the engineer should then consult with a porcelain enameler. Because of the number of enamels that are available it is quite difficult for the engineer, working on his own, to select the best enamel to meet a particular set of operating conditions. The best choice is usually made by mutual agreement between the designer and enameler.

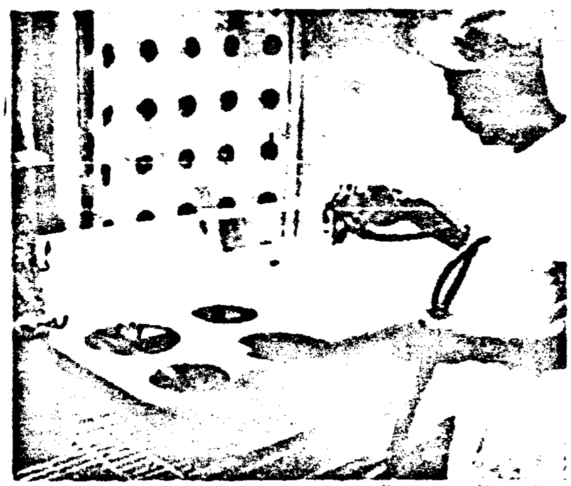
Base metals

Porcelain enamels can be applied to almost any metal that will not melt or volatize below the firing temperature of the coating. In addition to most ferrous metals, enamels can be applied to gold, copper, aluminum (as well as aluminum foil and aluminized steel), titanium, and a number of other nonferrous metals. Even molybdenum and magnesium can be coated if the enamel is fired in an inert atmosphere. Nevertheless, in most applications, porcelain enamels are applied to sheet iron or steel, cast iron, or aluminum.

Sheet iron and steel

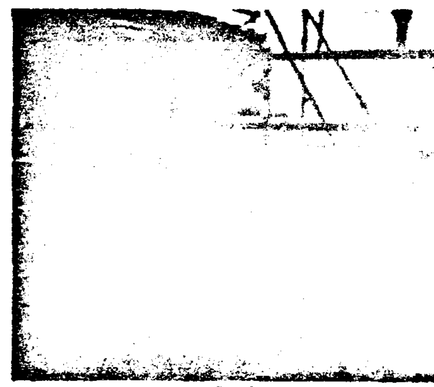
Porcelain enamels cannot be applied to all ferrous metals and practical use is limited to those metals with a low carbon content, few impurities, and a uniform surface structure. To suit these requirements, special enameling irons have been developed which are highly refined in open hearth furnaces to reduce carbon, manganese, sulfur, phosphorous and silicon content to the practical minimum. These irons are processed in special rolls that impart a tooth-like finish, promoting good enamel adhesion. Enameling irons are available in a general purpose commercial grade and in special deep drawing grades. All of the grades are designed to resist sagging at firing temperatures of 1500 to 1600 F. Plain steels, in contrast,

some typical uses

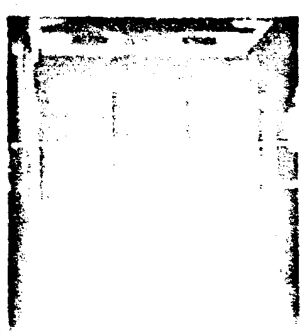


Westinghouse Electric Corp.

Range top *made from titanium-bearing steel does not require ground coat; it is covered directly with one porcelain enamel cover coat.*



Clothing chute *for dry cleaning equipment is coated with porcelain enamel to resist abrasion.*



Elevator cab *interiors are coated with porcelain enamels to produce a wide range of colors and surface finishes. Enamels withstand abuse of daily service and are easily cleaned.*

(Porcelain Enamel Institute)

Porcelain Enamel Institute

Kitchen appliances *and cabinets protected with porcelain enamels must be decorative and resist abrasion, acids, alkalis and heat.*

have more of a tendency to sag above 1300 F.

In addition to enameling irons, some cold rolled, low carbon steels are suitable for porcelain enameling. In general, these steels must be limited to 0.10 to 0.12% carbon, although up to 0.50% can be tolerated in special cases. Hot rolled steel is not generally suitable for enameling.

Because of their carbon and manganese content, the enameling properties of low carbon steels are usually not as good as those of enameling irons. Low carbon steels have a greater tendency to sag and produce surface defects. For this reason they are often used with enamels that are fired at low temperatures.

Another type of steel known as titanium enameling steel is also available. Properties of this steel are discussed under "one-coat enamels." Because of its comparatively high cost it is not as widely used as the enameling irons or low carbon steels.

Cast iron

Because of its high carbon content and impurities, cast iron is generally more difficult to enamel than sheet iron. Nevertheless, satisfactory enamels can be produced if chemical composition is held within certain limits. Castings should also have a dense and uniform structure and be free of porosity and inclusions. Surfaces should be free of defects and capable of withstanding sandblasting.

Aluminum

Porcelain enameling of aluminum is a recent development which, within a comparatively short period, has become widely used. Because of its light weight, good functional properties and decorative appeal, enameled aluminum is quite popular for transportation and architectural uses.

The successful application of enamels must, of course, take into account the low melting point of aluminum. The firing temperatures used in enameling aluminum may be above the melting point of some alloys. The following alloys are currently recommended for enameling: Sheet—1100, 3003, 6061; extrusions—1100, 3003, 6061, 6062, 6063; castings—43, 356, 344X. Of these, the 6061 alloy is the best for general enameling, especially for architectural applications.

A good deal of enameling has been done on aluminized steel. This combination provides the desirable corrosion resistance of an aluminum surface plus the strength and distortion resistance of a steel core.

Selection of the proper aluminum alloy and gage thickness is extremely important. In general, most of the design considerations that apply to sheet iron also apply to aluminum.

Types of enamels

Ground coats

With the exception of some one-coat enamels and aluminum enamels, most porcelain enamels are applied in two or more coats. The primary functions of the ground or base coat (analogous to a primer in painting) are to: 1) promote adhesion between the base metal and the enamel, 2) seal the metal and prevent evolution of gases during firing, and 3) act as a barrier to prevent any chemical reaction between the base metal and the topcoat(s).

The composition of some ground coats is relatively simple since they do not have to provide as many protective or decorative properties as topcoats. Most ground coats for sheet steels contain about 75 to 85% quartz, feldspar and borax. Feldspar is normally incorporated in the ground coat to extend the firing range and make the enamel more stable during firing. About 0.2 to 0.5% of cobalt oxide, the most important ingredient in promoting adhesion, is normally incorporated in the frit to promote bonding. Other oxides, such as those of nickel and manganese, are commonly used with cobalt oxide to control adhesion and color. In addition, a number of other materials are added to obtain specific physical and mechanical properties. Very often, two or three ground coat enamel frits with somewhat different properties are mixed together to extend the firing range of the enamel and provide greater latitude in processing.

In general, ground coats are applied in thicknesses of 3 to 5 mils by dipping or spraying. (Most porcelain enamels are applied by dipping or spraying. Brush and roller coating are used to a limited extent.) Ground coats for most ferrous surfaces are usually fired at 1450 to 1550 F for 4 to 6 min. However, as noted later, special low temperature enamels are fired at 1220 to 1350 F.

Cover coats

The primary functions of cover coat enamels are to provide protection against expected service conditions and to provide decorative appeal. A large number of enamels are available in a wide range of colors and gloss, with varying degrees of hardness and resistance to abrasion, impact, chemicals, corrosion and heat. In many cases a number of properties can be obtained in just one cover coat. However, in some applications two or more coats will be required to provide a specific group of properties. A cover coat enamel is generally applied thinner than a ground coat enamel. It is also fired at 30 to 40 °F below the melting point of the ground coat to prevent "reboiling."

The largest group of cover coat enamels in use today is formulated with titanium dioxide opacifiers. The main reasons for the popularity of these enamels are that they provide high opacity in thin coatings and they can be formulated with good acid resistance. Zirconium, antimony, fluoride, phosphate, molybdenum and other types of enamels are available where special properties are needed.

Cast iron enamels

Gray iron is ideally suited for use in sanitary products because of its low cost and its ability to be cast into a wide variety of shapes. Because of its comparatively poor appearance and corrosion resistance, the material often requires a protective and decorative coating. Porcelain enamels are ideally suited for this purpose and have long been used on cast irons to provide a decorative and long lasting product.

Cast iron parts can be covered with just one relatively heavy coat if a dark color can be tolerated. However, for white and pastel colors, both cover and ground are usually necessary. In addition to promoting adhesion and preventing reaction between the metal and cover coats, the ground coat prevents oxidation at high temperatures and seals and smooths surface irregularities.

Cast iron enamels may be more complicated than conventional enamels because of the more severe operating conditions that must be met. They are also applied by different methods and in greater thicknesses. The enamels are produced in a number of grades ranging from hard, acid resistant types, to softer types with lower resistance to acids and abrasion.

Two types of enamels can be used on cast iron.

Wet process enamels are used principally on small and medium size castings and are formulated and

Basic Enamel Terms You Should Know

acid resistance—Using a standard PEI test, enamels are classified into AA, A, and B groups depending on their degree of acid resistance. Class C and D enamels are called non-acid resistant enamels.

alligator hide—A severe case of orange peeling and tearing caused by too fast drying or heavy application of enamel.

anneal—In enameling, the process of heating black iron shapes and raw castings at 1200 to 1600 F to relieve strains, burn off grease and, in some cases, change the structure of the iron to promote better enameling.

bisque—The unfired, dried enamel coating. Bisque coatings must have enough film strength to avoid tearing and still allow for brushing.

black shapes—Raw iron parts as they exist before pickling.

black specking—Dark contaminating particles in a white or light colored cover coat.

boiling—Liberation of gases during firing of topcoat, which causes enamel defects.

brownies—Defects characteristic of white ground coats applied over steel that has not been properly prepared. See also *copperheads*.

brushing—A technique designed to remove the enamel topcoat and reduce overall enamel thickness in highly stressed areas. The thin ground coat remaining after brushing is better able to resist chipping and the effects of contact with adjacent surfaces.

checking—Raised lines on cast iron enamels caused by cracking of the ground coat.

copperheads—Reddish-brown defects in sheet iron ground coats which contain a base layer of oxidized iron and which destroy the continuity of the enamel.

cover coat—The top or last coat as distinguished from the first or ground coat. Some enamels are one-coat enamels, thus serving as ground and cover coat simultaneously.

cracking—The breaking of bisque enamels which usually produces tearing in the fired enamel. Breaking can be caused by rough handling of the bisque or by low dry film strength.

crackled enamel—An enamel with a novel patterned surface obtained by special application and handling.

crawling—A condition whereby topcoat forms into balls or islands during firing exposing ground coat. May be caused by too heavy application, improper drying conditions, or too finely ground enamel.

crazing—Almost invisible cracking extending down to base metal. Not to be confused with *hairlines*.

curtains—Darkened areas in the ground coat, presumably caused by boiling and blistering during firing. Sometimes called *loops* or *looping*.

drain lines—Pattern lines in the surface of fired enamel generally caused by irregular draining action.

dredging—Application of enamel powder to the hot casting in dry process enameling.

dry process enamels—Special enamels developed for finishing comparatively large cast iron parts.

eggshell finish—A matte surface texture.

enameling iron—Very low carbon steel or open hearth iron developed especially for enameling.

firing marks—Tiny indentations similar to pinholes which are caused either by firing supports or by excessive firing temperatures or firing times.

fish scale—Half-moon-shaped particles that pop off the surface of a ground coat. Also refers to holes left in surface. Condition may occur a considerable time after firing.

frit—Basic ingredient of porcelain enamels. Consists primarily of inorganic oxides, minerals, fluorides or salts.

graining—Process of applying an enamel finish that resembles a wood grain.

ground coat—A coating that is especially designed to promote adhesion and is applied directly to the base metal.

hairlines—Fine line defects produced by the ground coat showing through the topcoat. Can result from faulty firing, excessive enamel application, or metal strains. Do not affect serviceability.

jumpers—Bare spots where the enamel has flaked off. Usually caused by dirt, rust, scale or other foreign material.

marbleized—A color grained surface designed to give the appearance of variegated marble.

Mohs hardness—The hardness of a mineral gaged by its ability to scratch or be scratched by one of ten standard minerals: 1) talc, 2) gypsum, 3) calcite, 4) fluoride, 5) apatite, 6) orthoclase, 7) quartz, 8) topaz, 9) corundum, 10) diamond. Any mineral in the scale can be scratched by any other mineral with a higher scale number.

mottled ware—One-coat enamelware composed of a series of spots of various shades of gray and designed to give the appearance of coarse granite.

orange peel—Enamel defect characterized by an irregular wavy surface similar to the surface of an orange peel.

rusting—Formation of brown oxide spots during the drying of a wet enamel on a ferrous metal base.

sagging—Referring to enamel: Flow of enamel in waves on surface that is fired in a vertical position. Referring to metal: Any permanent deformation of metal during firing.

shading—A decorative effect produced by spraying a dark enamel over a lighter background.

shiners—A sheet iron defect similar to fish scaling, except that the particles are very minute and the affected surface in reflected light appears as though it were covered with tiny diamonds.

shivering—Chipping of dry process enamels.

shore lines—More or less concentric wavy lines that appear in the surface of fired enamel.

slip—The liquid enamel as it comes from the mill after the wet grinding operation.

specking—Discoloration of a surface caused by the impregnation of foreign particles in the enamel.

stippling—Application of fine drops of enamel to a background enamel with a different color.

tearing—A topcoat defect distinguished by minute breaks, cracks or tears.

For further definitions see ASTM C286-57T, Definitions of Terms Relating to Porcelain Enamel.

applied much like conventional sheet steel enamels. However, they usually do not contain cobalt oxide, since good adhesion can be obtained by mechanical bonding between the enamel and the rough cast iron surface. In the past, leaded enamels were widely used for cast iron. However, in recent years they have largely been replaced by leadless types containing titanium, zirconium or antimony opacifiers. These enamels are generally fired at 1200 to 1400 F. Firing times are generally longer than with sheet iron parts because of the thicker sections involved.

Dry process enamels are applied in much greater thicknesses than wet process enamels and are usually used on comparatively heavy castings. Ground coats are applied in much the same way as wet process enamels; however cover coats are applied by heating the casting to about 1700F, dusting a dry, fine frit on the surface, and returning the casting to the furnace. The final coating has a high gloss and is quite thick, usually around 40 mils or above.

Low temperature enamels

Probably the most significant development in porcelain enamel in recent years has been low temperature enamels for ferrous sheet. Most of these enamels are designed for firing at 1250 to 1350 F, about 150 to 250 deg lower than conventional enamels. Extra low temperature enamels are also under development for firing in the range of 1000 to 1100 F.

Advantages and limitations—The principal advantage of these enamels is that they reduce the danger of metal warpage, since they can be fired at low temperatures. Consequently, they can often be used over thinner sections, with possible cost savings. It has been reported that the amount of sagging when firing 20 gage metal at 1300 F is comparable to that when firing 16 gage metal at 1500 F. Thus, a 4-gage reduction in metal thickness can sometimes be realized where structural strength is not a factor.

Low temperature enamels require close control over metal preparation, enamel application and firing temperatures. These enamels are generally more expensive than conventional enamels; however, their higher cost is often offset by the use of thinner metals.

Base metals—In general, low temperature enamels can be applied to the same base metals as conventional enamels. An important advantage of the enamels is that they can be applied to so-called non-premium metals. Consequently, these enamels are most frequently applied to low carbon, cold rolled steels, usually 16 gage and lighter.

Metal preparation—Base metals for low temperature enamels are usually prepared by conventional pickling techniques. However, a somewhat heavier nickel flash is required to promote adhesion. Sandblasting alone, without the use of a nickel flash, is not recommended.

Application—Because of their fineness and heavy consistency, low temperature enamel slips are usually applied by spraying, not by dipping. A typical firing cycle for both ground and cover coats is 3 to 5 min at 1340 F. In general, edges and welds are covered better with low temperature enamels, and less burnoff is encountered because the base metal oxidizes less at the lower temperature.

Thickness — Low temperature ground coats are usually applied in thicknesses of 2 to 3 mils. Cover coats range from 3 to 5 mils; however, a minimum of 4 to 4½ mils is usually required to produce good color reproducibility.

Color and gloss—Low temperature enamels generally look the same as conventional enamels. With few exceptions, low temperature enamels are available in a wide range of strong and semi-pastel colors and in gloss or matte finishes. In some cases it appears that color stability may be better than in conventional enamels. Most low temperature frits are titania-opacified.

Acid and alkali resistance—In general, low temperature enamels have poorer acid and alkali resistance than conventional enamels. Enamels can be formulated with Class A acid resistance, but Class AA resistance cannot be attained. However, chemical resistance of the best low temperature enamels is equivalent to that of most conventional enamels and is highly satisfactory for most applications.

Other properties—Adhesion of low temperature enamels is about the same as that of conventional enamels. Compared to conventional enamels, low temperature enamels have poorer resistance to abrasion, scratching, and thermal shock; equal resistance to impact and weathering; and equal or better resistance to torsion and chipping.

Extra low temperature enamels—In addition to the low (1250 to 1350) temperature enamels described above, much research has been devoted to enamels that can be fired as low as 1000 to 1100 F. These enamels are generally lead-bearing. Fired enamels somewhat resemble organic coatings in appearance and, because of their thinness, can be applied to surfaces originally designed for organic coatings.

Some problems of adhesion exist; however, the enamels have better acid resistance than the enamels fired at 1250 to 1350 F. Both Class A and AA acid resistance can be obtained. Alkali resistance also appears to be quite good.

The extra low temperature enamels have a uniform finish which, however, is not as smooth or as opaque as that of conventional enamels. Abrasion and scratch resistance is not as good as for conventional enamels but is much superior to that of organic coatings.

Uses—Some of the products on which low temperature enamels can be used include small appliances, architectural panels and structures, signs, ventilating hoods, prefabricated clothes closets and bathrooms, etc. Some discretion is necessary where high thermal, chemical and abrasion resistance is required.

Aluminum enamels

Aluminum enamels are used primarily in architectural applications and to a lesser extent in consumer and industrial products. Depending on the kind of protection that is required, they can be applied in one or more coats. In general, the properties of aluminum enamels are quite similar to those of the low temperature (1250-1350 F) enamels for ferrous surfaces described above. However, the similarity ends here, as aluminum enamels are basically composed of lead borosilicate glasses with a high coefficient of expansion and are designed to be fired at much lower temperatures—about 930 to 980 F.

Advantages—The principal advantage of aluminum enamels is that they allow aluminum to be used in a number of applications for which it would not normally be considered. Aluminum is distinguished for its light weight, and when coated with a porcelain enamel it can be provided with a greater variety of decorative finishes and added resistance to chemicals, corrosion and damage.

An important advantage of enameled aluminum compared to enameled steel is that it can be sheared, sawed, and drilled without causing any damage or corrosion at rough edges. In addition, panels can be welded on the reverse side without marring the coating in any way.

Disadvantages—The principal disadvantage of aluminum enamels is that they require very close control during application. Good base metal preparation is extremely important, and more steps are required than with conventional enamels. In general, enameled aluminum is not as good as enameled steel where high strength, low cost or abrasion resistance are important factors.

Metal preparation—In order to produce a satisfactory coating it is essential that aluminum surfaces be cleaned and made receptive to the enamel. All of the alloys must have an inert layer in order to provide spalling resistance. Since the 1100 and 3003 alloys obtain an oxide layer immediately on contact with air they only have to be cleaned in a solvent or alkaline cleaner before enameling. Other aluminum alloys, however, require special surface treatment to build up an oxide layer. For further processing and design details the reader is referred to *Recommended Processing Methods for Porcelain Enamel on Aluminum Alloys*, published by the Porcelain Enamel Institute.

Thickness—Depending on the degree of protection and the color required, the overall thickness of ground and top coat enamels ranges from 2 to 6 mils. Composition and number of topcoats depends on the alloy used as well as the color and end-use properties required.

Color and gloss—Aluminum enamels can be produced in a large number of colors from light pastels to bold dark colors. Colors are available in finishes from a dull matte to a very high gloss, and in stippled, mottled or rippled textures.

Acid and alkali resistance—In general, the acid and alkali resistance of aluminum enamels is quite good, though not as good as in conventional enamels. White and pastel colors have Class A acid resistance; other colors have Class B resistance. The enamels do not stain, streak or fade when exposed to some alkalis and salt spray.

Other properties—It is claimed that the rigidity of aluminum sheet is increased up to 60% by the application of an aluminum enamel. This factor can permit a reduction in metal thickness in some designs. Resistance to thermal shock has been demonstrated by the ability of panels to withstand quenching in cold water after being heated to 1000 F. The dielectric properties of enamels are also good, on the order of 500 v per mil. Impact resistance of aluminum enamels is quite good.

Uses—Aluminum enamels are primarily used in transportation and architectural applications. Some transportation applications include: railway car interiors, ship bulkheads and paneling, pipe and fittings. Some architectural uses include: curtain walls, panels, tiles, door and window frames, hardware, lighting fixtures and sanitary ware. Other uses: kitchen ware, furniture, signs and displays, and cabinets.

Special one-coat enamels

Because of the cost savings that can be realized, much research has been devoted to finding a way of applying a single coat of porcelain enamel to ferrous metals without the use of a ground coat. In order to meet operating requirements it is obvious that any one-coat system must perform at least as well as a multiple coat system. In general, the problem has been approached in three different ways with varying degrees of success.

Special enamel formulations—In order for these enamels to have any cost or production advantages they must be applicable to conventional enameling irons without requiring any unusual surface treatments. To obtain satisfactory adhesion, one-coat enamels usually require special mill additions which, in some cases, reduce other coating properties to a certain extent. Development of satisfactory one-coat enamels has largely been held back by this factor. With the exception of some special enamels for heaters, light reflectors and some architectural applications, one-coat formulations are not widely used. However, as noted previously, conventional ground coat enamels are sometimes used alone where appearance is not an important factor.

Special surface preparation—This method of producing a one-coat system involves the formation of an adhesion-promoting layer on the metal. Most of the systems developed consist of an etching treatment plus a heavy nickel flash treatment which forms a nonreactive surface and promotes bonding. However, one of the most successful surface treatments developed consists of cleaning the surface of enameling iron or cold rolled steel, chemically converting the surface to a phosphate coating, and then prefiring the coating in a conventional enameling furnace to form an oxide layer about 1 mil thick (as compared to about 3 mils for a conventional ground coat). The phosphate coating controls oxidation during prefiring and produces a smooth and adherent oxide with the proper physical and chemical properties to directly accept a one-coat porcelain enamel of conventional formulation.

A good deal of research has been devoted to this process and it appears to have considerable promise. However, it is still in the experimental stage and difficulties have been encountered; very pure water is required in the rinse stages to prevent surface defects, and very close furnace control is required during prefiring to form a satisfactory oxide film.

Special enameling steels—In addition to the aluminum enamels de-

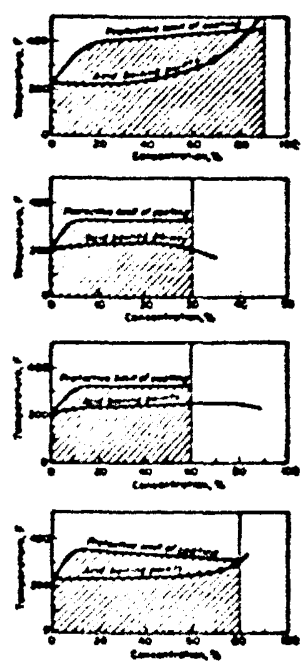


Fig 3—Resistance of special porcelain enamels to various concentrations of four common acids. From top to bottom: sulfuric acid, hydrochloric acid, nitric acid, and phosphoric acid.

scribed above, probably the most satisfactory one-coat enamel systems available are those which utilize special enameling steels. Ordinarily, when a cover coat is applied directly to conventional metals, surface defects are produced by the gases given off by the reaction of carbon in the metal and hydrogen in the frit. This condition is prevented in the special one-coat enameling steels by controlling and stabilizing the carbon. A special titanium-bearing killed steel (Ti-Namel) contains titanium (0.20 to 0.50%) which combines with the carbon in the steel, theoretically in the ratio of 4 to 1, to form titanium carbide. This compound is comparatively stable at enameling temperatures. The titanium also combines with and neutralizes the nitrogen, sulfur and hydrogen in the steel.

In general, conventional cover coat enamels can be applied directly to these steels. However, the colors that can be used are limited, enamel white being the most popular shade. Satisfactory white finishes are obtained in thicknesses of 6 to 9 mils, depending on whether interior or exterior use is intended.

Cost of the titanium-bearing steel is higher than conventional enameling irons; however, they are reported to have better resistance to sagging during firing than conventional irons of the same thickness. Some enamels, particularly the antimony-bearing type, produce an excellent bond when fired for 2 to 3 min at about 1500 F. Zirconium-type enamels generally require a firing cycle of 4 to 5 min at 1520 F.

In addition to the titanium-bearing steels, another one-coat enameling steel has been used experimentally. This steel is treated with nickel and decarburized after rolling to form a relatively inert surface which is receptive to a one-coat enamel.

Properties of porcelain enamels

With the exception of low temperature enamels, whose special properties have already been described above, the following properties apply to all single and multiple-coat enamel systems. Because of the large number of enamels and base metals available it is difficult to pinpoint exact properties; however, these data can be used as a good working guide for most product designs. In general, all porcelain enamels are resistant to normal atmospheres, oils and neutral organic solvents.

Chemical and corrosion resistance

Water—Porcelain enamels can be used in contact with water up to 150 F; however, water at temperatures over 150 F, especially when pressurized, can be quite damaging to some enamels. Nevertheless, many special formulations are available that provide extreme resistance, as evidenced by their trouble-free use in hot water heaters. Some of these enamels will last for several thousand hours under conditions that would break down galvanized steel in 48 hr.

Acids—Porcelain enamels are available in varying degrees of acid resistance, ranging from fair to excellent. Most enamels have fairly high acid resistance and can be used in contact with mild organic acids, photographic solutions and food products. As shown in Fig 1, special enamels can also be produced that will resist all organic acids and all inorganic acids except hydrofluoric (which dissolves silica, a major component of glass). In all cases, the enameler should be consulted when selecting an acid resistant enamel.

A helpful test for acid resistance is recommended by the Porcelain Enamel Institute; in this test enamels are classed by an AA, A, B, C or D rating, depending on their appearance after exposure to a 10% solution of citric acid for 15 min at 80 F. Another test, which determines resistance to boiling acids, measures the weight loss of enamels after exposure to a boiling 6% solution of citric acid for 2½ hr.

It is difficult to conceive of an enameled product that will not be subject to acid attack in one form or another, whether by the weak acids of citrus fruits or by concentrated mineral acids. On kitchen appliances where prolonged exposure to food acids may be encountered, enamels with an acid resistance of A or better are usually specified.

Alkalis—Until recently, most porcelain enamels possessed limited alkali resistance. However, concurrent with the increased use of detergents and household appliances, many new formulations have been developed that have excellent alkali resistance. Enamels are now available that are highly resistant to such alkalis as boiling 5% sodium pyrophosphate or 3% sodium hydroxide. Formulations can be produced that withstand a pH up to 12 at 212 F.

Weathering—The excellent weathering resistance of porcelain enamels has been demonstrated in a recently completed, 15-year test conducted at four principal locations in the United States. A number of significant observations were made:

1. In all cases where there was good initial coverage and no mechanical damage, the base metal was protected against corrosion for the entire fifteen year testing period.

2. In general, the enamels with the best acid resistance suffered the least gloss deterioration.

3. There was no noticeable fading of Class AA or A acid resistant enamels, nor was there any objectionable fading of Class B enamels. However, almost all Class C and D colored enamels showed very noticeable color changes.

Hardness and abrasion resistance

One of the most distinguishing characteristics and advantages of porcelain enamels is their excellent hardness and abrasion resistance. Depending on formulation, the hardness of enamels ranges from 3½ to 6 on the Mohs scale or about 150 to 560 Knoop. Surfaces are also characterized by their smooth, glassy appearance and low coefficient of friction.

The abrasion resistance of six typical enamel formulations is given in Fig 2. As indicated, the titanium-opacified enamels provide exceptional wear resistance. Poorest abrasion resistance is exhibited by the antimony-opacified, non-acid resistant enamel. Even the ground coat enamel, the antimony-opacified acid resistant enamel and the zirconium-opacified enamel showed a weight loss five to six times greater than the titanium enamels after extensive testing.

In some applications porcelain enamels exhibit greater hardness than many metals. For this reason, enamels are often used in abrasion resistant sanitary ware and in heavy duty industrial applications, such as coal and package chutes, pump pistons, and bucket and screw-type conveyors.

Stiffness

It is not widely appreciated that porcelain enamels can considerably improve the stiffness of metal parts. It has been shown that the stiffness of enameled parts is a function of the cube of the sum of metal thickness and one-half the enamel thickness. This strengthening effect is shown in Fig 3, which compares the deflection of plain and enameled 22-gage specimens at various loads. Because of these stiffening properties, enamels often permit the use of thinner gage metals with resulting cost and weight savings.

Impact resistance

The impact resistance of porcelain enamels ranges from fair to excellent. Actually, impact resistance is dependent on a number of factors other than enamel formulation. These are: 1) the moduli of elasticity of the metal and the falling body, 2) the radius of curvature of the surface receiving the impact, and 3) the thickness of the metal and the enamel.

Because of the number of variables involved it is difficult to predict accurately the impact resistance of an enameled product. However, a comparison of various enamels and base metal designs can be made by using a standard impact test for porcelain enamels such as ASTM C284-51T.

Typical impact properties of a porcelain enamel are given in Fig 4, which shows the effect of radius of curvature on impact resistance. The impact resistance of surfaces with large curvature is due to the fact that the impact force is distributed over a large area.

Torsion resistance

The torsion resistance of porcelain enamels is important for such products as ranges and refrigerators that are likely to be subject to bending or twisting during shipping or installation. Torsion resistance of an enamel depends on a number of factors, such as number of coats, coating thickness (torsion resistance is generally inversely proportional to thickness), weight of nickel flash coat, etc.

For a thorough evaluation of enamel systems the engineer should use a standard test such as the Porcelain Enamel Institute *Torsion Test for Porcelain Enameled Iron and Steel*. This test measures the number of degrees of twist required to produce failure along the apex of an enameled metal angle.

Color

An almost unlimited variety of colored enamels have been made available because of the increased demands of consumers for colored products. Titanium-opacified enamels, formerly available only in white and light pastels, are now available in several stronger colors. Metallic finishes such as copper, bronze, gold and gunmetal, and even luminescent finishes, are now being produced. A wider variety of speckled finishes are also available.

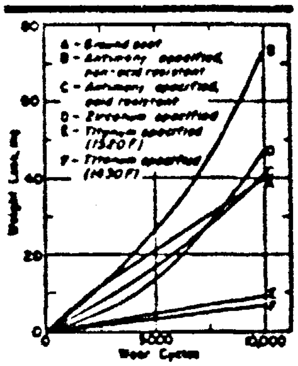


Fig 2—Comparative abrasion resistance of six types of porcelain enamels.

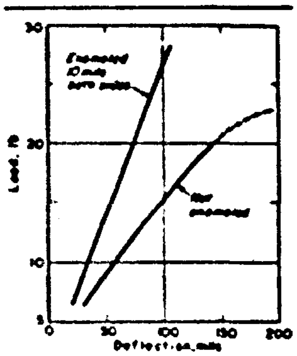


Fig 3—Improved stiffness is produced by using heavy porcelain coating on thinner metals.

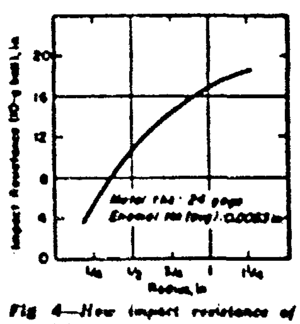


Fig 4—How impact resistance of porcelain enamels varies with base metal curvature.

In general, the strongest and brightest colors, such as the cadmium-selenium reds and oranges and cadmium yellows, are produced in clear glasses. Moderately strong to bright colors can be obtained with semi-opaque antimony and zirconium frits.

Semi-opaque titanium frits are suitable for light to moderately strong colors and are widely used on home appliances. The most stable colors are ivory-yellow, yellow, yellow-brown and blue-green. Pink, gray and other decorator colors are also being used despite the fact that relatively expensive raw materials are sometimes required. The semi-opaque enamels must usually be applied about 20% thicker than conventional enamels.

Opaque titanium frits are suitable chiefly for weak or light pastel colors. Strong colors in opaque titanium enamels require such a high proportion of pigment that the enamels must be ground finer than usual to prevent speckling, and it is difficult to adjust the working properties of the enamels.

Reflectance

Porcelain enamels are available in varying degrees of reflectance. For lighting fixtures the diffuse reflectance of an enamel should not be less than 0.85. In other applications where light reflectance is not too important the reflectance of white porcelain enamels should not be below 0.65 and is usually 0.75 or higher.

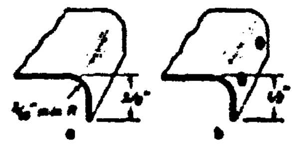
Thermal properties

As described in a later section, special porcelain enamels are available for high temperature applications up to 2100 F. However, unless they are specially formulated, most conventional enamels can only be used at temperatures up to 700 F. A rough rule that has been suggested is that an enamel's maximum operating temperature is about 500°F lower than its firing temperature. In general a conventional enamel can withstand a sudden temperature change of 350°F without failure. Special enamels can withstand temperature changes up to 800°F.

Electrical properties

Because of their high inorganic content, porcelain enamels have good dielectric strength, ranging from 500 to 1000 v per mil. Dielectric

Consider These Factors When Designing Enameled Parts



Flange dimensions. *Flanges are usually required on the edges of flat sheets to: 1) stiffen the sheet and prevent warping during firing, 2) round off rough edges and prevent chipping of the enamel, and 3) provide a mounting or fastening surface. Generally, radius of the flange bend should not be less than 3/16 in.; smaller radii create excessive surface tension in the coating, tending to produce thin spots which burn off during firing.*

As shown in a, all flanges should have a minimum height or width of ¼ in. If mounting holes are incorporated in the flange, as in b, depth should be at least ½ in.

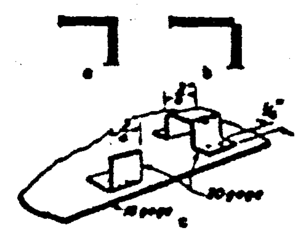
Bolt and screw holes. *Holes for bolts and screws should have a minimum diameter of 5/16 to 3/8 in. to prevent clogging of holes during dip enameling. Also, holes should be made an additional 1/16 to 1/8 in. oversize to allow for edge coating by the enamel. If screw heads are to be recessed as shown, the edges of the bolt holes should be turned down. Radius of the turned down edge should be at least 3/16 in. to provide good enamel adhesion.*

Enamel adjacent to holes can be prevented from chipping by thinning, or brushing away, the topcoat. If this is not possible, nonrusting eyelets, grommets or washers should be used to distribute fastening loads over a wide area.

Welded joints. *Certain precautions are necessary in enameling welded joints. The weld must be sound and free from cracks, crevices, bubbles or inclusions to prevent enamel defects. In designing corner welds, joints as in a should be avoided, since only one edge of the metal is exposed for welding and a weak joint is liable to be produced. A much better joint with more welding area is provided if the edges are positioned as in b. The joint should be peened and rounded over after welding to facilitate enameling.*

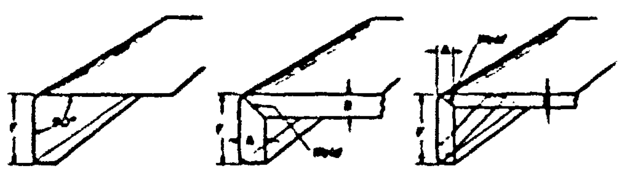
Attachments have a tendency to break loose during firing because of unequal expansion. Where attachments are not spot welded to sheet, the space between the spot welds should not be greater than 1 in. For this reason seam welding is preferred where feasible.

As shown in c, spot welded lugs or clips should be at least two gages



lighter than the base sheet. To prevent underfiring in the vicinity of attachments, the double-thickness area of contact should be kept as small as possible. The dimensions shown are typical.

Porcelain enamel cannot be applied over soft soldered or brazed joints. Riveted joints can only be enameled under ideal conditions, and movable joints, such as hinges, should not be enameled.



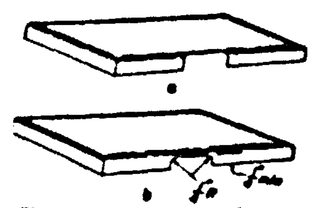
a Weak design. Flange F will change angle in firing

b Good design. A=B=⅓F Flange F is properly supported and will hold angle

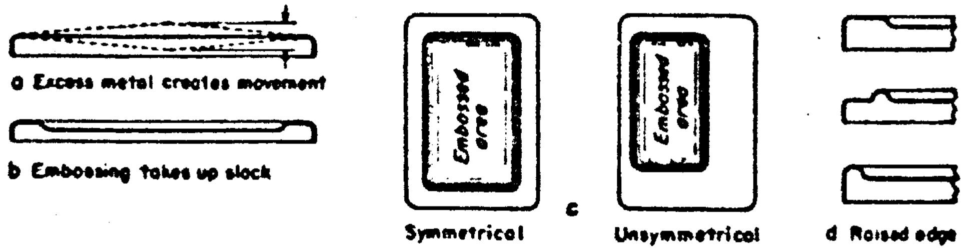
c Alternative method. If A & B are less than ⅓F additional support can be provided by spot welded strap

Flange stability. *Where a large flange (1 in. or more) is visible in the final assembly, it must usually be kept entirely straight and at an exact angle, usually 90 deg as in a. This can be done by providing two end flanges. These end flanges are usually welded together for greater rigidity. However, welding may be dispensed with if the corners are not visible or if the parts to be finished are in black or dark colors. As shown in b, end flanges should be equal in width and should be at least one-third the width of the large flange, i.e., A=B=⅓ F.*

On large parts where end flanges do not give proper support they may be braced with a removable strap that is installed just during firing, as in c.

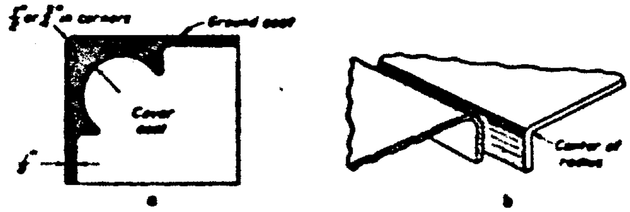


Flange cutouts. *Cutouts that completely interrupt the flange (a) should be avoided as they weaken the structure and create stress concentrations at the corners of the cutout which are transmitted to flat surfaces. If cutouts are absolutely required they should have corner radii of at least ¼ in., and at least ¼ in. of metal should be left between the top of the cutout and the face of the piece (b).*



Stiffening. *Large flat areas as in a are easily displaced or moved (sometimes called an "oil can effect"). Excess slack in the metal can be taken up by stretching or embossing the metal as in b. In all cases embossing should be symmetrical with the outline of the piece (c), as unsymmetrical embossing tends to create uneven stresses and distortion.*

Waviness along flat edges can often be overcome by providing raised edges, as in d. However, care should be taken to work the excess metal out to the edge and not to the center; otherwise, an oil can effect may be produced.



Brushing. *Chipping or handling damage can sometimes be reduced by brushing, a special technique developed to decrease the thickness of enamel at edges and corners. During brushing (or edging, as it is sometimes called) the finish enamel is removed right down to the base coat. Because of the development of superior enamels, brushing is no longer very common; however, it is still used on some heavy duty products.*

Brushing is essentially a shop operation. Nevertheless, since it can affect the appearance of the product, the designer should be concerned with how it can be controlled to harmonize with the overall design. As shown in a, the minimum width of brushing should be ⅛ in. Wider brushing should be in multiples of this width. Brushing at corners should be increased to ¼ or ⅜ in. This increase in width can usually be made decorative, as indicated in the sketch.

Where a flange contacts another surface, as in b, it should be brushed over its entire length, as well as over the center of the radius. Brushed areas around holes should have a radius of at least 1/16 in. more than screw heads or washers. Similarly, the edges of cutouts should be brushed to at least ⅛ in.

strength varies with formulation and operating temperature. The effect of coating thickness is not as great at temperatures above 250 F as it is at room temperature, and consequently actual values should be determined under simulated operating conditions.

Design of porcelain enameled parts

In designing parts to be porcelain enameled, the effect of high firing temperatures must always be kept in mind. A part may be fired many times, and each time it may be subject to sagging or to distortion and stresses due to unequal heating rates.

Parts should always be designed so that minimum stress is imposed on the enamel (see design data on p 112). If there is any question about a design a porcelain enameler should be consulted, as he can usually suggest changes that will minimize firing problems and produce a more durable design.

Selecting metal thickness

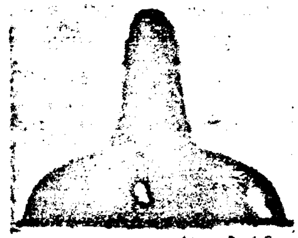
Selection of the proper metal thickness is extremely important to prevent such defects as warping, sagging, hairlining and chipping. For example, a drawn part containing a large flat area usually tends to be subject to warping because of the creation of unequal stresses in the metal; difficulties may be overcome by switching to a heavier gage.

Following is a table of thicknesses that can be used as a rough guide for designing medium sized parts that require moderate rigidity and flatness and are to be finished in white or light colors. All areas that are marked with an asterisk should be embossed, flanged or otherwise suitably reinforced. All parts larger than indicated should be made from 18-gage or heavier metal.

Gage	Width, in.	Area, sq ft
24	6	½
24	12	3*
24	18	6*
22	6	1
22	12	2½
22	18	6*
22	24	8*
20	6	1½
20	12	5
20	18	8*
20	24	10-15*

Chicago Vitreous Corp.

***Switch plate** for a fractional horsepower motor is enameled on conical portion to resist scoring action of a rapidly moving felt wheel.*



Armco Steel Corp.

***Light reflector** made from enameling iron is porcelain enameled to facilitate cleaning and promote long life.*

Chicago Vitreous Corp.

***Cast iron exhaust pipe** is protected with porcelain enamel coating against heat and atmospheric corrosion.*

In some cases end-use, rather than application, factors may determine gage thickness. Heavy thicknesses, of course, are required in applications such as hot water storage tanks where hydrostatic pressure is involved. Also, in architectural enamels a heavier gage may be required because of flatness requirements. Small sign pieces may be made as light as 24 or 26 gage, but larger units that are subject to wind pressure may require a stronger metal of 18 or 16 gage. The required degree of rigidity in plumbing ware is usually obtained by using nothing lighter than 14 gage.

Allow for surface build-up

Enamel thickness must be allowed for in the design stage of a product. Though the thickness of enamel in the center of a flat surface may be about 0.015 in., the build-up at edges may run as high as 0.06 in. Consequently, a clearance allowance of about 1/16 in. must be allowed at edges.

Even greater clearances are often needed. A ½-in. clearance should be allowed where parts fit into an enameled corner, since the ground coat has a tendency to accumulate in corners during draining. A similar allowance must be made for excess metal on the inside of welded corners, as the welding metal tends to run through the joint and build up on the inside.

Ceramic coatings

Ceramic coatings received their first real impetus 15 years ago with the successful development of the A-19 coating by the National Bureau of Standards. The original coatings were developed primarily to permit the use of noncritical, low carbon steels for military applications during World War II. Since that time a wide variety of coating formulations for military and commercial applications have been developed.

Ceramic coatings are principally designed to:

1. Protect base metals against oxidation and permit their use at high temperatures. In performing this function ceramic coatings can permit the use of less expensive, noncritical metals, or else raise the temperature limit of premium alloys.
2. Provide a hard and abrasion resistant surface.
3. Protect the base metal against corrosion and certain types of chemical attack.

Any one or all of these functions can be provided by a coating through suitable formulation.

Ceramic coatings can be classified into three broad categories, each distinguished for a special group of properties: 1) mixtures of porcelain enamel frits and refractory oxides, 2) refractory oxide coatings, and 3) cermet coatings. The last type is not discussed in detail in this manual (see box, p 116).

Enamel-refractory oxide mixtures

Most ceramic coatings in use today are largely made up of special high temperature porcelain enamel frits plus one or more refractory oxides such as aluminum oxide, chromium oxide, titanium oxide, cerium oxide, etc. Following are the principal coatings in this category that are available to the designer.

NBS A-19

The A-19 coating is the first successful one developed by NBS for protecting noncritical steels against oxidation at high temperatures. The coating is still being used today. It consists largely of oxides of silicon, aluminum, boron, calcium, sodium and potassium, plus calcined alumina, enameler's clay, citric acid crystals and water. The coating is primarily intended for one-coat application on low carbon steels and high temperature austenitic alloys.

In general, metals must be more deeply etched than when using conventional porcelain enamels. Sandblasting is recommended where feasible, but satisfactory adhesion can be obtained by pickling. Grease must be completely removed prior to pickling. Also, a nickel flash should be used after sandblasting.

The A-19 coating is usually applied in thicknesses of 2 to 3 mils. Thicknesses greater than 3 mils can be used, but heavier applications reduce resistance to thermal shock, blistering and chipping. The coatings can be applied by spraying, but parts requiring an interior coating must usually be dipped.

Firing temperature on ordinary steels is 1550-1600 F. Time of firing varies with metal thickness, size and shape of the piece, and the furnace used. A typical schedule for simple 18-gage steel parts is 4 to 5 min.

The operating temperature of low carbon steel parts coated with A-19 is usually limited to below 1350 F because the base metal rapidly loses strength above this temperature. When used on high temperature austenitic alloys the coating affords protection at temperatures up to 1550 F. Military specifications state that protection of base metals against oxidation must be such that a 2¼ x 3-in., 18-gage specimen of enameling iron shall not gain more than 0.03 gm in weight after 44 hr at 1200 F. Also, it is specified that 18-gage tubes 6 in. long x 2½ in. in dia must withstand five quenches from 1200 F without visible damage.

NBS A-31

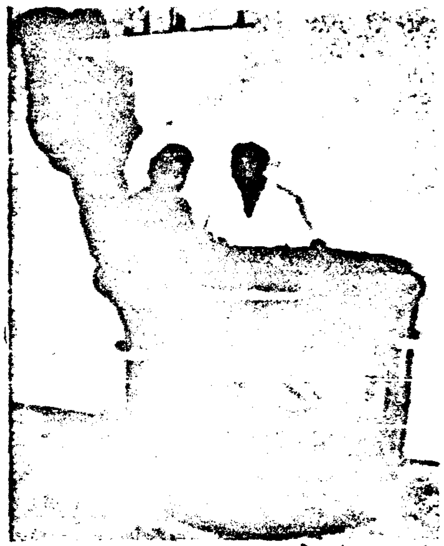
In properties and composition the A-31 system is quite similar to the A-19 coating. Because it must be applied in two coats it is not widely used except for specialized applications.

The A-31 system consists of an A-19 ground coat applied in 2 to 3 mils, followed by a 2 to 3-mil A-30 topcoat. The A-30 topcoat is quite similar in composition to the A-19 ground coat. In general, the A-31 coating is limited to steels with a carbon content of less 0.15%.

NBS A-417

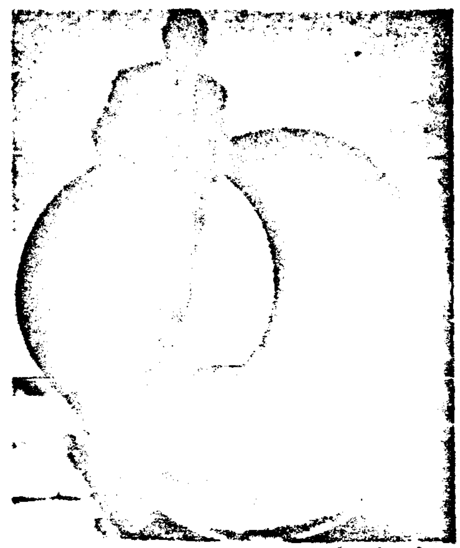
The A-417 coating was quite popular at one time but has been largely supplanted by the A-418 coating. Actually, there is very little difference between the two coatings except that the A-418 formulation does not contain any beryllium oxide. Some objections were raised to the A-417 coating because of the hazards of using beryllium oxide. However, the

Ceramic coatings: some typical uses



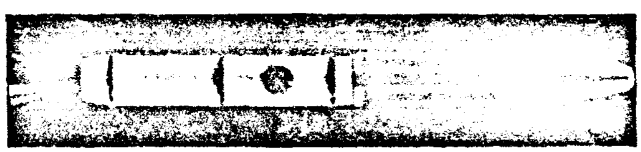
Ryan Aeronautical Co.

Engine exhaust *system is coated with NBS A-417 ceramic coating to protect base metals against high temperature oxidation.*



Solar Aircraft Co.

Afterburner shroud *is provided with reflective ceramic coating on interior and emissive coating on exterior to reduce operating temperatures.*



Norton Co.

Explorer satellite *is coated with eight ⅛-in. aluminum oxide stripes to control temperature inside instrumentation package.*

Bearings *can be coated with special ceramic coatings which have smooth, low friction, abrasion resistant surfaces.*

beryllium oxide in the A-417 coating is chemically combined in the frit and there have been no reports of any deleterious effects after coating thousands of parts.

NBS A-418

The A-418 coating, along with the NBS A-19 coating and other proprietary coatings, is one of the most popular enamel-refractory oxide coatings in use today. The coating frit is made up of oxides of silicon, boron, barium, calcium, zinc, aluminum and zirconium, and is mixed with chromic oxide, enameler's clay and water.

The coating is not recommended for low carbon steels, since the high firing temperature required (1875 F for 3 to 10 min) tends to distort and warp all but the simplest shapes. However, the coating performs extremely well on heat resisting steels, and has been used with good results on Inconel, Inconel X, Nimonic 75, HS-21, S-816, and 18-8, 19-9 and 25-20 stainless steels. The coating considerably extends the life of these alloys at operating temperatures up to 1750 F. It has also been successfully used with other alloys; however, final selection should be checked with the enameler.

Base metal pretreatment usually consists of a light sandblasting. Final coating thickness is about 1 to 2 mils.

NBS N-143

The N-143 coating was developed for use in nuclear reactors and consists of an alkali- and boron-free barium-beryllium silicate frit, plus cerium oxide, enameler's clay and water. It was designed for alloys such as 310 stainless steel, Nichrome V and Inconel, and affords appreciable protection against oxidation at temperatures up to 2050 F. An outstanding feature is its very low absorption coefficient for thermal neutrons.

Proprietary coatings

In addition to the above NBS coatings, a wide variety of proprietary enamel-refractory oxide ceramic coatings are also available from enamelers. Some of these proprietary coatings are just variations of the basic NBS coatings; however, most of them are unique formulations which are designed to improve the oxidation resistance of base metals at temperatures up to 2100 F. When required, they can be made to provide varying degrees of resistance to abrasion, corrosion and galling. Depending on formulation, a wide range of base metals and operating conditions can be accommodated. The following coatings are just typical of those that are available.

1. For low carbon and low alloy steels. These coatings are fired at 1600 F and are designed to improve the oxidation and corrosion resistance of metals at temperatures up to 1400 F. They have a gray, matte appearance and are intended for use on such equipment as space heaters, heat exchangers, combustion chambers and exhaust pipes.

2. For 300 and 400 series stainless steels. Several formulations are available for protecting these metals. One of the principal formulations is fired at 1700 F and can be used on all of the 300 and 400 series stainless steels except the free-machining grades and those containing more than 0.5% carbon. It can also be used on nickel and cobalt-base alloys that contain at least 10% chromium, provided they do not contain 15% or more of molybdenum or tungsten. The coating has extended the service life of parts 400% when used at operating temperatures up to 1800 F. Principal uses have been for turbojet combustion chamber liners, tail cones and afterburner liners; manifolds and turbo hoods; and industrial furnace baffles, combustion chambers, electric heating elements and bellows. Modified formulations are also available for use on parts subject to unusual corrosive or abrasive attack at temperatures up to 2000 F.

3. For aluminum. Several proprietary formulations have been developed in the past year for all of the

Cermet Coatings

In contrast to porcelain enamels and ceramic coatings, which are made up primarily of inorganic oxides, cermet coatings consist essentially of a combination of metallic and nonmetallic elements which may or may not be diffusion-bonded to the base metal. Cermet coatings can often provide certain design and cost advantages not obtainable in porcelain enamels or ceramic coatings. Following is a brief summary of the principal cermet coatings:

Tungsten carbide — Extremely hard and wear resistant layers of tungsten carbide can be deposited on metal surfaces with a specially constructed gun. Coatings range in thickness from 2 to 10 mils and have an overall hardness of about 1350 Vickers. Practically all metals can be coated, and since base metal temperature seldom exceeds 400 F, changes in mechanical properties are negligible. (For further information see "Try Flame-Plated Coatings Where Service is Severe," MATERIALS & METHODS, Feb '56.)

Chromium carbide—Chromizing can be used to produce a hard and wear resistant chromium carbide surface on low carbon steels, many alloy steels, high chromium and stainless steels, cast iron and iron powder parts. (For further information see Manual No. 134, "Hard Coatings and Surfaces for Metals," MATERIALS & METHODS, Jan '57.)

Silicon carbide—Silicon carbide coatings are used primarily to improve the erosion resistance of graphite parts at high temperatures. Coatings can be formed in thicknesses of 2 to 30 mils and are more resistant to oxidation than pure carbon. These coatings can be used up to 4000 F and are highly resistant to acids and alkalis. Knoop hardness is 2500 at 100-gm test load.

Aluminum-ceramic coatings—These coatings are comparatively new and consist essentially of a mixture of aluminum alloy powders and ceramic frits. They are applied to carbon steels, low alloys and cast iron by spraying or dipping. The coatings are diffusion-bonded to the base metal after firing between 1235 and 1600 F, and have a metallic finish. They are quite inert at temperatures up to 1100 to 1200 F, and have very high resistance to thermal shock and impact. They can be applied in thicknesses up to 30 mils; however, adequate long term protection is generally provided by 3 to 4 mils.

Nitriding—Although it is not usually thought of as such, a nitrided case is essentially a cermet. Nitriding, which is limited to certain grades of steel, forms an extremely hard case (1000 DPN) which retains hardness up to 1100 F and is not subject to fatigue. (For further information see Manual No. 96, "Surface Hardening of Steels and Irons," MATERIALS & METHODS, Oct '53.)

standard aluminum alloys as well as some of the high strength alloys. The coatings consist primarily of a low melting glass, plus refractory oxides and fluxing agents.

Normally, wrought aluminum alloys melt at temperatures between 1250 and 1350 F and begin to soften at considerably lower temperatures. However, aluminum surfaces treated with the new coatings have been reported to withstand temperatures of 1500 to 1550 F before softening occurs.

The coatings are usually applied in thicknesses of 0.0015 in. either on one or both sides of the metal. They are said to have excellent adhesion and good resistance to thermal shock, flame impingement and impact. Resistance to chemicals and abrasion, however, is limited, and the coatings are said to produce a 10 to 12% reduction in the tensile strength of the base metal as a result of the firing operation.

4. For titanium. These coatings are intended primarily for titanium aircraft parts operating at about 1500 F. Coatings are fired at 1800 F and have a glossy blue appearance.

5. For thin-gage metals. These coatings are especially designed for metals from 1 to 10 mils thick operating at temperatures up to 1750 F. They are used largely on the 300 series stainless steels, but can be adapted for the 400 series stainless steel and the superalloys. Principal uses have been for afterburner insulating blankets and high temperature solenoid coil insulators.

6. For extra high temperatures. Special enamel-refractory oxide coatings are available for use up to 2100 F. These coatings require special surface processing and are fired at 1900 F. They can be applied to all of the stainless steels with the exception of the free-machining grades. They are recommended for use on alloys containing 45% of the combination of chromium, cobalt and nickel (with a minimum of 10% chromium).

7. For resistance to galling. These coatings are designed to provide low friction, prevent galling, and minimize fretting corrosion at temperatures from 300 to 1650 F. Depending on formulation, a wide variety of base metals can be coated including those described in 2, above, all of the ferrous alloys, the nickel and cobalt-base alloys, the cupro-nickels and pure copper.

Refractory oxides

For many years the use of pure unbonded refractory oxides as coating materials was held back by the lack of suitable application methods and equipment. Recently, however, a number of successful techniques have been developed for applying these materials. The most important methods are flame spraying (for materials in rod or powder form), Flame-Plating, and solution ceramic techniques. These methods have been used to produce a wide range of refractory oxide coatings, including: aluminum oxide, zirconium oxide, zirconium silicate, aluminum silicate, titanium dioxide, iron titanate, cerium oxide and magnesium oxide. The properties of a number of these materials are summarized in the accompanying table. To date, the aluminum oxide, zirconium oxide and zirconium silicate coatings have proved to be the most successful.

Aluminum oxide (alumina)

Aluminum oxide coatings can be applied by all three of the methods mentioned above. The coatings are noted principally for their high resistance to wear and abrasion; however, they also provide good thermal insulation and high resistance to oxidation. Because of the low application temperatures involved during spraying, they can be applied to almost every ferrous and nonferrous metal as well as some plastics and other nonmetallic materials.

The excellent abrasion resistance of aluminum oxide coatings at room and elevated temperatures is largely due to their high macrohardness, which is equivalent to Rockwell C45. Despite the fact that the coatings are secured by a mechanical bond, adhesion and impact strength are reported to be quite good. A 1/16-in. thick sheet with a 0.010-in. coating can be bent 45 deg with no evidence of failure.

Aluminum oxide coatings are non-

PROPERTIES OF REFRACTORY OXIDE CERAMIC COATINGS[a]

Type	Aluminum Oxide	Zirconium Oxide	Zirconium Silicate	Aluminum Silicate	Titanium Dioxide	50% Iron Titanate; 50% Gamma Aluminum	Iron Titanate	Rare Earths (50% cerium oxide)
APPLICATION PROPERTIES								
Deposition Rate, sq ft/hr/10 mils	15-16	4-10	—	16	10	10	10	8
Thickness Range, mils	5-50[b]	5-50[c]	5-80	—	—	—	—	—
Finish After Polishing, μin. rms	2-50[d]	15-50[d]	30-90	52-77	6-43	36-38	7-52	32-48
THERMAL PROPERTIES								
Melting Point, F	3600-3700	4500-4800	3000	3700	3000	2500	2500	—
Coef of Ther Exp, 10^{-6} per °F	4.0-4.3[d]	5.4-6.4[d]	4.2	2.5	4	—	—	5
Ther Cond, Btu/hr/sq ft/°F/in.	19-20	7-8	15	25	46	—	—	30
Shock Resistance	Good	Very good	Good	—	—	—	—	—
OTHER PROPERTIES								
Dielectric Strength, v/mil	700	380[e]	Nonconductive	—	Conductive	Conductive	Conductive	—
Vickers Hardness (DPH, 25-gm load)	1400	400	1000 Knoop	650	1500	800	700	600
Porosity, %	8-12	8-12	8-12	—	—	—	—	—
Density, lb/cu in.	0.12	0.19	0.14	—	—	—	—	—

[a]Properties generally apply to flame sprayed coatings. Properties of solution coatings may differ somewhat.
[b]Thicknesses up to 0.125 in. can be produced for special applications.
[c]Thicknesses over 0.10 in. can be produced for special applications.
[d]Varies with method of application.
[e]Nonconductive at room temperature; conductivity increases rapidly above 2100 F.

ally used in thicknesses of 0.001 to 0.060 in. and occasionally in thicknesses up to 0.125 in. Surface finish is often an important factor, since the coatings are frequently used in bearing applications. The as-coated finish ranges upward from 125 μin. rms depending on the application method; however, finishes of 1 to 2 μin. rms after a fine diamond lap have been reported.

The coatings are very useful for high temperature applications since they do not oxidize or melt at temperatures up to 3600 F. Resistance to thermal shock is also excellent. The coatings have a coefficient of thermal expansion of 4.0-4.3 x 10^{-6} per °F over a temperature range of 100 to 2100 F. Thermal conductivity is about 19 Btu/hr/sq ft/°F/in. at 1000 F.

In general, the coatings are not attacked by common acid or salt solutions, by oxidizing or reducing atmospheres, or by many low temperature molten liquids. They are attacked by hydrofluoric acid and hot sodium hydroxide, and may be attacked by many molten salts and metal oxides. Porosity of flame sprayed coatings ranges from 8 to 12%, whereas porosity of Flame-Plated coatings is claimed to be less than 1%.

Because of their excellent combination of properties, aluminum oxide coatings can be used in a variety of applications requiring varying degrees of resistance to abrasion, heat or corrosion. Actual and potential applications include: seals operating under heat and in corrosive atmospheres, thrust bearings, pump plungers, aircraft and missile engine parts, and insulation for electronic components.

Zirconium oxide (zirconia)

In common with aluminum oxide, zirconium oxide coatings can be applied to almost all metals, as well as some nonmetallics. Because of their higher melting point (4500 F), zirconium oxide coatings are more widely used for high temperature applications; however, they are not as hard or as resistant to abrasion as aluminum oxide coatings.

Zirconia coatings are usually applied by flame spraying. They can also be applied by solution ceramic techniques, but to date this method of application has not been widely used. They cannot be applied by Flame-Plating. The coatings can be applied in thicknesses from 0.005 to 0.050 in., but are frequently used in a thickness of about 0.010 in. to obtain an adequate compromise of oxidation resistance, refractory properties and resistance to impact. Thicknesses over 0.010 in. can be applied for special applications.

As the table indicates, zirconium oxide has somewhat higher thermal expansion than other refractory oxide coatings. Thermal conductivity, however, is quite low—on the order of 5 Btu/hr/sq ft/°F/in. at 1000 to 2000 F. The coating is not electrically conductive at room temperature, but conductivity begins to increase rapidly above 2190 F. So far, the coatings have been used principally to protect high temperature missile and rocket parts against oxidation and corrosion and to provide thermal insulation.

Zirconium silicate

Zirconium silicate coatings are formed during flame spraying through the dissociation of zircon (in rod form) into zirconium oxide and silica. The final coating consists of 65% zirconium oxide and 34% silica.

Many of the properties of zirconium silicate coatings are similar to those of aluminum oxide coatings. Coatings are hard and adherent and can be used up to about 3000 F before the glass phase begins to soften. They have excellent corrosion resistance and are nonconductive.

Impregnated coatings

Quite often the impact and abrasion resistance of flame sprayed ceramic coatings can be improved by impregnation. Phenolics, furane, silicones, epoxy-base formulations, and a variety of other organic and inorganic impregnants have been successfully used. Phenolic and furane impregnants have proved particularly good because of their good physical properties. The heat-cured types of impregnants are preferred, but both catalyzed and air dried types have proved acceptable.

Most impregnants have been used with flame sprayed, powdered aluminum oxide coatings. Coatings impregnated with a baked or catalyzed phenolic have been used on fan blades to improve their resistance to severe abrasive conditions. Also, extra corrosion resistance to specific reagents can be supplied by impregnating the coatings with an appropriate sealer such as a microcrystalline wax. Solid lubricants such as molybdenum disulfide or graphite can also be added to improve friction properties and galling resistance.

Insulating coatings

In most applications refractory oxide ceramic coatings are simply applied over surfaces that have been sandblasted to promote mechanical bonding. However, recent research conducted for the Wright Air Development Center indicates that the useful range of some ceramic coatings may be considerably extended by using some type of reinforcing mechanism. Aluminum oxide and zirconium oxide coatings, as well as other ceramic coatings, have been applied to expanded steel mesh sections which are first seam welded to the base metal. Excellent insulating properties have been obtained, and the reinforced coatings have produced appreciable thermal drops at operating temperatures of 2000 to 3000 F.

In general, brush and spray application of the coatings has not been very successful; best results have been obtained by pressure rolling heavy-bodied, dough-like compositions. Much development work remains to be done on these coatings, and despite promising results it is difficult to say at this early stage if they will prove commercially acceptable.

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