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FLUORSPAR

carefully regulate the smelter to assure the presence of an oxidizing atmosphere. And, if a large amount of fluorspar is used, the amount of nitrate in the batch mix must be increased. Although some enamel compositions are said to require up to 11% fluorspar, the consensus is that amounts in excess of 3% lower acid resistance.

If the smelting operation is sufficiently intense to drive off the fluorine, then acid resistance will not be impaired, but experience has shown that this point is not always reached. The nature of the enamel, its viscosity and the amounts of boric oxide and other raw materials present also are important factors.

The fact that fluorspar lowers the fusion point of enamels more than does an equivalent amount of calcium carbonate indicates that it is either not completely decomposed or that the fluorine recombines in some form in which it can act as a flux. If the fluorine from the fluorspar is all driven out of the enamel, the compound resulting is probably not materially different from what is obtained when calcium carbonate is used as the source of lime. It also is important to note that the loss of silica from an ordinary enamel would be only about 3%, even if all of the fluorine were liberated as SiF_4, since an enamel seldom contains more than 8% fluorspar. While this would be a decided loss in silica, it would not be sufficient to make a substantial difference in fusibility or corrosion resistance.

Additions of 10% fluorspar to some enamels have been found to cause extreme crawling, which decreases as part of the fluorspar is replaced by cryolite. Fluorspar in cobalt ground coats makes the enamel more mobile and easy to work, but an excess causes a pimply surface. In cover-coat enamels, fluorspar seldom exceeds 5% of the batch because greater amounts impair color and tend to give a slightly pimply appearance. Fluorspar also has a negative effect on the color of enamels in which antimony oxide is the opacifier, imparting a bluish-green tint. This discoloration can be avoided by using antimony pentoxide (Sb_4O_5). The opacifying phase is $Ca_4F_2 \cdot Sb_4O_{13}$ (calciumfluorantimonate). When substituted for cryolite or sodium silicofluoride, fluorspar decreases the coefficient of thermal expansion and, therefore, should be a desirable addition in some glazes to diminish or prevent crazing.

The chief use of fluorspar in the glass industry is as an opacifier for opal glass. In this application, it is often used with a nearly-equal amount of feldspar. A sample composition has 20 lb each of fluorspar and feldspar per 100 lb of sand. With the introduction of a little cryolite and an increase in the amount of feldspar, less fluorspar is needed. The new mix: 20 lb feldspar, 10 lb fluorspar and 3 lb cryolite per 100 lb sand.

Smaller amounts of fluorspar, however, are often used in the manufacture of transparent glasses because of its beneficial fluxing action, its ability to aid glossiness and its activity as a decolorizer. Fluorspar also is valuable in optical glass batches because it has a low index of refraction and small dispersion. These same optical properties create a small demand for flawless transparent fluorspar crystals to correct color and spherical aberration errors in lenses for spectroscopes, microscopes and small telescopes. Generally, in the manufacture of glasses, as well as enamels, the fluorine content is kept as low as possible to reduce corrosion of refractories by silicon tetrafluoride gas. (Some authorities, however, question whether SiF_4 is a strong corrosive.)

Fluorspar has received scattered attention as a constituent in whiteware bodies and glazes, but has never been systematically evaluated in sufficient detail to permit fair appraisal of its possibilities. Fluorspar has been found to offer promise in glazes as a substitute for whiting, tending to promote more fusible glazes. During firing, fluorspar in contact with silica and clay is thought to dissociate into gaseous SiF_4, a fluoride of aluminum and calcium metasilicate. The volatile fluoride may in time promote destruction of kiln refractories, which dictates the necessity for ticularly where firing temperatures are pinholing also may be a problem if firing are not properly controlled. It is probable and other fluorine compounds have u ceramic glazes, but their successful ger tion will require the development of additional information relative to advantages and limitations. As much as 15% CaF_2 is used in one-fire textured glazes for floor tile.

As a whiteware body constituent fluorspar offers greatest promise as an auxiliary flux in promoting decreased porosity or lower firing temperatures. Amounts as low as 2.5% have been found effective in vitreous sanitaryware, semivitreous sanitaryware and electrical porcelain bodies. Apparently, fluorspar particle size is an important factor—coarser grades tend to promote pinholing.

FLUX. Any material that lowers the melting temperature of another material or mixture of materials. Fluxing substances may occur as natural impurities in a raw material. Thus, the alkali content of a clay will flux the clay. In other cases, fluxes are separate raw materials. Example: use of feldspar to flux a mixture of clays and flint.

An auxiliary flux is a third component that may make the primary flux more effective. Thus, addition of 2% dolomite, talc or fluorspar to a whiteware mixture that contains 25% feldspar will produce a substantial decrease in vitrification temperature. The auxiliary constituent may be incapable of producing the same result (or too expensive to use) as the sole flux.

Compounds of alkali metals (sodium, potassium and lithium) are popular fluxes for clay bodies. Compounds of alkaline-earth metals (calcium, magnesium and, to a lesser extent, barium and strontium) are common auxiliary fluxes. However, they also may be primary fluxes for such products as low-loss dielectrics. Lead and boron compounds are important fluxes for glasses, glazes and enamels. And premelted glasses or frits may be used to flux clay or other bodies.

The term flux also may be used to specify a low melting glass used in decorating glass products or an overglaze for clay ware. Pigments are mixed with the powdered glass flux and then applied to the object to produce a vitrifiable coating at temperatures <650°C. These glasses contain large quantities of lead oxide. A typical composition: 50% lead oxide, 36% silica, 10.8% boric oxide, 3.2% soda.

FORSTERITE. $2MgO \cdot SiO_2$. Synthetic-fused material typically containing 56% magnesia and 43% silica. Higher purity, fine-particle-size material used extensively in **electronic ceramic** formulations and **ceramic-metal seals** because its high CTE matches that of some metals. Higher purity materials require higher maturing temperatures.

FRIT. Mixture of inorganic substances fused together in a furnace and quenched rapidly by either a water bath or water-cooled metal rolls.

Frit is a complex combination of oxides. Its purpose is to render solubles and hazardous components insoluble by combining them with silica and other oxides.

The fritting is done either on a continuous basis by introducing raw batch into a properly heated furnace or on a batch basis in crucibles or a rotary furnace. Frit then is used in combination with clay and possibly other suspending agents to produce a coating material for whiteware, which is applied, dried and fired to produce the glassy deposit called a glaze.

Frit also is used with clay and electrolytes for coating steel, aluminum, cast iron and other metals. This coating—called porcelain enamel—is used on major household appliances, sanitaryware, cast iron and aluminum cookware and architectural panels.

The coating may be applied by wet spraying or dipping. Frit is wet milled with clay and electrolytes. Drying and firing follow application. Dry application of powdered frit to pretreated metal by electrostatic spraying also is possible. Frit is milled with organic components. The drying step is eliminated.

Use of frit is not only beneficial from the standpoint of stabilizing hazardous materials and controlling solubles, but it also helps develop a more uniform coating that generally fires at lower temperatures, all of which results in increased surface and color unifor-

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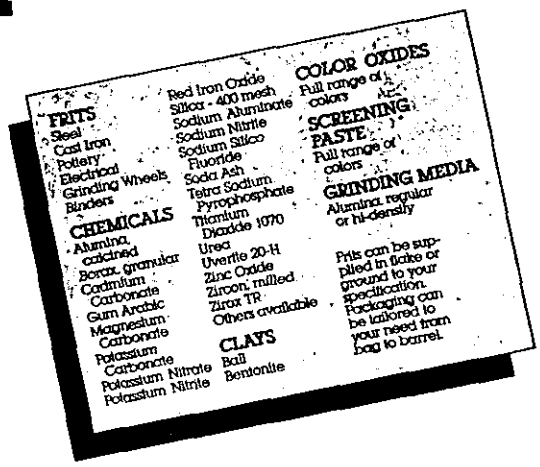

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mity and better process control.

Frit also may be used as a component for bonding grinding wheels, as a body flux to lower vitrification temperatures and as a flux for glass-decorating enamels. Frit can be used as a mold lubricant in continuous casting of steel, as a lubricant for metal extrusion, and as coatings for jet engine parts, rocket components, auto exhaust systems and solar heating panels. High-temperature paints and stabilizers for nuclear waste are other applications.

FUCHSINE DYE. An analine dye which, when dissolved in ethyl alcohol, may be used to test the porosity of wet-process electrical porcelain and other ceramic bodies. In dye-testing of wet-process insulators, a pressure of 60,000 lbf is commonly used.

The material also may be used as a dye for body identification prior to firing. As little as 0.01 to 0.2% is sufficient.

GADOLINIUM OXIDE. Gd_2O_3. Mol. wt. 362.5; density 7.41 g/cm^3. Cubic crystals soluble in acids, only slightly soluble in water. Gd_2O_3 undergoes a crystal inversion at ~1300°C. The oxide has seven stable isotopes ranging from 0.20-24.9%. Its major impurities are yttrium oxide and europium oxide.

A rare earth available in purities of 25-99.99%, Gd_2O_3 has the highest thermal neutron cross section of all the elements (46 × 10^{-25} m^2/atom), making it a candidate for nuclear control rods. Gd_2O_3 also forms garnets having useful ferromagnetic properties. Applications in addition to those in the nuclear field include dielectric ceramics, microwave garnets, bubble memory substrates (e.g. GGG) and as a special phosphor activator.

Pressed compacts of Gd_2O_3 containing about 2% terbium were sintered at 1500°C. Properties: density, 7.60 g/cm^3 (theoretical density = 7.64 g/cm^3); modulus of rupture, 2840 psi; modulus of elasticity, 18 × 10^6 psi; CTE (15-100°C), 10.5 × 10^{-6}/°C.

GALLIUM. Ga. Used in metallizing of ceramics.

GALLIUM ANTIMONIDE. GaSb. Mol. wt. 191.5; m.p. 705.9°C. Crystallizes in zinc blende structure, lattice constant 6.095 × 10^{-3}. Crystals are hard, brittle and of metallic appearance. Oxidizes readily in air at elevated temperatures. Prepared by melting together pure gallium and antimony under an inert or reducing atmosphere. Subsequent zone-refining is necessary for high purity. Single crystals are grown by melt-pulling.

GaSb is of interest as a semiconductor. Of the several Group III-Group V element compounds with semiconducting properties, GaSb's most closely approximate those of germanium. Its forbidden gap width, for example, is ~0.8 eV; germanium's is 0.75 eV. Both p-n junction and point-contact rectifiers have been prepared.

GALLIUM ARSENIDE. GaAs. Mol. wt. 144.6; m.p. 1240°C. Crystallizes in zinc blende structure. Prepared by melting together stoichiometric quantities of gallium and arsenic in a sealed ampoule to prevent loss of arsenic by volatilization. Purification by zone refining is also carried out in sealed ampoules. Fused silica containers have been successfully used. Single crystals may be grown by melt-pulling.

GaAs is of interest for microwave diodes and high-temperature rectifiers and transistors. Its relatively large energy-band gap of 1.34 eV and electron mobility of ~6500 cm^2/Vs at room temperature give this semiconductor advantages over both germanium and silicon. Positive-carrier mobility is ~650 cm^2/Vs. Uses have been found for GaAs as: photovoltaic devices; lasers operated by injection of minority carriers instead of by optical pumping; tunnel diodes for switches and oscillator amplifiers; power transistors and infrared-energy generators.

GALLIUM FERRIC OXIDE. $Ga_{2-x}Fe_xO_3$. Composition is variable, with x ranging between 0.7 and 1.4. When x = 1 ($GaFeO_3$), single crystals form which are rectangular, prismatic and transparent in thin sections. They're magnetic below ~260 K (-13°C), and are piezoelectric from room temperature down to that of liquid nitrogen (-195°C). It is possible to produce crystals that are both magnetic and piezoelectric at and above room temperature.

GALLIUM NITRIDE. GaN. Semiconductor—4.0 × 10^3 Ω·cm.

GALLIUM OXIDE. Ga_2O_3. Mol. wt. 187.44; density 6.44 g/cm^3; m.p. 1900°C. White powder insoluble in water but soluble in hot alkalis and acids.

GALLIUM PHOSPHIDE. GaP. Mol. wt. 100.7. Crystallizes in zinc blende structure, lattice constant 5.447 × 10^{-8}. Crystals are transparent with orange coloration. Prepared by melting gallium and phosphorus in a sealed silica tube and freezing slowly from one end.

GaP is of some interest as a semiconductor. Its energy gap is ~1.3 eV at room temperature; infrared absorption cut-off is ~0.5 µm.

GERMANIUM. Ge. At. wt. 72.6; m.p. 958.5°C; density 5.32 g/cm^3. Gray-white, brittle, metallic-appearing crystals with diamond structure. Germanium metal as well as germanium dioxide is produced in the United States, Belgium, France, Germany, the Soviet Union and the People's Republic of China. The metal is prepared by reduction of GeO_2 by hydrogen, or from certain ore residues by fractional distillation of $GeCl_4$, its volatile tetrachloride.

In addition to its use as the oxide (see GERMANIUM DIOXIDE), germanium itself is an important electronic material. Ultrahigh-purity metal, obtained by zone refining germanium reduced from high-purity oxide, is required. Impurity levels as low as 1 part in 10^{10} have been obtained. Single crystals are prepared by drawing from a melt which has been doped with the required elements.

As a semiconductor, germanium exhibits an energy gap of 0.75 eV and, in the case of highly perfect crystals, unusually long minority carrier lifetimes (up to 1 ms) and relatively high carrier mobilities. Its chief limitation is a low operating temperature—100°C max—imposed by the energy gap.

Germanium combines semiconduction, insulation and electroluminescence in a single material.

GERMANIUM DIOXIDE. GeO_2. Mol. wt. 104.6; sp. gr. 4.25 (commercial grade); m.p. 1115°C; slightly soluble in water. Another form has a sp. gr. of 6.2, m.p. of 1086°C and is insoluble in water, hydrofluoric acid and ammonium hydroxide, but is slightly soluble in a strong (5N) solution of NaOH at 100°C. Germanium dioxide (and germanium metal) is continuously produced in the United States, Belgium, France, Germany, the Soviet Union and the People's Republic of China.

At red heat, germanium metal will oxidize rapidly in air to GeO_2. Germanous oxide (GeO) also is known, and its color and physical characteristics depend upon the method of preparation. It may be formed by the controlled reduction of GeO_2 at elevated temperatures, by the hydrolysis of a dihalide or by the reduction of a germanic salt in solution.

GeO_2 may be used to replace silica in glass batches. It is capable of producing glasses of high refractive index. Fused GeO_2 has a refractive index of 1.607; that of fused silica is 1.4588.

GeO_2 may be very useful for such limited applications as microscope objectives. Other properties which it may impart to glass are greater dispersion, density and expansiveness; equivalent hardness; considerably lower fusion temperatures and higher transmissivity for infrared radiation. Germanium is especially important for military night sights. And its use in optical fibers continues to rise. The major application for high-purity material is a source of germanium crystals which are subsequently used for semiconductors. Germanium oxide complexes and solid solutions with good piezoelectric and ferroelectric properties are being investigated.

GERMANIUM NITRIDE. Ge_3N_4. Nonconductor—>108 Ω·cm.

GLASS BONDED MICA. (See GLASS-MICA COMPOSITE.)

GLASS ENAMEL. (Vitrifiable glass colors.) Fine-powder mixtures of low melting flux and calcined ceramic pigment, usually produced in a 9:1 flux: pigment ratio. The enamels may be mixed with suitable vehicles, applied to glass articles and fired to a smooth, hard enamel coating at temperatures below the deformation point of the ware. A glass enamel must have an expansion coefficient closely matching that of the base glass; a low enough fusion point to permit development of a good glass at a permissible temperature; and a sufficient degree of chemical resistance to materials to which the article may be exposed. The preparation of glass enamels has become a highly complex art.

Enamels are compounded for maximum acid, alkali and detergent resistance. Firing temperatures range from 1000-1250°F. Colors and transparent colors in satin etch, matte and full gloss finishes are available. Special enamels are offered for use on Pyrex and low-coefficient glass. Applications for glass enamels include: containers, dinnerware, drinking ware, lighting goods, building exterior and interior panels, chalk boards and signs.

GLASS-MICA COMPOSITE. (Glass-bonded mica.) Moldable and machinable ceramic material available in several grades for a variety of applications. Can be used at operating temperatures up to 1200°F (650°C), and some grades can withstand even higher temperatures. Each grade has its own combination of such properties as arc resistance, moldability and machinability. Dielectric constant range is 6.7-8.8 at 1 MHz. Glass-mica composites are made by bonding high-temperature glass frit with natural or synthetic mica.

These materials have an unusual combination of properties for high-temperature, high-frequency electrical and electronic applications. Dimensional stability, arc resistance, excellent dielectric properties, moldability with or without metallic inserts, lack of mold shrinkage and resistance to radiation effects are featured in addition to heat resistance. When made with natural muscovite mica, glass-mica composite will withstand temperatures up to 750°F (machining grades) and 650°F (molding grades). Glass-mica composite made with synthetic mica (a "ceramoplastic" material) can withstand continuous temperatures up to 1100°F (machined) and 1300°F (molded).

GLASS SAND. (See SILICA.)

GLAUBERS SALTS. (See SODIUM SULFATE.)

GLAZE STAINS. Prepared calcined ceramic pigments which, when mixed with a glaze before it is applied to the ware, give a uniform color throughout the glaze layer. Most glaze stains function as pigments. Some remain as precipitates, while others are dissolved in the fired glaze. Color range of glaze stains is very wide at lower fires. At cone 8 or higher, many glaze stains become unstable and the range of obtainable colors narrows.

GLAZES. Generally homogeneous, thin silicate mixtures fused on the surface of a clay body. They are glasses in their physical and chemical nature: hard, slightly or completely insoluble excepting in strong acids or bases, and impermeable to gases and liquids. Also like glasses they are not definite chemical compounds but instead are complex mixtures sometimes described as undercooled solutions because many of their properties are analogous to those of ordinary solutions.

Glazes usually are more or less lustrous, generally with a highly reflective or glossy surface. However, by dispersing selected crystals in the glaze, a matte finish can be produced. The surface of a matte glaze can be compared with the appearance of a glacé kid, and all gradations of glossiness or matteness may be observed.

Glazes may be colored, colorless, transparent, translucent or opaque. Regardless of its appearance, a glaze (or similar coating) is used to make clayware impermeable to liquids and gases and/or to provide decoration. Designing a glaze to "fit" a given body is a complex problem involving such variables as tempera-