NOTE ON CERTAIN CHARACTERISTICS OF PORCELAIN.¹

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Porcelains vary widely in their physical properties such as modulus of elasticity, coefficient of thermal expansion, heat conductivity and electrical resistance at different temperatures. It is not uncommon for instance, to find differences in the modulus of elasticity as far apart as 6,600,000 and 1,200,000. Again, the coefficient of thermal expansion is subject to decided variations for different porcelains as well as for the same material at different temperatures. With reference to the electrical conductivity, the values observed for different temperatures are subject to equally wide variations.

These facts are not at all surprising and are explained by the various stages of development represented by different porcelains. In practically all of them we have conditions far removed from such equilibria as we find in glasses depending upon the composition, the fineness of grinding and intimacy of blending, the rate and the ultimate temperature of firing, and finally the rate of cooling. As a result, the amounts of undissolved quartz or cristobalite, of glassy matrix, of undecomposed clay and of sillimanite fluctuate within wide variations. It is obviously of great importance whether the quartz content is high or low, whether it is comparatively coarse or fine, whether the percentage of feldspar is small or large or whether additional or different fluxes are introduced, and last but not least, what the temperature treatment has been. It is only through more refined and exact measurements that we may obtain a clear notion of the relation between the physical properties of porcelain and the several factors governing them.

In the low-fired porcelains—those fired to about cone 10—it is evident that the amount of undissolved quartz is comparatively large and that of sillimanite small. It is to be expected, therefore,

¹ By permission of the Director, Bureau of Standards.

that this product is subject, upon heating, to the changes in specific volume coincident with the transformations of quartz and cristobalite. It is not unlikely that some of this type of porcelain, when made into heavy pieces, is in a state of stress—due to its heterogeneous structure which has not been modified by high temperature treatment. It is to be expected, on the other hand, that the structure would gradually approach a more balanced, because more homogeneous, state, as higher firing temperatures, which cause far-reaching solution of the quartz and practically complete dissociation of the clay substance into sillimanite, are employed. The development of the latter mineral is desirable owing to its stability, being subject to no transformation changes, its density, 3.031, and its low coefficient of thermal expansion.

The undesirable characteristics of quartz in heavy porcelains are well understood by the manufacturers of sanitary ware who avoid its introduction as much as possible and insist upon the use of French flint—a partially amorphous modification of silica which inverts into cristobalite much more quickly and probably is also dissolved more readily by the fused feldspar. It is not unlikely that the objectionable property of “dunting” and its minor manifestations do not appear until the amount of quartz exceeds a certain value which has not yet been established. In the case of electrical porcelain subject to high tensions, it is more than likely that the permissible content of free quartz remaining in the porcelain is very much lower if maximum stability is desired. In advocating a high clay content for chemical porcelain subject to severe duty, E. T. Montgomery, therefore,¹ proceeds on sound principles and his conclusions deserve careful attention.

In the Pittsburgh laboratory of the Bureau of Standards a large series of porcelains have been made in which quartz has been replaced both by clay and by synthetic sillimanite. In both cases porcelains of excellent stability have been obtained as shown by the resistance of the bodies to sudden heating and cooling. Particularly was this the case by the use of the sillimanite which was prepared by grinding together 258 parts of kaolin, 102 of anhydrous alumina and 7.2 of boric acid, and heating the mix-

¹ *Trans. Am. Ceram. Soc.*, 18, 88-92 (1916).

ture to the softening temperature of cone 20. The calcined material consisted largely of sillimanite with a small amount of uncombined alumina. It was again ground and introduced in the body, replacing the flint. As a type, these porcelains, especially that in which 40 per cent of sillimanite calcine was used together with 40 per cent of clay and 20 per cent of flux, when fired to cone 16, not only showed excellent resistance to sudden heating and cooling but also high mechanical strength. At the same time the sillimanite increased the firing range of feldspar porcelain decidedly. By raising the amount of sillimanite to even larger proportions, porcelains of still more marked stability could be produced. Similar results were obtained through the introduction of other minerals not subject to molecular transformations, such as fused alumina, zirconium oxide, etc. The thermal expansion is decreased with the replacement of quartz by such constituents. The body obtained with the use of the zirconia seemed to be especially desirable for purposes where high mechanical strength was necessary.

It has been known for some time that the dielectric strength of porcelains is greatly reduced upon heating. Messrs. Henderson and Weimer¹ found that when heated from 24° to 275° C, a body fired to cone 9 showed a reduction in the puncturing voltage down to $\frac{1}{30}$ of the initial value. The same experience holds true also for the electrical resistance of vitrified bodies. In fact, the conductivity of such materials increases very rapidly with temperature—according to the law of compound interest at the rate of about 2 per cent per degree C. That this introduces an important factor in the case of porcelains exposed to higher temperatures, such as spark plugs, high tension insulators used in Cottrell process installations, etc., is obvious.

In order to secure information concerning the effect of composition upon these phenomena, a large number of porcelains were made and tested. The specimen used for this purpose was a cup of 60 mm. outside diameter, 65 mm. height and having a thickness of wall of 2.5 mm. The cup was placed in a suitable electrically heated furnace. Electrical contact was provided by

¹ *Trans. Am. Ceram. Soc.*, 13, 469-475 (1911); also Weimer and Dunn, *Ibid.*, 14, 280-292 (1912).

the use of molten solder on the inside of the cup and its immersion in a shallow metal bath on the outside.

Alternating current, 60 cycle, of 500 volts, was employed—since direct current gave rise to disturbing polarizing effects. The current passing through the porcelain was measured by means of a very sensitive milliammeter or a dynamometer wattmeter. The temperature was determined by means of two insulated thermocouples immersed in the molten solder of the inside of the cup.

The results of the resistance measurements were plotted as the $\log_{10} R$ against the temperature, in degrees C. The plots were approximately straight lines expressed by the relations

$$\log_{10} R = a - bt,$$

where R = resistance of the specimen, in ohms,

t = temperature in degrees C, and a and b are constants.

By computing a resistivity factor, based on the dimensions of the cup, it was possible to calculate the resistance per cubic centimeter of the porcelain. The criterion used in comparing the merits of each body was the temperature Te at which the material has the definite resistance of one megohm per centimeter cube.

The electrical measurements and computations were made in the electrical laboratory of the Bureau of Standards at Washington.

A characteristic curve for a feldspar porcelain is shown in the diagram of Fig. 1, for which the value $Te = 335^\circ \text{C}$. Upon studying the resistance curves of a number of porcelains it was soon apparent that the feldspar was the important factor in lowering the electrical resistance at these temperatures. Invariably, the higher the feldspar content the lower was the resistance and the value Te . By eliminating the feldspar and carrying the maturing temperature to a high point, say cones 18–20, bodies of good resistance at the temperatures involved were obtained. The same result was reached when the feldspar was replaced by synthetic silicates containing beryllium oxide, magnesia or other alkaline earths. Through the elimination of the feldspar it was found possible to reach a Te value as high as 800°C , which is quite satisfactory when one considers that fused quartz gave the result of 880°C .

FIG. 1.

It also appeared that with higher feldspar content the polarization phenomena became more prominent, indicating clearly that this constituent of porcelain plays a rôle of an electrolyte. It is evident, therefore, that for conditions where a high tension porcelain insulator is exposed to elevated temperatures it is neces-

sary to reduce the content of the feldspar and to replace it by some other flux.

For porcelains intended to be used under severe electrical and heat conditions, it would appear desirable, therefore, to eliminate both the quartz and the feldspar as constituents of the body in the manner suggested above.