SPECIAL SPARK-PLUG PORCELAINS.¹

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Requisite Properties of Porcelains for Spark Plugs.—The average commercial porcelain does not fulfill the conditions required for spark-plug service, nor for any other conditions where high-tension currents are employed and the temperature is considerably above atmospheric conditions. From the standpoint of the electrical resistance at the temperatures reached in airplane engines, the feldspathic porcelains begin to break down at a rate rapidly increasing with temperature, due to electrolytic effects. This is indicated also by the polarization which is observed in using direct current. The leakage thus taking place may become a serious factor.

The average porcelain is likewise not constant in volume and the volumetric changes are greater than can be explained solely by thermal expansion. Aside from the thermal expansion, the quartz content of porcelain, when heated or cooled, is subject to certain modifications in crystalline structure, accompanied by definite volume changes. Thus, the form of quartz permanent at atmospheric temperature, is alpha quartz which inverts to beta quartz at 570° C, a transformation which is reversed by cooling. On the other hand, if, in the firing of porcelain, the quartz is inverted to its high-temperature form, cristobalite, there is again the transformation of the alpha to the beta modification to be considered, which takes place at 230° C. In either case, volume changes are unavoidable in all porcelains containing free quartz in large amounts, due to the inversion noted. In a good spark-plug porcelain, the quartz should be eliminated from the composition and replaced by a substance not subject to these inversions.

Another defect of the ordinary porcelain is that the coefficient of thermal expansion is by no means constant at different tem

¹ By permission of the Director, Bureau of Standards.

peratures. It may be 19×10^{-6} between 30–200° C and 5×10^{-6} between 400–500° C.

With respect to mechanical strength, also, great variations are possible. A series of tests of commercial electrical porcelains, conducted at the Pittsburgh laboratory of the Bureau of Standards, showed variations in the modulus of elasticity of from 1,600,000 to 6,000,000.

Methods of Testing Spark-Plug Bodies.—For the purpose of studying porcelains from the standpoint of their electrical conductivity at the high temperatures obtained in airplane ignition systems, a large number of typical compositions were made up in the form of test cups of 60 mm. outside diameter and 65 mm. high, the thickness being 2.5 mm. These mixtures were usually prepared in 10 kg. batches, carefully weighed out and ground wet in porcelain-lined ball mills for three hours. The suspension of clay was pumped into a filter press to remove the water and then kneaded in a mixing machine to the consistency required for shaping the mass on the potters wheel. This was done by the use of plaster molds in which the cups were “jiggered” in the usual manner. The specimens were then dried, placed in saggers and burned in a down-draft kiln fired with natural gas to the finishing temperature. The latter was controlled both by means of thermocouples with the necessary galvanometers, and pyrometric cones. Each cup was examined for non-absorption by the application of ink. The testing of the specimens was done at the Washington laboratory. The characteristic expression for the resistivity of the porcelains is the “Te” value, which represents the temperature in degrees C at which a cubic centimeter of the material still shows a resistance of one megohm.¹

Replacement of Feldspar.—Upon comparing the “Te” value of the different porcelains it was noted that there exists no definite relation between the composition and the electrical conductivity. On the other hand, the higher the maturing temperatures of the porcelains, the higher was the “Te” value. This is practically equivalent to saying that, roughly speaking, the electrical resistance at higher temperatures is the greater, the lower the feldspar content, since small amounts of this flux make it neces-

¹ *J. Am. Ceram. Soc.*, 1, 700 (1918).

sary to carry the porcelain to a higher burning temperature. The relation, however, is not sharply defined, as may be observed from the results compiled in the following table:

TABLE 1.

No. of body.	Per cent feldspar.	Maturing temperature in cones.	"Te" value.
16.....	16	16	560
17.....	18	15	390
18.....	20	14	440
22.....	28	14 ($1/2$ over)	370
23.....	30	13	450

It is quite evident that the micro-structure of the porcelains is an important factor in this connection, since it cannot be immaterial how much kaolin or quartz has been dissolved by the fused feldspar and how much sillimanite has been formed. The evidence, however, was considered sufficient to warrant the replacement of the feldspars by other fluxes, the oxides of magnesium and beryllium being used for this purpose.

Owing to the evolution of carbon dioxide from magnesite and the artificially prepared basic magnesium carbonate during the firing process, and the very large shrinkage accompanying their use as a flux, it was decided to introduce the magnesia in the form of a calcine; that is, a silicate mixture previously fired to vitrification. The mixtures employed for this purpose corresponded to the formulas: $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ and $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. Of these, the first and the second were most used in this work. The preparation of the calcines consisted in dry ball-mill-grinding and firing the mixtures made up into balls with just sufficient water. After calcination, the material was crushed and ground and introduced into the bodies in this form. The beryllium oxide was brought in through the use of the mineral beryl (which has the general composition $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) without any previous heat treatment.

With the use of magnesia as the principal flux the electrical resistance, and hence the value "Te," was found to increase quite decidedly, though with no well defined regularity as referred to

percentage content of magnesia. It was seen again, in this connection, that the structure of the porcelain plays an important part especially as it is known that MgO accelerates the crystallization of sillimanite most vigorously. Not only the number but also the size of the sillimanite crystals is of significance in determining the texture of the body, whether it is to be fine-grained, glassy, or coarsely crystalline. The rate of cooling the porcelain is likewise of importance since a rapid drop in temperature invariably causes the structure to be closer and of more vitreous character than when a longer time is taken in cooling down the kiln. For this reason smaller kilns are to be preferred to larger ones since they permit of more rapid cooling. The effect of magnesia, added in the form of synthetic silicate, is strikingly shown by the high "Te" values of bodies Nos. 77 and 78 (see Table 4).

It is a fact that the magnesian silicates show electrolytic effects which are much less prominent than when feldspar is used as a flux. It likewise appears that the higher the firing temperature of the porcelain the greater its electrical resistance, at temperatures up to 700° C, or somewhat above this point.

With reference to the use of beryllium oxide, it was found that this flux behaves similarly to the magnesia in showing high electrical resistance and "Te" values. This is indicated by the following table:

TABLE 2.

No.	Per cent beryl.	Per cent clay.	Per cent flint.	Maturing temp. of porcelain in cones.	"Te" value.
193....	25	50	25	12	624
194.....	35	50	15	11	784
195.....	45	50	5	11	798

It is evident from these results that beryllium oxide, used in the form of the mineral beryl, is a valuable flux from the standpoint here under consideration. It requires, however, careful temperature control in firing, since the beryllium porcelain is subject to sudden deformation as the vitrification temperature is exceeded. The experiments have proven that beryllium oxide

is worthy of consideration for the production of such porcelain, and the high "Te" value obtained, 798, is exceedingly promising. The firing temperature of these bodies is quite low, from cones 11 to 12.

Another interesting fact was that the thermal expansion of the beryllium porcelain was found to be lower than that of the feldspathic bodies commonly employed. The average coefficient was found to be 1.63×10^{-6} for the temperature interval 26° to 200° C; 2.95×10^{-6} for 200° to 400° ; 3.60×10^{-6} for 400° to 570° ; and 2.33×10^{-6} for 26° to 400° .

Replacement of Quartz.—From a general study of porcelains, it appears desirable to eliminate the quartz, as has been pointed out in a previous paragraph. Some of the materials available for this purpose are calcined kaolin, synthetically prepared sillimanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), sintered or fused alumina, and zirconium oxide. These substances have been introduced in a number of compositions. The effect of adding calcined kaolin in general was beneficial; even with a feldspar content of 13.5 per cent (body No. 63) a fair "Te" value, 540, was obtained. This particular composition contained 50 per cent raw kaolin, 13.5 per cent feldspar, 1.5 per cent calcium carbonate, and 35 per cent calcined kaolin. The maturing temperature of this porcelain was that corresponding to cone 16. It is evident that by raising the content of calcined kaolin still more at the expense of the feldspar a higher "Te" value would be obtained. The introduction of plastic ball clay to replace kaolin, invariably and in all types of bodies, reduces the electrical resistance within the temperature range here under consideration.

The use of fused alumina in any extensive work was prohibited by the lack of material low in iron content. The commercial substance is unsuited for this purpose. The total amount of white, fused alumina available was not more than two pounds. To bring about the necessary impervious and dense structure the use of 17.6 per cent of feldspar was required. A mixture consisting of 45 per cent kaolin, 17.6 per cent feldspar, 4.4 per cent calcine No. 13, and 33 per cent fused alumina, resulted in a very tough porcelain which showed a "Te" value of 620. Cal-

cine No. 13 was compounded, according to the formula $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, from 84 parts, by weight, of magnesium carbonate, and 258 parts of plastic kaolin from Florida and Georgia. Here again the reduction of the feldspar content and its replacement by calcine No. 13, or beryl, or a combination of these two, would be certain to raise the "Te" value considerably and at the same time would result in a porcelain of excellent mechanical properties. The cost of the fused, white alumina would be quite high, but would be justified under the circumstances. Furthermore, a single calcine could be readily produced by combining the raw materials of calcine No. 13, the kaolin and magnesite, with uncalcined alumina from any convenient source, and firing the mixture to a point of constant volume, which could be accomplished at temperatures not exceeding cone 18. At the same time this procedure would simplify the process of preparation very considerably.

Sillimanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is a normal component of all hard-fired porcelains, and this constituent, if not present in the form of large crystals, imparts to the material constancy in volume upon heating, lowers the thermal expansion, and increases the refractoriness and the resistance to sudden heating and cooling. For this reason it was thought desirable to produce the mineral synthetically and to introduce it in the porcelain composition in place of the quartz. This was done by combining 70.2 per cent of plastic kaolin, 27.8 per cent anhydrous alumina, and 2 per cent boric acid. After grinding this mixture in the dry state in a ball mill, it was made up with water to form a plastic mass which was molded into balls which were calcined to a temperature corresponding to that of cone 20, or approximately 1530°C . At this temperature the mass sintered to a dense structure, subject to but little additional shrinkage and containing only a small amount of uncombined alumina. The boric acid was added to assist in bringing about the necessary shrinkage and closing up of the pores, and it is quite probable that most of this constituent is volatilized at the final temperature of calcination. This calcine (No. 19) was then crushed separately, passed over a magnetic separator and then ground together with the other materials of the body with the addition of water, in the ball mill. In preparing

this type of body the feldspar was eliminated, on the basis of the results discussed above, and replaced by a calcine corresponding to the formula $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ (No. 14). This porcelain (No. 152) was composed of 30 per cent kaolin, 10 per cent ball clay, 40 per cent sillimanite calcine and 20 per cent fluxing calcine No. 14, and fired to a temperature of cone 16 or higher. The resultant material had excellent electrical qualities and an average "Te" value of 690. The structure of this body should be fine and dense, a condition which requires quite rapid cooling of the kiln. Slower cooling results in the formation of coarser sillimanite crystals which produce a structure much less resistant to sudden heating and cooling.

The preparation of this body may be simplified by the combination of the two calcines into one. Thus, by employing the composition of flux No. 13 ($\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) the combined calcine would be composed of 75.10 per cent plastic kaolin, 8.77 magnesite, and 16.13 per cent anhydrous alumina. The boric acid content has been eliminated. Body No. 152 would then consist of 30 per cent kaolin, 10 per cent ball clay, and 60 per cent of the combined calcine. Wherever the working conditions permit, the ball clay should be eliminated, and an effort made to employ the body containing 40 per cent of plastic kaolin, which can usually be done by allowing the mixture to age before molding it.

The tendency of the body to crystallize may be diminished also, by replacing the fluxing calcine in part by beryl, so that these two components are present in the ratio of 1 to 1. If, then, the combined fluxing- and sillimanite-calcine is employed, the resultant composition would be: kaolin 60.94 per cent, anhydrous alumina 18.38 per cent, boric acid 1.32 per cent, magnesite 4.58 per cent, and beryl 14.78 per cent. The body, as before, would consist of 60 per cent of this calcine and 40 per cent of kaolin. The fusion point of this mixture is so low that it would be quite possible to eliminate the boric acid entirely. At the same time the vitrification point of the body is lower and closer to the normal kiln-temperatures.

Attention might be called to the fact that the use of a silicious porcelain is not objectionable from the electrical standpoint, but only from consideration of the mechanical strength, resistance

to sudden temperature changes, etc. This is shown by the results upon high silica porcelains, bodies Nos. 116 and 119, which show a very high "Te" value, namely 730. This type of porcelain contains 50 per cent clay, 30 per cent free quartz (flint) and 20 per cent magnesia calcine (Table 3). In No. 116, the calcine corresponds to the formula $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and in No. 119 to $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$. It is fair to state that these porcelains would give excellent results, considered from the dielectric standpoint, when used under conditions not so extreme with reference to temperature and shock—as is the case with spark plugs used in airplane engines.

Zirconium oxide was used only in two porcelains, due to the comparatively limited supply available. The material at hand was zircon which contained 52.74 per cent of ZrO_2 and 43.46 per cent of silica. As received, the mineral was high in iron, which, however, was eliminated by treatment with chlorine¹ at a temperature of 800° C. In this manner all but a trace of the iron was removed. Owing to the fact that these zircon porcelains were produced comparatively early in the work, feldspar was employed as the flux. The result was that the electrical resistance, and hence the "Te"

TABLE 3.

Body No.	Per cent clay.	Per cent quartz (flint.)	Per cent MgO-calcine.	Formula of MgO-calcine.	Sillimanite calcine, per cent.	Coefficient of thermal expansion $\times 10^{-6}$.			
						Degrees centigrade.			
						30–200°	200–400°	400–550°	30–400°
114	50	20	30	$\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	..	19.45	9.35	5.52	13.99
116	50	30	20	$\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	..	7.34	6.11	4.68	6.68
117	50	20	30	$\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	..	8.93	4.43	4.05	6.51
119	50	30	20	$\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	..	19.61	11.13	8.08	15.03
120	50	20	30	$\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	..	10.45	5.43	4.45	7.74
152	40	..	20	$\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	40	3.36	4.19	4.78	3.81

¹ A. J. Phillips, *J. Am. Ceram. Soc.*, 1, 791 (1918).

value, was low, being 500 and 450, respectively. With the use of the magnesia- or beryllium-fluxes much better products could undoubtedly be produced. The mechanical strength of these porcelains was excellent in every respect. The composition of these bodies, Nos. 72 and 73, is given in Table 4.

The effect of the quartz in porcelain upon the thermal expansion of the body is shown in the results compiled in Table 3.

TABLE 4.

Number of body.	16	17	18	22	23	24	28	32	35	36	39	40
	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.
Kaolin	45.00	45.00	45.00	45.00	45.00	50.00	50.00	55.00	55.00	55.00	55.00	60.00
Feldspar	16.00	18.00	20.00	28.00	30.00	16.00	24.00	14.50	20.50	22.50	28.50	16.00
Potters flint	39.00	37.00	35.00	27.00	25.00	34.00	26.00	29.00	23.00	21.00	15.00	24.00
Whiting- (CaCO ₃)	...	...	...	...	...	...	...	1.50	1.50	1.50	1.50	...
Ball clay	...	...	...	...	...	...	...	...	...	...	...	...
Calcined- kaolin	...	...	...	...	...	...	...	...	...	...	...	...
Calcine No. 3	...	...	...	...	...	...	...	...	...	...	...	...
Calcine No. 19	...	...	...	...	...	...	...	...	...	...	...	...
Calcine No. 20	...	...	...	...	...	...	...	...	...	...	...	...
Zircon	...	...	...	...	...	...	...	...	...	...	...	...
Maturing temperature in cones	16	15	14	14	13	15	14	14	12	12	12	13
"Te" value.	560	390	440	370	450	380	358	400	460	400	390	410

TABLE 4 (Continued).

47	48	49	50	55*	63	70	72	73	74	77	78	79
%.	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.
60.00	50.00	50.00	51.00	50.00	50.00	50.00	37.00	37.00	...	5.00	10.00	10.00
30.00	24.00	22.00	25.00	28.50	13.50	16.40	22.00	17.60	...	...	...	...
10.00	5.00	12.00	...	...	...	...	...	...	...	...	...	...
...	1.00	1.00	1.50	1.50	1.50	1.00	...	...	...	...	...	...
...	...	...	...	...	...	...	5.00	5.00	15.00	10.00	10.00	15.00
...	20.00	15.00	...	20.00	35.00	...	...	...	...	...	...	...
...	...	...	...	...	...	4.10	...	4.40	...	...	...	...
...	...	...	22.50	...	...	28.50	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	85.00	85.00	30.00	75.00
...	...	...	...	...	...	...	36.00	36.00	...	...	...	...
10	14	14	14	14	16	14	13	13	13	13	13	13
400	410	400	390	400	540	460	500	450	640	800	790	640

TABLE 5.

Number of body.	88 %	94 %	95 %	107 %	109 %	116 %	152 %	180 %	193 %	194 %	195 %
Kaolin.....	50.00	45.00	40.00	47.00	25.00	50.00	30.00	69.00	40.00	40.00	40.00
Feldspar.....	8.00	17.60		14.00							
Potters' flint....	30.00		42.00	21.00		30.00		5.75	25.00	15.00	5.00
Mag. carbonate				10.00				4.58			
Ball clay.....		 ⁴		8.00	20.00		10.00	9.15	10.00	10.00	10.00
Calcined kaolin					35.00						
Calcine No. 8a					20.00						
Calcine No. 13	12.00	4.40				20.00					
Calcine No. 14			18.00				20.00				
Calcine No. 19							40.00				
Calcine No. 20											
Calc. Al ₂ O ₃		33.00						11.52			
Beryl.....									25.00	35.00	45.00
Maturing tem- perature in concs.....	15	16	20	12	16	18	16	20	12	11	11
"Te" value....	590	620	630	480	610	730	690	640	624	784	798

TABLE 6.—COMPOSITIONS OF CALCINES.

Calcline number.	MgCO ₃ . %.	Kaolin %.	Flint %.	Calc. Al ₂ O ₃ . %.	Boric acid. %.	Calcination temp. (cones).
3.....	39.50	60.50	...	...	...	10
8a.....	14.40	44.30	41.30	...	...	12
13.....	23.85	76.15	...	...	...	12
14.....	18.20	56.00	25.80	...	...	13
19.....	...	70.20	...	27.80	2.00	20
20.....	34.30	...	65.70	...	...	16

It is at once evident from a comparison of these figures that the thermal expansion of these magnesia porcelains increases with the silica content of the body, and at the same time, is subject to decided variation within the temperature limits of 30–550° C. On the other hand, the porcelain in which the clay is lower, and all the quartz has been replaced by sillimanite, shows both the lowest thermal expansion and the least variation in the value of the coefficient. However, the composition is not the only determining factor and the importance of the micro-structure must be realized.

Summary.

The work, the results of which have been given, has been successful in showing: first, the injurious quality imparted to electrical porcelains by the use of feldspar as a flux; and second, in bringing out the desirability of replacing the quartz by minerals, or synthetically prepared materials, which are more constant in volume when heated. The remedial procedures advocated are, hence: (1) The replacement of feldspar by other fluxes, such as silicates of the type $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, or $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, or other silicates of beryllium and the alkaline earths, either natural or prepared artificially. (2) The elimination of quartz and the substitution of substances not subject to inversions or other volume changes. These may be highly calcined kaolin, alumina, zirconia or sillimanite, either natural or produced synthetically.

The compositions of the most typical porcelains produced in this work are compiled in Tables 4, 5 and 6, in which the "Te"

value is given for each body, so that these tabulations may be consulted for detailed information.

All of the electrical measurements as well as the determinations of the thermal expansions of the porcelains have been made in the Washington laboratories of the Bureau of Standards.

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