

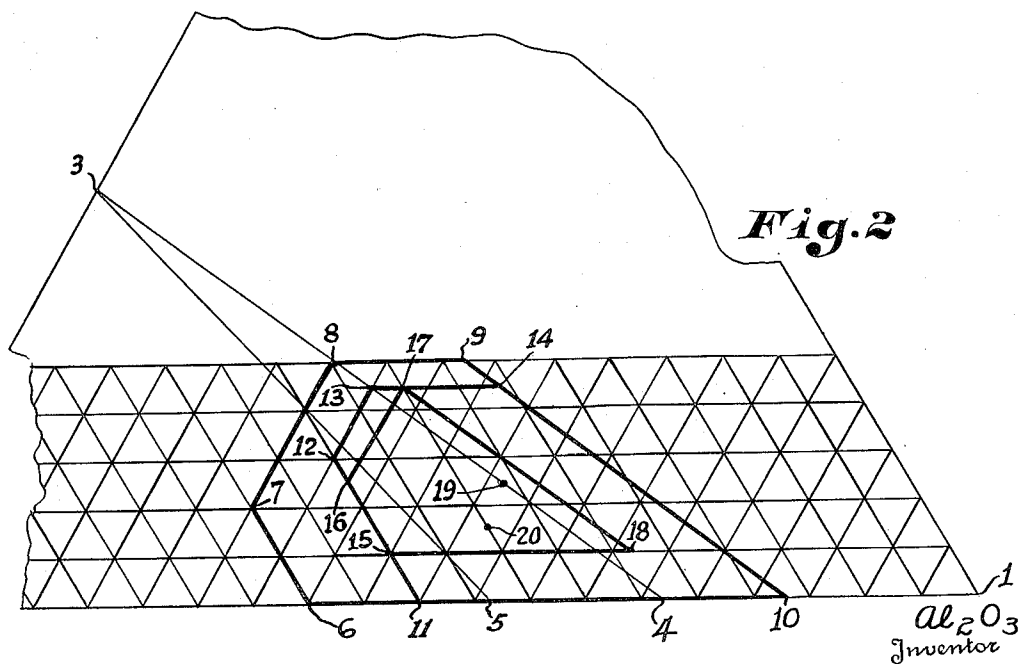
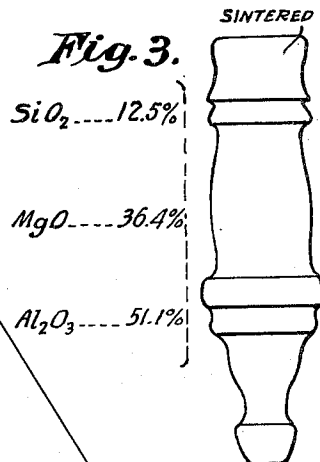
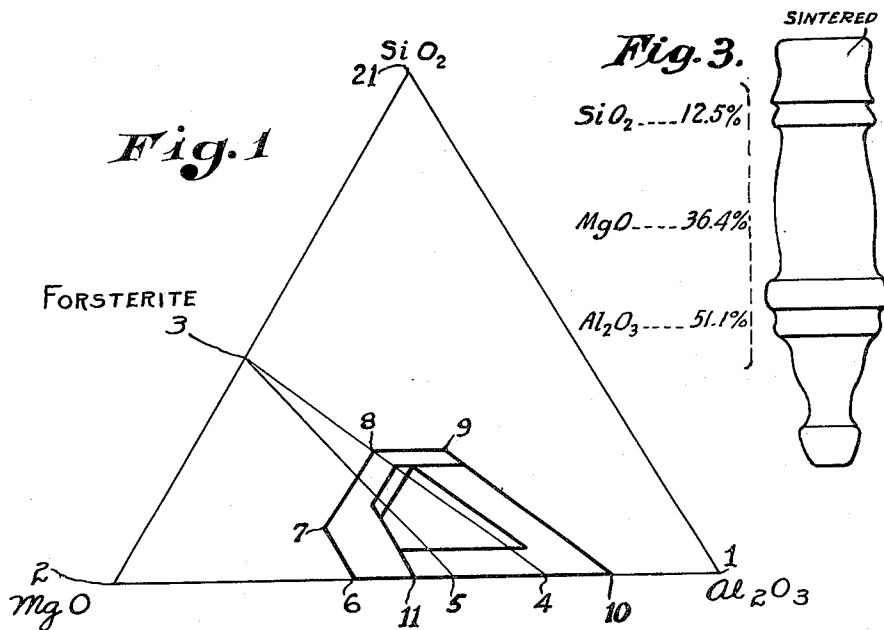
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ELECTRICAL INSULATOR AND METHOD OF MAKING THE SAME

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ELECTRICAL INSULATOR AND METHOD OF MAKING THE SAME

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This invention relates to electrical insulators and a method of making the same, and particularly to those insulators which are used in conjunction with electrical conductors and are subjected in use to high temperatures, sudden temperature changes and other exacting conditions, as is the case with spark plug cores.

The object of the invention is to provide an insulator of such a composition and with the ingredients so prepared and united, that the insulator has combined in it the various qualities desirable for spark plug cores and other insulators subjected to some or all of the trying conditions under which spark plug cores are used.

A spark plug core should be an electrical insulator at normal temperatures, and it should retain its insulating quality when heated by compressed and burning gases by which it is surrounded. It must have the mechanical strength to withstand the sudden variations in pressure and mechanical shocks to which it is subjected, and it must be able to withstand the heat shock of contact with suddenly flaming gases, even when the core itself is at the cold temperatures reached in winter. It should transmit heat sufficiently readily to prevent its inner end from becoming so hot as to cause preignition, and also as an aid in withstanding heat shock. Relatively good conductivity of heat and good electrical insulation, especially at high temperatures, are not qualities commonly found together. Also, the core must resist chemical or other corroding effects of the hot gases with which it comes in contact. Conductors generally have a higher coefficient of heat expansion than insulators, so that an unusually high coefficient of heat expansion (for an insulator) is desirable for a spark plug core in order that it may maintain close, non-leaking, contact with its central electrode and shell through widely and rapidly varying temperatures, and also in order to reduce the danger of splitting the core, due to the greater heat expansion of the central electrode.

It has been found that, when properly prepared, formed, and fired, mixtures or compounds containing certain proportions of magnesia and alumina, with a permissible addition of a limited amount of silica, form insulating bodies which combine many desirable qualities.

Details as to the desirable proportions of ingredients, and the manner in which the desirable qualities vary with the proportions, will be pointed out, and then the methods of preparing, compounding, shaping and firing the materials will be discussed, together with some of the effects of

the methods of preparation upon the desirable qualities.

In the accompanying drawing, Fig. 1 is a conventional chart of the three component system Al_2O_3 , MgO , SiO_2 , with the preferred portion of the field indicated thereon, while Fig. 2 is an enlargement of the preferred portion of the field indicated on Fig. 1—Fig. 3 is an elevation of a spark plug core with an indication of a preferred composition.

On Fig. 1, point 1 indicates 100% Al_2O_3 , point 2 indicates 100% MgO , and point 21 represents 100% SiO_2 .

It will be readily understood that any intermediate point on the boundary line indicates a mixture containing the two ingredients which the terminals of the lines indicate and in proportion in accordance with the distance between the point and the respective terminals. Accordingly point 3, which divides the line between points 21 and 2 in proportion of 57 to 43, represents a mixture of 57% MgO and 43% SiO_2 , the proportion in which MgO and SiO_2 combine to form forsterite ($2\text{MgO} \cdot \text{SiO}_2$). Point 4 indicates approximately 28% MgO and 72% Al_2O_3 , or the so-called spinel ratio corresponding to the compound $\text{MgO} \cdot \text{Al}_2\text{O}_3$, or MgAl_2O_4 . Likewise any point on the line 1—4 indicates a mixture of spinel and alumina and any point on the line 4—2 indicates a mixture of spinel and MgO . Point 5 indicates a proportion of 44 MgO to 56 of Al_2O_3 , which is found to be the eutectic proportion between spinel and periclase.

Any point within the boundary lines indicates a mixture of the three ingredients, the amounts of the several ingredients being proportional to the distances between the point and the several boundary lines, the amount of each ingredient being represented by the perpendicular distance of the point from that boundary line opposite the apex indicating 100% of that ingredient. For convenience, in the detail figure, intermediate reference lines parallel with the three boundary lines are drawn at such distances that the distance between each pair of parallel lines indicates 5% of the mixture.

Along the line from point 3, representing forsterite, to point 4, representing spinel, each point indicates a mixture of forsterite and spinel in proportions corresponding to the distances of the point from 4 and from 3, respectively, providing of course that the materials are combined so as to form the maximum theoretically possible amounts of forsterite and spinel.

Spark plug cores having many good qualities

may be made from mixtures or compounds of magnesia and alumina without any silica, but it is difficult to obtain and keep the materials free from silica, and moreover some silica renders the bodies easier to mature in firing. However, a magnesia-alumina body having too much silica therein has too narrow a sintering range. In other words, such bodies are difficult to fire in a ceramic kiln without either underfiring or over firing, i. e., being either porous or vesicular. For this reason, about 25% silica is the desirable limit, and this only if there is sufficient magnesia present to form forsterite with the silica.

It is deemed advisable to introduce not over 60% magnesia because uncombined magnesia is attacked by steam at high temperatures and pressures, and also seems to reduce the resistance of the body to heat shock as well as the mechanical strength and the firing range. It is best to have only about the amount of magnesia theoretically sufficient to form forsterite with all the silica present and/or spinel with all the alumina present. The difficulties from too much magnesia increase only slowly until the eutectic proportion of spinel-periclase is reached. In speaking of the eutectic mixture, the spinel-periclase eutectic is always understood.

At least 30% alumina is desirable because it produces high strength in the body; but alumina in excess of that sufficient to form spinel with magnesia tends to produce bodies which cease to be good insulators. Possibly this may be due in part to the soda which is almost always present as an impurity in commercial alumina, but whether this is the reason or not, alumina much in excess of the spinel ratio is not desirable from the standpoint of hot dielectric resistance. Alumina has a lower coefficient of thermal expansion than magnesia, but the effect of alumina on this property of the body and also upon the hot dielectric property varies only slowly in the field below and to the left of the line 3-4.

While, for reasons just given, it is preferred that the alumina shall not bring the body far to the right of the line 3-4, yet in cases where the desirability of strength, or other considerations, overbalance the decreased heat expansion and hot dielectric resistance, alumina may be added so as to constitute up to 40% of the entire body, in addition to the alumina theoretically sufficient to form spinel with all magnesia not required to form forsterite.

The degree to which the ingredients actually unite to form forsterite and spinel depends upon their preparation and heat treatment, but it is assumed, for convenience, in discussing proportions of the ingredients that magnesia unites with silica to form forsterite, while the remainder of magnesia forms spinel, with alumina or periclase left over, whichever is in excess of the spinel ratio.

Referring once more to the drawing, it will be understood from the above discussion that the desirable compositions of insulator bodies discussed above are limited along line 6 to 7 by the objection to more than 60% magnesia; along line 7 to 8 by the objection to less than 30% alumina; along line 8 to 9 by the objection to more than 25% silica, and along line 9 to 10 by the objection to more than 40% extra alumina.

Furthermore, a limitation along line 11 to 12 to 50% magnesia, which is but little beyond the eutectic proportion, along line 12 to 13 by as much as 35% alumina, and along 13 to 14 by not more than 22½% silica, limits the field to bodies gen-

erally preferable for insulating purposes. The best bodies for spark plug cores, when availability of ingredients and ease of manufacture are considered, along with the desirable qualities of the cores, are formed within the narrower field beginning with 5% silica at 15, including not more than 50% magnesia to 16, as much as 37% alumina to 17, and not more than 10% excess alumina to point 18.

Point 19, indicating 12.5% silica, 36.4% magnesia and 51.1% alumina, or 30% forsterite and 70% spinel, is a very desirable spark plug body, while point 20 indicates a body composed of about 7.5% silica, 40% magnesia and 52.5% alumina, corresponding to 17.5% forsterite, 73.1% spinel and 9.4% periclase. The qualities of these particular bodies will be pointed out in some detail later. All of the forsterite need not be present in the crystalline form but may appear as inclusions of glass.

The desired body may be obtained by using one or more natural minerals, or one or more synthetic compounds, or a combination of one or more natural minerals with one or more synthetic compounds, any of these or any combination of these being used in the batch in the raw, calcined, vitrified, or fused state. Mineralizers or accelerators may be added.

Materials that may be used

Magnesium oxide.—A number of different materials, either natural or synthetic, such as magnesite, or other magnesium carbonates; periclase; magnesium oxide; the hydrate of magnesia, either the artificial hydrate or mineral hydrate brucite; talc; serpentine; steatite and other magnesium compounds yielding the oxide or a silicate (when silica is required) on heating. Also minerals containing a combination of MgO and Al₂O₃ such as spinel, or a combination of MgO, Al₂O₃, and SiO₂ (magnesium aluminum silicate) such as rumpffite or other members of chlorite group from which the iron may be removed.

Alumina.—Alumina may be introduced by using bauxite, diaspore, corundum, and similar alumina bearing minerals, also artificially prepared or refined products such as concentrated bauxite ore, electrically fused alumina, etc. Minerals of the sillimanite group, clay and other aluminum silicates, either natural or synthetic, may be used in suitable proportions when silica is to be introduced into the body batch.

The degree of purity and the character of the impurities in the materials have a marked effect on the final product. Soda is particularly objectionable from the standpoint of current leakage at higher temperatures and should be avoided. Potash is also objectionable but to a lesser extent. On account of the extremely refractory character of the compounds formed within the field specified, it is not necessarily objectionable to use materials having suitable fluxes occurring in them as impurities, as these will assist in lowering the temperatures required for fabrication.

Silica is an impurity that is extremely difficult to exclude, and its presence is not necessarily objectionable unless extreme refractoriness is required and is frequently desirable for lowering working temperatures.

The melting point of the eutectic mixture of magnesia and alumina is 2030° C. ± 20°, while bodies within the described field and having a content of about 12½% silica melt at a temperature of around 1900° C. With about 22½%

silica the melting point drops to around 1800° C., or in the neighborhood of the melting point of mullite.

It should be understood that the mixtures need not be carried to the state of complete fusion but only to the sintering point which permits the desired reactions to be completed more slowly at a lower temperature and with a minimum degree of deformation.

Preparation of the body batch

The degree of fineness of the grinding of the raw materials depends upon the method of processing. If the ingredients are to be fused separately in an electric arc or other furnace, it is usually most satisfactory to crush them to small lumps, the largest being under about one inch. For calcines or fusions of mixtures of raw materials, the materials should be ground, proportioned, mixed, and ground together to preferably finer than 100 mesh. Wet grinding is preferable as the resulting filter cake can be handled easily either for fusion in the arc or for calcining in lumps in a kiln. If wet grinding is not practical on account of the solubility of some of the ingredients, dry grinding may be done or liquids of suitable character substituted for water.

The materials may be used in the raw state and the product formed from these. But when this is done, the reactions may cause excessive strains and shrinkages. Higher temperatures are also required, and in no instance is it permissible to carry the temperatures beyond the point where deformation of the product would be caused. Although the above process is entirely feasible, it is preferable to complete most or all of the chemical and physical reactions by pre-calcining, sintering, or melting the ingredients. The advantages are several. The final forming of the product can be brought about at lower temperatures with lower shrinkages and fewer strains.

A more complete combination is made possible in many instances through the use of higher temperatures, and then crushing the resulting products, grinding them, forming them into desired shapes, and sintering them at lower temperatures.

In some instances it is desirable to recrystallize the grains in the final product. This can be accomplished by the above process when the ingredients are of a suitable nature and the thermal reactions properly carried on.

When the three ingredients, magnesia, alumina and silica, in proportions within the range above indicated as preferred, are heated together to substantial equilibrium, the aforementioned assumption that magnesia and silica form forsterite, magnesia and alumina form spinel, and any excess of magnesia is left as periclase, is substantially correct. Forsterite has a melting point of 1890° C. $\pm 20^\circ$. Spinel fuses at 2135° C. $\pm 20^\circ$, and increase of magnesia decreases the melting point until the eutectic ratio is reached with a melting point of 2030° $\pm 20^\circ$ C.

It is not necessary that the reactions be carried to complete equilibrium, but it is preferred that such a state shall be approached, as it improves the quality of the body, in particular its resistance to heat shock.

The following are some examples of methods by which I have successfully prepared the body batch, and from it fabricated the finished product:

Batch composition

- (1) Artificial MgCO_3 + artificially prepared fused Al_2O_3
- (2) Artificial MgCO_3 + artificially prepared calcined Al_2O_3
- (3) Natural magnesite + artificially prepared calcined Al_2O_3
- (4) Fused magnesite + artificially prepared calcined Al_2O_3
- (5) Fused MgO + artificially prepared calcined Al_2O_3
- (6) Fused MgO + artificially prepared fused Al_2O_3
- (7) Fused magnesite + artificially prepared calcined Al_2O_3
- (8) Fused MgO + artificially prepared fused Al_2O_3 + flint

The above combinations are intimately mixed and wet ground with water in a ball mill for eighteen hours which will reduce substantially all of the material to at least 325 mesh, or they are ground for a shorter period if the above degree of fineness is not required, then filter-pressed to remove the major part of the water and subsequently dried until they are practically moisture free.

The dried cake is then sintered together in any suitable type of kiln or furnace such as a potter's periodic kiln or continuous kiln either car tunnel or rotary; or, if desired, actually fused in an electric arc furnace such as commonly used in the fusion of alumina, periclase and the like.

If, for example, combinations No. 1 and 6 compounded in the proportions of 1 MgO , 1 Al_2O_3 , are calcined they will require a temperature equivalent to cone 32 down to bring about the necessary reactions. The time required, gas quality for burning, etc., can readily be determined by those skilled in the ceramic art. A combination of 30% MgO , 15% SiO_2 , 55% Al_2O_3 , will require about cone 20.

Most of the calcines low in silica require at least cone 32 for satisfactory calcining.

For actual fusions in the electric arc much higher temperatures are required and easily obtainable.

Fabrication of the final product

This may be accomplished by several methods.

It is first necessary to crush and grind the calcined or fused compounds to the desired grain size, preferably 325 mesh and finer. If the several ingredients used are mixed together before grinding no additional mixing is required. If the ingredients are ground separately, it is necessary to mix them thoroughly. This is most easily done by placing them together in a suitable pebble mill and running it for a short time.

The final forming may be done by several methods well known in the art, such as casting in plaster molds, dust pressing in metal molds, jiggering, extruding, or extruding and turning, etc. On account of the extremely "short" or nonplastic nature of the final product, organic compounds, electrolytes and/or plasticizers may be necessary. It may also be desirable to fuse the constituents in an electric arc furnace and to form products by pouring into suitable molds, chilling and/or annealing.

My preferred method of forming differs in certain respects from the above mentioned methods. I prepare the grain or dust by mixing it with about one percent by weight of dextrine, or other binder, and from 4 to 6% water. The mixing must be carried on long enough to secure a thorough distribution of the moisture and binder.

This can also be accomplished in a somewhat better manner by making a slip of the grain or dust and binder by the addition of enough water or other liquid to form a suspension which can be poured. This is run through a spray dryer and dried to a suitable moisture content for dry forming. In this process the dried particles are spherical and sufficiently hard enough so they will easily run or pour and hence be ideal for filling a mold cavity in a uniform manner.

If more convenient, the thoroughly mixed ingredients may be filter-pressed and dried, and the filter cake may be ground to form dust.

The dust, formed by either of the two or similar processes, is then formed to the desired shape in a flexible mold under a high hydraulic pressure such as from 3 to 7 or 8 thousand pounds pressure per square inch. This may be the final form or a semi-finished form. If semi-finished, the final form is made by turning or other suitable process. Drying is usually necessary after forming and prior to final finishing, if the latter is done.

The formed piece is fired to a suitable temperature to bring about the desired properties in the final product. The piece may be glazed, or not, as desired. The glaze may be applied prior to firing or prior to a second firing at another temperature, as seems best. Special glazes are required for bodies of this character.

It is preferable to fire the bodies so that they will approach equilibrium, as this tends to develop resistance to heat shock. If the materials have been previously prepared so as to develop approximately the maximum amounts of forsterite and spinel, the final firing may be shortened, but where the preparation has not brought the materials so nearly to equilibrium, it is preferable to fire the bodies for a prolonged time in the lower portion of the firing range rather than firing them more quickly at a higher temperature. The firing may be varied so as to control the degree of crystallization of the final product.

A body with a composition indicated as at point 19 and prepared in accordance with the foregoing description has a specific gravity over 3, as compared with ordinary spark plug porcelains which are materially under 3. Such a body has satisfactory mechanical strength and resistance to heat shock, and has a higher thermal conductivity, is a better electrical insulator at high temperature, and has approximately twice as great a coefficient of thermal expansion as the widely used spark plug porcelains containing considerable mullite.

A body with approximately the composition indicated at point 20 has a still higher coefficient of thermal expansion and retains its electrical insulating quality at a higher temperature, but it does not have as great mechanical strength or resistance to heat shock as body 19 and matures at a higher temperature.

In general, those compositions are preferred which have 5% or more of silica, sufficient magnesia to form forsterite with it, as well as having enough remaining magnesia to combine with the alumina, in the range between the spinel and the spinel-magnesia eutectic, since they combine ease of preparation with a combination of qualities suitable for spark plugs. Wider variations may

be made in the composition, but such wider variations are accompanied by difficulty in manufacture or lessening of some quality desirable in spark plug cores. Nevertheless, bodies within the wider range of compositions indicated in Fig. 2 constitute improvements over spark plug cores now in general use, and for other insulators requiring some but not all of the characteristics of spark plug cores, some of the marginal bodies may be even preferable.

What I claim is:

1. A fine grained vitreous electric insulator consisting essentially of the following constituents fired together: not over 25% silica, at least 30% alumina, and magnesia not over 60% and at least enough to form forsterite with all silica present and to form spinel with any excess of alumina over 40%.

2. An electric insulator in accordance with claim 1, and in which the magnesia is not over 50%.

3. An electric insulator in accordance with claim 1, and in which the alumina is at least 35%.

4. An electric insulator in accordance with claim 1, and in which the alumina is at least 37.5%.

5. An electric insulator in accordance with claim 1, and in which the silica is at least 5%.

6. An electric insulator in accordance with claim 1, and in which the silica is not over 22.5%.

7. An electric insulator in accordance with claim 1, and in which there is not over 10% more alumina than enough to form spinel with the magnesia in excess of the amount necessary to form forsterite with all the silica present.

8. A sintered, fine grained, vitreous electric insulator formed by firing together magnesia, alumina and silica within the following proportions: between 5% and 22.5% silica, at least 37.5% alumina, and magnesia not over 50% and at least enough to form forsterite with all silica present and spinel with all but 10% of the alumina present.

9. A sintered, fine grained, vitreous electric insulator formed by firing together materials in the following proportions: not over 25% silica, magnesia enough to form forsterite with all silica present, and the balance of the mixture composed of magnesia and alumina in proportions from the spinel proportion to the eutectic proportion, inclusive.

10. A spark plug core consisting essentially of fine grains of the following constituents fired together to substantial equilibrium: not over 25% silica, at least 30% alumina, and magnesia not over 60%, and at least enough to form forsterite with all silica present and to form spinel with any excess of alumina over 40%.

11. The method of forming an electric insulator which consists in preparing a fine grained mixture composed essentially of the following ingredients: not over 25% silica, at least 30% alumina, and magnesia not over 60% and at least enough to form forsterite with all silica present and spinel with any excess alumina over 40%, forming the mixture into insulators, and firing until approximate equilibrium is established.

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