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METHOD OF MAKING FIRED VITREOUS PRODUCT

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The discovery and invention relate in general to compositions of matter for vitreous products and the like, and for vitrifiable bodies and the like, and methods of making the same.

The discovery and invention particularly relate to substances requiring high temperatures for vitrification, and more particularly to compositions of matter including aluminum oxide, and this application is a division of my application, Serial No. 456,414, filed August 27, 1942 now Patent No. 2,413,441, Dec. 31, 1946.

Products made by vitrifying or firing at high temperatures body compositions having as their principal constituent aluminum oxide are used as spark plug insulators, particularly for aircraft engines, wear resistant and similar parts having extreme hardness, and for other purposes.

Spark plug insulators adapted for use in a high compression internal combustion engine such as an aircraft engine or motor become increasingly difficult to produce, the higher the compression of the engine, and the tendency is always to increase the compression of an aircraft engine whenever possible.

Mica has been used for the insulators of aircraft engine spark plugs, but most mica having the required special mineral and physical properties must be imported into the United States, the forming and machining of mica insulators is relatively costly, and the quality of mica insulators is not always satisfactory.

Mica being a natural mineral and containing a varying amount of chemically combined water of crystallization in its composition, tends to decompose when heated giving up its water of crystallization and deteriorating in crystalline form to that of an anhydrous powder, and thus deteriorates rapidly from its initial characteristics when used as a spark plug insulator in a high compression engine.

With the development of higher compression motors, mica becomes increasingly unsatisfactory as an insulator for the spark plugs for the motors, and other substances have been used including ordinary porcelain and mullite porcelain.

Ordinary porcelain, such as a composition of feldspar, pure clay, and flint fired to a temperature of 2300° to 2500° F., constitutes a superior form of burned clay product, but for spark plug insulator use has relatively poor resistance to the thermal shock imposed upon the spark plug insulators of a high compression motor.

Furthermore ordinary porcelain has a low dielectric strength, particularly when hot, and is in fact an electrical conductor when hot. Ordinary

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porcelain also has insufficient thermal conductivity for use as a satisfactory aircraft engine spark plug insulator, and furthermore is subject to attack by the lead compounds present in the combustion gases of high octane tetra ethyl lead gasolines.

Mullite porcelains, composed chiefly of clay and silica minerals, such as sillimanite, fired together at a temperature of approximately 2700° F., develop into strong crystalline structures having improved mechanical strength and improved hot dielectric strength as compared to ordinary porcelains, but still lacking sufficient thermal conductivity and chemical stability necessary for use as spark plug insulators in high compression aircraft motors.

It has been determined to be desirable for use as spark plug insulators in high compression aircraft motors to provide a fired composition of matter having the greatest attainable combination of the following properties:

1. Vitreousness to a high degree and extremely low porosity;
2. Hot dielectric strength in excess of 100 meg-ohms at 1000° F.;
3. Resistance to thermal shock so as not to be subject to fracture when quenched in water at room temperature from a temperature of 400° F.;
4. Mechanical strength greater than 100,000 lbs. per sq. in. in compression;
5. Thermal expansion of 7.00×10^{-6} ;
6. High thermal conductivity;
7. Hardness and resistance to wear such that the hardness is 9 or over on Mohs' scale;
8. Inert with common acids at normal temperatures, that is not subject to appreciable loss in hot or cold HCl, H₂SO₄, HNO₃, or H₃PO₄;
9. Resistant to corrosion in molten lead oxide;
10. Absorptive of radiant energy.

Pure aluminum oxide has been found to attain a combination of the above properties satisfactory for use in the vitrified state as insulators for aircraft engine spark plugs.

The commercial production of vitrified articles from pure aluminum oxide, or alumina, has not been found practicable because of the extremely high temperatures required to bring about the condensation of a pure alumina body to the point of complete vitreousness free from porosity, and because the lack of plasticity of pure alumina renders its formation as a body into any particular shape such as that of an insulator very difficult.

By the present discovery and invention, it has been found that the presence of a very small

amount of substantially any other inorganic substance in a body otherwise including substantially all alumina will produce a pronounced depression in the temperature necessary for the vitrification of the body composition, and will improve the forming adaptability.

It has further been discovered that a combination of a relatively great variety of other substances to a total of a very small amount in a body, the remainder of which is substantially all alumina, has a more pronounced effect in depressing the vitrification temperature than when only one or two other substances with alumina are used for the body.

It has further been discovered that by using a combination of four or more other substances with alumina in the body, that the total amount of the added substances can be kept very low in proportion to the alumina and that in this way the properties of the body and the fired product are predominantly those of alumina, and stability is attained in the production of the fired products without the sacrifice of any substantial amount of the desired properties of the major ingredient alumina.

Plotting the effects of the various added substances on a phase rule diagram reveals a levelling off of the effects through the combination of the various added ingredients, so that instead of sharp changes affecting the combination, the changes are more gradual and the firing range of the combination is greatly extended and stabilized.

Furthermore, the addition of a relatively great variety of substances to the predominant alumina provides a factor of safety against the variations that normally exist in the commercial forms of the substances, so that a more stable and dependable body is obtained through the use in the body composition of a wide variety of substances added to the alumina.

Also it has been discovered that regardless of the specified substance added to the alumina, if added in minute amount, the effect on the alumina will be about in the same degree. The alumina in the resultant mixture or body is overwhelmingly the predominant material, and the resultant body has substantially the properties of that of pure alumina.

In attaining a combination of the highest degree of the above enumerated properties for a fired composition of matter for use as aircraft engine spark plug insulators, it has been found preferable to use body combinations of aluminum oxide with the addition of chromium oxide in a minor quantity plus the addition of small quantities of other inorganic substances preferably the oxides of the other metals.

In particular the chromium oxide produces in the fired article a strong pink or rose color at room temperature. Without the chromium oxide the fired articles are white in color. The strong pink or rose color produced in the fired article by the chromium oxide changes when hot, as when the article is in use as an insulator in an aircraft engine spark plug, to black which imparts to the insulator the property of greater heat absorption by the absorption of radiant heat from the gases of combustion in the engine cylinder, the radiant heat being otherwise reflected by white or coated bodies.

To the predominant alumina, the chromium oxide is added and small quantities of other substances selected from a wide variety of metallic oxides and compounds.

The total amount of the added substances should preferably not exceed 8% of the total composition, the remaining 92% being alumina. It is preferable that the total number of added substances be more than three.

All the added substances are selected from the following metals in their oxide or other compound forms:

Aluminum	Mercury
Antimony	Molybdenum
Arsenic	Nickel
Barium	Osmium
Beryllium	Platinum
Bismuth	Potassium
Boron	Praseodymium
Cadmium	Rubidium
Caesium	Scandium
Calcium	Selenium
Cerium	Silicon
Chromium	Silver
Cobalt	Sodium
Columbium	Strontium
Copper	Tantalum
Dysprosium	Thallium
Gallium	Thorium
Germanium	Tin
Gold	Titanium
Indium	Tungsten
Iridium	Tellurium
Iron	Uranium
Lanthanum	Vanadium
Lead	Yttrium
Lithium	Zinc
Magnesium	Zirconium
Manganese	

The above metals are included in groups 1—2—3—4—5—6—7—8 of the periodic table of elements of matter.

While it has been found that the presence of the alkalis of group 1 of the periodic table of elements, particularly sodium and potassium, are deleterious to the fired composition in causing a reduction in hot dielectric strength, it is a practical impossibility to avoid traces to measurable amounts of these substances in the body.

Furthermore, it has been found that a proportion of these alkalis not in excess of .05% does not sufficiently deteriorate the body dielectrically to cause any seriously harmful results, and that their presence in combination with other substances, particularly the alkaline earths of group 2 of the periodic table of elements and boron, develops low fusion combinations and intensifies the fluxing action of the mass. Therefore allowance for the presence of these alkaline substances is made in the particular body compositions of the present discovery and invention.

The alumina in the body composition or mixture should be in excess of 92% and preferably in excess of 95%. It has been found impractical from a firing standpoint to vitrify mixtures much in excess of 95% alumina. However the properties of the product are much improved as the alumina is increased, and laboratory products have been made at temperatures of 3400° F. in which compositions as high as 98% of alumina were vitrified, yielding an excellent product, but impractical to produce in commercial practice at present because of the exceedingly high temperature required.

The alumina is preferably in excess of 99% Al_2O_3 and as stated free from alkalis in excess of .05% and also free from silica in excess of .05%.

The silica content of the body is minimized by

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avoiding silica contamination in the processing, and by using silicates as little as possible in the body composition. Where calcium, magnesium, chromium, beryllium, and barium are used in the body composition, the forms of these substances may be in the compounds including fluorides, carbonates, oxides, phosphates, sulphates, etc., to avoid the silicates. All the added substances should be preferably in the dehydrated form, and free from the alkalis, lithium, sodium, and potassium.

However, by the introduction of fluorides into the body composition, silicates of the metals, such as magnesium in the form of talc may be used to a limited extent without harmful results from subsequent silica contamination, because the fluorine set free by the reaction resulting from the firing of the body composition combines with the silica to form gaseous silicon tetrafluoride which escapes and constitutes a volatilization of the silicon.

Describing one particular composition of matter or body composition I of the discovery and invention and the method of making the same, the principal ingredient of the body composition is calcined aluminum oxide, which before use in the compounding of the body is highly refined and freed of soluble impurities by lixiviation after being ground to a sub-microscopic grain size.

To 92 parts by weight of this purified and finely ground alumina Al_2O_3 is added and thoroughly mixed $1\frac{1}{2}$ parts of calcium fluoride CaF_2 and $1\frac{1}{2}$ parts magnesium phosphate $Mg_3(PO_4)_2 \cdot 4H_2O$, 4 parts of plastic ball clay $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and 1 part of chromic oxide Cr_2O_3 .

In the grinding of the alumina to sub-microscopic grain size quartz stones are generally used as grinding media, and in the grinding the abrasiveness of the calcined alumina on the quartz grinding stones causes about $1\frac{1}{2}$ to 2% of silica to be ground into the alumina so that the alumina after grinding has a composition of 98 to 98 $\frac{1}{2}$ % Al_2O_3 and $1\frac{1}{2}$ to 2% SiO_2 .

In the preferred manner of grinding the alumina for the bodies of the present invention, a rubber lined mill is used, and the grinding balls are formed of fired alumina, thereby avoiding the pick-up of silica in the ground alumina.

It has further been discovered that the initial calcination of the fluxing ingredients alone or in combination with part or all of the alumina is desirable before the final body is formed and the final firing effected.

Eutectics are formed between alumina and a combination of various other substances. However the formation of these eutectics requires initially a very high temperature, at which point the firing range of the mixture is very short due to the sudden depression of the melting point at the temperature of the formation of the eutectics.

When however the mixture is fused or calcined and then ground and re-formed, as the final body composition, upon the second heating, the sintering point is reached at a much lower temperature because of the previously formed eutectics.

A combination of many ingredients yields a superior result than when only few are used, since the eutectics formed between alumina and a wide variety of substances in combination provides a wide range of temperature over which the various eutectics are active, whereas with a lesser number, the range is correspondingly shorter.

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The above described body composition I after the second firing to a temperature of over 3000° F., produces a fired product consisting of aluminum in excess of 92%, and the oxides of the added metals, silicon, calcium, chromium, and magnesium, the fired product having desired properties as set forth herein for use as an aircraft spark plug insulator, and other purposes.

Examples of other body compositions, made according to the present discovery and invention, and processed as set forth herein to produce the improved fired product including alumina and other metallic oxides, are as follows:

Body composition II

	Per cent
Alumina, aluminum oxide	92.25
Talc, magnesium silicate	1.25
Fluorspar, calcium fluoride	2.00
Clay, aluminum silicate	3.50
Chromium oxide	1.00
	100.00

Body composition III

	Per cent
Alumina, aluminum oxide	91.68
Talc, magnesium silicate	1.25
Whiting, calcium carbonate	2.57
Clay, aluminum silicate	3.50
Chromium oxide	1.00
	100.00

Body composition IV

	Per cent
Alumina, aluminum oxide	92.04
Talc, magnesium silicate	1.25
Barium carbonate	0.89
Whiting, calcium carbonate	0.44
Clay, aluminum silicate	3.50
Chromium oxide	1.00
Beryllium silicate	0.88
	100.00

The embodiments of the compositions of matter and the method steps of making the same described herein are by way of example, and the scope of the present discovery and invention is not limited to the same or to the particular details thereof, but is commensurate with any and all novel subject matter contained herein which may at any time properly under the United States patent laws be set forth in the claims hereof or originating herein, and the elements of any such claims are intended to include their reasonable equivalents.

I claim:

1. The method of making a fired vitreous product from a body including upwards of 92 per cent by weight of calcined alumina, which includes lixiviating the calcined alumina, making a mixture of the alumina and more than three other metallic compounds, forming the mixture, and firing the formed mixture to vitrification, and thus producing a fired product consisting of aluminum oxide of upwards of 92 per cent and oxides of the added metals.

2. The method of making a fired vitreous product from a body including upwards of 92 per cent by weight of calcined alumina, which includes lixiviating the calcined alumina, making a mixture of the alumina and more than three other metallic compounds, forming the mixture, and firing the formed mixture to vitrification, and thus producing a fired product consisting of aluminum oxide of upwards of 92 per cent and oxides

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of the added metals, the alumina before calcining and lixiviation comprising in excess of 99 per cent aluminum oxide and free from alkalis in excess of 0.05 per cent.

3. The method of making a fired vitreous product from a body including upwards of 92 per cent by weight of calcined alumina, which includes lixiviating the calcined alumina, making a mixture of the alumina and more than three other metallic compounds, forming the mixture, and firing the formed mixture to vitrification, and thus producing a fired product consisting of aluminum oxide of upwards of 92 per cent and oxides of the added metals, the alumina before calcining and lixiviation comprising in excess of 99 per cent aluminum oxide and free from alkalis in excess of 0.05 per cent and free from silica in excess of 0.05 per cent

4. The method of making a fired vitreous product from a body including upwards of 92 per cent by weight of alumina, which includes lixiviating the alumina, making a mixture of the alumina and more than three other metallic compounds,

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forming the mixture, and firing the formed mixture to vitrification, and thus producing a fired product consisting of aluminum oxide of upwards of 92 per cent and oxides of the added metals, the alumina before lixiviation comprising in excess of 99 per cent aluminum oxide and free from alkalis in excess of 0.05 per cent.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
Re. 22,648	Heany	June 5, 1945
2,033,300	Reichmann	Mar. 10, 1936
2,278,442	Heany	Apr. 7, 1942
2,308,115	Schwartzwalder et al.	Jan 12, 1943
2,310,953	Heany	Feb. 16, 1943
2,336,182	McDougal et al.	Dec. 7, 1943
2,391,454	Heany	Dec. 25, 1945