

UNITED STATES PATENT OFFICE

2,434,236

CERAMIC INSULATOR

Evert Johannes Willem Verwey and Marinus Gerard van Bruggen, Eindhoven, Netherlands, assignors to Hartford National Bank and Trust Company, Hartford, Conn., as trustee

No Drawing. Application January 18, 1943, Serial No. 472,782. In the Netherlands November 25, 1940

Section 1, Public Law 690, August 8, 1946
Patent expires November 25, 1960

6 Claims. (Cl. 106—39)

1

Various low-loss ceramic insulating materials are known both of the kind having a high and having a low dielectric constant. More particularly with materials having a high dielectric constant the temperature coefficient is often of great importance. In conjunction with their purpose the composition may be so chosen that the temperature coefficient of the dielectric constant is positive or negative or very slightly different from zero.

In the present case the expression temperature coefficient of the dielectric constant of an insulating material is to be understood to mean the value obtained from measurements of the capacity of a condenser, having a dielectric made from this material, at different temperatures without any correction in regard to variations occurring due to thermal expansion.

The present invention permits to extend the field of low-loss insulating materials having a high dielectric constant obtained by ceramic means utilizing ceric oxide.

By sintering ceric oxide which in accordance with its purity can be sintered to compactness at temperatures of 1450 to 1600° C. the invention permits the obtainment of products having a dielectric constant of 35 and a slightly positive temperature coefficient of the dielectric constant viz. $+80 \times 10^{-6}$ per °C.

In order to reduce the sintering temperature or to act upon the dielectric properties use may be made, if desired, of ceramic admixtures such as clay or soapstone. In this case, however, it is to be taken into account that materials containing alkali generally increase the dielectric losses. Furthermore it must be considered that the said admixtures have a low dielectric constant, say about 5, and a high positive temperature coefficient of the dielectric constant, say 500×10^{-6} per °C., so that by addition thereof the dielectric constant is reduced and the temperature coefficient is raised.

When making use of titanium dioxide to constitute the admixture, which has a high dielectric constant and at the same time a high negative temperature-coefficient, good results in dielectrical respect can be obtained for certain applications, since in this way the temperature coefficient of the dielectric constant can be made less positive, equal to zero and, if desired, even negative and furthermore the dielectric constant itself is considerably raised.

As is customary admixtures are used in limited quantities always amounting to less than one half of that of the mixture.

2

It is well-known that when making use of titanium dioxide for ceramic insulating materials care must be taken to prevent reduction to a conductive lower oxide. This can be ensured by making use of a sufficiently oxidising atmosphere. On the occurrence of a slight reduction during the sintering operation this can be set off either by cooling so slowly from the sintering temperature to below the temperature at which oxygen began to split off or by after-heating for such a time at a lower temperature, at which oxygen can be absorbed, as to obtain a thoroughly oxidised product.

Although to a less extent than with titanium dioxide there is also a risk of the formation of a conductive lower oxide in the case of ceric oxide, which must be prevented with the insulators according to the invention. To this end sintering in the air is generally sufficient. When making use of titanium dioxide to constitute the admixture it is desirable to counteract the reduction to a greater degree, for instance, by making use of ventilation or an oxygen atmosphere. When splitting off of oxygen occurs to a slight degree during the sintering operation the method of slowly cooling or after-heating, as stated above in regard to titanium dioxide, permits the reduced oxide to be completely oxidised again.

Furthermore, in order to obtain ceramic insulators of titanium dioxide having low dielectric losses it has been suggested to cool rapidly from a temperature of at least about 1100° C. after the sintering operation. With the insulators according to the invention and in particular when containing titanium dioxide one may also act accordingly to reduce the dielectric losses, thus obtaining products having a $\tan \delta$ of less than 10^{-3} measured at 200 metres.

The insulators according to the invention which have a low temperature coefficient of the dielectric constant are particularly adapted for use as a dielectric of condensers designed to be used in circuit arrangements in which dependency of the capacity with respect to temperature is undesirable; moreover, these insulators have the advantage of a high dielectric constant.

For certain circuit arrangements, for instance for compensating the influence of the temperature of condensers having dielectrics with a high negative temperature coefficient and a high dielectric constant, for instance, dielectrics consisting entirely or partly of titanium dioxide, use may be made with advantage, especially in conjunction with the size, of dielectrics according to the invention which have a high positive tempera-

ture coefficient and a still fairly high dielectric constant. To this end use may, for instance, be made of species of clay having a poor alkali content and a high positive temperature coefficient to constitute the admixture and this to a maximum, for instance, of about 30% by weight of the mixture, since otherwise the dielectric constant becomes too low.

The invention will be more fully explained by giving several examples.

Example I

Powdered cerium oxide (analysis 98.8% of CeO_2 , 0.3% of SiO_2 , 0.55% of Fe_2O_3 , 0.31% loss due to burning) is pressed at a high pressure to form a plate and sintered in the air for half an hour at 1500°C . followed by cooling to room temperature in about half an hour. The product sintered to compactness thus obtained has a dielectric constant of 35, a $\text{tg}\delta$ of 4.10^{-4} at 200 metres and a temperature coefficient of the dielectric constant of $+80 \times 10^{-6}$ per $^\circ\text{C}$.

Example II

A mixture of 90% by weight of cerium oxide (analysis 98.4% of CeO_2 , 1.24% of SiO_2 , 0.06% of Fe_2O_3 , 0.14% loss due to burning) and 10% by weight of clay (analysis 46.1% of SiO_2 , 39.3% of Al_2O_3 , 0.8% of Fe_2O_3 , 0.15% of CaO , 0.15% of $\text{Na}_2\text{O} + \text{K}_2\text{O}$, 13.4% loss due to burning) is mixed with a aqueous tragacanth solution to form a pastic mass from which is pressed a tube which is sintered in the air for 20 minutes at 1350°C . followed by rapid cooling.

Example III

A mixture of 95% by weight of cerium oxide (analysis 99.6% of CeO_2 , 0.09% of SiO_2 , 0.2% of Fe_2O_3 , 0.15% loss due to burning) and 5% by weight of titanium oxide (analysis 98.6% of TiO_2 , 0.2% of Fe_2O_3 , 0.3% of Al_2O_3 , 0.5% of SO_3 , 0.2% of P_2O_5 , 0.1% loss due to burning) is, similarly to Example II, pressed to form a tube, heated for half an hour at about 1300°C . in a stream of oxygen, followed by cooling to 1100°C . in 10 minutes and by subsequent rapid cooling in the air.

The product sintered to compactness thus obtained has a dielectric constant of 36, a $\text{tg}\delta$ of 8.1×10^{-4} at 200 metres and a temperature coefficient of the dielectric constant of $+8.4 \times 10^{-6}$ per $^\circ\text{C}$.

Example IV

A mixture of 90% by weight of cerium oxide and 10% by weight of titanium oxide (of the same analysis as in Example III) is treated similarly to Example III.

The product sintered to compactness thus obtained has a dielectric constant of 39, a $\text{tg}\delta$ of 6.2×10^{-4} at 200 metres and a temperature coef-

ficient of the dielectric constant of -64×10^{-6} per $^\circ\text{C}$.

What we claim is:

1. An electrical insulator particularly suitable as a condenser dielectric consisting of a mass of at least about 90% by weight of ceric oxide and the remainder consisting of a low-loss dielectric material, said mass being sintered to compactness.
2. An electrical insulator as claimed in claim 1 containing an alkali-poor ceramic as an admixture.
3. An electrical insulator as claimed in claim 1 containing titanium dioxide as an admixture.
4. A method of making an electric insulator consisting of a mass of preponderantly ceric oxide which comprises the steps of forming a mass consisting of at least about 90% of ceric oxide and the remainder consisting of low-loss dielectric material, and sintering the said mass to compactness in an oxidizing atmosphere.
5. A method of making an electric insulator as claimed in claim 1 in which the mass is cooled from a temperature of at least 1100°C . to the ambient temperature within approximately one-half hour so that the dielectric loss factor, measured at a wave length of 200 meters, is less than about 10^{-3} .
6. A method of making an electric insulator consisting of a mass of preponderantly ceric oxide which comprises the steps of forming a mass consisting of at least 90% by weight of ceric oxide and the remainder consisting of titanium dioxide, sintering the said mixture for approximately one-half hour at a temperature of about 1300°C . in an oxygen atmosphere, cooling said heated mixture to 1100°C . in about 10 minutes, and thereafter cooling said mixture to the ambient temperature within approximately one-half hour.

EVERT JOHANNES WILLEM VERWEY.
MARINUS GERARD VAN BRUGGEN.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,071,452	Bloch	Feb. 23, 1937
2,152,655	McDougal et al.	Apr. 4, 1939
2,177,943	McDougal et al.	Oct. 31, 1939
2,214,931	McDougal et al.	Sept. 17, 1940

FOREIGN PATENTS

Number	Country	Date
116,129	Australia	1942
391,919	Germany	1924
445,269	Great Britain	1936
588,271	Germany	1933