CERAMIC MATERIALS WITH A HIGH DIELECTRIC CONSTANT

by E. J. W. VERWEY and R. D. BüGEL.

In electrical engineering, ceramic materials are very widely used for insulation purposes and as dielectric for capacitors. In the latter instance preference is given to a material having a high dielectric constant and low dielectric losses and here the choice is limited almost exclusively to pure titanium dioxide (rutile), or a mixture in which the latter figures as chief ingredient. Admixtures, sometimes necessary for the purpose of reducing the dielectric losses to a value below the permissible maximum, tend also to reduce considerably the dielectric constant of the TiO₂, and the purpose of this article is to investigate in how far the value of this constant is related to other properties of the material. A disadvantage of pure titanium dioxide is that the temperature coefficient of its dielectric constant is highly negative, The Philips Laboratories at Eindhoven have worked out various methods for reducing this temperature coefficient to zero by using suitable admixtures. By way of example, a description is given of a series of capacitors of small dimensions with a ceramic dielectric as used in radio receivers and other equipment incorporating high-frequency circuits.

Ceramic materials are widely employed for insulating purposes in electrical engineering: high values of the capacitance of the insulated conductors to earth, or in respect of other conductors, will, in general, involve a certain amount of hazard and such capacitances are therefore kept low by exercising care in the design and by employing a suitable ceramic material, i.e. one having a low dielectric constant.

The requirements imposed on insulating materials used as dielectric in capacitors are very different, however: here a high dielectric constant is usually an advantage, and certain ceramic materials can be produced which possess this property. Further, a suitable choice of the raw materials and methods of preparation will ensure that the resultant material meets certain other requirements to which capacitors usually have to conform, e.g. that the dielectric losses will not be too high and that the dielectric constant will not vary too much with the temperature.

Dielectric constant of titanium dioxide and the effects of admixtures

Those materials which have a high dielectric constant and which have so far been adopted for electrical purposes usually contain a major proportion of titanium dioxide, owing to the fact that this material (as also a number of titanates) belongs to the very small group of substances the dielectric constant of which is exceptionally high. In nature titanium dioxide (TiO₂) occurs in the form of three different modifications, namely anatase, brookite and rutile. Wherever titanium dioxide is mentioned in the following we mean rutile, this being the stable modification, having at the same time the greatest density as well as the highest index of refraction and dielectric constant.

The two last mentioned qualities are dependent, moreover, on the orientation of the (tetragonal) crystal. In the direction of the major axis they are higher than in either of the two transverse axes: the indexes of refraction are 2.903 and 2.661 (for light of the wavelength of the D-line) and the respective values of the dielectric constant are 172 and 86 (as measured on a large crystal of the mineral rutile). In a close-sintered specimen 1), which will contain a large number of arbitrarily oriented small crystals, an average value of approximately \((172 + 86 + 86) / 3 = 115\) may be obtained for the dielectric constant, but in actual practice it is very difficult to reach this figure. In the first place a titanium dioxide compound sintered to such an extent as to seal effectively all the pores on the crystal faces, and this has the effect of reducing considerably the apparent dielectric constant. Moreover, such a compound inevitably contains certain impurities, the dielectric constant of which is generally on the low side, so that in actual fact the dielectric constant \(\varepsilon\) of technical mixtures is generally lower than that of the pure titanium dioxide. If an impurity becomes dissolved in the titanium dioxide lattice, producing mixed crystals, it is not immediately clear why this should produce such a marked effect in the way of a decrease in the value of \(\varepsilon\), but if the impurity occurs as a secondary distinct phase, having in itself a much lower \(\varepsilon\) value, then as a rule the dielectric constant of the

mixture will obviously be considerably reduced by the presence of this secondary substance.

Let us suppose, for the sake of convenience, that the secondary phase occurs in the form of layers perpendicular to the direction of the electric field, so that the lines of force traverse a dielectric whose constant is alternately high and low. The example may be further simplified by taking the case of a capacitor consisting of only two layers, i.e. a flat capacitor of which the two electrodes are a distance \( d \) apart, with a dielectric comprising a layer of titanium dioxide the \( \varepsilon \)-value of which is \( \varepsilon_1 \), and another layer, in contact with it, of a substance having a low dielectric constant \( \varepsilon_2 \) and a thickness of \( xd \). According to the theory of dielectrics, the field in a capacitor of this kind will conform to the requirement that the product of field strength and \( \varepsilon \) must be constant throughout. The potential difference \( V \) between the two electrodes is then divided (see fig. 1) into two parts \( V_1 \) and \( V_2 \), so that:

\[
\frac{V_1 \varepsilon_1}{(1-x)d} = \frac{V_2 \varepsilon_2}{xd} = \frac{V}{d}, \quad \ldots \ldots (1)
\]

where \( q \) is the apparent dielectric constant of the whole. Since \( V = V_1 + V_2 \), expression (1) gives us:

\[
\frac{1}{\varepsilon} = \frac{1-x}{\varepsilon_1} + \frac{x}{\varepsilon_2}. \quad \ldots \ldots (2)
\]

Let \( \varepsilon_1 = 100 \) and \( \varepsilon_2 = 5 \). The following values of \( \varepsilon \) will then be found in relation to \( x \):

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>110</td>
</tr>
<tr>
<td>0.005</td>
<td>99</td>
</tr>
<tr>
<td>0.01</td>
<td>91</td>
</tr>
<tr>
<td>0.05</td>
<td>54</td>
</tr>
<tr>
<td>0.10</td>
<td>36</td>
</tr>
</tbody>
</table>

Although this is only a very simplified example, it nevertheless demonstrates the marked reduction in the value of \( \varepsilon \) produced by the smallest admixtures in the dielectric: impurities to the extent of only about 0.5% immediately reduce the value of \( \varepsilon \) to a point below 100. Generally, such impurities are already present in the raw materials, or may be introduced in the course of the further processing. Small air-gaps between the crystals of the sintered mixture, or cavities within the mass, have an even more pronounced effect (since in that case \( \varepsilon_2 = 1 \)). It therefore follows that the value of \( \varepsilon \) can be raised to 100 or slightly more only by taking the most stringent precautions.

It is hardly to be expected that expression (2) will provide an accurate quantitative criterion of the effect of admixtures or air-occlusions in titanium dioxide upon the value of \( \varepsilon \), since we have based our

\[\text{Fig. 1. Diagram showing the drop in potential in a double-layer capacitor. The thickness of the layers is indicated by } xd \text{ and } (1-x)d; \text{ the dielectric constants are respectively } \varepsilon_1 \text{ and } \varepsilon_2.\]

example on an extremely simplified case which will certainly not be met with in general practice. It is possible, none the less, in the same way to construct expressions in respect of other, rather more complex examples, for instance where the one medium, in the form of ellipsoidal particles arbitrarily oriented, is enclosed within the other. The appropriate expression may then be readily simplified to suit spheroidal particles, more or less flat particles (in which case one dimension of the ellipsoid is small in relation to the others), or needle-like particles (with one dimension large in contrast with the others). It may be anticipated that such hypotheses would more closely approximate actual conditions.

We are more particularly interested in the case where the secondary substance occurs in the form of flat, plate-like particles. If titanium dioxide be contaminated with a small quantity of a secondary substance it may be expected, in general, that the latter will accumulate at the crystal boundaries and thus reveal some analogy to flat particles having a low dielectric constant. When the calculation is carried out in respect of this particular case, to determine the effect of admixtures on the value of \( \varepsilon \), it will again be found that the addition of relatively small quantities of substances having a low dielectric constant produces an exceptionally

\[\text{2) D. Polder and J. H. van Santen, Physica, 12, 257-271, 1946.}\]
Reasons for the high dielectric constant of TiO$_2$

Let us for a moment investigate the causes of the extremely high dielectric of titanium dioxide.

The dielectric constant of a substance is defined as follows: when the space between the electrodes of a capacitor is filled with an insulating substance of dielectric constant $\varepsilon$, the charge on the electrodes, at a given potential, is $\varepsilon$ times as great as when that space is empty; this constant is always greater than unity. The effect of such a medium, of which $\varepsilon > 1$, upon the charge in a capacitor is an outcome of the fact that it is built up of positive and negative charge-carriers which are able to migrate among themselves but which are nevertheless limited to their positions of equilibrium.

In a substance such as TiO$_2$ two possibilities have to be taken into account: firstly the chemical structure is strongly polar, so that TiO$_2$ may be imagined, as an approximation, as being built up from Ti$^+$-ions and O$^-$-ions which are able to undergo a limited amount of displacement in an electric field. Each ion, moreover, consists of a positively charged nucleus within a cloud of negatively charged electrons which in turn will also move with respect to each other in an electric field.

Consequently, in a homogeneous substance every volumetric element $dV$ will have a dipole moment $PdV$ equal to the product of the displaced charge and the distance over which the negative charge has been displaced, with respect to the positive charge. The dipole moment per cubic centimetre (the polarisation $P$) is nil when $\varepsilon = 1$ and is proportional to $\varepsilon - 1$. Further, provided the field is not too strong, the displacement of the charge is proportional to the applied electric field $E$. This is expressed by:

$$ P = \frac{\varepsilon - 1}{4\pi} E \quad \ldots \ldots \ldots \ldots (3) $$

The magnitude of the polarisation, and therefore also that of the dielectric constant of the material, is very closely related to the degree to which the above-mentioned charge displacement takes place in the electric field.

The atomic characteristic determining such charge displacements in the atom is what may be termed the polarisability of the atom. Let us first assume that this is the only active characteristic. In the case of a substance consisting of only one type of atom the same electric field influences each of the atoms. Suppose that the value of this field at the atom be $F$, then the dipole moment $\mu$ generated in the atom is proportional to $F$ and also to the polarisability $a$, so that:

$$ \mu = aF. $$

If the number of atoms per cubic cm be $N$, then the polarisation is:

$$ P = N\mu = NaF. \quad \ldots \ldots (4) $$

The effective field strength in the immediate vicinity of the atom however is not identical with the external field strength as applied, since the dipoles generated in the other atoms produce an additional field. The relation between $F$ and $E$ within a space of cubic symmetry is rendered by:

$$ F = E + \frac{4\pi}{3} P, $$

(as given by Lorentz), so that formula (3) immediately gives us:

$$ F = E + \frac{\varepsilon - 1}{3} E = \frac{\varepsilon + 2}{3} E \quad \ldots \ldots (5) $$

Elimination of $P$ and $F$ from (3), (4) and (5) then finally yields:

$$ \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} Na \quad \ldots \ldots (6) $$

Expressions (3) to (6) are given in electrostatic units, but according to the rationalised Giorgi system they would take the following form:

From the formula:

$$ D = \varepsilon_0 \varepsilon E = \varepsilon_0 E + P, $$

in which $\varepsilon_0$ is the (absolute) dielectric constant of a vacuum, whilst $\varepsilon_0$ represents the (relative) dielectric constant of the material, it follows that:

$$ P = (\varepsilon_0 - 1) \varepsilon_0 E \quad \ldots \ldots \ldots \ldots (3') $$

In the local field $F$ the dipole moment is:

$$ \mu = aF, $$

where $a$ is again the polarisability, but which, as will be seen presently, now has another physical dimension. If $N$ be the number of atoms per cubic metre then:

$$ P = N\mu = NaF \quad \ldots \ldots \ldots \ldots (4') $$

The relation between $E$, $F$ and $P$ is now:

$$ \varepsilon_0 F = \varepsilon_0 E + \frac{1}{3} P, $$

from which, in view of (3'), it follows that:

$$ F = E + \frac{\varepsilon_0 - 1}{3} E = \frac{\varepsilon_0 + 2}{3} E \quad \ldots \ldots (5') $$

Elimination of $P$ and $F$ from (3'), (4') and (5') then gives us 4):
\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3} \varepsilon_0 \quad \ldots \ldots \ldots \ldots \quad (6')
\]

If we ascribe to the term \(a'\varepsilon_0\) the form \(a'\), then \((6')\) can be written as:
\[
\frac{a' - 1}{a' + 2} = \frac{1}{3} \varepsilon_0' \quad \ldots \ldots \ldots \ldots \quad (6'a)
\]

The quantity \(a'\), as also \(a\) in \((4)\) and \((6)\), has the dimension of a volume; on the other hand, \(a\) in \((4')\) and \((6')\) bears the dimension \(\text{cm}^2\).

The dielectric constant in question, being determined by a term \(p\) which is proportional to both the number of atoms \(N\) per cubic cm and their polarisability \(a\). In a substance such as TiO\(_2\), which is composed of two kinds of atoms, \(p\) is governed by the polarisability of the Ti\(^{4+}\)-ion and the O\(^{2-}\)-ion together. Thus, \(N\), the number of TiO\(_2\) "molecules" per cubic cm and \(a\) is the sum of the polarisability values of the individual atoms.

The second term of expression \((6)\) is designated as \(p_e\), in which the index \(e\) indicates that the electrons are displaced in the atom. From the derivation it thus follows that the dielectric constant is determined by a term \(p_e\) which is proportional to both the number of atoms \(N\) per cubic cm and their polarisability \(a\). In a substance such as TiO\(_2\), which is composed of two kinds of atoms, \(p_e\) is governed by the polarisability of the Ti\(^{4+}\)-ion and the O\(^{2-}\)-ion together. Thus, \(N\), the number of TiO\(_2\) "molecules" per cubic cm and \(a\) is the sum of the polarisability values of the individual atoms.

The dielectric constant in question, being determined exclusively by the displacement of the electrons in the atoms with respect to the nucleus, may be measured in an alternating field of so high a frequency that displacement of the ions in respect to each other does not take place: for this purpose electromagnetic waves at a frequency higher than about \(10^{13}\) i.e. of visible light, can be employed, so that it is permissible to use Maxwell's law:

\[
\varepsilon_{\text{opt}} = \eta^2,
\]

where \(\eta\) is the index of refraction of the substance having \(\varepsilon_{\text{opt}}\) as the optical dielectric constant.

Conversely, it is possible to proceed from the index of refraction to obtain some idea of the magnitude of \(p_e\) and \(a\). For TiO\(_2\) the average value of \(n\) is about 2.74. As far as the electronic contribution to the polarisability is concerned, TiO\(_2\) should therefore have a value of \(\varepsilon_{\text{opt}} = 7.5\). Applying formula \((6)\) in this case \(^5\), \(p_e\) would then be \(6.5/9.5 = 0.68\).

\(^5\) Admittedly this is not strictly correct, since the crystal lattice of TiO\(_2\) does not conform to the condition that the encompassment of each ion shall be cubic-symmetrical. Nevertheless, it is quite feasible to apply this formula as an approximation, especially considering that we are employing the average value of \(n^2\) (average of the three crystal planes). The difference is not so great as to affect the final conclusion in any way.

It is necessary, further, to take into account the polarisation arising from the displacement of the ions with respect to each other, and in this case we can similarly define a term \(p_i\); hence:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = p = p_e + p_i.
\]

It will now be clear that in a substance such as TiO\(_2\), of which the index of refraction is already relatively high, the part played by \(p_i\) in the total value of \(p\) — in comparison with \(p_e\) — need be only small in order to yield a high value of \(\varepsilon\), since, if \(p = 1\), the value of \(\varepsilon\) would already be infinitely high. From the experimental value of \(\varepsilon = 110\) it follows that in the case of titanium dioxide \(p = 0.97\), which is a close approximation of \(p = 1\). For the contribution in respect of the ion displacement we now have \(p_i = 0.29\), which, compared with the polarisability of other ion crystals, may be considered normal.

Our conclusion is that the high dielectric constant is due to the combination of a high index of refraction \(n\) and the fact that the value of \(p_i\) is not too low.

The dielectric losses of titanium dioxide and the effects of admixtures

It now having been ascertained that \(\varepsilon\) is high in the case of TiO\(_2\) in the pure state and that admixtures result in a sharp decline in this value, the obvious aim will be to maintain the greatest possible purity in the preparation of this substance, before processing it in the form of ceramic material. This, however, is easier said than done, for the preparation and processing of TiO\(_2\) involves a number of difficulties, added to which is the fact that a high value of \(\varepsilon\) is not the only requirement to which insulating materials have to conform. In many cases it will be found that admixtures to the TiO\(_2\) are unavoidable.

When TiO\(_2\) is to be used as basic material for capacitors there is no doubt that a high value of \(\varepsilon\) is very important, but it is also essential that the dielectric losses shall be low, especially in cases where the capacitor is to be employed in circuits working on high frequencies. The amount of these dielectric losses is customarily expressed as the value of \(\tan \delta\), in which \(\delta\) represents the angle of loss. Material which is to be employed for high-frequency capacitors usually has to conform to a value of \(\tan \delta\) not exceeding \(10^{-4}\) to \(10^{-3}\) \(^6\).

\(^6\) For comparative purposes the average value of \(\tan \delta\) with respect to certain non-ceramic insulating materials may be noted, viz: mica \(1 \times 10^{-4}\), ebonite \(21 \times 10^{-4}\), paper \(140 \times 10^{-4}\), celluloid \(450 \times 10^{-4}\).
Material prepared from reasonably pure titanium dioxide has a high value of $\varepsilon$, but its dielectric losses are intolerably high, partly owing to the high sintering temperature and its pronounced tendency at this temperature to evolve oxygen and revert to lower oxides, such as Ti$_2$O$_3$, which are semi-conductors 7) and therefore useless for dielectric purposes. Even the smallest proportion of such oxides, too small to be determined by chemical analysis, will be sufficient to increase the loss factor $\tan\delta$ far beyond the permissible limit. This reducing effect becomes all the more marked according as the surrounding gases during the firing contain less oxygen and greater proportions of reducing agents.

It is, however, difficult to avoid these unwanted constituents. Owing to the dissociation just mentioned, it is impossible to indicate the melting point of titanium dioxide with any accuracy, but it is certainly above 1700 °C. A temperature of about 1500 °C — which is relatively close to the melting point — is therefore necessary to sinter the material closely, and such high temperatures are best obtained by gas firing; in the large kilns generally employed in the ceramic industry. It will be readily understood, then, that the exclusion of reducing gases from the firing space is an extremely difficult matter; in fact, when titanium dioxide material is fired in a gas kiln considerable reduction does actually take place.

One way of counteracting this effect is to add other substances to the TiO$_2$. Several substances, for instance clay, reduce the sintering temperature of the mixture, so that these lower oxides are not so easily formed. Various substances will, moreover, decrease the tendency towards the actual reduction itself, and in this way a raw material can be produced the loss factor of which is within the prescribed limit. In the meantime, however, $\varepsilon$ will be found to have dropped as low as 60 or 80. Efforts have therefore to be made to evolve a composition, as well as a method of preparation, which will ensure satisfactory values both of $\varepsilon$ and $\tan\delta$.

It has been found possible in some cases to effect this by cooling the fired product in such a way as to introduce re-oxidation and thus nullify the reducing effect of the sintering process; this may be done by re-heating to a slightly lower temperature (about 1200 °C) in air or, even more simply, by retarding the cooling of the titanium dioxide products after the normal sintering. In this way a temperature zone is passed through in which the oxygen dissociation-pressure of the material is sufficiently low to permit of the re-formation of stoichiometrically pure titanium dioxide, the reaction rate remaining high enough to allow this re-formation to take place within the space of a few minutes. None the less, from the fact that the two measures referred to do not always yield the desired result, or at any rate not to a sufficiently high degree, it follows that the above mentioned partial reduction of the material is not the only source of a high loss factor.

There is no certainty regarding the origin of the dielectric losses occurring in the purest possible TiO$_2$ after full re-oxidation has been assured, but means have been found to limit these losses to a considerable extent by observing certain special precautions in the processing of the product. The first of these essential, is a rapid cooling after sintering and subsequent re-oxidation to stoichiometric TiO$_2$, which means that the sintered product is first cooled slowly to about 1100 °C, after which the cooling rate is accelerated.

The fact that we can obtain in this way a material with a low loss factor has led to the assumption that the previously mentioned dielectric losses (which appear to be present after complete re-oxidation) must be ascribed to the presence of impurities in the material. Closer investigation has shown, in fact, that traces of alkali metals (Na, K), and especially alkaline earth metals (Ca, Ba), have a very adverse effect on the dielectric losses.

Once this was known, a second method of reducing the loss factor to within the proper limits was made available to us. We therefore start with the purest possible titanium dioxide, in which the content of the deleterious oxides mentioned has been reduced to the technical minimum and in which the effects of any remaining unwanted oxides have been neutralised by the addition of small quantities of other oxides. It might be argued in spite of this, as mentioned above, that even one or two tenths of one per cent of impurities would be enough to reduce the dielectric constant from 110 to less than 100, but in actual practice the method in question has yielded satisfactory results. By basing the product on TiO$_2$ which is extremely pure by technical standards, so that any necessary additions may be limited to a minimum, it has been found possible to produce a titanium dioxide having an $\varepsilon$-value of 100 to 105, with $\tan\delta$ at most a few times $10^{-4}$ (at a frequency of 1500 kc/s).

It is a noteworthy fact, too, that the method in question enables us to obtain a ceramic material the loss factor of which is low not only at 1500 kc/s but also at 10 kc/s. If use is made of TiO$_2$
containing a large percentage of clay the most favourable case will yield dielectric losses which are low at 1500 kc/s but high at 10 kc/s, as demonstrated in fig. 2, in which tanδ is shown plotted as a function of the frequency, with the two different mixtures as parameters.

![Graph](image)

Fig. 2. The value of tanδ as a function of the frequency of the alternating current applied. The frequency v of the current in c/s and the value of tanδ are shown plotted on logarithmic co-ordinates. Curve a refers to titanium dioxide to which a high percentage of clay has been added, and curve b to technically pure TiO₂ in which the inevitable impurities, of oxides of alkaline-earth metals, have been neutralised by small quantities of other oxides.

**Temperature coefficient of the dielectric constant**

Once it has been assured, by a careful choice of the composition and the method of preparation of the ceramic material, that the final product will have a high value of ϵ and a low tanδ, attention must be paid to a final factor, the temperature coefficient of the dielectric constant, for, in the case of titanium dioxide, the value of ϵ is very highly dependent on the temperature. Curiously enough, this temperature coefficient, in contrast with that of nearly every other material, is negative, i.e. 1/ρ·dρ/dT = −8.10⁻⁴. This means that an increase of, say, 12.5 °C in the temperature of a capacitor having TiO₂ as dielectric causes the capacitance to decrease by 1%.

In certain applications such a high coefficient is a decided disadvantage. Take as an example the case of a capacitor in the tuning circuit of a radio receiver tuned at room temperature to a given station: as soon as the capacitance changes, which it will do after a little while owing to the increase in the working temperature of the set, the tuning will be upset. On the other hand there are cases where the high negative temperature coefficient may prove an advantage in compensating the coefficient in other components in the circuit, which is usually of the opposite sign.

It may well be asked what the relation is between the temperature coefficient of the dielectric constant and the other characteristics of titanium dioxide. According to expression (6), the temperature coefficient of ϵ is determined by that of Na. Clearly, as a result of the thermal expansion the number of atoms per cubic cm decreases as the temperature is raised; in other words, the dielectric constant decreases with rising temperature. This effect may be counteracted by the variation in a with T, but in the case of a substance such as TiO₂ it appears that the value of a as calculated from the rather approximate formula (6) depends very little upon the temperature, so that the temperature coefficient of ϵ is determined almost wholly by the thermal expansion. At high values of ϵ, small variations in N result in relatively marked changes in ε, as will be seen from the relationship between these quantities in accordance with expression (6). The high temperature coefficient of TiO₂ is thus directly related to the high value of ϵ.

In the case where de/dT ≈ 0, as roughly approximated in TiO₂, the following may be derived from formula (6):

\[
\frac{1}{\epsilon} \frac{d\epsilon}{dT} = \frac{(\epsilon-1)(\epsilon+2)}{3\epsilon^2} \frac{1}{N} \frac{dN}{dT} \ldots \ldots (7)
\]

If we introduce an average linear coefficient of expansion:

\[
\beta = \frac{1}{3N} \frac{dN}{dT}
\]

expression (7) may be written in the form:

\[
\frac{1}{\epsilon} \frac{d\epsilon}{dT} = \left(\frac{\epsilon-1}{\epsilon} + 2\right) \beta \ldots \ldots (8)
\]

which, at high values of ϵ, becomes:

\[
\frac{1}{\epsilon} \frac{d\epsilon}{dT} = -\beta \epsilon \ldots \ldots (9)
\]

The temperature coefficient is thus negative in such substances and is also proportional to the average linear coefficient of expansion.

It is necessary here to stress the fact that there are also many substances, especially those whose dielectric constant is low, in regard to which variations of a with the temperature also play a part.

It has already been mentioned that the high negative temperature coefficient is a disadvantage in many applications of the material in question. By adding other substances having a positive temperature coefficient it is possible to produce a mixture the temperature coefficient of which is very low, or even zero, but this can be done only at the cost of a high value of ϵ, as may be expected in the light of the remarks made in the opening paragraphs of this article. Let us now look at one or two examples of ceramic mixtures of this kind.
For many years MgO has been known as a suitable constituent; the sintered product in this case yields a material consisting in part of magnesium titanate, and provided the proportions are suitably chosen $1/\varepsilon \, d\varepsilon/dT$ is for all practical purposes zero. The dielectric losses of this material are very low ($\tan\delta = 1 \times 10^{-4}$ at 1000 kc/s) but the dielectric constant is not much more than 12 to 18.

Another method consists in the addition of steatite, which will also give an ultimate temperature coefficient of 0, with very low losses, but $\varepsilon$ is then only about 10.

Philips have developed a special mixture, using CeO$_2$ as a constituent. It was found that the dielectric constant of this substance is still fairly high, viz. about 35, whilst the temperature coefficient, dependent to some extent on the purity of the oxide, is generally weakly positive $^8$). Therefore, mixtures prepared from CeO$_2$ and TiO$_2$, the temperature coefficient of which is to be roughly zero, must contain a very large proportion of CeO$_2$, a typical example being 85 mol% CeO$_2$ and 15 mol% TiO$_2$. This mixture is thoroughly sintered at 1220 °C, a temperature very much lower than that required for pure TiO$_2$. The dielectric constant is approximately 40, with $\tan\delta$ approx. $8 \times 10^{-4}$ at 1000 kc/s.

Another possibility which we have investigated concerns admixtures of SnO$_2$. 50 mol% SnO$_2$ and 50 mol% TiO$_2$ yields a temperature coefficient of roughly zero. The firing temperature is certainly very high, being 1550 °C, but the losses are extremely low ($\tan\delta \approx 1 \times 10^{-4}$ at 1000 kc/s), whilst for the mixing ratio in question $\varepsilon$ is 25.

Finally, mention should be made of ZrO$_2$ as a possible constituent: this may be introduced in a number of ways. In the first place, if not more than 1 or 2 % zirconium oxide is added, $\varepsilon \approx 60$ and $\tan\delta \approx 5 \times 10^{-4}$ at 1000 kc/s, but $1/\varepsilon \, d\varepsilon/dT$ is then still markedly negative ($-6 \times 10^{-4}$). Alternatively, the admixture of ZrO$_2$ can be increased until $1/\varepsilon \, d\varepsilon/dT$ is for all practical purposes zero. According to the rule of Gevers and du Pré (Philips Techn. Rev. 9, 91-96, 1947, (No. 3), for this material that contribution towards the temperature coefficient which is related to the dielectric losses is roughly equal to $0.06 \tan\delta$; at $\tan\delta = 10^{-3}$ this is therefore $+0.6 \times 10^{-4}$.

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$^8$) The spreading of the values is related partly to the losses. According to the rule of Gevers and du Pré (Philips Techn. Rev. 9, 91-96, 1947, (No. 3), for this material that contribution towards the temperature coefficient which is related to the dielectric losses is roughly equal to $0.06 \tan\delta$; at $\tan\delta = 10^{-3}$ this is therefore $+0.6 \times 10^{-4}$. 

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Fig. 5. Two groups of ceramic capacitors as supplied ready for use. On the left 4 capacitors of the "A" type; on the right the "B" type.
≈ 0, but, although this shows the same dielectric losses, ε will be found to have dropped to the order of 30. In this case, moreover, a high sintering temperature is needed.

From these examples it will be seen that variations in the ceramic mixtures will produce widely divergent dielectric properties, and it is on the basis of these experimental results that the composition of ceramic materials is determined, to meet the particular requirements to which any given product may have to conform.

Capacitors made of ceramic material

We close the present article with a brief reference to one particular application of ceramic materials for capacitors: these comprise a range of miniature capacitors for which a high dielectric constant is required to suit the capacitance values concerned. Figs 3 and 4 show the method of construction.

These components, the length of which varies from 15 to 40 mm \(^{9}\), are manufactured in capacitances varying from 33 to 1200 pF. The tolerance ranges are 20, 10, 5 and 1%, although the maximum guaranteed accuracy is ± 1 pF. The maximum working voltage is 600 V, but each capacitor is factory-tested on 1500 V, A.C. 50 c/s, for 1 hour. As far as the dielectric losses are concerned, tanδ is less than 20 × 10\(^{-4}\) in the "A" type (at 1500 kc/s) and less than 10 × 10\(^{-4}\) in the "B" type. The insulation resistance is higher than 5000 megohms. On the score of mechanical strength it may be said that the ends of these small capacitors can be loaded to the extent of 2 kg without rupture.

Fig. 5 illustrates a group of these components. These may be employed in radio receivers and other high-frequency circuits.

\(^{9}\) In the very low capacitance values (3.3 to 27 pF, similar capacitors are made with glass as dielectric. The dimensions then lie between 15 and 30 mm.