

March 10, 1959

A. H. IVERSEN

2,877,144

VITREOUS COATED MAGNETIC MATERIAL

Filed May 19, 1954

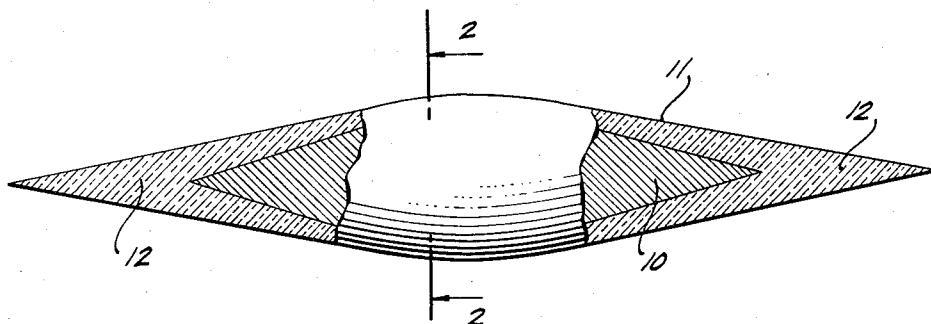


FIG. 1.

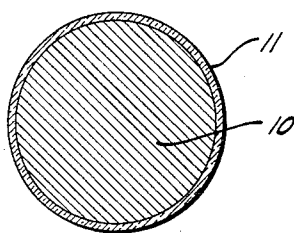


FIG. 2.

INVENTOR.

ARTHUR H. IVERSEN,

BY

Ronald J. J. J.

ATTORNEY.

1

2,877,144

VITREOUS COATED MAGNETIC MATERIAL

Arthur H. Iversen, Santa Monica, Calif., assignor to Hughes Aircraft Company, Culver City, Calif., a corporation of Delaware

Application May 19, 1954, Serial No. 430,841

4 Claims. (Cl. 117—215)

This invention relates to hermetically-sealed ferromagnetic dielectric materials and a method for sealing the same, and more particularly to vitreous-coated ferromagnetic dielectric compacts and a method for applying a vitreous coat to such materials.

Ferromagnetic dielectric materials, known in the art simply as ferrites, are crystalline ceramics in which the major constituent is iron oxide. These ceramics are generally formed into a compact by a closely-controlled sintering process from a powder mixture which includes a plurality of bivalent-metal oxides. Ferrite compacts have a wide range of physical and electrical properties which are dependent on their composition and the sintering technique employed in their formation.

The ferromagnetic dielectrics are particularly useful in microwave applications because at these frequencies they exhibit a characteristic known as the "Faraday" effect. However, in use, the heating effect, power factor, and polarization rotating ability of the ferrite compacts are adversely affected by increasing moisture content.

An example of such utilizations of the ferrite compacts is shown in copending application, Serial No. 419,259, by Willard A. Hughes, filed on March 29, 1954. In this example the ferrite compact is utilized to rotate incident wave energy 45 degrees for transmission to a load. The reflected energy is rotated another 45 degrees in again traversing the ferrite compact so that it has a final polarization at the source end of the ferrite which is normal to that of the incident energy. This relationship between the planes of polarization of the incident and reflected energy makes it feasible to divert the reflected energy out of the working system and so prevent it from traveling back to the source.

In addition to the utilization of the ferrites in microwave transmission systems, they are also useful in certain types of electron discharge devices such as, for example, the traveling wave type. The susceptibility of the ferrites to release occluded gases over a long period of time is an impediment to this type of use because of the necessary high vacuum which must be maintained in the electron discharge device. It follows that this problem can be obviated by hermetically sealing the ferrite compact in accordance with the present invention. Accordingly, it follows that if the ferrite compacts can be hermetically sealed in an envelope or skin in a dry condition, their usefulness will be very much enhanced. The manner in which the ferrites are utilized, as well as their inherent physical properties, interposes a number of difficulties in the way of achieving a satisfactory hermetic envelope.

The ferromagnetic dielectric compact or ferrite is utilized in high intensity microwave applications which cause considerable heating of the compact. It follows that a sealing skin for the compact must be capable of withstanding a temperature of at least several hundred degrees centigrade without deterioration, cracking or otherwise developing porosity. The substances capable of

2

performing a sealing function at these temperatures are the vitreous products, notably, glass.

An obstacle in the way of utilizing a vitreous skin on ferrite compacts is the inherent susceptibility of the compact to deterioration, i. e., cracking, due to thermal shock. That is, the tensile and compressive strengths of the ferrite compact are insufficient to prevent disruption of the compact due to sudden heating to a high temperature of the outer surfaces thereof. Consequently, since a glass surface must be applied to the compact at the molten temperature of the glass, it is necessary to utilize a glass which has a temperature of melting which is not so high as to cause breakup or cracking of the compact. On the other hand, because, as previously mentioned, the ferrite compact can become quite hot in operation, it is necessary to utilize a glass which has a high enough melting temperature to withstand deterioration of the glass skin or envelope.

In addition to the above problems involved in providing a ferrite compact with a vitreous coat or skin, it is also necessary that the compact with its vitreous skin withstand variations in temperature over several hundred degrees centigrade without deterioration of either the compact or seal. This requires that the vitreous substance utilized for sealing the compact have a coefficient of thermal expansion sufficiently similar to that of the ferrite compact to limit the stresses in either the skin or the compact itself so as to avoid deterioration of either the skin or the compact.

It follows that a prime objective of this invention is to provide a sealing coat or skin onto a ferromagnetic dielectric compact.

A further objective of this invention is to provide a method for applying a vitreous coating to ferromagnetic dielectric compacts.

The novel features which are believed to be characteristic of the invention, both as to its organization and method of operation, together with further objects and advantages thereof will become apparent from the following description considered in connection with the accompanying drawing, made a part of this specification.

In the drawing:

Fig. 1 is a partial broken section of a hermetically sealed ferromagnetic ferrite device of the present invention; and

Fig. 2 is an enlarged cross-sectional view, section 2—2', of the device shown in Fig. 1.

Referring to the figures of the drawing, a typical embodiment of the present invention is shown comprising an elongated ferrite compact or slug 10 having a glass coating or skin 11 which hermetically seals the compact 10 from the surrounding medium. In the embodiment shown, the diameter of the middle portion of the compact is of the order of from 0.1 to 1.0 inch and its length is generally within the range of from one to four inches, the dimensions being determined by the particular application. Inasmuch as ferrites may be used in numerous other forms such as, for example, hollow or solid cylinder, it is readily apparent that the scope of the present invention is not limited to the sizes mentioned or particular configuration shown.

In order to provide a suitable glass skin on the ferrite compacts, it is first necessary to determine the physical properties of the ferrite. Ferrites of many varied and diverse compositions are commercially available. Many different compositions are employed because of the unusually large number of combinations of different useful physical properties exhibited by all of them. Representative samples of a ferromagnetic ferrite may contain the following constituents: MnO, MnO₂, CuCO₃, ZnO, ZnO₂ (unstable), BaO, CaO, Zr, ZrO₃. The ferrites are nor-

mally chemically reactive with lead peroxides and borates but they are not reactive with oxides of aluminum or magnesium or the carbonates of sodium or calcium.

The mineral magnetite, FeOFe_2O_3 , is the well-known ferro-ferrite occurring in nature. Past experiments have led to success in making "synthetic" ferrites with both "soft" and "permanent" magnetic properties. Due to the absence of metal components and in view of their dense structure, ferrites have relatively high volume resistivity and high permeability in comparison to powdered iron materials. Their specific gravity lies between 4 and 5 and their dielectric constant is about 9. These and other peculiar properties have led to a wide field of applications, many of which, as previously mentioned, require ferrites to be hermetically sealed.

The thermal coefficient of expansion of ferrites is primarily limited to the range 71 to 93×10^{-7} inch per inch per $^{\circ}\text{C}$. They have a relatively high modulus of elasticity and their ultimate strength is usually about 10,000 p. s. i., i. e., pounds per square inch, in compression and 2000 p. s. i. in tension. These three physical properties are generally the most important when correlated with those of glass, the thermal expansion coefficient normally being the most important of the three.

To produce a hermetic seal that will withstand high vacuum and large temperature variations, glass probably has better physical and chemical properties than any other material. In obtaining a glass seal for a material it is necessary for the glass to "wet" and to "match" the material. Since most all glasses "wet" metal oxides, there is obviously no problem presented with respect to this requirement in coating ferrites since they are almost totally constituted of the oxides of bivalent metals. What is normally meant by "matching" a glass to a material is to seek out a glass having a thermal coefficient of expansion near enough to that of the material to prevent a structural failure in either by stresses set up by differential expansion.

In the manufacture of a good seal, being able to match a glass and a material from the standpoint of thermal expansion, i. e., being able to keep the strains in the glass or the material below their breaking strength in case their thermal expansions do not match, is not sufficient when accomplished only at room temperature because the glass and material must first of all be heated to a high temperature in order to make the seal. For this purpose, the glass is heated to its working temperature, the temperature above that at which it begins to soften or change its shape. In fact, the glass should be rendered plastic or fluid-like so that it will "wet" the material and stick thereto. Such a temperature is in the neighborhood of 800°C . or higher, although, as it will be seen, one type of useful glass has a working temperature of 560°C .

The working temperature of a glass is to be distinguished from the "softening" temperature which may be as low as 440°C . and which is defined as being the temperature at which the glass becomes sufficiently yielding so that strains are relieved at an extremely rapid rate or within a very short period, for example, less than one minute. The seal is then allowed to cool directly to room temperature or, as is the more usual case, the cooling process is temporarily arrested at a predetermined elevated temperature, termed the "annealing" point or the lowest temperature below the "softening" temperature at which 90% of the internal stresses of the glass will be removed in about fifteen minutes.

In choosing a suitable glass in which to seal a ferrite, it is to be noted that a considerable choice as to which and how many raw materials, in addition to sand, are to be incorporated into a batch of a useful silicate glass. Silica glass or fused quartz and fused silica, made from a batch consisting of sand alone, appears to be the ideal in glass in nearly all its physical and chemical properties. However, if too high a percentage of sand is utilized, the glass formed in such a batch requires, for melting, tem-

peratures of about 1700°C . which temperatures are too expensive and impractical to achieve even with the best commercial glass-furnace refractories. Also, the resultant glass is so viscous, even at melting temperatures, that it can be homogenized and shaped only with great difficulty. Consequently, for fluxing or lowering the melting temperature, some sodium, or potassium oxide, or both, usually 3–19% total, and some correlated amounts of one or more of the stabilizing and modifying oxides such as calcium, magnesium, zinc, barium, aluminum, and lead oxides are included.

In the trade, the commercial silicate glasses, excluding two-component silicate glasses, which are unsuitable for making glass articles because of water solubility or devitrification, i. e., crystallization, are classified in five chemical types: soda-lime glasses, sometimes called simply "soda glasses" and sometimes "lime glasses"; lead glasses; and three new low-expansion and therefore heat-resistant type glasses, namely, borosilicate glass; and 96% silica glass, and pure silica glass or quartz. This listing is more or less in order of increasing silica content, increasing mechanical durability, improving electrical properties, increasing cost, increasing shaping difficulty, and decreasing thermal expansion coefficient.

The composition of these types, given in Table I, are the analyses of the finished glasses for elements, except oxygen, converted to oxide equivalent.

Table I.—Compositions of commercial glasses

Component	Composition, percent*				
	Soda-lime	Lead	Borosilicate	96% Silica	Silica glass
SiO_2	70–75 (72)	53–68 (68)	73–82 (80)	96	99.8
Na_2O	12–18 (15)	5–10 (10)	3–10 (4)		
K_2O	0–1	1–10 (6)	0.4–1		
CaO	5–14 (9)	0–6 (1)	0–1		
PbO		15–40 (15)	0–10		
B_2O_3			5–20 (14)	3	
Al_2O_3	0.5–2.5 (1)	0.2	2–3 (2)		
MgO	0–4 (3)				

*The figures in parentheses give the approximate composition of a typical member.

In order to make a successful seal, the expansion of ferrite 10 and glass 11 must be substantially the same over the temperature range within which the glass is elastic. A large difference in expansion between them produces stresses which may cause either or both to crack when cooled to room temperature. Some degree of differential expansion, however, is tolerable and sometimes desirable. The relaxation characteristics of the glass determine the upper temperature limit to which matched expansion is essential. Obviously, at temperatures where the glass is substantially plastic, equal expansion is no longer necessary.

The glasses which are most useful in practicing the present invention are then the "soft" glasses, the soda-lime glasses and the lead glasses. The thermal coefficients of each of these types have the following respective ranges: 67 to 105 and 9 to 140×10^{-7} inch per inch per $^{\circ}\text{C}$. Although soft glasses may go lower to possibly 65×10^{-7} inch per inch per $^{\circ}\text{C}$., few will go as high as 140×10^{-7} inch per inch per $^{\circ}\text{C}$. Fused silica or 100% silica glass has a coefficient of expansion which is too low for the present purposes, being about 5.5×10^{-7} inch per inch per $^{\circ}\text{C}$. and 96% silica glass likewise has too low a coefficient of expansion, being about 8×10^{-7} inch per inch per $^{\circ}\text{C}$. The glasses called borosilicate glasses contain 5% or more of boric oxide. They are also usually too hard to seal a ferrite, the range of their thermal expansion coefficients being about 13 to 60×10^{-7} inch per inch per $^{\circ}\text{C}$.

Glass in general has an ultimate strength in compression and tension ranging respectively from 90,000 to 180,000 and from 4,000 to 1,000,000 p. s. i. The ultimate

mate strength in tension is normally much less than 1,000,000 p. s. i. except for very small glass fibers. It is however, pertinent to note that the use of any glass with a ferrite demands that the thermal expansion coefficients be well matched to prevent a structural failure particularly in the ferrite because of the low ultimate strength of the latter.

Next in importance to the thermal expansion coefficient is the modulus of elasticity of a glass. This is true because the glass should also be pliable at low temperatures to be able to take a large deformation with very little stress, i. e., its modulus of elasticity should be as low as possible. Young's modulus does not appear to be especially related to the "hardness" of a glass or to any particular element of its composition. It is also true that there appears to be no correlation between Young's modulus and the thermal expansion coefficient. This modulus of elasticity, however, does not normally vary appreciably for soft glasses of common compositions and is, therefore, not nearly so important as the thermal expansion of glass. For example, all Young's moduli of glasses fall within the range 65 to 127×10^{-7} p. s. i. Some go as low as 76×10^{-7} p. s. i. with a thermal expansion coefficient of 79.6×10^{-7} inch per inch per $^{\circ}$ C. The moduli of hard glasses are scattered over an equally wide range, going as low as 68×10^{-7} p. s. i. for a glass having a thermal expansion coefficient of 32×10^{-7} inch per inch per $^{\circ}$ C. and going as high as 127×10^{-7} p. s. i. for thermal expansion coefficient of 42×10^{-7} inch per inch per $^{\circ}$ C.

Although the soft glasses are generally satisfactory for coating a ferrite, there are a few glasses which may be used to particular advantage to reduce the risk of structural failures during the manufacture of the seal and especially during the handling of the component materials. For example, in the case of ferrites having a thermal expansion coefficient falling within the range $71 \times 86 \times 10^{-7}$ inch per inch per $^{\circ}$ C., it has been an effective expansivity between 65 and 100×10^{-7} inch per inch per $^{\circ}$ C. A glass having characteristics approximating these is commonly known as "lime glass." This glass is composed of 73.3% SiO_2 ; 15.6% Na_2O ; 5.4% CaO ; 3.8% MgO ; 1.4% R_2O_3 ; 0.5% K_2O and has an effective expansivity of $92 \pm 2 \times 10^{-7}$ inch per inch per $^{\circ}$ C., and a Young's modulus of 98×10^{-7} p. s. i.

It has also been found that a seal between the soft glasses known to the trade as 0080 and 7570 manufactured by the Corning Glass Company may be used in hermetically sealing the ferrites of the above description. The Corning Glass Company designates "clear sealing bulb glass" and "solder glass" with the number 0080 and 7570, respectively. These glasses are kept as closely as possible to a standard chemical composition at all times.

In order to apply the glass coating 11 to the ferrite slug 10, a suitable glass of the above-described types is first powdered and then suspended in a liquid such as, for example, water, methyl alcohol, or a solution of nitrocellulose in amyl acetate. This suspension of powdered glass is then brushed or sprayed uniformly over the ferrite slug 10 or alternatively, the ferrite slug 10 may be immersed in a suspension of powdered glass in the solution of nitrocellulose in amyl acetate.

The ferrite slug 10 covered with the suspension of powdered glass is then heated in a controlled atmosphere to the working temperature of the glass and then slowly cooled. This process is repeated until the glass coating 11 has a glaze finish and is of a suitable thickness. The thickness of glass coating 11 depending on the uses to which the ferrite is to be put is of the order of from 0.003 inch to more than 0.06 inch, the thinner coatings being used where permissible in that the electrical losses are less.

Referring again to Fig. 1, it is seen that glass coating 11 of the device has elongated pointed ends 12 where

the glass is considerably thicker than the remaining portions of the coating. The device, as previously mentioned, is employed to rotate the plane of polarization of the electric field of a propagated wave. In order to accomplish this, it is necessary for the electromagnetic wave to propagate through the medium of the device. In that the dielectric constant of ferrite is quite high, there is generally an impedance mismatch between the medium surrounding the device and the medium of the ferrite slug 10. Thus, if the glass has a dielectric constant approximately equal to the geometric mean of the dielectric constants of the surrounding and ferrite mediums, it may be employed to substantially improve the impedance match of the ferrite slug 10 to the surrounding medium. The thickness of glass points 12 for optimum matching as measured along the longitudinal axis of the device is of the order of one-half guide wavelength.

A glass suitable for making the glass points 12 is known as Corning glass 0120. This glass has the particularly low dielectric constant of 6.6 which is necessary to approximate the aforementioned geometric mean of the dielectric constants of the surrounding medium and the ferrite. The Corning 0120 glass is a "clear potash soda lead" glass having a thermal expansion of 89×10^{-7} inch per inch per $^{\circ}$ C., and a Young's modulus of 80×10^{-7} p. s. i. which is suitable for use in conjunction with the glass constituting the glass coating 11.

It has been found in attempting to hermetically seal some ferrites that they are sufficiently porous so as to continuously absorb the glass when heated to the fluid state. This effect is to be avoided in that the characteristics of the ferrite are deleteriously effected. According to the present invention, ferrites of this type are sealed by first applying a coating of glass having a high working temperature to the ferrite. This coating will generally not effectively seal the ferrite but it will prevent subsequent coatings of glass having a lower working temperature from being absorbed into the ferrite.

More particularly, this process of hermetically sealing a porous ferrite is as follows:

- (1) Suspend powdered Corning glass 0080 in water.
- (2) Brush glass 0080 onto the ferrite.
- (3) Heat glass 0080 in an oven in air to its sintering temperature, i. e., the temperature at which substantial fusion but not fluidity is indicated, e. g., $700-800^{\circ}$ C.
- (4) Allow the glass and the ferrite to cool.
- (5) Brush a liquid suspension of powdered Corning glass 7570 over the sintered 0080 glass.
- (6) Heat the ferrite and glasses to the working temperature of the 7570 glass, i. e., about 560° C.
- (7) Allow both glasses and ferrite to cool.

Corning glass 7570 by itself has utility in the manufacture of the ferrite seal of the present invention in that its working temperature is 560° C. whereas most other glasses have a working temperature above 800° C. The use of this glass reduces the risk of structural failure due to the low thermal shock resistance of ferrites. Corning glasses 7570 and 0080 have thermal expansion coefficients of 84 and 92×10^{-7} inch per inch per $^{\circ}$ C., respectively, and in this regard are useful in preventing differential stresses. Young's modulus of Corning 7570 is within the usual soft glass range. Likewise, Corning 0080 has a Young's modulus of 98×10^{-7} p. s. i.

A few other glasses may also be used to hermetically seal a ferrite material. Among these glasses are "clear sealing glass" which is designated by the present Corning number code by 8870. Its application is somewhat limited particularly because of its high dielectric constant, viz., 9.5; however, its thermal expansion coefficient is 91×10^{-7} inch per inch per $^{\circ}$ C. and a large advantage accompanying its employment is its modulus of elasticity, 76×10^{-7} p. s. i., which is comparatively low.

What is claimed is:

1. A device comprising an element composed of a porous ferromagnetic dielectric ceramic, said element hav-

ing predetermined physical characteristics; a sintered layer of a first type of glass covering the exposed surface of said element, said first type of glass having a predetermined working temperature; and a coating of a second type of glass disposed on top of said sintered layer, the working temperature of said second type of glass being more than 80° C. lower than said predetermined working temperature, and said first and second types of glasses having thermal coefficients of expansion of from 65 to 120×10^{-7} inch per inch per degree centigrade, whereby said first and second types of glass provide a seal having physical characteristics substantially equivalent to said predetermined physical characteristics of the ferrite element.

2. The method of hermetically sealing a normally porous ferromagnetic dielectric compact employing first and second types of glasses having first and second predetermined softening temperatures, respectively, said first softening temperature being higher than said second softening temperature, said method including the steps of producing first and second liquid suspensions of said first and second types of glasses, respectively; applying said first liquid suspension to the surface of said compact; heating said compact to the fusing temperature of said first type of glass to produce a coating of said first type of glass on said compact that partially seals the surface thereof; applying said second liquid suspension to the coated surface of said compact; and heating said compact to a temperature not less than the softening temperature of said second type of glass and less than the softening temperature of said first type of glass.

3. A device comprising an element composed of a porous ferromagnetic dielectric ceramic, said element having predetermined physical characteristics; a sintered layer of a first type of glass disposed on the exposed sur-

face of said element, said first type of glass having a predetermined working temperature; and a coating of a second type of glass disposed on top of said sintered layer, the working temperature of said second type of glass being less than said predetermined working temperature, whereby said first and second types of glass provide a seal having physical characteristics substantially equivalent to said predetermined physical characteristics of the ferrite element.

4. The method of hermetically sealing a normally porous ferromagnetic dielectric compact employing first and second types of glasses having first and second predetermined softening temperatures, respectively, said first softening temperature being higher than said second softening temperature, said method comprising the steps of producing a glaze of said first type of said glasses over the exposed surface of said compact, and producing a glaze of said second type of said glasses over the exposed surface of said first type of said glasses.

References Cited in the file of this patent

UNITED STATES PATENTS

612,839	Gallinowsky	Oct. 25, 1898
1,221,561	Meyer	Apr. 3, 1917
1,663,660	Hottinger	Mar. 27, 1928
2,076,869	Tanner	Apr. 13, 1937
2,568,881	Albers-Schoenberg	Sept. 25, 1951
2,570,299	Zademach et al.	Oct. 9, 1951
2,598,371	Gusdorf	May 27, 1952
2,643,336	Valensi	June 23, 1953
2,677,055	Allen	Apr. 27, 1954
2,685,539	Woodburn et al.	Aug. 3, 1954
2,745,069	Hewitt	May 8, 1956
2,748,353	Hogan	May 29, 1956

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,877,144

March 10, 1959

Arthur H. Iversen

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 70, for "MnO," read -- MgO, --; column 4, line 39, Table I, third column, for "0.2" read -- 0-2 --; line 62, for "65 X 10⁻⁷" read -- 67 X 10⁻⁷ --.

Signed and sealed this 30th day of June 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,877,144

March 10, 1959

Arthur H. Iversen

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 70, for "MnO," read -- MgO, --; column 4, line 39, Table I, third column, for "0.2" read -- 0-2 --; line 62, for "65 X 10⁻⁷" read -- 67 X 10⁻⁷ --.

Signed and sealed this 30th day of June 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents