

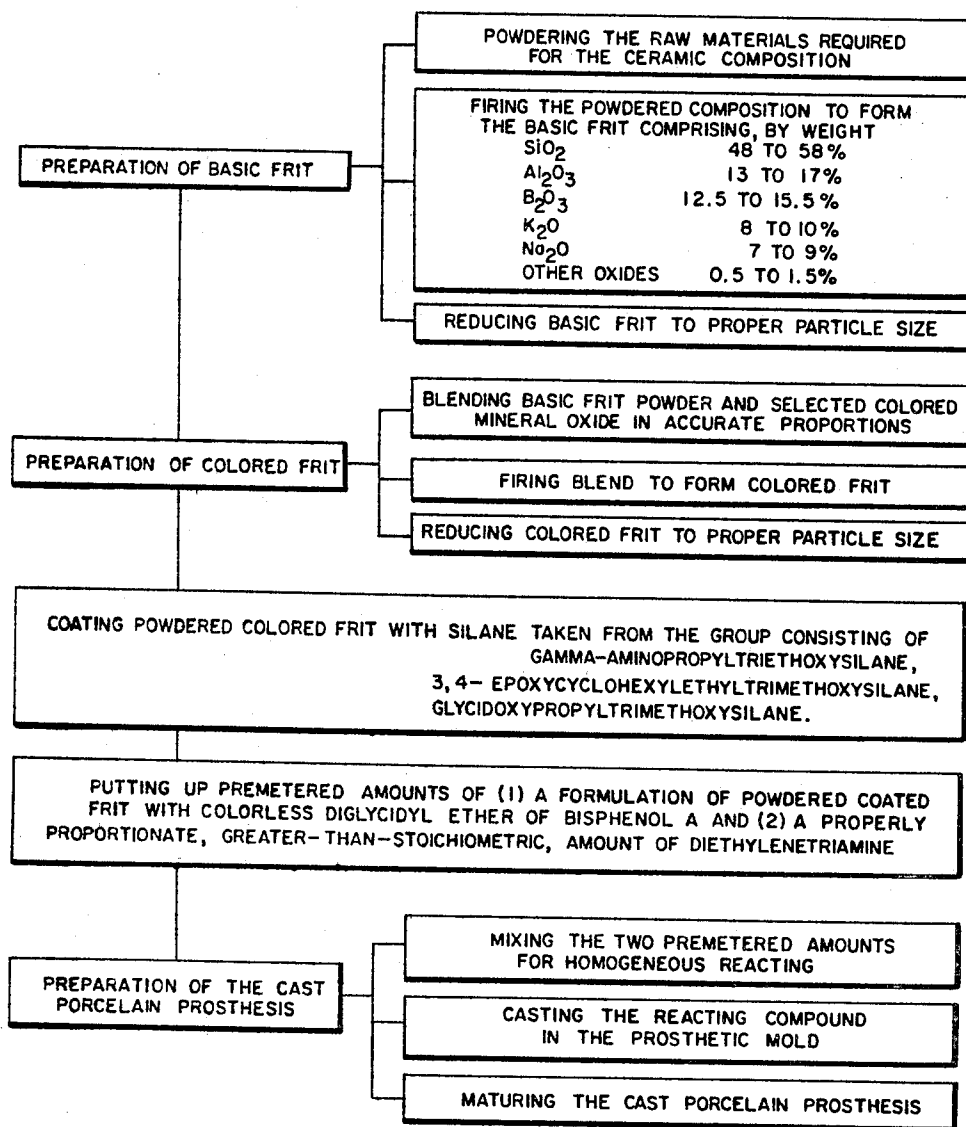
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CAST PORCELAIN PROSTHESIS AND METHOD OF MAKING THE SAME

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CAST PORCELAIN PROSTHESIS AND METHOD OF MAKING THE SAME

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This invention relates to a porcelain material cast to form a dental prosthesis and the method of making the same. Specific prostheses of this new type may be an inlay, an onlay, a crown, a pontic or artificial tooth, a facing, a fixed or removable partial denture, a complete denture or a saddle, a liner or other auxiliary part of any such prosthesis.

We can most readily illustrate the invention by taking the dental inlay as an example, for its requirements are perhaps the most exacting in restorative dentistry and therefore reflect both particular and general problems with which the dentist practicing the prior art is confronted.

Almost all dental inlays are presently formed of gold alloys by the lost wax technique of casting. It is well known, however, that gold inlays present such problems as (a) discomfort and danger to the pulp from thermal and galvanic shock, (b) unsightliness, which results in reluctant use in posterior teeth and virtually no use in interiors, and (c) questionable fit due to nonuniform compensation for its shrinkage in casting by expansion of the investment.

Porcelain being the medium of choice in restorative dentistry, attempts have been made to form an inlay by applying a slurry of conventional dental porcelain to a matrix of platinum foil adapted to a die (a replica of the prepared tooth), drying and shaping it, removing it from the die and baking it to maturity. However, as dental porcelains shrink 15 to 20%, it is necessary either to repeat this process with additional porcelain one or more times or to overbuild the first application 20 to 25% and hope for the best. As a result, not only is the fit questionable but the fine margins tend to round off when the porcelain is baked to a glazed condition, thus widening the cement line and inviting seepage. Finally, thin sections of baked porcelain are subject to fracture in service. If by chance a successful inlay is formed of baked porcelain, the process of achieving it is prohibitively costly in labor time. Few if any such inlays are found in actual use.

Baked porcelain can also be found in some few inlays made of suitable dental metal to which a thin porcelain covering has been fused, following the teachings of Patent 3,052,982 for the making of fused porcelain-to-metal teeth in general. By this method, the unsightliness of gold is eliminated and galvanic and thermal shock are minimized but the problems of fit and service remain as for the gold inlay. Moreover, somewhat deeper preparation of the host tooth and higher skills in fabrication are required than when attempting an inlay of baked porcelain alone, especially in matching the color of adjacent dentition, and it is therefore extraordinarily expensive in labor cost.

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Resins, although widely used in dentistry because of ease in fabrication and for lack of superior, truly adequate materials, exhibit known deficiencies when used as other dental prostheses and are not used at all as inlays, primarily because they are too far below the cast gold inlay in strength, hardness and corrosion resistance and too far above it in rate of shrinkage, acrylic, for example, shrinking as much as 7%. Authorities state that no ideal resin has yet been found which meets all the requirements of mouth service such as optically esthetic appearance and stability; dimensional fit and stability; adequate strength, resilience and abrasion resistance; impermeability to mouth fluids, insolubility and noncorrosion; resistance to food clingage and ability to be cleaned in ways such as mouth tissues are cleaned; freedom from taste, odor, toxicity and irritation to tissues; thermal conductivity normal to the mouth and low specific gravity, with a softening temperature well above that of hot foods or liquids taken orally; and ease of repair and fabrication with simple equipment.

Reinforced resins, infrequently attempted for use in dentistry, likewise are not used at all as inlays and exhibit known deficiencies when used as other indirect dental prostheses. A direct filling material comprising a combination of fused silica and a resin has been described in Patent 3,066,112. Use of it for inlays and other indirect dental prostheses is contraindicated in view of its admitted volumetric shrinkage of 2%. Similarly, direct filling materials now in common use, such as silicate cements and amalgam (silver-tin-mercury), have no application in the field of indirect dental prostheses.

Accordingly, it is an object of our invention to provide new indirect dental prostheses formed of a new cast porcelain material which endows such prostheses with virtually 100% dimensional accuracy and stability and which enables them to eliminate thermal and galvanic shock; to possess improved esthetics; to function durably with sufficient strength and a surface hardness approaching that of cast gold, resisting abrasion, corrosion, discoloration and dissolution in mouth service; to provide normal hot-and-cold sensations, with a softening temperature well above that of hot foods or liquids taken orally; to resist food clingage and be easily cleaned; to be free from taste, odor, toxicity and irritation, functioning benignly when in permanent contact with tissue; to be capable of tenacious adhesion to metal for secure embedment of metal denture extensions; and to be easily fabricated or altered.

Further objects are to provide a porcelain material that can be durably pigmented with fired colors in the shades of the tooth spectrum or of other oral tissues such as the gums, that is highly translucent for delicate shading, that will blend with the color and texture of natural teeth, simulating them as does baked porcelain, and that can be easily cast in a suitable dental mold.

Such desirable pigmentation and esthetic texture could not, we have found, be achieved by the known coloring techniques and materials used in dental resins, because of fading, discoloration, and the difficulty in obtaining permanent dental spectrum shades.

These and other objects of the invention are accomplished and the new results obtained as will be apparent

from the porcelain material and fabrication methods hereinafter described, particularly pointed out in the attached claims, and outlined in the form of a flow diagram on the attached drawing.

The material comprises a frit of unique composition which is reduced to a specific particle size range, specifically fired with mineral oxide colors suitable for this porcelain, prepared for chemical bonding by coating it with a selected colorless silane, compounded with a purified form of diglycidyl ether of bisphenol A, which is colorless, and hardened in a special manner with diethylenetriamine, which also is colorless. Matured in an appropriate mold, the resulting product is an indirect dental prosthesis the major portion of which is colored porcelain, with its desirable esthetic and physical properties when used in the mouth, now possessing, among other new advantages, the property of exact fit instead of the 15 to 20% shrinkage characteristic of baked porcelain.

Preparation of the basic frit

The existing dental porcelains and dental grade feldspars known in the prior art were examined and none was found that could give us the optical qualities required for our porcelain base. Either they exhibited undesirable color characteristics or they lacked the requisite strength or they were unable to retain the desired mineral oxide colors when brought high into their fusing ranges. Known frits, also, exhibited undesirable color characteristics, inadequate strength and a general inhospitality to the true orange shades of the tooth spectrum. However, we discovered a composition, comprising substantially the following ingredients by weight, in the range which proved satisfactory:

	Percent
SiO ₂ -----	48-58
Al ₂ O ₃ -----	13-17
B ₂ O ₃ -----	12.5-15.5
K ₂ O -----	8-10
Na ₂ O -----	7-9
Other oxides -----	0.5-1.5

The source materials were blended in powdered form and fired in a crucible to about 2050° F. over a 3½ to 4 hour period or until the resulting frit was thoroughly fused and could be poured in a sluggish stream into water. The fired frit was dried and ground. We found that best results were obtained when using as our basic frit those particles which passed a U.S. No. 200 sieve but not a U.S. No. 325 sieve.

A spar known as Buckingham S-1 feldspar was found which, when mixed 80 parts by weight of spar with 20 parts by weight of anhydrous borax, had a constituent range which fell within our composition formula, namely SiO₂, 52.97%; Al₂O₃, 14.93%; B₂O₃, 13.84%; K₂O, 9.38%; Na₂O, 8.24%; CaO, 0.56%; Fe₂O₃, 0.06%; and MgO, 0.02%. Other substances may be added which do not reduce the strength, hardness and translucency required in the final product.

Preparation of colored frits

Generally from 97.5 to 99.975% of the basic frit is fused with mineral oxides to produce the colored frits. For example, 99.975% of the basic frit was refritted with 0.025% of a mixture containing chromium, ferric and vanadium oxides that has been sintered to the spinel form, known as Drakenfeld mineral oxide No. 41229, sold by B. F. Drakenfeld Co. of Washington, Pa., to produce a grayish colored frit. Usually a powdered blend is made of the basic frit and the required mineral oxide and the blend fired in the same manner as the basic frit itself, then dried and reduced to 200/325 mesh particle size for use.

Firing of the colored frit must be limited to tempera-

tures which do not reduce the colored mineral oxides. In some few instances, a particular colored frit may require firing to a temperature of 1900° F. and then be reduced from the boule form to proper particle size for use as prepared colored porcelain frit.

Coating the porcelain frit

We have found that we can chemically bond the basic or colored frit particles with the reaction product of the diglycidyl ether of bisphenol A and the diethylenetriamine by first coating the particles with a silane of the group:

Gamma-aminopropyltriethoxysilane,
3,4-epoxycyclohexylethyltrimethoxysilane,
Glycidoxypropyltrimethoxysilane.

The last of these three silane monomers is our preferred coupling agent. Optimum properties for the bond are obtained by judicious control of the application of the coupling agent to the frit particles. This coating also serves to lubricate the particles, prevent agglomeration and impart water repellency.

A vessel is charged with a weighed amount of distilled or purified water, 1% by weight of the selected silane is added and mixed for an hour at moderate speed and then the particulated frit is added, in an amount about equal in weight to that of the water, and mixed for 2 hours at moderate speed, after which the entire charge may be put through a spray dried to yield the coated frit in its original particle size, discrete and dry, or the same result approached by more primitive means.

Preparation of the porcelain casting formulation

The only material we have found suitable to make a useful porcelain casting formulation is a purified form of diglycidyl ether of bisphenol A which is transparent and colorless and is shown in Patent 3,095,429. Such a material has a melting point of 39 to 43° C., an epoxy content of from 24.4 to 25.3% and an epoxide equivalent weight of 173 to 179. Such a material may crystallize at room temperature but can be warmed back to liquid form at slightly elevated temperatures and then, even when in the prepared formulation, remain liquid at room temperature for substantial periods of working time adequate to all our purposes.

A vessel is charged with a weighed amount of the diglycidyl ether of bisphenol A and, while it is stirred at moderate speed, 150 to 233% by weight of the coated frit is added gradually, depending on the viscosity desired in the formulation, and the entire charge is then thoroughly mixed at moderate speed for 4 hours, the resulting homogenized formulation thus consisting of coated frit and diglycidyl ether of bisphenol A in a ratio of from 60:40 to 70:30, respectively.

The formulation may then be put up in small quantities in wide-mouth jars, as a practical matter, to await the time when, with the hardener added, it is to be used to form a cast porcelain dental prosthesis. Such a procedure would be followed to assure availability within a reasonable time of a porcelain casting formulation of a certain shade of color to form a prosthesis desired by the dentist to be of that shade.

Compounding the porcelain casting formulation

Of all the known materials available to harden our casting porcelain formulation, we have found only one to be right for all our purposes and this one only after devising a special system for it. This is diethylenetriamine, referred to as DETA. It is transparent and colorless. Its five active hydrogen atoms bring about the most effective reaction in our prepared formulation when used in the unusual proportion we discovered to be right, thus providing optimum heat distortion temperature and optimum chemical resistance, as well as strength and related

properties, factors important for a material to be used in the mouth.

Moreover, used in the quantities of formulation put up appropriately small enough for handily forming dental prostheses, its exotherm is low enough and the temperature at which it matures is low enough to avoid discoloration of the prosthesis and deformation or degeneration of molds commonly used for the purpose. Finally, the elements of working-time and maturing-time are within ranges of practicality.

Our example again is the most exacting of all indirect dental prostheses, the inlay. In a system involving diglycidyl ether of bisphenol A and DETA, the direct ratio of mass to exotherm and the inverse ratio of mass to working-time and maturing-time become critical factors when the mass has the tiny dimensions of a dental inlay, which will usually weigh less than a gram. The problem presents itself even more critically in our prepared formulation, in which the two exothermic reactants make up a minor part of the mass.

We found it important not to follow the teaching that stoichiometric amounts of DETA bring best results. The stoichiometric amount of DETA for our particular material is 11.5 parts by weight per 100 parts of diglycidyl ether of bisphenol A, which proportion, in a prepared formulation in which the coated frit accounts for 60% of the total weight, is equivalent to only 4.6 parts per 100 parts of formulation.

We obtained a superior reaction product by using 15 parts of DETA per 100 parts of diglycidyl ether of bisphenol A, i.e., 6 parts of DETA per 100 parts of formulation, an amount more than 30% in excess of the stoichiometric. Tests showed, unexpectedly, that, instead of producing adverse effects, the intensified reaction resulted in a superior product.

We believe, as part of the explanation of this phenomenon, that the heat capacity of the porcelain frit in the formulation exerts the beneficial effect of regulating the thermal aspect of the reaction so that, in the early stages, the frit particles act as storehouses of heat, robbing the reaction of all excessive exotherm, and, in the later stages, assure uniform distribution of heat throughout the formulation.

Accordingly, we have found it desirable to employ 15 parts by weight of DETA per 100 parts of diglycidyl ether of bisphenol A as the guide in putting up vials of DETA as premeasured hardener to match, in proper proportion, the amounts of premeasured formulation put up in wide-mouth jars, in which the two are to be thoroughly mixed by hand at the time when a cast porcelain prosthesis is to be formed; and we have fixed upon the processing schedule as follows:

Working-time: About 20 minutes elapses between the time the hardener and the formulation have been mixed and the time that significant hardening has begun. As it is best that they not be actively disturbed thereafter, all prostheses to be cast from the particular mix should be cast within the 20-minute period.

Bench treatment: The cast prosthesis, in its mold, is then allowed to stand at room temperature (approximately 77° F.) for 2 hours, regardless of its size or mass.

Heat treatment: It is then placed, mold and all, in a regulated oven and allowed to mature at a temperature of 180° F. to 200° F. for a period of from 4 to 16 hours, depending inversely on the mass of the casting. An extremely small prosthesis, such as an inlay, where fullest hardening and maximum edge strength are required in the tiny flanges at the margins, should go the full 16 hours (overnight, in the usual practice), whereas at the other extreme in mass, a full-arch denture can be assumed to have matured after 4 hours—and intermediate-size prostheses at commensurate times in between, although no harm is done if a casting is heated at the regulated temperature longer than the time indicated for its size. The

casting should be cooled to room temperature before being removed from the mold.

Patterns and molds

A pattern of the desired cost porcelain dental prosthesis to be formed may be made in wax in a manner known to the art, on a die or model commonly in use, and the mold in which the prosthesis is to be cast may also be made in ways known to the art and of materials commonly used. Certain special considerations however, should be taken into account, in view of some of the new and unique properties in the material of our invention, primarily such properties as its 100% dimensional trueness and stability and its high fidelity to the texture of the surface against which it is cast.

Indirect dental prostheses are dependent on the art of replication and there can be a loss of the advantages we provide if the die and model materials employed or the mold materials employed are of a type which expands on setting or otherwise changes dimension or which exposes a rough, porous surface or which, when subjected to temperatures up to 200° F., gives off reactants capable of discoloring or otherwise adversely affecting our material. Fortunately, there are some die and model materials and mold materials available which exhibit none of these negative characteristics and it is from among such materials that a choice is made to aid in forming our cast porcelain dental prosthesis with optimum results.

General considerations

Our cast porcelain dental prosthesis may be formed entirely of our own material, as for example inlays, crowns, fixed or removable partial or full dentures and prefabricated facings, crowns or pontic teeth for use in connection with such dentures, or for use as part of other such dentures. Applicants have found in many clinical tests that after the prosthesis has been cured, which curing always takes place in the laboratory and outside the mouth, the inserted prosthesis has no skin irritant effect and is actually benign to tissue. DETA, in its skin irritant form, does not exist in the final completely cured product.

Many variations are possible, most noteworthy perhaps being those which utilize the tenacious adhesion of our material to metal as for example, in veneer crown and bridge work. In this particular field, as an illustration, the dentist's primary choice in the prior art is between acrylic cured on metal, with its known deficiencies, and the much superior but substantially more expensive fused porcelain-to-metal. When used for this purpose, our invention provides the economy and easy fabrication of the first with many of the superior attributes of the second, together with advantages not present in either of them.

Variations may be made in the various constituents as follows, by weight. The porcelain casting compound may comprise the porcelain frit in amounts varying from 55 to 68% and the reaction product in amounts varying from 45 to 32% and the reaction product itself may comprise the diglycidyl ether of bisphenol A in amounts varying from 75 to 90% and the diethylenetriamine in amounts varying from 25 to 10%. The porcelain frit could comprise 80% Buckingham S-1 feldspar and 20% anhydrous borax and could constitute 56.1% of the porcelain casting compound, of which the other constituents could be: 0.5% the silane, such as glycidoxypropyltrimethoxysilane; 37.7% the diglycidyl ether of bisphenol A; and 5.7% the hardener, such as diethylenetriamine.

We consider that our product possesses a unique dental coloring for oral prostheses which results solely from firing mineral oxide colors in the colorless porcelain frit and compounding it with colorless diglycidyl ether of bisphenol A and the colorless hardener, creating a unique formulation wherein the color resides solely in the frit particles.

We have thus described our invention but we desire it understood that it is not confined to the particular forms or uses shown and described, the same being merely illustrative, and that the invention may be carried out in other ways without departing from the spirit of our invention, and therefore we claim broadly the right to employ all equivalent materials coming within the scope of the appended claims, and by means of which objects of our invention are attained and new results accomplished, as it is obvious that the particular embodiments herein shown and described are only some of the many that can be employed to attain these objects and accomplish these results.

We claim:

1. A cast colored porcelain dental prosthesis made of substantially homogeneous material, having two areas, one a smooth surface for moving contact with oral tissue in the mouth and another area conforming to the supporting surface to which it is to be fixed in position, said prosthesis comprising a chemically bound combination of a powdered colored porcelain frit, wherein the basic frit comprises approximately, by weight:

	Percent
SiO ₂ -----	48-58
Al ₂ O ₃ -----	13-17
B ₂ O ₃ -----	12.5-15.5
K ₂ O -----	8-10
Na ₂ O -----	7-9
Other oxides -----	0.5-1.5

said frit having a particle size of from 200 to 325 mesh coated with a silane taken from the group:

gamma-aminopropyltriethoxysilane
3,4-epoxycyclohexyltrimethoxysilane
glycidoxypopyltrimethoxysilane

a colorless diglycidyl ether of bisphenol A and colorless diethylenetriamine, said prosthesis characterized by exact dimensional conformation to a replica of the supporting surface for exact fitting thereto.

2. The porcelain dental prosthesis of claim 1, wherein the homogeneous material comprises by weight: 55 to 68% a powdered frit constituted basically of:

	Percent
SiO ₂ -----	48-58
Al ₂ O ₃ -----	13-17
B ₂ O ₃ -----	12.5-15.5
K ₂ O -----	8-10
Na ₂ O -----	7-9
Other oxides -----	0.5-1.5

which is coated with a silane taken from the group: gamma-aminopropyltriethoxysilane, 3,4-epoxycyclohexylethyltrimethoxysilane and glycidoxypopyltrimethoxysilane; and 45 to 32% the resinifiable mixture which contains 75 to 90% of the purified diglycidyl ether of bisphenol A and 25 to 10% of the diethylenetriamine.

3. The porcelain dental prosthesis of claim 1, wherein the basic frit comprises Buckingham S-1 feldspar fired with anhydrous borax.

4. A porcelain composition comprising a chemically bound combination of a powdered frit, having a particle size of from 200 to 325 mesh, having basic constituents by weight of:

	Percent
SiO ₂ -----	48-58
Al ₂ O ₃ -----	13-17
B ₂ O ₃ -----	12.5-15.5
K ₂ O -----	8-10
Na ₂ O -----	7-9
Other oxides -----	0.5-1.5

which is coated with a silane taken from the group:

gamma-aminopropyltriethoxysilane
3,4-epoxycyclohexylethyltrimethoxysilane
glycidoxypopyltrimethoxysilane

and a resinifiable mixture which contains, by weight, 75 to 90% a purified diglycidyl ether of bisphenol A and 25 to 10% diethylenetriamine.

5. The porcelain composition of claim 4, in which the coated porcelain frit comprises 55 to 68% of its weight and the reaction product 45 to 32%.

6. The porcelain composition of claim 4, having constituents by weight of approximately 56.1% a powdered frit which, in its uncolored state, comprises:

	Percent
SiO ₂ -----	52.97
Al ₂ O ₃ -----	14.93
B ₂ O ₃ -----	13.84
K ₂ O -----	9.38
Na ₂ O -----	8.24
CaO -----	0.56
Fe ₂ O ₃ -----	0.06
MgO -----	0.02
Glycidoxypopyltrimethoxysilane -----	0.5
Purified diglycidyl ether of bisphenol A -----	37.7
Diethylenetriamine -----	5.7

7. The porcelain composition of claim 4, wherein the diethylenetriamine is used in excess of 12 parts by weight per 100 parts of diglycidyl ether of bisphenol A.

8. A cast porcelain dental prosthesis made of substantially homogeneous material, having two areas, one a smooth surface for moving contact with oral tissue and another area conforming to the supporting surface to which it is to be fixed in position, said prosthesis comprising a chemically bound combination of a powdered porcelain frit having a particle size of from 200 to 325 mesh, colorless diglycidyl ether of bisphenol A and colorless diethylenetriamine, said prosthesis characterized by exact dimensional conformation to a replica of the supporting surface for exact fitting thereto, said porcelain material consisting by weight of approximately 56.1% a powdered frit comprising:

	Percent
SiO ₂ -----	52.97
Al ₂ O ₃ -----	14.93
B ₂ O ₃ -----	13.84
K ₂ O -----	9.38
Na ₂ O -----	8.24
CaO -----	0.56
Fe ₂ O ₃ -----	0.06
MgO -----	0.02
Glycidoxypopyltrimethoxysilane -----	0.5
Purified diglycidyl ether of bisphenol A -----	37.7
Diethylenetriamine -----	5.7

9. The method of preparing a porcelain dental prosthesis which comprises making a pattern having two areas, one a smooth surface for moving contact with oral tissue and another area conforming to the supporting surface to which it is to be fixed in position, and preparing a mold therefrom, into which is poured a porcelain composition having the following constituents approximately by weight, 56.1% a powdered frit comprising, in its uncolored state:

	Percent
SiO ₂ -----	52.97
Al ₂ O ₃ -----	14.93
B ₂ O ₃ -----	13.84
K ₂ O -----	9.38
Na ₂ O -----	8.24
CaO -----	0.56
Fe ₂ O ₃ -----	0.06
MgO -----	0.02
Glycidoxypopyltrimethoxysilane -----	0.5
Purified diglycidyl ether of bisphenol A -----	37.7
Diethylenetriamine -----	5.7

said porcelain composition having been made by firing the constituents of the said powdered frit to about 2050°

F., cooling and powdering it, adding a powdered colored mineral oxide thereto, firing the colored mixture to from 1900° F. to 2100° F., cooling and powdering it to a particle size of from 200 to 325 mesh, coating the particles with said glycidoxypropyltrimethoxysilane, drying and returning them to their previous particle size, mixing the coated particles with said purified diglycidyl ether of bisphenol A, putting up the resulting formulation in appropriate quantities for use and, when needed, compounding said porcelain composition by mixing said formulation with said diethylenetriamine; thereafter allowing the molded product to stand for 2 hours at room temperature and then heating it to about 180° F. for from 4 to 16 hours.

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