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3,147,225

RADIOACTIVE SOURCES AND METHOD FOR MAKING

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FIG. 1

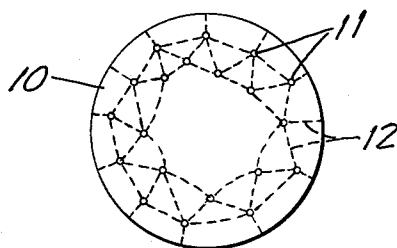
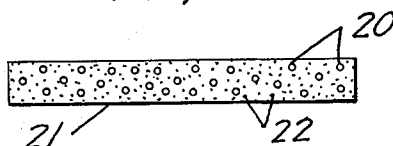


FIG. 2



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3,147,225 RADIOACTIVE SOURCES AND METHOD FOR MAKING

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This invention relates to small discrete weather-resistant refractory particles in which radioactive ions are widely dispersed and firmly fixed so as to resist removal. The particles hereof constitute discrete sources of radioactivity which may conveniently be handled with a minimum of hazard.

My particles have an inorganic refractory matrix which not only resists discoloration and degradation by radiation, but also permits substantial transmission of radioactive emanations therethrough. This matrix serves as a barrier against actual contact between radioactive ions entrapped therein and an individual who may accidentally or intentionally touch the articles. It is highly resistant to damage by weathering, and by acid and alkaline chemicals. While the matrix is translucent or transparent to light, and is formed using a glassy material, it is actually composed of inorganic refractory materials which are present in such amount that one cannot, in face, form a glass from a raw material batch of such composition by merely using ordinary glassforming temperatures up to about 1000° C. (or in most cases even 1500° C. or higher). Yet, in affixing radioactivity in such a matrix to form my articles, it is unnecessary to exceed about 1000° C., or so; and desired results may be gained using much lower temperatures.

Radioactive isotopes are dispersed in essentially ionic form within the refractory inorganic matrix aforementioned, and are mechanically entrapped so as to resist dislodgment. It is also likely, as will be explained, that the radioactivity in my articles is held in position by forces of ionic attraction, or is chemically bound in place so as to resist migration from the matrix. The strongest chemical bonding (and mechanical bonding) is achieved particularly in cases where higher temperatures of affixation are employed, as illustrated hereinafter.

Ions or particles of non-radioactive material may be affixed in or about the matrix of my radioactive source particles; and such additional constituents may or may not function in combination with the entrapped radioactivity to produce a useful result.

In use, my articles may be subjected to varied temperature conditions, from freezing temperatures well below 0° C. up to temperatures as high as approximately 1000° C., or even higher, without danger of radioactive material loss. They may be employed as sources of radioactivity in high temperature environments where all other small sources of radioactivity known to me deteriorate and allow escape of radioactive material, thus creating unwanted hazards. For example, particles of this invention may be used in applications around molten metals (e.g., in a liquid level indicator apparatus where the radioactive source would be inside the furnace and a detector outside its walls), in combination with phosphors as a heat resistant self-luminous marker on the exterior of rockets and missiles, in spark-gap equipment to introduce pre-ionization; and in a multitude of other applications, particularly where the hazards associated with radioactivity migrating from a source are to be avoided. At temperatures at least as high as about 1000° C., sources hereof still remain as discrete entities without fusing or flowing together.

The size, and therefore weight, of my articles may

easily be controlled so that they will not remain suspended in air to create unwanted hazards; thus, intake of the sources with air in breathing can be obviated. The hazards ordinarily associated with accidental or intentional ingestion of radioactivity are reduced to a minimum in using my sources. Indeed, in cases where the radioactive emanations from a particular source hereof are on the order of those tolerable by an individual for short periods, ingestion and egestion of particles of this invention by an individual can be accomplished without any significant harmful effect. Experiments indicate that only very little, or insignificant, residual radioactive material of the source would be left behind in the individual. However, I do not recommend wanton ingestion of my sources; rather I point out here that they show promise of being suitable for medical use in such manner, and that a minimum of hazard is encountered in the case of accidental ingestion. Other medical uses for my articles are also contemplated.

Insofar as I am aware, no other source of radioactivity is as easily and safely prepared, is as conveniently handleable, and additionally possesses all of the herein-noted advantageous properties of my articles. Known glassy sources of radioactivity are not resistant to higher temperature deterioration or fusion as aforementioned, and become discolored readily due to radiation, or lose radioactive substance readily when placed in solutions of acid or alkaline chemicals. While some sources of radioactivity have been prepared where the radioactive substance is dispersed, none of these prior art sources have possessed the extraordinary high temperature resistance and resistance to leaching exhibited by my articles; and none have been capable of a concentration of radioactive substance even approaching that possible in the case of my articles. It is estimated that the possible concentration of dispersed radioactive ions per unit of volume in my articles is up to about five times greater than is possible in the case of fused montmorillonite prior art sources containing widely-dispersed radioactive material.

A drawing made a part hereof schematically illustrates in FIGURE 1 an enlarged cross-sectional view of a radioactive source article of this invention. As shown in FIGURE 1, the article is preferably a small sphere or spheroid in shape and comprises a matrix 10 in which radioactive isotopes 11 are dispersed and entrapped. Dotted lines 12 are representations of the shrunken, and even obliterated, pores of the matrix in which the radioactive isotopes are bound. These radioactive isotopes are held within the chemically-resistant matrix by physical forces, i.e., by the pinching action of the walls of the shrunken pores around the radioactive atoms. However, as may be gleaned from the discussion to follow, chemical forces also play a very important part in retaining the radioactive ions or isotopes in fixed position within the matrix.

FIGURE 2 of the drawing is a schematic representation in side elevation of a sheet layer of self-luminous material, wherein radioactive source articles 20 of this invention are held in a plastic matrix or layer 21 in intimate association with a phosphor compound 22 (represented by dots in the plastic layer of this figure).

In making my source articles I employ the following convenient and simple procedure: First a batch of inorganic oxide ingredients selected to provide a particular glass on melting at ordinary glassforming temperatures is heated to a fluid state, using temperatures generally between about 1100° C.—1500° C., and quenched in a bath of water to form glass frit particles. These particles may then, if desired, be formed into sphere-like bodies by dropping them through a radiant heating zone wherein they will become fluid while free falling and assume a generally spherical shape due to forces of surface

tension. While free falling, they are cooled so as to retain their glassy nature and spherical shape. Then I place these glassy particles in an acid solution so as to leach therefrom a substantial amount of the acid soluble, non-refractory constituents of the original glassforming batch. As illustrated in the examples to follow, the resulting leached refractory glassy particles, having very high ion exchange properties, are then placed in solutions containing radioactive ions. The radioactive ions are rapidly picked up and absorbed by ion exchange within the leached pores of the glassy particles. From the solution which contained radioactive ions, the particles are dried and then raised to a temperature of at least about 350° C. up to approximately 1000° C., or even higher, under which treatment the pores of the glassy matrix actually shrink and seal the radioactive ions within the matrix, even though this temperature treatment is totally insufficient to effect a fusion or melting of the leached matrix. It has been noted that when temperatures on the order of around 350° F. up to approximately 700° C. are employed, the glassy nature of the matrix is largely preserved; whereas in the case of employing temperatures in excess of approximately 700° C., a crystalline phase develops in the refractory matrix of the article. For highest resistance to acid and alkaline attack, it is preferable to heat the refractory matrix above about 700° C., preferably about 1000–1200° C. so as to largely devitrify the matrix to a substantially crystalline phase. After this heat treatment, the articles, still in a translucent or transparent condition, and still as discrete articles (i.e., not fused together), are subjected to a brief treatment with acid solution so as to remove exposed radioactive ions which may have clung to the outer surfaces of the particles. They are then dried and are ready for use.

For convenience of handling and use in sheet material applications, the particles so formed are preferably in the range of about 10 to 150 microns average diameter. While larger sized particles may be formed where desired for specialized uses (e.g., thicknesses of about 2 mm. or even greater for the particles or layers), it has been found most practical to keep the size of particles usually within a range capable of passing through a screen of about 50 mesh (i.e., about 200 microns).

In an early preliminary experiment to test the principles of this invention, the following was done: A solution of strontium-90 in the form of strontium chloride was shaken for five hours with leached beads of about 125 to 175 microns average diameter and of the type hereinafter described in Example 1. The beads were then washed with water, dried overnight at about 54° C., and placed in an oven and heated to 250° C. over a period of 4 hours. They were then raised rapidly to 500° C. and maintained at that temperature overnight. Then, they were raised rapidly to 1000° C. and held for 6 hours, after which they were cooled gradually over a period of about 18 hours to room temperature. The shrunken beads were then immersed in an acid wash consisting of 0.1 normal HCl for two weeks to remove radioactive ions on the exposed outer surfaces of the beads. The amount removed was noted (less than 1%). Such beads were then tested for leach resistance and found to lose less than 0.0004% (i.e., less than four parts per million) of their entrapped radioactive ions in a water exposure test at 54° C. lasting 42 days. Such resistance to leaching, insofar as I am aware, has never been approached in discrete small radioactive sources. Indeed, one could drink the water used in this leaching test without harmful effects.

A wide variety of radioactive materials may be used in making the articles hereof. The particular radioactive isotope selected must be capable of ionization. Radioactive isotopes are commonly recognized as those which are unstable and decay to a less unstable state with the emission of penetrating radiation from the nucleus. From the illustrative examples, it is seen that a variety of wellknown radioactive materials of widely differing half-

life, radioactive particle or ray emanation, valence, etc., are suitable to employ.

In describing the composition of the preferred matrix of the articles hereof, I set forth the individual inorganic constituents as being presumptively present in oxide form, in accordance with general practice in glass and related arts. Also, for convenience and in the interest of accuracy, the various constituents of the matrix are set forth in terms of unit cations, combined with just sufficient oxygen to satisfy the valence of the particular cation (e.g., $\text{BO}_{1.5}$ instead of B_2O_3); and the "mol percent" of the various inorganic constituents of the matrix is calculated on the basis of these unit cation formulas.

The following examples are offered to illustrate this invention, but are not to be construed as limitative thereof.

EXAMPLE 1

A raw material batch of inorganic oxides having a compositional analysis in mol percent consisting of about 6.0% ZrO_2 , 9.0% $\text{AlO}_{1.5}$, 33.0% $\text{BO}_{1.5}$, 20.0% $\text{PO}_{2.5}$ and 32.0% $\text{NaO}_{0.5}$ is melted to a homogeneous mass at about 1350° C., and then quenched by pouring the melt in a cool bath of water so as to form small fractured glass particles (frit) of varied shapes.

The glass particles are then formed into spheres. Suitably this can be done by passing them through a radiant heating zone or high temperature flame where they soften sufficiently to permit surface tension forces to form them into spheres while they are freely moving through air. They are then cooled rapidly to prevent devitrification. Beads or spheres averaging about 50 to 100 microns in diameter are formed.

About 10 parts by weight of beads so formed are immersed in about 150 parts by weight of a five normal solution of nitric acid for about 6 hours with continuous agitation at room temperature, after which the beads are washed with water. The resulting leached beads, on chemical analysis, show an inorganic composition, set forth in mol percent, consisting of about 33% ZrO_2 , about 2% $\text{AlO}_{1.5}$, about 64% $\text{PO}_{2.5}$ and traces of small amounts of $\text{BO}_{1.5}$ and $\text{NaO}_{0.5}$. The wash water is drained from the beads, but the beads are not dried. They have an ion exchange capacity of about 6.8 milliequivalents per gram, as may be determined by the following test: To a one gram sample of beads is added 100 ml. of 0.1 normal sodium hydroxide solution and the whole shaken to equilibrium for about 24 to 72 hours. Thereafter, the solution is drained from the sample and titrated with 0.1 normal solution of hydrochloric acid. The milliequivalents of hydrochloric acid used in titration ($32 \text{ ml.} \times 0.1 \text{ N} = 3.2 \text{ meq.}$) subtracted from the milliequivalents of sodium hydroxide added to the sample ($100 \text{ ml.} \times 0.1 \text{ N} = 10 \text{ meq.}$) gives the ion exchange capacity (6.8 meq.) of the sample in milliequivalents per gram.

These leached beads have an effective surface area of about 670 square meters per gram, as may be determined by the Brunauer-Emmett-Teller (B.E.T.) method, the method being set forth in an article by P. H. Emmett appearing on page 95 et seq. of a published volume entitled Symposium on New Methods for Particle Size Determination in the Subsieve Range, containing the minutes of the Washington spring meeting, March 4, 1941, of the American Society for Testing Materials.

About three grams of the leached beads of this example, from which excess water had been drained, were then shaken for 24 hours with five millicuries of promethium-147 in the form of PmCl_3 , dissolved in 100 ml. of a very dilute acid solution. The promethium-147 was supplied by Oak Ridge National Laboratories and contained less than about 0.1% europium and less than about 15 mg. of neodymium per curie of Pm-147. It was in about 0.1 to 1.0 normal HCl water solution. At the end of 24 hours, the supernatant was decanted and counted to determine the percent of Pm-147 adsorbed by the beads. About

99% of the Pm-147 was found to have been adsorbed by the beads from solution.

The beads were then rinsed with water, dried in air a few hours, and raised to 500° C. over a period of about 4 hours. They were fired at 500° C. for about 18 hours, and then raised over a period of 3 hours to 1000° C. where they were maintained for about 4 hours, after which they were cooled to room temperature gradually over a period of about 16 hours. No sintering together of the beads occurred even though firing was accomplished while they were piled in a mass. During firing, the leached pores throughout the beads contracted and the ionically-bonded radioactive Pm-147 ions become an integral part of the structure. They were mechanically and chemically entrapped therein. X-ray diffraction analysis of the inorganic matrix of the bead indicated that a large percentage of the matrix was converted by the heating step to a crystalline phase, and thus I characterize the resulting matrix as "devitrified." (Analysis of beads of this example fired at various maximum temperatures indicated that at about 700° C. the tendency for the matrix to devitrify is noticeable, and that at 1000° C. devitrification is substantial.)

After shrinking the pores of the matrix, the beads containing affixed Pm-147 were shaken for one hour with a 100 ml. aliquot of one normal aqueous H₂SO₄ to remove any small amount of Pm-147 which may have clung to the outer surfaces of the beads. This acid wash was then repeated as an added precaution to remove residual surface radioactive ions, and then the product was rinsed with water and dried in air.

The resulting articles were spherical in shape and had a substantially devitrified refractory matrix within which Pm-147 was chemically and mechanically entrapped. The extent to which Pm-147 was entrapped and resistant to removal by leaching was tested, as set forth in Table I below.

The articles of this example have further been employed in sign and marker applications. They show every promise of being what might be termed a "safe" source for radioactive emanations in signs and markers.

Using the procedure and leached beads of this example, the following varied radioactive isotopes, ionized in water solution with an acid anion such as a chloride or nitrate, have been affixed, as described, to provide the new and improved sources of this invention: Sr-90, Tl-204, Co-60, Zn-65, Ag-110, Fe-59, Na-22, Ca-45, and Cs-134. In each case refractory damage-resistant radioactive sources were formed which were highly resistant to loss of their radioactive ions by migration and leaching. For illustrative purposes, the results obtained in testing the articles formed using Sr-90 are set forth in Table I.

EXAMPLE 2

The procedure of Example 1 was followed except that different leached glassy articles were employed. These glassy articles were formed from a raw material batch having an analysis in mol percent consisting of about 1.1% TiO₂, 5.7% ZrO₂, 5.7% SiO₂, 5.7% AlO_{1.5}, 25.0% BO_{1.5}, 17.6% PO_{2.5}, 33.0% NaO_{0.5}, and 6.2% KO_{0.5}, using a melting temperature of 1350° C. The quenched glass particles were formed into beads of about 50 to 200 microns average diameter and then leached for four hours under conditions otherwise as specified in Example 1. The resulting glassy matrices exhibited an ion exchange capacity of about 5.9 milliequivalents per gram and had an effective surface area of about 450 square meters per gram. Their leached composition analyzed to contain, in mol percent, about 5.1% TiO₂, 26.8% ZrO₂, 7.4% SiO₂, 1.6% AlO_{1.5}, 0.5% BO_{1.5}, 56.9% PO_{2.5}, 1.7% KO_{0.5}, and a trace of NaO_{0.5}.

About 94% of Pm-147 ions was adsorbed by the matrix

of these articles, after which the articles were processed as specified in Example 1.

EXAMPLE 3

A raw material batch analyzing to contain, in mol percent, 6.0% TiO₂, 6.0% HfO₂, 36.0% BO_{1.5}, 22.0% PO_{2.5} and 30.0% CaO was melted at 1350° C. and quenched in a cool bath of water to form glass frit particles. The particles were converted to beads of about 50 to 200 microns average diameter and leached for a period of 30 hours using conditions set forth in Example 1. Analysis of the leached product showed its composition to be, in mol percent, about 13.9% TiO₂, 19.1% HfO₂, 63.5% PO_{2.5}, 3.5% CaO, and a trace of BO_{1.5}. Its ion exchange capacity measured to be about 5.7 milliequivalents with an effective surface area of about 530 square meters per gram.

About 93% of the Pm-147 was adsorbed by these particles, after which the articles were processed as in Example 1.

EXAMPLE 4

The materials, procedure and conditions of Example 1 were duplicated, except that the matrix was formed using a raw material batch analyzing to contain, in mol percent, 8.0% TiO₂, 29.0% BO_{1.5}, 21.0% PO_{2.5}, 4.0% ThO₂, 6.0% CdO, and 32.0% NaO_{0.5}. After leaching, the matrix had a mol percent analysis of 30.0% TiO₂, 15.5% BO_{1.5}, 46.5% PO_{2.5}, 1.0% ThO₂, 0.5% CdO, and 6.5% NaO_{0.5}. It had an ion exchange capacity of about 4.6 meq. and an effective surface area of about 490 square meters per gram. About 95% of the Pm-147 was adsorbed and affixed in this matrix.

Table I

Example	1		2	3	4	M ²
	Pm-147	Sr-90				
Reagent test ¹						
a. H ₂ O	0.007	0.002	0.007	0.053	0.008	2.0
b. 5% NaCl	0.002	0.002	0.002	0.014	0.018	1.4
c. 5% Versene	0.044	0.011	0.002	0.052		2.0
d. 5% Na ₂ CO ₃	0.10	0.16	0.080	0.16		0.09
e. 0.1 N HCl	0.17	0.022	0.070	0.11	0.12	48.8

¹ About one gram of the articles of the examples was soaked in 100 ml. of each specified reagent at 50° C. for one week. Reagents b, c, and d are set forth in percent by weight in water solution. All reagents contain, in addition to the component listed in the table, about 0.01 percent by weight of CeCl₃, which served to occupy sites on the vessel in which the test was conducted, and therefore, inhibited the radioactive isotope from occupying such sites. In this manner, essentially accurate readings of the quantity of the isotope removed from the articles was insured. (The use of CeCl₃ may be omitted, except in the case of testing sources in which the radioactive isotope is a rare earth, such as Pm-147.)

² This column of test results is for a montmorillonite article of the type known heretofore in the art. The montmorillonite article was made by exposing the montmorillonite clay for 24 hours to Pm-147 ions in water solution containing chloride as the anion. About 94 percent of the Pm-147 ions were adsorbed from solution, after which the montmorillonite was subjected to the same heat treatment as set forth in Example 1. Instead of remaining as powder particles, it fused into a plurality of relatively larger particles under this heat treatment. It was then washed with acid as specified in Example 1 hereof, before conducting the tests here set forth.

There is a vast difference between the characteristics and behavior of the refractory materials of my articles and the material of fused montmorillonite articles such as set forth in the table. The highly refractory matrix of my articles, contrary to that of montmorillonite, cannot be fused at temperatures up to about 1000° C. Test results in the table further illustrate that montmorillonite sources have poor resistance to leaching, and thus are unsuitable for use in many weathering applications,

whereas the articles of this invention satisfy the requirements for use in such weathering applications. For example, it may be noted that my articles lost less than 0.1% of their entrapped radioactivity in water exposure tests lasting for one week at 50° C., whereas montmorillonite articles lost 2% as aforementioned in the table.

While a wide variety of materials may be used in forming a refractory matrix of the infusible character and other properties specified herein, it is preferable to employ, as illustrated in the examples, a particularly highly refractory matrix comprised in essential respects of at least one phosphate complex selected from the group consisting of titanium phosphate, zirconium phosphate and hafnium phosphate. A more detailed teaching of such inorganic-oxide matrices may be found in U.S. patent application Serial No. 513,156, filed June 3, 1955, by Warren R. Beck and George C. Hann, now Letters Patent No. 2,943,059, having a common assignee with this application. Leached matrices which satisfy the following compositional analysis, in mol percent, are particularly suitable to employ in the practice of this invention:

Table II

TiO ₂ -----	0-40
ZrO ₂ -----	0-35
HfO ₂ -----	0-35
TiO ₂ +ZrO ₂ +HfO ₂ -----	10-40
SiO ₂ -----	0-40
AlO _{1.5} -----	0-10
BO _{1.5} -----	0-25
PO _{2.5} -----	20-70
PO _{2.5} +BO _{1.5} -----	20-70
Fluxes -----	0-15
BO _{1.5} +fluxes -----	0-25
Total of listed ingredients -----	90-100

where fluxes, if present, are selected from alkali and alkaline earth oxides.

As further evidence of the striking properties possessed by the sealed sources of this invention, several rats were fed my articles and then sacrificed after various periods of time to determine the radioactive material retained in their bodies. Specifically, each rat was fed a capsule containing about 0.5 millicuries of Sr-90 affixed within a matrix as described in Example 1 hereof. Those rats which were sacrificed at the end of 4 days were found on analysis to have only a small harmless amount of radioactive substance in their systems. Based on the amount of radioactive substance initially fed to them, less than 0.001% remained in their bodies. Such a residual low amount of radioactive substance would not produce harmful effects.

Leach tests on my sources also indicate that they are highly resistant to weathering under acid, alkaline, and high ionic strength conditions, and thus may be used in many outdoor environments where other sources would be unsatisfactory. For example, they may be used in applications of a nautical nature, where salty air and spray may be expected to contact them.

A particularly interesting use of my articles lies in the area of providing new types of self-luminous sheet materials, signs, markers, etc. For example, two parts of the articles of Example 1, formed so as to range in size from about 40 to 80 microns, were mixed with 3 parts of phosphor (e.g., a zinc sulfide phosphor) excited by radioactive emanations (such as beta particles from Pm-147), and about 5 parts of a solution of 30% ethyl methacrylate polymer solids in xylene. The solvent mixture was then coated on a low adhesion surface at a thickness of about 60 mils, and dried at about 140° F. for one-half hour and at about 200° F. for 15 minutes. The resulting sheet layer may be used as a low intensity self-luminescent marker, or as a light source in applications where electrical illumination is impractical or undesired, e.g., under battle conditions in remote areas.

The foregoing is offered to illustrate but not limit my invention, as further set forth in the appended claims.

That which is claimed is:

1. As a new article source of radioactivity: a particle having a thickness no greater than 2 mm. and consisting essentially of a weather-resistant refractory matrix at least partially devitrified and characterized by remaining as a discrete entity not bonded to a like particle of identical matrix even when subjected to 1000° C. in contact with said like particle, and a radioactive isotope dispersed in said matrix by ion exchange and structurally bonded within shrunken pores of said matrix, said particle being characterized by an ability to withstand water exposure for one week at 50° C. with less than 0.1% weight loss of said structurally bonded radioactive isotope.

2. A composition comprising a plurality of particles as defined in claim 1 in intimate association with a radiation-excitabile phosphor.

3. A self-luminous article comprising a plastic material having therein a plurality of particles as defined in claim 1 in intimate association with a radiation-excitabile phosphor.

4. As new article sources of radioactivity: a mass of particles capable of passing through a screen of about 50 mesh, each of said particles consisting essentially of an at least partially devitrified weather-resistant inorganic-oxide refractory matrix and a radioactive isotope dispersed in said matrix by ion exchange, said radioactive isotope being firmly and substantially insolubly affixed within shrunken pores of said matrix without substantial attenuation of radioactive emanations from said isotope, said mass of particles being characterized by remaining as a mass of discrete entities not fused and not sintered to each other even when subjected to 1000° C. in contact with each other, and being further characterized by an ability to withstand water exposure for one week at 50° C. with less than 0.1% weight loss of said affixed radioactive isotope.

5. As a new article source of radioactivity: a particle having a thickness no greater than 2 mm. and consisting essentially of a weather-resistant refractory devitrified matrix comprised essentially of at least one inorganic complex selected from the group consisting of titanium phosphate, zirconium phosphate and hafnium phosphate, and a radioactive isotope dispersed in said matrix by ion exchange and structurally bonded within shrunken pores of said matrix.

6. A composition comprising a plurality of particles as defined in claim 5 in intimate association with a radiation-excitabile phosphor.

7. A self-luminous article comprising a plastic material having therein a plurality of particles as defined in claim 5 in intimate association with a radiation-excitabile phosphor.

8. As a new article source of radioactivity: a particle no larger than about 200 microns having a weather-resistant refractory devitrified matrix comprised essentially of at least one inorganic complex selected from the group consisting of titanium phosphate, zirconium phosphate, and hafnium phosphate, and containing a radioactive isotope dispersed in said matrix by ion exchange and firmly mechanically and substantially insolubly bound within shrunken pores of said matrix.

9. As new article sources of radioactivity: a mass of small spherical sealed sources of radioactivity having an average diameter smaller than 150 microns, and each source comprising a radioactive isotope dispersed and substantially insolubly affixed within shrunken pores of a weather-resistant refractory matrix, said matrix being characterized by remaining as a discrete entity not bonded to like particles of identical matrix even when subjected to 1000° C. in contact with said like particles, and being characterized further by serving as a barrier against actual physical contact of the radioactive isotope entrapped therein, the chemical analysis of said matrix being such

as to satisfy the requirements of the following table wherein amounts are set forth in mol percent:

TiO ₂ -----	0-40
ZrO ₂ -----	0-35
HfO ₂ -----	0-35
TiO ₂ +ZrO ₂ +HfO ₂ -----	10-40
SiO ₂ -----	0-40
AlO _{1.5} -----	0-10
BO _{1.5} -----	0-25
PO _{2.5} -----	20-70
PO _{2.5} +BO _{1.5} -----	20-70
Fluxes -----	0-15
BO _{1.5} +fluxes -----	0-25
Total of listed ingredients -----	90-100

said fluxes being selected from the group consisting of oxides of alkali and alkaline earth metals.

10. As new article sources of radioactivity: particles of small sealed sources of radioactivity having an average particle size greater than 10 microns and smaller than 2 mm. in thickness, and each comprising a radioactive isotope dispersed and chemically and mechanically affixed within shrunken pores of a weather-resistant inorganic-oxide refractory matrix, said matrix being infusible at temperatures below 1000° C. and serving as a barrier against actual physical contact of the radioactive isotope entrapped therein, the chemical analysis of said matrix satisfying the requirements of the following table wherein amounts are set forth in mol percent:

TiO ₂ -----	0-40
ZrO ₂ -----	0-35
HfO ₂ -----	0-35
TiO ₂ +ZrO ₂ +HfO ₂ -----	10-40
SiO ₂ -----	0-40
AlO _{1.5} -----	0-10
BO _{1.5} -----	0-25
PO _{2.5} -----	20-70
PO _{2.5} +BO _{1.5} -----	20-70
Fluxes -----	0-15
BO _{1.5} +fluxes -----	0-25
Total of listed ingredients -----	90-100

said fluxes being selected from the group consisting of oxides of alkali and alkaline earth metals.

11. Method of preparing small sealed sources of radioactivity comprising (1) contacting a solution of radioactive cations in ion exchange relationship with small, leached, highly-porous, refractory, cation - exchanging glassy articles infusible at temperatures below 1000° C., said glassy articles being comprised essentially of at least one inorganic complex selected from the group consisting of titanium phosphate, zirconium phosphate, and hafnium phosphate, (2) allowing a period of time for said radioactive cations to be adsorbed within the pores of said glassy articles, then (3) heat-treating said articles to a temperature above 350° C. to shrink the pores of said articles and substantially insolubly affix the radioactive cations in the form of a radioactive isotope within said shrunken pores of said articles, and (4) washing said articles in acid water to remove from the outer exposed surfaces of said articles incidental radioactive cations

which may have been adsorbed on said outer surfaces during the time of conducting steps (1) and (2) afore-saith.

12. A composition comprising radiation-excitabile phosphor in intimate association with particulate sources of radioactivity having a weather-resistant inorganic-oxide refractory matrix and containing radioactive isotope for excitation of said phosphor, said radioactive isotope being dispersed in said matrix by ion exchange and structurally bonded within shrunken pores of said matrix, said matrix being at least partially devitrified and characterized by an ability to withstand 1000° C. in contact with separate particles of identical matrix without sintering and without fusing to said separate particles of identical matrix, and said particulate sources of radioactivity being characterized by an ability to withstand water exposure for one week at 50° C. with less than 0.1% weight loss of said structurally bonded radioactive isotope.

13. A self-luminous article comprising a plastic material within which radiation-excitabile phosphor is mixed with particulate sources of radioactivity having a weather-resistant inorganic-oxide refractory matrix and containing radioactive isotope adapted to excite said phosphor, said radioactive isotope being dispersed in said matrix by ion exchange and structurally bonded within shrunken pores of said matrix, said matrix being at least partially devitrified and characterized by an ability to withstand 1000° C. in contact with separate particles of identical matrix without sintering and without fusing to said separate particles of identical matrix, and said particulate sources of radioactivity being characterized by an ability to withstand water exposure for one week at 50° C. with less than 0.1% weight loss of said structurally bonded radioactive isotope.

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