Whereas, there has been presented to the Commissioner of Patents a petition praying for the grant of letters patent for an alleged new and useful invention the title and description of which are contained in the specification of which a copy is hereunto annexed and made a part hereof, and the various requirements of law in such cases made and provided have been complied with, and the title thereto is from the records of the Patent Office in the claimant(s) indicated in the said copy, and whereas, upon due examination made, the said claimant(s) is (are) adjudged to be entitled to a patent under the law.

Now, therefore, these letters patent are to grant unto the said claimant(s) and the successors, heirs or assigns of the said claimant(s) for the term of seventeen years from the date of this grant, subject to the payment of issue fees as provided by law, the right to exclude others from making, using or selling the said invention throughout the United States.

In testimony whereof, I have hereunto set my hand and caused the seal of the Patent Office to be affixed at the city of Washington this twelfth day of March, in the year of our Lord one thousand nine hundred and sixty-eight, and of the Independence of the United States of America the one hundred and ninety-second.

Attest: Estin G. Johnson Attesting Officer.

Edward J. Berger Commissioner of Patents.
RADIOACTIVE FLUOROPHOSPHATE GLASS COMPOSITION

GLASS FORMATION REGION OF THE SYSTEM $\text{UO}_3^{8/3}$-NaF-Al(PO$_3$)$_3$

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This invention relates to glass containing uranium, and more particularly it pertains to fluophosphate glass having an unusually high content of uranium.

Uraniun contained in glass either in the form of thin glass fibers or small glass particles has been proposed as a fuel for nuclear reactors. In either form, glass is a convenient means for introducing uranium into a reactor. During fission, uranium breaks down into fission fragments most of which travel only a short distance (about \(\frac{1}{2}\) mil or less) which is sufficient for free migration from the individual glass fibers or particles. The released fission fragments are then free to produce a highly ionizing energy source for chemical reactions.

Prior attempts to introduce large amounts of uranium into a glass have resulted only in maximum concentrations of 20% of uranium by weight. Such concentrations have not been sufficient to sustain fission in a limited space. The present invention involves a glass having over 40% uranium by weight which will facilitate the sustaining of fission in a nuclear reactor.

From earliest times the basis of glass technology has involved reacting various mixtures of silica, soda, and lime combined in a relatively narrow range of compositions. One difficulty with silicate mixtures particularly when uranium is introduced, however, has been a requirement of high temperatures, of the order of 2000° C. for melting such glasses. This is higher than is normally available in most ordinary laboratory furnaces and is difficult to obtain in many industrial furnaces. Another difficulty has been introducing more than 20% of uranium into a silicate type of glass having and retaining the vitreous state.

It has been found that certain phosphates and fluorides may be combined with certain uranium compounds to provide a glass having a relatively low melting point containing large amounts of uranium. In particular alumina or beryllium phosphates, with alkali metal fluoride or oxide may be combined with an oxide or fluoride of uranium to provide a homogeneous glass with a sufficiently high level of uranium to sustain fission in a nuclear reactor. Thorium oxide or plutonium oxide may be substituted for at least a part of the uranium compound.

Accordingly, it is a general object of this invention to provide a fluophosphate glass containing a sufficient percentage of uranium to sustain fission in a nuclear reactor.

It is another object of this invention to provide a fluophosphate glass containing up to about 40% elemental uranium, or 46% of uranium oxide by weight.

It is another object of this invention to provide a fluophosphate glass having a relatively low melting point for facilitating the preparation of batch mixtures containing approximately 40% elemental uranium, or 46% of uranium oxide by weight.

Finally, it is an object of this invention to provide a fluophosphate glass that accomplishes the foregoing objects and requirements in a simple and effective manner.

For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description and drawing in which the single figure is a triaxial diagram plotting glass composition on a mol and weight percentage basis.

Broadly, the glasses containing uranium are basically three component fluophosphate glasses. The phosphate component of the glass comprises aluminum or beryllium phosphate, or mixtures of the two, as a major component by weight. The fluoride may be present as an alkali metal fluoride in which event it comprises from 52 to 82 mol percent of the glass, or uranium fluoride. When alkali metal fluoride is present it is preferred that at least the major proportions of the uranium be present as UO₂₃ (UO₂), or UO₃, or UO₂, or mixtures of two or more of such oxides. For the purpose of this invention UO₂ is designated as UO₂/3. When the uranium is present as U₅/₄, the glass preferably comprises as the third component a monovalent oxide of lead, such as lead oxide, such as sodium oxide, potassium oxide, limestone oxide, calcium oxide, strontium oxide, barium oxide, and zinc oxide, and mixtures of two or more.

The preferred fluophosphate crucibles, in which the fusion preferably includes but is not limited to mixtures of from 15 to 30 mol percent of Al(PO₄)₃, from 52 to 80 mol percent of NaF, and from 1 to 25 mol percent of UO₂, namely, the portion of curve X of the triaxial diagram of the drawing. On a weight basis, the aluminum phosphate comprises from 34 to 75%, sodium fluoride comprises from 15% to 43%, and the uranium oxide from 2 to 46%, represented by curve Y of the drawing. Beryllium phosphate may be used as a "glass former" instead of aluminum phosphate by replacing all or a part of the latter on an equimol basis. Fluorides of the other alkali metals may be substituted for all or a part of a sodium fluoride, namely, the fluorides of lithium, potassium, rubidium, and cesium. Moreover, UO₃, UO₂, and UF₆ may be substituted for all or a part of the UO₂/3.

The main elements in chemically combined form used in the glass compositions are: M₁, M₂, Al, P, U, F, and O, where M₁ is an alkali metal or a combination of two or more monovalent alkali metals, and M₂ is a bivalent element, including Be, or a combination of bivalent elements. A small amount of the oxide or fluoride of any other element or elements may be added to this system so long as it does not detrimentally affect the formation of glass by Al(PO₄)₃ and NaF reacting with the uranium compound.

The uranium may be natural uranium or enriched uranium, for example 10% enriched. Depleted uranium may be used if a glass for non-reactive purposes is desired.

The preferred systems are UO₂/₃NaF-Al(PO₄)₃ and UF₆-M₃O-Al(PO₄)₃. The specific system UO₂/₃NaF-Al(PO₄)₃ is discussed in the examples below.

It is known that the individual compounds UO₂/₃, NaF, or Al(PO₄)₃ alone will not form a glass when cooled from the liquid melt. However, with a suitable combination, in the proportions indicated above, of these compounds a glass results by melting the mixtures of the compounds and cooling to room temperature. The melts are usually prepared in crucibles within a temperature range of from 800° C. to 1350° C. With higher proportions of sodium fluoride or other monovalent alkali metal fluorides, the melt temperatures are progressively lower. With higher proportions of UO₂/₃, UF₆, M₃F₅, or Al(PO₄)₃, the melt temperatures are higher. The time of melting depends upon the amount and composition of mixture. For a 50-gram melt a time of about five minutes under stirring is usually sufficient. Larger melts will require longer times up to an hour.

The control of temperature and time is important. To avoid vaporization of some of the fluorides the liquid
melt should not be heated to too high temperatures or too long. After the melt becomes a clear liquid, it is stirred to uniformity and poured into a mold that has been previously heated to a temperature ranging from 350° C. to 500° C. to prevent cracks in the solidified glass body. On cooling, a glassy glass ordinarily results. The drawing is a ternary diagram of the ternary system \( \text{UO}_2 \cdot \text{NaF} \cdot \text{Al} \left( \text{PO}_4 \right)_3 \) with the solid curve Y showing the glass forming region in weight percent and the dashed curve X showing mol percent. If larger amounts of glass are melted, it is preferred to employ compositions within the borders of curves X and Y by one or two percent in order to secure a good vitreous product. As indicated in the diagram, the amount of \( \text{UO}_2 \) that can be introduced in the glass can be as high as 46% by weight, corresponding to over 40% of uranium. Preferred compositions are within the portion B–C–D of curve Y, or portion 2–3–4 of curve X. Other alkali metal fluorides may be substituted on a mol for mol basis for the sodium fluoride.

The table gives the compositions and density of some high uranium-containing glasses, as well as two compositions with no uranium, wherein the melt charge composition is given.

**TABLE—COMPOSITIONS AND DENSITY OF SOME HIGH URAMIUM CONTAINING GLASS**

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Mol Percent</th>
<th>Weight Percent</th>
<th>Wt. U. Percent</th>
<th>Density, gm./ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{UO}_2 )</td>
<td>( \text{NaF} )</td>
<td>( \text{Al} \left( \text{PO}_4 \right)_3 )</td>
<td>( \text{UO}_2 )</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>80</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>25</td>
<td>25</td>
<td>67.7</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>60.3</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>25</td>
<td>45</td>
<td>47.7</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>25</td>
<td>65</td>
<td>40.9</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>25</td>
<td>60</td>
<td>46.3</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>25</td>
<td>50</td>
<td>49.0</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>25</td>
<td>40</td>
<td>51.6</td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>25</td>
<td>30</td>
<td>54.4</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
<td>25</td>
<td>20</td>
<td>54.9</td>
</tr>
<tr>
<td>11</td>
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<td>25</td>
<td>10</td>
<td>56.3</td>
</tr>
<tr>
<td>12</td>
<td>80</td>
<td>25</td>
<td>0</td>
<td>57.7</td>
</tr>
</tbody>
</table>

Compositions are as charged.

Corresponding values for mol and weight percentages, weight of uranium, and density for Glass Nos. 1 to 12 are listed in the table. Glass Nos. 1 to 4 are included simply for comparison purposes, the preferred range comprises Glass Nos. 5 to 12 which show increasing amounts of uranium oxide from 10 to 22 mol percent and 25.5 to 44.4% by weight. Experiments indicate that using larger proportions of uranium oxide than 46% by weight results in lack of formation of a glass. The enclosed areas within the curves in the drawing are the glass formation regions for this system. The composition of Glass Nos. 1–12 are within those regions. The optimum proportions of fluoride glass of the present invention include by weight 38.0% aluminum phosphate, 17.6% sodium fluoride, and 44.4% uranium oxide. Those weight percentages correspond to 22 mol percent aluminum phosphate, 58 mol percent sodium fluoride, and 20 mol percent uranium oxide.

Glass No. 12 is one of the best compositions for certain nuclear applications because of the highest amount of uranium oxide, i.e., 22 mol percent or 44.4% by weight. However, other glasses usable in nuclear work include Glass Nos. 3 to 11 having from 10 to 22 mol percent or from 25.5 to 41.5% uranium by weight, respectively. The uranium content of these glasses was analyzed chemically and found to be substantially within the charge proportions.

It was also found that the density of the glass can be calculated from the following equation:

\[
1/d = 0.124/\text{UO}_2 + 0.315/\text{NaF} + 0.309/\text{AlPO}_4
\]

where \( d \) is density in gm./ml. of the glass and \( f_{\text{UO}_2}, f_{\text{NaF}}, f_{\text{AlPO}_4} \) are weight fractions of \( \text{UO}_2 \), NaF, and \( \text{AlPO}_4 \), respectively. The resistivity against moisture attack was found to be high for the glasses containing a high amount of uranium.

This specific glass system may be modified to yield glasses of other desirable properties. For example, other alkali metal fluorides such as potassium fluoride may be used in place of, or in addition to, NaF: B\(_2\)O\(_3\) may be added in small amounts to the glasses of the present invention. ThO\(_2\) or plutonium oxide, or both, may be substituted for a part of the UO\(_2\) for instance up to 40% by weight. Phosphates other than the meta-phosphate may be used. All such changes may be included to give improved results without deviating from the spirit of the present invention. Small amounts of the order of a few percent of other components such as SiO\(_2\) may be added without altering the basic effectiveness of the glass of the invention. Thorium fluoride or plutonium fluoride, or both, may be substituted for a part of the uranium fluoride.

The glass may be drawn into fibers or reduced to small beads having diameters from 1 to 50 microns. The resulting gold-colored glass particles or fibers may be disposed in fuel elements with a binder. The glass beads may be suspended in a moderator, such as water, or in a gas, and employed as the fuel for a fluidized bed nuclear reactor.

The glass compositions also have utility as color filters for photographic and other purposes. The glasses are green, and with the higher uranium content become an extremely dark green. Also, the green glasses of this invention may be used for various illuminating and decorative applications, particularly when depleted uranium is used for the uranium oxide or uranium fluoride.

It will be understood that the above description and drawing are illustrative and not limiting.

**1.** A stable fluorophase glass melting about above 800° C. consisting essentially of by weight from 34 to 75% of at least one phosphate of a metal of the group consisting of aluminum and beryllium; 15 to 35% of at least one fluoride or oxide selected from the group consisting of a univalent metal fluoride, a bivalent metal oxide, and boron oxide; and 2 to 46% of at least one compound selected from the group consisting of uranium oxide, uranium fluoride, plutonium oxide, plutonium fluoride, thorium oxide and thorium fluoride, with the proviso that there be present a fluoride selected from either of the last two groups.

**2.** The fluorophase glass of claim 1, consisting essentially of by weight from 34 to 41% of at least one phosphate of metal of the group consisting of aluminum and beryllium; 15 to 35% of at least one fluoride or oxide selected from the group consisting of a univalent metal fluoride, a bivalent metal oxide, and boron oxide; and 20 to 46% of at least one compound selected from the group consisting of uranium oxide, uranium fluoride, plutonium oxide, plutonium fluoride, thorium oxide and thorium fluoride.

**3.** The fluorophase glass of claim 1, consisting essentially of by weight from 38.0% of at least one phosphate of metal of the group consisting of aluminum and beryllium; 17.6% of at least one fluoride or oxide selected from the group consisting of a univalent metal fluoride, a bivalent metal oxide, and 44.4% uranium oxide.
of at least one compound selected from the group consisting of uranium oxide, uranium fluoride, plutonium oxide, plutonium fluoride, thorium oxide and thorium fluoride.

4. The fluophosphite glass of claim 1, consisting essentially of an aluminum phosphite; at least one alkali metal fluoride selected from the group consisting of fluorides of lithium, potassium, rubidium, and cesium; and uranium oxide within the area defined by A-B-C-D-E of curve X of the drawing.

5. The fluophosphite glass of claim 1, consisting essentially by weight of 34 to 75% of aluminum phosphate; 15 to 43% of at least one alkali metal fluoride selected from the group consisting of fluorides of lithium, sodium, potassium, rubidium, and cesium; and 2 to 46% of uranium oxide.

6. The fluophosphite glass of claim 1, consisting essentially by weight of 34 to 41% of aluminum phosphate; 15 to 35% of at least one alkali metal fluoride selected from the group consisting of fluorides of lithium, sodium, potassium, rubidium, and cesium; and 20 to 46% of uranium oxide.

7. The fluophosphite glass of claim 1, consisting essentially by weight of 38.0% of aluminum phosphate; 17.6% of at least one alkali metal fluoride selected from the group consisting of fluorides of lithium, sodium, potassium, rubidium, and cesium; and 44.4% of uranium oxide.

8. The fluophosphite glass of claim 1, consisting essentially of 34 to 75% of aluminum phosphate, 15 to 34% of a compound selected from the group consisting of alkali metal oxide and alkali metal fluoride, and 2 to 46% uranium oxide, all parts by weight.

9. The fluophosphite glass of claim 1, consisting essentially by weight of 34 to 41% of aluminum phosphate, 15 to 35% of a compound selected from the group consisting of alkali metal oxide and alkali metal fluoride, and 20 to 46% of uranium oxide.

10. The fluophosphite glass of claim 1, consisting essentially by weight of 38.0% of aluminum phosphate, 17.6% of a compound selected from the group consisting of alkali metal oxide and alkali metal fluoride, and 44.4% of uranium oxide.

11. The fluophosphite glass of claim 1, consisting essentially of an aluminum phosphite, a fluoride of a univalent metal, and uranium oxide within the area B-C-D of curve Y of the drawing.

12. The fluophosphite glass of claim 1, consisting essentially of by weight 34 to 41% of an aluminum phosphate, 15 to 35% of an oxide of a bivalent metal, and 20 to 46% uranium fluoride.

13. The fluophosphite glass of claim 1, resulting from fusion of a batch consisting essentially of by weight 38.0% of an aluminum phosphate, 17.6% of sodium fluoride, and 44.4% of uranium oxide.

14. The fluophosphite glass of claim 1, resulting from fusion of a batch consisting essentially of by weight 38 to 55% aluminum phosphate, 14 to 27% sodium fluoride, and 20 to 45% uranium oxide.

15. The fluophosphite glass of claim 1, resulting from fusion of a batch consisting essentially of by weight: 38 to 55% aluminum phosphate, 14 to 27% sodium fluoride, and 20 to 45% uranium oxide.

16. The fluophosphite glass of claim 1, consisting essentially of by weight 34 to 41% aluminum phosphate, a compound selected from the group consisting of an alkali metal fluoride and a bivalent metal oxide, and 20 to 46% by weight uranium oxide.

17. The fluophosphite glass of claim 1, consisting essentially by weight of 34 to 54% aluminum phosphate; 15 to 30% of a compound selected from the group consisting of an alkali metal fluoride and a bivalent metal oxide, and one compound selected from a group consisting of uranium oxide and uranium fluoride in an amount having 30 to 45% by weight uranium.

18. The fluophosphite glass of claim 1, consisting essentially by weight of 34 to 45% aluminum phosphate; 15 to 25% of a compound selected from the group consisting of an alkali metal fluoride and a bivalent metal oxide, and one compound selected from a group consisting of uranium oxide and uranium fluoride in an amount having 40 to 45% by weight uranium.

19. The fluophosphite glass of claim 1, consisting essentially of aluminum phosphate, sodium fluoride, and uranium oxide within the area defined by 2-3-4 of curve X of the drawing.

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