United States Patent Office

3,493,514
Patented Feb. 3, 1970

3,493,514
RADIOISOTOPE-CONTAINING MICROSPHERES

George E. Ashby, Highland, Adolfo MacCragh, Ellicott City, and Jean G. Smith, Baltimore, Md., assignors to W. R. Grace & Co., New York, N.Y., a corporation of Connecticut

No Drawing. Filed June 20, 1967, Ser. No. 647,312
Int. Cl. C09k *3/00;* G21c *19/42;* G21g *3/00*
U.S. Cl. 252—301.1 10 Claims

ABSTRACT OF THE DISCLOSURE

A process for preparing radiation sources in a form that can be easily handled and can be prepared with a minimum of risk by impregnating a base with the desired quantity of the radioisotope material. The base may be inert or it may be a material that reacts with the radioactive ion to form a compound.

This invention relates to a process for the preparation of radioisotopes in the form in which they can be easily handled and transported. The process involves impregnation of a porous base, preferably in microsphere form, with a solution of a salt of the radioisotope or with a colloidal suspension (sol) of the isotope.

Radioisotopes have many uses. Strontium-90, for example, has many useful applications in industrial medicine and food processing irradiations, in leak testing and thickness testing and as a heat source for thermo-electric devices. However, they are highly dangerous and extreme care must be taken in the preparation of radiation sources containing these radioisotopes to prevent contamination.

One of the difficulties arising in radiation source preparation technology results from the extreme toxic nature of these materials. Strontium-90, for example, is a strong source of gamma radiation. In the normal method of preparing these sources, the equipment used must be very carefully shielded. It is obvious that it would be advantageous both from the standpoint of cost and health hazards to carry out as much as possible of the preparation under conditions that do not require the shielding needed with present techniques.

We have found that radioisotopes can be converted into a form that is safe and convenient to handle in an effective and economic process by impregnating a matrix and insolubilizing the radioisotope in the pores of the matrix. In the preferred method, the matrix is one that is capable of reacting with a given radioisotope to form an insoluble residue. The final product may be in any desired shape. We have found that a very desirable product can be prepared by impregnating the radioisotope into an oxide or carbide matrix in the form of a microsphere.

These colloidal residues may be prepared by any conventional technique. For example, a microsphere may be obtained by solvent drying of sol droplets. The microspheres, as we prepare them, are obtained as colloidal residues, providing the necessary surface energy for strong adsorption of the impregnant and later for interaction with it during sintering.

In some cases, the matrix can also be prepared directly from a solution in a process in which a solution of a salt of the matrix material is admixed with a water soluble resin that increases in viscosity in an alkaline medium. The droplets of solution are fed into an aqueous alkaline solution to form microspheres or spheroids. The particles are recovered, dried, and are then ready for impregnation.

For purposes of simplicity, our process will be described in terms of our preferred microsphere impregnation process.

Our preferred process comprises the following steps:

(1) Dissolution of the matrix raw materials.
(2) Preparation of sols of these materials.
(3) Formation of microspheres from the sols.
(4) Washing and drying the microspheres.
(5) Introducing the radioactive additive into the microsphere product and, if necessary, fixing it.
(6) Sintering the microsphere containing the additive to the desired temperature.

In the first step of our process, the radioactive component, as well as the material to be used as matrix, are selected. The matrix materials are preferably oxides capable of interacting with a given radioisotope to form an insoluble compound.

Several oxides are suitable for this purpose, including those of tin, titanium, aluminum, molybdenum, niobium, arsenic, vanadium, lead, antimony, bismuth, tellurium, rhenium and zinc. The preferred oxides are the oxides of titanium, silicon, zirconium, aluminum, niobium and vanadium. The matrix material is selected on the basis of the properties desired in the final product. The radioisotope is selected on the basis of the application. Radioisotopes are becoming increasingly available from spent nuclear fuel reprocessing and are converted to solutions of the proper salts or to sols for the impregnation. Examples of useful radioisotopes include strontium-90, cesium-137, cerium-144, promethium-147, plutonium-238, polonium-210, and curium-242.

The titanium or other salt used to prepare the matrix is dissolved to obtain a solution of the chloride, nitrate, etc., and the solution is converted to sol form. The method used to prepare the sol depends, of course, on the material being selected for the matrix. Suitable sols can be prepared by any one of several methods such as, for example, peptization, electrodialysis, and ion exchange.

In the next step of our process, the sol of the oxide selected as a carrier for the radioisotope is converted to microspheres. The method of preparing these microspheres is not part of the invention. It is covered in copending application Ser. No. 541,519, filed Apr. 11, 1966, now U.S. Patent No. 3,331,785. Briefly, the process comprises forming the sol into droplets and drying the sols in a column of solvent passed in counter-current direction to the sol particles. The formed microspheres are removed from the bottom of the column and washed, if necessary.

The washed microspheres are dried and the microspheres in the size range desired for the preparation of our product are selected by separation using a sieve having openings in the desired range.

In the next step of the process, the radioisotope is incorporated into the microspheres by the impregnation technique. The concentration of the impregnant is calculated on the basis of the required isotope loading. A solution of a salt of the impregnant or a sol is prepared in a concentration sufficiently high to give the desired radioisotope content to the microspheres.

The impregnation may be done at any temperature in which the impregnant exists in solution or sol form. Since the solubilities of most salts increase with temperature, higher temperatures of impregnation may be desirable if a high isotope loading is desired and a salt is used as the impregnant. Sols as impregnants are generally prepared and used at lower temperatures since the ability of the sol to interact with the matrix decreases as the temperature is raised. Also, successive impregnations can be made with drying in between to increase isotope loading. Excess salt solution may be washed from exposed surfaces and reused.

In some instances, it is desirable to fix the impregnant within the sphere by treating the spheres with an agent that will form an insoluble compound with the isotope. For

example, the isotope may be converted to the hydroxide by treating with either aqueous or gaseous ammonia or it may be converted to the oxalate with oxalic acid, or to the carbonate with ammonium carbonate. The agent is preferably a substance which contributes only ions which can be decomposed later during sintering. Likewise, the impregnating solution is preferably a salt of a volatile acid, although interfering ions can be removed from the spheres by washing if the isotope is first fixed in insoluble form, as described above.

The solution of the radioactive isotope is added in an amount sufficient to fill the internal pores of the microspheres.

The impregnation may be carried out in any suitable manner. For example, the microspheres may be simply stirred with the impregnant. Another satisfactory laboratory method is to divide the microspheres to be impregnated into 20 gram batches. The batches of the microspheres are transferred to a fritted disc filter funnel. An atmosphere of an inert gas is passed upwardly through the microspheres to agitate them gently. The impregnating solution is made up to contain the desired amount of the radioisotope. The solution is admitted dropwise from a burette into contact with the microspheres.

After the impregnation step, any necessary fixation of the impregnant is accomplished; then the spheres are dried in a vacuum drier over a period of about 10 hours. The temperature is increased from room temperature to about 120° C. over this period.

The impregnated spheres are then ready for sintering. The spheres may be sintered to whatever temperature is necesary to interact the isotope with the matrix to form the desired compound (titanate, zirconate, etc). The preferred combinations of isotope and matrix are those which form thermally stable compounds that are water-insoluble. Strontium titanate, for example, is such a compound. It is prepared by impregnating microspheres of titania with a solution of a strontium salt in the required quantity and then sintering the dried microspheres to promote interaction between the two components to form strontium titanate.

A suitable sintering temperature for strontium on a titanium matrix, for example, is 1000° to 1500° C. After the sintering temperature is reached, it is maintained for 1 to 12 hours.

Obviously changes can be made in the impregnation technique. In certain cases, it may be desirable to impregnate with radioisotopes that have physical properties that make it impossible to use conventional solution and impregnation techniques. In that case, the spheres can be sintered to about 90 percent of theoretical density, impregnated and the final sintering step completed. The radioisotopes may be converted to sols by electrodialysis, peptization or any other technique and used to impregnate the matrix. The spheres can also be impregnated using gaseous systems as well as the liquid system described above.

Our invention is further illustrated by the following specific but non-limiting examples.

EXAMPLE I

This example describes a process for preparing a titanium microsphere sample to be used as the matrix for impregnation with radiostrontium and as a precursor to forming a microsphere of strontium titanate.

A 34 cc. volume of purified titanium tetrachloride and an 80 cc. volume of concentrated aqueous ammonia (29% NH_3) were added dropwise from separate funnels into a flask that contaned 320 cc. of deionized water. Stirring was maintained continuously. The flask was cooled with an ice bath that kept the temperature of the reactants at 0° C. throughout the addition. The rate of addition was such that the pH of the liquid in the flask was between 7.5 and 9 at all times.

The milky suspension of titania obtained in the hydrolysis reaction was separated on a Buchner funnel and the solids washed with very dilute ammonia solution until chloride ions could not be detected in the washings and then washed with deionized water to remove the ammonia. The titania was then mixed with water in a flask and the pH of this suspension adjusted to 1.1 with hydrochloric acid; the total volume of the mixture was 275 ml.

The system was heated for 2 hours at 80° C., with stirring under reflux. This treatment transformed the titania suspension into a stable, opaque white sol having a pH of 1.4. The sol contained 90 grams of TiO_2 per liter.

The titania sol was converted into spheres by injecting it through a 24 gauge hypodermic needle into a column of n-butanol. The column was operated at a temperature of 30° C. The product spheres were collected from the bottom of the column, washed with acetone to remove the butanol layer and dried at 50° C.

EXAMPLE II

This example illustrates the preparation of strontium titanate microspheres from the titania spheres obtained in Example I. The titania spheres were soaked for 2 hours in a saturated solution of strontium nitrate. They were dred at 150° C. and placed in a porcelain boat in an oven; the temperature was raised to 1000° C. and held there for 2 hours. The x-ray diffraction spectra of the calcined material gave a well defined pattern for strontium titanate, principally $SrTiO_3$, with some $Sr_3Ti_2O_7$. The product spheres ranged in diameter between 60 and 200 microns.

It is apparent from the data presented in Examples I and II above that our process can be used to prepare a microsphere containing strontium-90, a well-known radioisotope. Since the chemistry of the radioactive isotope is the same as the chemistry of the non-radioactive isotope of the same element, these techniques can be used in the same way to handle radioisotopes.

Obviously many modifications and variations of the invention may be made without departing from the essence and scope thereof, and only such limitations may be applied as are indicated in the appended claims.

What is claimed is:

1. A process for preparing a radiation source which comprises the steps of:

(a) preparing a sol of the matrix oxide, by peptization, electrodialysis or ion exchange,

(b) solvent drying the sol particles to prepare microspheres,

(c) washing and drying said microspheres,

(d) introducing a radioisotope into the microspheres by impregnation,

(e) treating said microspheres with a decomposable precipitant to precipitate the radioisotope in the pores,

(f) sintering said microspheres to convert the radioisotope to an insoluble form.

2. The process according to claim **1** wherein the radioisotope is selected from the group consisting of cesium-137, plutonium-238, curium-242, cerium-144 and promethium-147.

3. The process according to claim **1** wherein the radioisotope is treated with oxalic acid, ammonium carbonate or ammonia to precipitate the radioisotope into the pores of the matrix.

4. The process according to claim **1** wherein the microspheres are prepared by drying droplets of the sol in a column of a dehydrating solvent.

5. The process according to claim **1** wherein the impregnated microspheres are sintered at a temperature of about 1000 to 1500° C. for about 1 to 12 hours.

6. A process for preparing a radiation source which comprises forming a colloid of a matrix material consisting essentially of an inorganic oxide selected from the group consisting of tin, titanium, aluminum, molybdenum, niobium, arsenic, vanadium, lead, antimony, bis-

muth, tellurium, rhenium, and zinc adding a radioisotope selected from the group consisting of strontium-90, cesium-137, cerium-144, promethium-147, plutonium-238, polonium-210 and curium-242 to said colloid, sintering at a temperature sufficient to immobilize the radioisotope and recovering the product radiation source.

7. The process according to claim **6** wherein the matrix is titania in microspheroidal form and the radioisotope is strontium, and the microspheres are sintered at a temperature of about 1000 to 1500° C. for about 1 to 12 hours.

8. The process according to claim **6** wherein the dried colloid is microspheroidal in form and the radiation source is prepared by impregnating the microspheres with a solution of a salt of the radioisotope.

9. The process according to claim **6** wherein the dried colloidal residue is microspheroidal in form and the radiation source is prepared by impregnating the microspheres with a sol of the radioisotope.

10. As a composition of matter a radiation source comprising an inorganic oxide matrix composed of dried colloidal particles in microspheroidal form impregnated

with a radioisotope wherein said radioisotope has been immobilized by precipitation within the pores of the inorganic oxide matrix.

References Cited

UNITED STATES PATENTS

3,145,181	8/1964	Courtois et al.	252—301.1
3,303,140	2/1967	Heinemann et al.	252—301.1
3,320,177	5/1967	Halva	252—301.1
3,320,178	5/1967	Dewell	252—301.1
3,329,817	7/1967	Walz	252—301.1 X
3,331,785	7/1967	Fitch et al.	252—301.1
3,334,050	8/1967	Grotenhuis et al.	252—301.1
3,340,202	9/1967	Olombel et al.	252—301.1
3,360,477	12/1967	Acree et al.	252—301.1

CARL D. QUARFORTH, Primary Examiner

M. J. SCOLNICK, Assistant Examiner

U.S. Cl. X.R.

176—89; 250—845; 264—5