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3,334,050

**ORGANIC CARBONACEOUS MATRIX WITH
RADIOISOTOPE DISPERSED THEREIN**

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This invention relates to radioactive sources and more particularly to radioisotopic sources having the radioactive material firmly and non-leachably bound therein; and to processes for producing the same.

It has been proposed heretofore to incorporate radioisotopes into the structure of synthetic resins, and articles containing tritium or carbon 14 incorporated into the structure of synthetic resins or plastics have been produced. However, such articles are relatively soft in that they possess the physical properties of such plastics; and they have low potential specific activity. They are not resistant to relatively high temperatures and are limited with respect to the type of ions which can be incorporated therein.

The suggestion has also been made that radioactive isotopes be adsorbed on clays such as montmorillonite, followed by firing to produce a hard, refractory structure. On firing, however, such material fuses to a solid, brittle mass, which, if it is to be used in particulate form, must be ground up or comminuted, with the result that the contained radioactivity is exposed on the fresh surfaces produced and thus becomes leachable. Furthermore, in the case of such clays, only very low specific radioactivity can be introduced into the fired mass. The utility of such substances is limited and probably is directed chiefly to disposal of radioactive wastes.

It is an object of this invention to prepare radioactive particles consisting of carbonaceous matrices having firmly bound radioisotopes dispersed therein.

It is another object of this invention to provide heat-resistant, mechanically strong sources of high specific radioactivity, in which an organic matrix contains the radioactive material firmly bound therein.

It is a further object of the invention to provide a process for the production of such radioactive sources.

Still further objects of the invention will be apparent from the disclosure hereinafter made.

In accordance with the above and other objects of the invention, radioactive sources having advantageous properties are formed by contacting a solution containing radioactive ions with a particulate organic ion-exchange resin for a period of time sufficient to bring about significant ion exchange, removing the resin from the solution and heat-treating the resin, which now contains radioactive ions exchanged therein, at a temperature up to about 450° C. The heating step causes shrinking and weight loss, e.g., by dehydration, of the resin, which is converted to a carbonaceous, non-ion-exchanging form. In this form, the radioactive ions are firmly and structurally bound in the particles and can no longer be leached therefrom, even using solutions containing ions which normally would displace them.

Such particles are physically strong, unaffected by heat, at least up to the temperatures at which they were fired in the process of making them, and capable of containing very high specific radioactivity. Up to 30 percent by weight of radioisotope ions can be incorporated into the particles.

The original shape of the particles is not materially changed by the heat treatment. Thus, spherical resin beads remain spherical and shrink somewhat to shiny

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dark brown or black spherules. Irregular particles likewise remain of the same general configuration.

The particles thus produced can be used for purposes of making luminous signs and markers, when combined with a phosphor. They also find particular utility in connection with medical uses of radioisotopes. Thus they can be employed for diagnosis or therapy and because of their favorable specific gravity, which can be adjusted by regulating the amount of and type of ion which is employed, they can be made to approximate the specific gravity of the blood so that they will be suspended therein and carried through the blood vessels without settling or collecting in low points. Furthermore, because of these favorable density characteristics, they are much more easily suspended in pharmaceutical media for use in diagnosis or treatment.

The particles prepared by the process of the invention are highly resistant to leaching of radioactive material therefrom. Thus, they can be suspended in aqueous or physiological fluids for extended periods of time, without significant portions of the radioactivity being leached from the particles. Even when cracked or broken, the rate of leaching is not increased, although a slight amount of radioactive material may be leached from the broken surface. It is thus apparent that the radioactive material is in some way structurally bonded within the pores of the ion exchange resin after firing. The exact nature of this bond is not understood, but it is considered that it is a chemical bond as well as a mere physical entrapment of the ions within the pores.

Broadly speaking, any radioactive isotope which is capable of existing as an ion in solution can be employed in the process of the invention. Special treatment may be necessary when volatile radioisotopes are employed, such as firing the resin particles containing the adsorbed ions under pressure. Particularly useful radioisotopes are the short-lived isotopes such as yttrium-90, ytterbium-169, scandium-46, chromium-51 and the like. These substances are characterized by having half-lives of the order of less than 100 days. However, the particles of the invention are not limited to use of such materials, and long-lived isotopes can be employed where these are required for particular purposes. When longer lived radioisotopes are employed, resins are used which are more radiation resistant. Such materials are known to the art and can readily be selected for use in situations where radiation resistance is required.

The ion exchange resins which can be employed in the process of the invention are anionic or cationic organic ion exchange resins. Many such resins are known, and it is well-known that they can be obtained in forms which will permit exchange with particular ions, or can be placed in such form by treatment with the proper reagent.

Examples of the useful ion exchangers include the strongly acidic sulfonated polystyrene resins, phenolic resins containing methylene group linked sulfonic groups, polystyrene resins containing phosphonic groups, acrylic resins containing carboxylic groups, polystyrene resins containing quaternary ammonium groups, pyridinium group substituted polystyrene resins, epoxy-polyamine resins containing tertiary and quaternary ammonium groups, polystyrenes containing weakly acidic iminodiacetic groups and polystyrene resins containing polyamine groups. These resins are available in particulate form, such as tiny spherules having diameters of the order of 10 to 200 microns, irregularly shaped particles and even films or sheets can be made of such resins. Any of such forms can be employed in the process of the invention; and while there are no limitations on the size of particles which can be employed herein, preferably spherules or irregular particles of a size of the order of about 10 to 150

microns are employed. Larger particles can be used for particular, specific purposes; however, as a practical matter the particle size is kept to that which passes a 50 mesh screen, i.e., about 200 microns. For medical diagnostic or therapeutic purposes, the particles are preferably spherical; and they can be graded, as by sieving, to insure that only particles of a narrow size range are obtained. In this way, particles suitable, e.g., for introduction into the blood stream, can be produced.

The solutions employed in the ion-exchange step of the process of the invention are commonly aqueous solutions, but organic solvents in which the radioisotopes are ionized can also be employed. Thus, for example, solutions of radio-isotopes in lower aliphatic alcohols or ketones can be employed, or aqueous solutions containing organic solvents can be used. To these solutions can be added appropriate pH control agents, either acidic or basic as the case may be. Such expedients are well known to the art, inasmuch as the first step of the process is a normal ion exchange step and is carried out according to the normal practice in this respect. The techniques likewise are well known, and the operation can be carried out simply by slurrying the ion exchange resin particles with the solution, or by passing a solution over a column of the material. Obviously, suitable precautions are to be taken in accordance with the radioactive nature of the isotopes employed.

The firing of the particles containing the radio-active ions is carried out in a furnace or oven, for example, a conventional electrical resistance-heated furnace capable of reaching the temperatures required. Glass containers are quite suitable for the purpose and have the advantage of permitting observation of their contents. In general, dried (solvent-free) particles are placed in the container, heated in the oven over a period of about 1 hour to the temperature desired, and then permitted to remain at that temperature for a period of about 4 hours. During this time, the particles shrink, water vapor and other gases are evolved, and the particles become black in color, but do not fuse together or become adhered in any way. The particles are then allowed to cool and are ready for further treatment.

Typical changes in composition of the beads after firing are shown by results obtained on elementary analysis of a sulfonated polystyrene resin ion exchanger before and after firing. Before firing, air-dried beads had the percentage composition C, 48.3; H, 5.1; O, 32.6; S, 13.4. After firing, the percentage composition was C, 67.5; H, 3.0; O, 21.0; S, 3.3. The weight loss was about 80 percent of the original weight. The beads ordinarily shrink to about 65% of their original diameter, on firing.

The temperatures used in firing range up to about 450° C. The nature of the ion and the particular resin employed govern the maximum temperature which is employed. The minimum temperature used is that at which the particles are converted to a carbonaceous, non-ion-exchanging form and, as shown by leach tests hereinafter described, the radioisotopic ions are firmly bound therein, in non-leachable form. Such minimum temperatures are of the order of 200–250° C. The upper limit is governed by the point at which the resin is completely degraded or decomposed. In general, all of the presently known ion exchange resins begin to decompose significantly at temperatures of the order of 500° C., so that after prolonged heating at such temperatures they are no longer capable of retaining the radioisotopes in the leach test.

The articles of the invention can be used as sources of radioactive rays, such as alpha, beta and gamma radiation. For example, particles containing alpha-emitting isotopes can be made into sheets, by attaching them to any suitable substrate, and used as static eliminators. For this purpose, the sheets can be positioned, for example, next to a traveling web; voltage charges about the web are reduced to essentially zero by ionization of the air which permits the charge to leak off.

By coating phosphors, e.g., in an organic binder, over the particles themselves or over particles mounted on a substrate, self-luminous markers, signs and the like can be produced.

Example 1

Two grams of a strongly acidic cation exchange resin of the sulfonated polystyrene type (Dowex-50), as spherical beads about 10 to 20 microns in diameter and in the hydrogen form were added to 50 ml. of a solution containing 3500 millicuries of yttrium-90 and citrate buffered to pH of 5.5. The slurry was boiled and then shaken for 1 hour, the solution was decanted and the ion-exchanger beads now containing 99.8 percent of the radio-isotope were washed with two 50 ml. portions of H₂O. The beads were air dried for about 1 hour and transferred to a furnace in a glass container. The temperature of the oven was raised to 350° C. over a period of 1 hour and then held at this temperature for 4 hours. The fired beads which were now shrunken in size and shiny black, but still spherical, were removed from the furnace and cooled. They were then treated with 50 ml. of 0.1 normal nitric acid for a period of 16 hours; only .1 percent of the 3500 millicuries contained in the beads was removed. The beads were further washed with two 50 ml. portions of water and then dried at 100° C. for 1 hour.

The product thus obtained was soak-tested by placing the spheres in 50 ml. of 0.9 percent sodium chloride solution and allowing them to remain there for a period of 16 hours. A sample of the supernatant liquid taken at this time and counted in a conventional end window Geiger-Muller counter showed that only 0.01 percent of the total yttrium-90 was contained in the soluble form in the supernatant fluid. The final product had a mass of 1.4 grams and a specific activity of 2500 millicuries per gram.

A further test of the non-leachability of these particles was made by soaking 0.1 gram of them in 10 ml. of human blood. Only 0.5 percent of the total radioactivity was present in the blood after soaking for 5 days with agitation at a temperature of 37° C.

Example 2

A solution of 2.41 grams of strontium nitrate in 50 ml. of distilled water containing 50 millicuries of Strontium 90 was passed over a column consisting of 5 grams of small beads of a strongly acidic cation exchanger of the sulfonated polystyrene type in the ammonium form. Analysis of the effluent solution after two passes over the column indicated that 94 percent of the Sr 90 had been absorbed by the ion exchange resin. The beads were removed from the column and air dried. After drying they were transferred to an oven and heated to 260° C. over a period of 1 hour. The oven was then held at this temperature for a period of 19 hours, after which time the beads were black and shrunken although still spherical and glossy. The beads were removed from the oven and cooled.

The radiative beads thus obtained weighed 3.5 grams, and contained 13.5 millicuries of Sr 90 per gram. This product was soaked in 50 ml. of water for 4 days at room temperature. Analysis of the supernatant solution by Geiger counting indicated that only 0.01 percent of the Strontium 90 had been leached out of the beads into the supernatant. The sample of beads was also soaked in 50 ml. of 0.9 percent sodium chloride solution for 28 hours, and 0.06 percent of the Sr 90 was found to have been leached from the beads after this period of time.

Example 3

Two ml. of an aqueous thallium nitrate solution, containing approximately 7.5 millicuries of Tl-204 per ml., was diluted to 7.5 ml. with water and the pH adjusted to approximately 6 with dilute nitric acid. About 0.2 gram of small beads of strongly acidic, sulfonated polystyrene

type cationic exchange resin in the hydrogen form was added to this solution and shaken for a period of 24 hours. Approximately 50 percent of the T1-204 was adsorbed by the resin during this period of time as shown by analysis of the supernatant. The supernatant fluid was decanted, and the resin dried for 1 hour at room temperature. Following drying, the resin was placed in a furnace and brought up to a temperature of 400° C. over a period of 1 hour. This temperature was held for 5 hours, at which time the resin was removed and cooled. The black beads were further treated with 20 ml. of 8 normal nitric acid for 5 hours at room temperature. The beads were then washed and dried at 100° C. for 2 hours. The final product weighed 0.13 gram and had a specific activity of 51.2 millicuries per gram. Only 0.12 percent of the T1-204 had been removed from the beads during the aforementioned treatment with nitric acid. The beads were further tested by soaking in 20 ml. of 0.1 normal HCl for a period of 16 hours. Analysis of the supernatant by conventional Geiger counting indicated that less than 0.01 percent of the T1-204 had been removed from the beads by this treatment.

Example 4

Fifty ml. of an aqueous solution containing 100 millicuries of S-35 in the form of sodium sulfate was shaken for 18 hours with 1 gram of a strongly basic anion exchange resin of the polystyrene type containing quaternary amine groups (Dowex-2) in the form of small beads of approximately 50 microns diameter. At the end of that time, examination of the supernatant fluid with a Geiger counter indicated that 98 percent of the S-35 had been exchanged onto the resin. The supernatant liquid was decanted, the resin was washed with 250 ml. portions of distilled water, and dried at 100° C. in air for 4 hours. The beads were then placed in a furnace at 350° C. and held there for 4 hours. After cooling, the beads were black and shiny in appearance and weighed approximately 0.6 gram. The specific activity of the product was 160 millicuries per gram.

The product thus obtained was tested for leachability by placing about 0.4 gram of the beads in 10 ml. of 0.1 normal hydrochloric acid, and subjecting the mixture to treatment with an ultrasonic generator for a period of 1 hour. Thereafter, the hydrochloric acid solution was tested and it was found that about 0.04 percent of the S-35 contained in the particles had been leached into the supernatant liquid. The same sample was then soaked in 50 ml. of 0.1 normal HCl for 5 days at room temperature. Thereafter, it was found that the supernatant liquid contained about 0.05 percent of the total S-35 activity.

A wide variety of radioactive materials of widely differing properties (such as half life, radioactive particle or ray emanation and valence) can be employed in the process of the invention. Among additional radioactive ions (both cations and anions) which can be utilized are Cs-134, Cs-137, Ag-111, U-235, Au-198, P-32 and C-14, as well as isotopes of iodine, iridium, calcium, barium, scandium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, indium, cadmium, the rare earths, mercury, lead, americium and neptunium.

The invention also includes metal-coated carbonaceous beads containing radioactive ions. The metal coatings increase mechanical strength and act as additional preventives of any possible release of radioactive materials, as by spalling, abrasion, etc. This is of great importance in many uses of the particulate radioactive sources, e.g., in the food industry. Thus, liquids can be passed directly through a bed of metal-coated radioactive particles to expose them to alpha, beta or gamma irradiation without fear of contamination by leached radioactivity. Among the metals which can be used to form protective coatings on the particles are nickel, cobalt, copper, silver, gold, niobium, tantalum, tungsten, zirconium, titanium, etc.

Coating is accomplished by various processes such as electroless and electro-deposition, vapor deposition (gas plating), etc. For example, the radioactive beads can be fluidized together with a dispersed (e.g. gaseous) metal carbonyl and the fluidized mixture heated to a temperature sufficient to decompose the carbonyl, thus to cause the metal to form and deposit on the surfaces of the beads. Another technique involves first rendering the particles electrically conducting (coating them with graphite, metal powder, vapor deposited metal, etc.) and then metal plating. Other processes can also be used.

Example 5

Radioactive beads made by the process of Example 2, (one gram) containing approximately 13.5 millicuries of Sr 90 which are soaked in about 100 ml. of a 10% aqueous solution of stannous chloride, then without drying are treated with about a 100 ml. of palladium chloride solution containing about 1 gram of palladium chloride per liter of water. The beads thus treated are removed from the solution and while still wet are added to an electroless nickel plating bath containing the following ingredients:

NiCl ₂ · 6H ₂ O	-----grams-----	30
NaC ₂ H ₃ O ₃	-----do-----	50
Na ₂ H ₂ PO ₄ · H ₂ O	-----do-----	10
Water to 1000 ml.		
pH	-----	4-4.5

The bath is heated to about 200° F. The beads are stirred in the bath for about 1 hour at that temperature, then removed, washed with distilled water and dried. A nickel coating about 5 to 8 microns thick is formed over the entire surface of the beads.

Similarly, using known electroless coating techniques, dense, impermeable, strongly adherent coatings of silver, copper, cobalt and gold can also be obtained on the beads or particles of the invention.

Particles so coated are exceptionally resistant to the accidental removal of radioactive materials and are therefore particularly advantageous in the many areas of utility in which this is of importance.

What is claimed is:

1. A fired radioactive particle consisting essentially of a solid, water-insoluble essentially organic carbonaceous matrix having a radioisotope dispersed therein by ion exchange and permanently structurally bonded within said matrix by chemical bonding and physical entrapment.

2. Tiny fired radioactive beads of the order of about 6 to 130 microns in diameter, consisting essentially of a solid, water-insoluble essentially organic, carbonaceous matrix having a radioisotope dispersed therein by ion exchange and permanently structurally bonded within said matrix by chemical bonding and physical entrapment.

3. A fired radioactive particle consisting essentially of a solid, water-insoluble essentially organic, carbonaceous matrix having radioactive ions dispersed therein by ion exchange and permanently structurally bonded within said matrix by chemical bonding and physical entrapment, and characterized by loss of not more than of the order of 0.01 percent of the total of the radioactive ions contained therein when soaked in an aqueous solution of 0.9 percent sodium chloride for 16 hours.

4. A radioactive particle according to claim 3, having yttrium-90 dispersed therein.

5. Tiny fired radioactive beads of the order of about 6 to 130 microns in diameter, consisting essentially of a solid, water-insoluble essentially organic, carbonaceous matrix having Strontium 90 dispersed therein by ion exchange and permanently structurally bonded within said matrix by chemical bonding and physical entrapment; and having an adherent coating of nickel over the entire surface thereof.

6. A fired radioactive particle consisting of a water-insoluble essentially organic, carbonaceous matrix having

a radioisotope dispersed therein by ion exchange and permanently structurally bonded within said matrix by chemical bonding and physical entrapment; and having an adherent coating of metal over the external surface thereof.

7. A process for the production of radioactive sources which comprises the steps of contacting a solution containing radioactive ions with an organic ion exchange resin capable of exchanging the radioactive ions in said solution, for a period of time sufficient to bring about significant ion exchange, removing said resin from said solution and heat-treating the resin containing the radioactive ions at a dehydrating temperature up to about 450° C. and below the temperature of complete degradation of said resin to shrink and dehydrate the resin and convert the resin to an essentially organic, carbonaceous, non-ion-exchanging form in which the said radioactive ions are permanently structurally bonded by chemical bonding and physical entrapment.

8. A process for the production of radioactive sources which comprises the steps of contacting a solution containing radioactive ions with a particulate organic ion exchange resin capable of exchanging the radioactive ions in said solution, for a period of time sufficient to bring about significant ion exchange, removing said resin from said solution and heat-treating the resin containing the radioactive ions at a dehydrating temperature up to about 450° C. and below the temperature of complete degradation of said resin to shrink and dehydrate the resin and convert the resin to an essentially organic, carbonaceous non-ion-exchanging form in which the said radioactive

ions are permanently structurally bonded by chemical bonding and physical entrapment.

9. A process for the production of radioactive sources which comprises the steps of contacting a solution containing radioactive ions with an organic ion exchange resin capable of exchanging the radioactive ions in said solution, for a period of time sufficient to bring about significant ion exchange, removing said resin from said solution, washing for a period of time sufficient to remove all non-adsorbed radioactive ions, and heat-treating the resin containing the radioactive ions under dehydrating conditions at a temperature up to about 450° C. and below the temperature of complete degradation of said resin to shrink and dehydrate the resin and convert the resin to a hard, essentially organic, carbonaceous, non-ion-exchanging form in which the said radioactive ions are permanently structurally bonded by chemical bonding and physical entrapment.

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