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ELECTROLYTIC PROCESS FOR CLEANING PLUTONIUM METAL

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This invention relates to a method of preparing metals with clean, lustrous surfaces and, more particularly, to a method for removing the impurities from the surfaces of plutonium objects.

Plutonium with clean, bright, lustrous surfaces is desirable for use in fabricating plutonium objects which must be prepared with the plutonium in pure form and which may not contain surface impurities such as plutonium oxides. Plutonium metal compositions with clean, bright, lustrous surfaces which are not readily converted to impurities such as oxides are also useful in neutronic reactors, in scientific instruments, and the like.

It is, however, difficult to obtain plutonium objects with clean, lustrous surfaces because the plutonium metal, plutonium alloys, or plutonium metal compacts containing a major proportion by weight plutonium are so active and the reagents which remove the impurities also excessively attack the plutonium metal causing a loss of the valuable metal and yielding a pitted surface. Moreover, even if clean plutonium surfaces are obtained in this manner, they oxidize rapidly in air causing the bright surfaces to turn a dull color because of the formation of plutonium oxide.

The object of this invention is, therefore, to provide a rapid, efficient method for cleaning the surfaces of plutonium metal compositions.

A further object of this invention is to provide a method for removing impurities from the surfaces of plutonium plutonium alloys or plutonium metal compacts containing a major proportion by weight plutonium which does not at the same time remove an appreciable amount of the pure plutonium metal.

A still further object of this invention is to provide a method for preparing plutonium metal compositions with clean, lustrous surfaces which will not readily be converted to the oxides.

Other objects and advantages of this method will be apparent from the following description.

The objects of this invention are achieved by the process of removing the impurities from the surface by making the plutonium metal bodies anodic in an electrolyte containing phosphate ions.

More specifically, a solution containing phosphate ions is placed in a container which may be of any material which is not attacked by the electrolyte and which does not absorb the solution containing the radioactive plutonium. For example, Pyrex glass may be used for small scale production while stainless steel containers are more satisfactory for larger scale production. The plutonium object which is to be cleaned is made the anode and a metal such as platinum or stainless steel is made the cathode. Potential is applied to the electrodes in the bath for a predetermined period of time. After electrolysis all the surface impurities such as plutonium oxide are removed without the loss of an appreciable amount of plutonium but the plutonium object is usually covered with a thin brown film which is probably a complex compound. Most of this film may be removed by washing the plutonium object in a stream of water. However, the film may be conveniently and completely removed by dipping the object in a solution containing nitrate ions, as pointed out in copending application SN. 23,864, filed Apr. 28, 1948, by the same inventor, now Patent 2,915,387, issued Dec. 1, 1959. This dipping in a solution containing nitrate ions also makes the plutonium surface passive. After the plutonium has been cleaned and made passive in a solution containing nitrate ions, it is washed in water and acetone.

In order to illustrate the method of this invention but not to limit its spirit or scope, the presently preferred embodiment of the invention is presented in the following example.

Example I

A piece of plutonium foil, 0.5 inch square and 0.1 inch thick and a platinum electrode are connected as anode and cathode respectively in a Pyrex container at room temperature containing approximately 100 cubic centimeters of concentrated (85 percent) orthophosphoric acid and 100 cubic centimeters of C.P. ethylene glycol. Potential is applied and the anode current density is adjusted to 0.5 ampere per square inch. The bath is operated at room temperature. The surfaces of the plutonium object are usually thoroughly cleaned with high current efficiency in about 5 minutes at this current density. When the surfaces are cleaned the current is turned off and the plutonium metal is removed from the bath. The plutonium object is immersed for from 15 to 60 seconds in a solution containing 600 grams of ammonium nitrate per liter of concentrated orthophosphoric acid. This immersion removes any brown stain formed during the previous electrolysis and also renders the plutonium surfaces passive. The object is then washed successively with water and acetone and is thoroughly dried. The plutonium object is placed in a cool, dry atmosphere. Under these conditions it will retain its clean, passive, lustrous surface.

The embodiment presented in Example I is preferred because a polyhydric alcohol such as ethylene glycol reduces the ionization and thus reduces even more the very small amount of plutonium which is dissolved when plutonium is made anodic in a solution containing phosphate ions in other solvents. A polyhydric alcohol such as ethylene glycol also has the advantage that it is not very volatile, it reduces the loss of salts due to the creeping of the solution, and it may be conveniently used in a closed system. The orthophosphoric acid and ammonium nitrate composition used for cleaning and making the plutonium passive may be conveniently used in a closed system.

However, despite the advantages of the embodiment presented in Example I, other embodiments are, of course, possible and even desirable under different conditions. For example, other polyhydric organic materials such as glycerol, diethylene glycol, erythritol, sorbitol and/or like like may be used. Solvents such as water may be used along with/or in place of the polyhydric alcohols. Sources of the phosphate ion, other than orthophosphoric acid, such as sodium monohydrogen phosphate, sodium dihydrogen phosphate, or trisodium phosphate may be used. After the electrolysis step the plutonium object may be washed with water or immersed in solutions containing nitrate ions supplied by other sources than the ammonium nitrate in orthophosphoric acid used in Example I. For example, the nitrate ions may be furnished by nitric acid. Some of these modifications are illustrated in the following Example II which is also not intended to be limiting on the spirit or scope of the invention.

Example II

A piece of plutonium foil 0.5 inch square and 0.1 inch thick and a platinum electrode are connected as anode and cathode respectively in a Pyrex dish containing 15 grams of trisodium phosphate in 100 cubic centimeters of aqueous solution. Potential is applied and the anode current density is adjusted to 1 ampere per square inch. The plutonium foil is rapidly cleaned at a high current efficiency. The current density gradually falls to a very low value as the oxide is removed so that at the end of the cleaning period the voltage may be increased to 12 volts or more without an appreciable flow of current. After cleaning, the plutonium metal is immersed in concentrated nitric acid. It is then washed with water, then acetone, and dried. The metal thus treated retains its bright, lustrous surface and does not dull when stored in a cool, dry atmosphere. The method is very efficient and may be carried out without any appreciable loss of the valuable plutonium.

In other embodiments of the method of the invention it is possible to use other equivalent aqueous phosphate salts in which the sodium is replaced by another monovalent cation. The cation may be, for example, the ammonium radical or alkali metals such as lithium and potassium. When an electrolyte consisting of an aqueous solution containing 120 grams per liter of potassium monohydrogen phosphate is substituted for the trisodium phosphate solution used in Example II, an anode current density of 0.8 ampere per square inch gives rapid cleaning with high current efficiency of the plutonium metal object. The object can then be used or made passive by the methods mentioned in Example I or II.

The time necessary for removing the impurities present on the surface of the plutonium varies with the sample. The current densities used in the examples may, of course, be varied. An anode current density of from 0.2 to 1.0 ampere per square inch will satisfactorily clean in from 3 to 10 minutes most plutonium surfaces on which the only impurity present is plutonium oxide.

The various embodiments of the method of this invention have the advantage that although the impurities such as oxides are removed, there is no appreciable removal of the plutonium metal since the electrolytes do not appreciably attach plutonium.

It is to be understood that when plutonium metal compositions are mentioned in the specification or in the claims, pure plutonium, or plutonium alloys, or plutonium metal compacts containing a major proportion by weight plutonium are meant.

The method also has the advantage that the rate of cleaning can be controlled within wide limits through simple current adjustments.

Although the conditions have been stated very specifically hereinbefore, because there are many possible embodiments of the method of the invention, it is not intended to limit its spirit or scope except as indicated in the following claims.

What is claimed is:

1. A process for cleaning plutonium metal compositions which comprises making a plutonium metal composition anodic in an electrolyte consisting essentially of from 15 to 75 percent by volume concentrated orthophosphoric acid and from 85 to 25 percent by volume ethylene glycol.

2. A process for cleaning plutonium metal compositions which comprises making a plutonium metal composition anodic in an electrolyte consisting essentially of equal parts by volume concentrated orthophosphoric acid and ethylene glycol.

3. A process for cleaning plutonium metal compositions which comprises making a plutonium metal composition anodic in an electrolyte consisting essentially of equal parts by volume concentrated orthophosphoric acid and ethylene glycol, and immersing the plutonium metal composition for at least 15 seconds in an oxidizing solution of the class consisting of nitric acid and a mixture of ammonium nitrate in orthophosphoric acid.

4. A process for cleaning plutonium metal compositions which comprises making a plutonium metal composition anodic in an electrolyte consisting essentially of equal parts by volume concentrated orthophosphoric acid and ethylene glycol, and immersing the plutonium metal composition for about one minute in concentrated nitric acid.

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