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1

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PROCESS OF FORMING PLUTONIUM SALTS  
FROM PLUTONIUM OXALATESClifford S. Garner, Redondo Beach, Calif., assignor to the  
United States of America as represented by the United  
States Atomic Energy CommissionNo Drawing. Application June 9, 1947  
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19 Claims. (Cl. 23—14.5)

This invention relates to a process of converting  
plutonium oxalate and, more particularly, lower valence  
plutonium oxalates to other compounds of plutonium by  
dry conversion methods.

Processes for converting plutonium oxalate to other  
plutonium compounds are desirable because the pure  
plutonium oxalate in aqueous slurry is the usual end  
product in a wet chemistry concentration and decon-  
tamination of plutonium made by neutron irradiation of  
uranium. The conversion processes are necessary in  
obtaining other desirable compounds of plutonium. They  
are also desirable for the preparation of pure plutonium  
metal because, while the plutonium oxalate cannot it-  
self be efficiently converted directly to the pure metal, a  
number of other compounds such as plutonium halides  
and especially plutonium tetrafluoride can be so con-  
verted. It may be seen that processes for efficiently con-  
verting the plutonium oxalate to other compounds are  
needed.

The object therefore of this invention is to provide  
methods for quickly and efficiently converting plutonium  
oxalate to other compounds of plutonium.

A further object of this invention is to provide a  
method for rapidly converting plutonium oxalate to com-  
pounds such as plutonium halides, cyanides and oxides by  
the methods of dry chemistry.

Still further objects and advantages of this invention  
will appear in the following description.

The objects of this invention are achieved by heating  
the dry plutonium oxalate to a high temperature while  
passing a vapor of a volatile, non-oxygenated, monobasic  
acid over the heated plutonium oxalate.

When it is desired to form a plutonium halide or  
cyanide, a hydrohalide or hydrocyanide may be passed  
over the plutonium oxalate while it is heated. It is  
desirable to carefully control the oxidation-reduction  
conditions under which the hydrohalide or hydrocyanide  
are admitted. When the vapors are passed over the plus  
three plutonium oxalate under non-oxidizing or reducing  
conditions or over plus four plutonium oxalate under re-  
ducing conditions the plus three salt of the corresponding  
halide or cyanide is formed. When the plus three oxalate  
is treated under oxidizing conditions or plus four  
plutonium oxalate is treated under non-reducing condi-  
tions the corresponding plus four salt is formed.

The conditions for efficiently preparing the hydrohalide  
or hydrocyanide vary with each of these compounds which  
it is desired to form, while the percent conversion depends  
upon the conditions used. The following example gives  
one embodiment of the invention for converting plus three  
plutonium oxalate in a reducing atmosphere to plus three  
plutonium chloride.

## EXAMPLE I

A 1 gram slurry of hydrated plus three plutonium  
oxalate is partially dried by passing air over it at a tem-  
perature of about 50° C. Drying of the slurry proceeds  
rapidly because plutonium plus three oxalate is very  
insoluble in water and hence the water present is substan-

2

tially at its normal vapor pressure. The dry plus three  
plutonium oxalate is then heated from room temperature  
to about 700° C. in two hours in a slow stream of hy-  
drogen plus hydrogen chloride vapor. On larger scales  
such as 5–10 grams it has been found necessary to carry  
out the preliminary heating to about 250° C. slowly in  
order to dehydrate the hydrated oxalate and to reduce  
splattering. It is sometimes convenient to dehydrate the  
oxalate overnight in a hydrogen stream at 225° C. and  
then proceed with the reaction heating. Experiments  
indicate that the oxalate first dehydrates and is then  
converted to a plus three chloride-plus three plutonium  
oxychloride mixture but subsequently converts to the  
plus three plutonium chloride. The use of hydrogen dur-  
ing the hydrochlorination helps convert the oxychloride  
to the trichloride. This process causes 100 percent con-  
version of the hydrated plutonium oxalate to plus three  
plutonium chloride. The product is light blue in color  
with a calculated density of 5.70 grams per milliliter, and  
melts at about 760° C., at which temperature its vapor  
pressure has been found to be about  $7 \times 10^{-3}$  millimeters  
of mercury. It is somewhat hygroscopic, slowly hydrating  
in air to form what is apparently  $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}$ .

Substitution of plutonium tetraoxalate in the example  
will similarly produce plutonium trichloride.

Another embodiment of the method of this invention  
is shown in the following example.

## EXAMPLE II

A slurry containing about 105 milligrams of plus three  
plutonium oxalate is heated to dryness in air at about  
50° C. Dry hydrogen bromide is passed over the dried  
oxalate for 2.0 hours at 275° C. While continuing the  
hydrogen bromide gas flow, the temperature is increased  
gradually to 425° C. and held for another hour. It is  
again slowly raised to 550° C. and maintained for one  
hour. The effect of varying the extent and duration of  
the reaction temperature can be shown by observing the  
percent conversion to bromide versus the treatment.  
This is illustrated by the summary of the data presented  
in the following table:

Table 1

PERCENT CONVERSION VERSUS HEATING  
TREATMENT

Heating treatment:	Percent conversion
2 hours @ 275° C.-----	69
1 hour @ 425° C. additional-----	80
1 hour @ 550° C. additional-----	100

It may be seen that the temperatures and time during  
which the temperature is continued directly affects the  
yield. The plutonium tri-bromide which is formed is  
a light green solid melting at about 685° C. and volatil-  
izing appreciably from the molten state. It hydrates  
in air to form  $\text{PuBr}_3 \cdot 6\text{H}_2\text{O}$ . Its calculated density is  
6.69 grams per milliliter. Tetraoxalate in place of tri-  
oxalate results in plutonium tetrabromide.

A still further embodiment of the method of the in-  
vention is shown in the following example:

## EXAMPLE III

One gram of plus three plutonium oxalate is slowly  
dried to the anhydrous salt by heating it to about 50° C.  
The anhydrous plutonium oxalate is then treated with  
a mixture of hydrogen fluoride and hydrogen, while the  
temperature is advanced in 50° C. increments every  
ten minutes. The temperature is then maintained at  
600° C. for one hour. The plus three plutonium oxalate  
is one hundred percent converted to the plutonium tri-  
fluoride which occurs in two forms, a black or gray form  
and a lavender form. Both of these forms have a cal-  
culated density of 9.32 grams per milliliter.

3

The previous examples have pointed out some embodiments of this invention for preparing plus three plutonium compounds from plutonium trioxalate. In other embodiments of the method of the invention, plus four plutonium compounds may be formed from the trioxalate. One such embodiment is shown in the following example.

## EXAMPLE IV

5 grams of plus three plutonium oxalate are dried to the anhydrous salt. A mixture of hydrogen fluoride and air is passed over the anhydrous oxalate while it is heated in 50° C. increments every five minutes to 350° C. The temperature is maintained at this value while the gas flow continues for one hour. The oxalate is 100 percent converted to the tetrafluoride.

In other embodiments of this invention, oxygen may be used with the hydrogen fluoride. This is shown in the following example.

## EXAMPLE V

160 grams of plus three plutonium oxalate is dried by heating at 50° C. overnight. It is then placed in the fluorinating furnace and heated to 200° C. A mixture of hydrogen fluoride and air is admitted while the oxalate is heated according to the following schedule:

0.5 hour at 200° C.  
 0.5 hour at 300° C.  
 0.5 hour at 400° C.  
 0.5 hour at 500° C.  
 1 hour at 600° C.

When treated according to this method a 96 percent yield of plutonium tetrafluoride results.

The plutonium tetrafluoride produced by either of these embodiments shown in Examples IV and V has a density calculated from the lattice constants of 7.0 grams per milliliter. The tetrafluoride is readily converted at an elevated temperature to trifluoride if hydrogen is present.

Tetraoxalate in Examples IV and V will also produce the corresponding tetrahalide salt.

In other embodiments of the method of this invention, hydrogen cyanide vapor is used instead of the various hydrohalides and a plutonium cyanide results. The product may be a plus three or plus four cyanide depending on the original valence of the oxalate and the oxidation conditions during the conversion as indicated in the examples.

The foregoing examples and procedures are given for the purpose of illustrating the present invention but are not intended to be limiting on the scope thereof. Since many widely different embodiments of the invention can be made without departing from the spirit and scope thereof, it is to be understood that this application is not to be limited except as indicated in the appended claims.

What is claimed is:

1. The process of converting lower valence plutonium oxalates to non-oxygenated salts of plutonium which comprises heating lower valence plutonium oxalate in the presence of a vapor of a volatile non-oxygenated monobasic acid.

2. The process of converting a lower valence plutonium oxalate to the plutonium salt of that lower valence state which comprises heating the lower valence plutonium oxalate to a temperature of from 300° C. to 700° C. under conditions which are neither oxidizing nor reducing in the presence of a vapor of a volatile non-oxygenated monobasic acid.

3. The process of converting plus three plutonium oxalates to plus three non-oxygenated salts of plutonium which comprises heating plus three plutonium oxalate under non-oxidizing conditions in the presence of a vapor of a volatile non-oxygenated monobasic acid.

4

4. The process of converting plus four plutonium oxalates to plus three non-oxygenated salts of plutonium which comprises heating plus four plutonium oxalate under reducing conditions in the presence of a vapor of a volatile non-oxygenated monobasic acid.

5. The process of converting plus three plutonium oxalates to plus four non-oxygenated salts of plutonium which comprises heating plus three plutonium oxalate under oxidizing conditions in the presence of a vapor of a volatile non-oxygenated monobasic acid.

6. The process of converting plus three plutonium oxalates to plus three non-oxygenated salts of plutonium which comprises heating plus three plutonium oxalate to a temperature of from 300° C. to 700° C. under non-oxidizing conditions in the presence of a vapor of a volatile non-oxygenated monobasic acid.

7. The process of converting plus four plutonium oxalates to plus three non-oxygenated salts of plutonium which comprises heating plus four plutonium oxalate to a temperature of from 300° C. to 700° C. under reducing conditions in the presence of a vapor of a volatile non-oxygenated monobasic acid.

8. The process of converting plus three plutonium oxalate to plus four non-oxygenated salts of plutonium which comprises heating plus three plutonium oxalate to a temperature of from 300° C. to 700° C. under oxidizing conditions in the presence of a vapor of a volatile non-oxygenated monobasic acid.

9. The process of converting a plus three plutonium oxalate to plus three plutonium chloride which comprises heating plus three plutonium oxalate under non-oxidizing conditions in the presence of a vapor of hydrogen chloride.

10. The process of converting plus four plutonium oxalate to plus three plutonium bromide which comprises heating the plus four plutonium oxalate under reducing conditions in the presence of a vapor of hydrogen bromide.

11. The process of converting a plus three plutonium oxalate to a plus four plutonium fluoride which comprises heating plus three plutonium oxalate under oxidizing conditions in the presence of a vapor of hydrogen fluoride.

12. The process of converting plus three plutonium oxalates to plus three plutonium chloride which comprises heating plus three plutonium oxalate to a temperature of from 300° C. to 700° C. under non-oxidizing conditions in the presence of a vapor of hydrogen chloride.

13. The process of converting plus four plutonium oxalates to plus three plutonium bromide which comprises heating plus four plutonium oxalate to a temperature of from 300° C. to 700° C. under reducing conditions in the presence of a vapor of hydrogen bromide.

14. The process of converting plus three plutonium oxalate to plus four plutonium fluoride which comprises heating plus three plutonium oxalate to a temperature of from 300° C. to 700° C. under oxidizing conditions in the presence of a vapor of hydrogen fluoride.

15. The process of converting plus three plutonium oxalates to plus three plutonium chloride which comprises heating plus three plutonium oxalate to a temperature of from 300° C. to 700° C. in the presence of a vapor of hydrogen chloride.

16. The process of converting plus four plutonium oxalates to plus three plutonium bromide which comprises heating plus four plutonium oxalate to a temperature of from 300° C. to 700° C. in the presence of a vapor of hydrogen and hydrogen bromide.

17. The process of converting plus three plutonium oxalate to plus four plutonium fluoride which comprises heating plus three plutonium oxalate to a temperature of from 300° C. to 700° C. in the presence of a vapor of oxygen and hydrogen fluoride.

18. The process of converting lower valence plutonium oxalates to non-oxygenated salts of plutonium which com-

**5**

prises heating lower valence plutonium oxalate in the presence of a vapor of a volatile non-oxygenated monobasic acid under controlled oxidation-reduction conditions.

19. The process of converting lower valence plutonium oxalates to non-oxygenated salts of plutonium which comprises heating lower valence plutonium oxalate to a temperature of from 300° C. to 700° C. in the presence of a vapor of a volatile non-oxygenated monobasic acid under controlled oxidation-reduction conditions.

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