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PURIFICATION OF METALS

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Fig. 1,

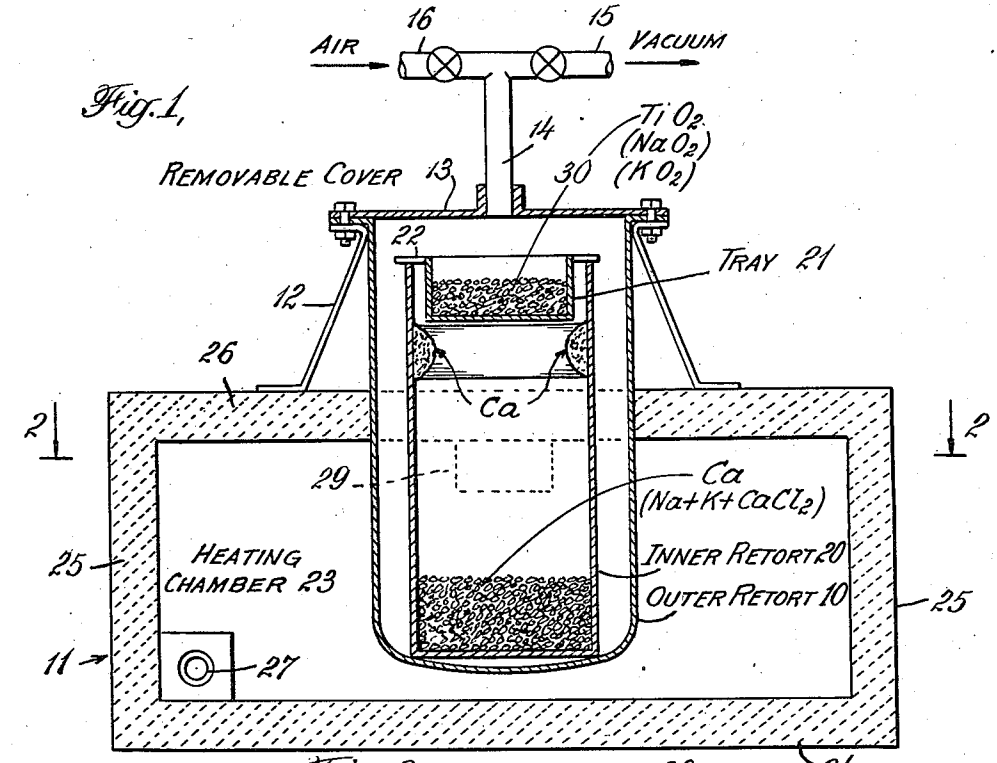
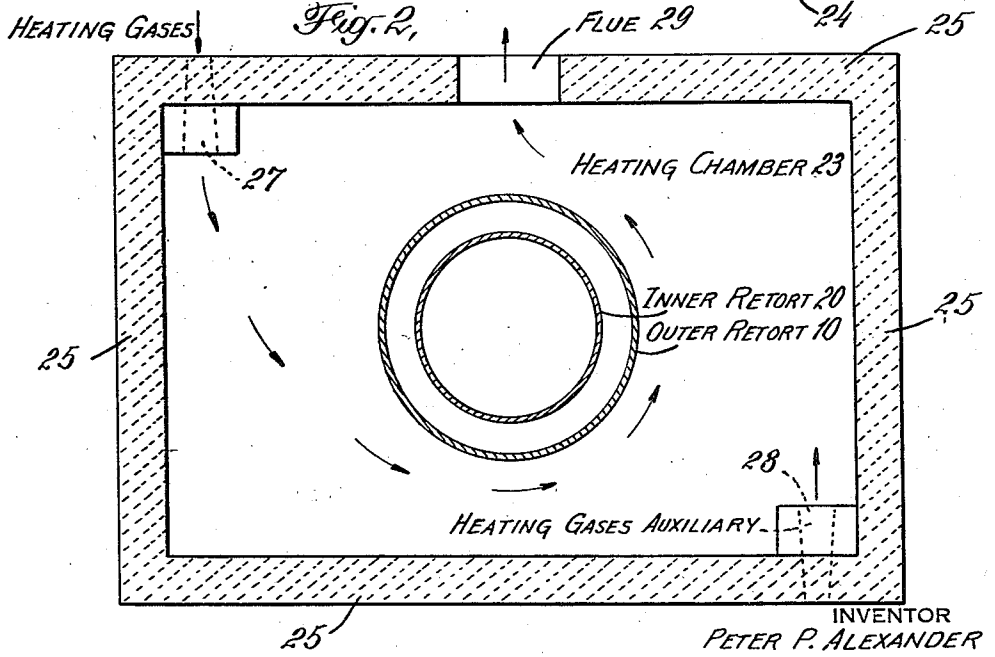


Fig. 2,



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PURIFICATION OF METALS

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22 Claims. (Cl. 75—67)

This invention relates to the purification of metals contaminated with metal impurities having a lower boiling point, and has for its object more particularly certain improvements in the method of purifying calcium, strontium and barium contaminated with sodium and potassium.

The alkaline earth metals, calcium, strontium and barium, are usually made by subjecting their fused chlorides to electrolysis. Since the salts of the alkali metals, sodium and potassium, are usually present in these chlorides, the resulting alkaline earth metal is usually contaminated with a small amount of alkali metal, as well as of the chloride of the alkaline earth metal itself. To purify the alkaline earth metal, it has been proposed to subject the metal to distillation in a closed retort that has been evacuated to remove objectionable air. The distilled metal is permitted to condense in a cooler part of the retort, usually in the form of a more or less spongy deposit. After cooling the retort, air is admitted, the retort is opened and the condensed metal is removed. The resulting product is so reactive that it frequently oxidizes rapidly on the surface and produces heat in sufficient amount to ignite the whole mass, with the result that fires are quite common. This objectionable result is all the more apt to occur because of the presence of the more highly reactive sodium and potassium. These alkali metals are also distilled and condense in a cooler part of the retort. The small deposits of sodium and potassium are so reactive that they almost invariably catch fire when the retort is opened and they come in contact with the oxygen of air.

As a result of my investigations, I have discovered that these disadvantages may be overcome for the most part. The alkali metals, sodium and potassium, may be segregated from the alkaline earth metals in a form to make them non-inflammable on exposure to the oxidizing influence of air. The alkaline earth metal may then be separately collected and at the same time be substantially freed of its chloride.

In accordance with the invention, the alkaline earth metal is heated in the absence of air to a temperature sufficiently high to distill the alkali metal impurity. The alkali metal vapor is selectively oxidized by bringing it in reactive contact with a refractory oxide, such as titanium oxide, zirconium oxide and chromium oxide, and collecting the oxidized alkali metal impurity as a solid separate from the alkaline earth metal to be purified. The alkaline earth metal itself is advantageously distilled and condensed separate from the oxidized alkali metal impurity.

These and other features of the invention may be better understood by referring to the accompanying drawing, taken in conjunction with the following description, in which:

Fig. 1 is a diagrammatic representation, being a side elevation in section, of an apparatus with which the method of the invention may be practiced; and

Fig. 2 is a horizontal section on the line 2—2 of Fig. 1.

The apparatus shown comprises an outer retort 10 supported within a heating furnace 11, the retort being held in position by means of two or more supports 12 resting on top of the heating furnace. The retort preferably consists of heat-resistant steel. It is provided with a removable cover 13 having attached thereto a vertical pipe 14 and lateral valved branches 15 and 16, connectable with a source of vacuum, and air, respectively. A removable inner retort 20, having an open top, rests within the outer retort. A removable tray 21 rests over the open top of the retort, being supported thereon by means of three or more lugs 22 extending over the wall of the inner retort. The heating furnace 11 consists essentially of a rectangular chamber 23 having a refractory bottom 24, side and end walls 25, and a top 26 having an opening of a size adapted to receive the outer retort. An expanding opening 27 is provided at or near a lower corner of one of the side walls of the chamber, for the introduction of heating gases into the chamber. A similar opening 28 is preferably provided at or near an opposite corner, as a spare or auxiliary means for introducing heating, or cooling, gases into the chamber. When not in use, the opening 28 is closed. A flue opening 29 extends through the same wall as the opening 27, preferably at a higher level, so that heating gases passed into the chamber through the opening 27 tend to pass around the retort before leaving the chamber through the flue opening 29.

The apparatus may be used as follows: A charge of calcium, for example, contaminated with sodium, potassium, and calcium chloride, is placed in the bottom of the inner retort 20. The inner retort is then placed in the outer retort 10. A layer of titanium oxide 30 is placed in the tray 21, which is in turn placed across the open top of the inner retort. The removable cover 13 is placed on the outer retort 10 and locked thereon to provide a sealed joint. The lateral branch 15 is then connected to a source of vacuum. With

the valve of this lateral branch open, and the valve of the other lateral branch 16 closed, the outer and inner retorts are placed under vacuum to remove objectionable air.

Heating gases are passed through opening 27 into the heating chamber, where they circulate almost completely around the retort and then pass through the flue opening 29 to the outside atmosphere. As the lower portion of the outer retort 10 is heated, the lower portion of the inner retort 20 is also heated. As the temperature rises, a point is reached where the sodium and potassium present in the calcium are distilled. The resulting sodium and potassium vapors rise to the upper and cooler portion of the retort where they come in contact with the titanium oxide 30 in the tray 21. Due to their great affinity for oxygen, the sodium and potassium are promptly oxidized and the titanium dioxide is reduced to titanium and a sub-oxide of titanium, according to reactions which may be indicated as follows:

$$Na+TiO_2 \rightarrow NaO_2+Ti$$
$$Na+4TiO_2 \rightarrow NaO_2+2Ti_2O_3$$
$$K+TiO_2 \rightarrow KO_2+Ti$$
$$K+4TiO_2 \rightarrow KO_2+2Ti_2O_3$$

As the temperature at the bottom of the inner retort continues to rise, a point is reached where the calcium is distilled and its resulting vapor tends to condense and settle out against the wall of the inner retort immediately below the tray 16. Some calcium vapor may of course rise sufficiently to come in contact with titanium dioxide in the tray and react with it in a manner similar to sodium or potassium vapor. The bulk of the distilled calcium may, however, be separately condensed and collected, as shown. A residue consisting essentially of calcium chloride, admixed perhaps with a small amount of sodium chloride or potassium chloride, or both, remains as a residue in the bottom of the inner retort.

The introduction of heating gases to the heating chamber is stopped and the retort is permitted to cool. The cooling operation may be accelerated by passing cooling air through the heating chamber, for example, through the opening 28, or by removing the outer retort and its contents from the heating chamber. After the retort has been suitably cooled, lateral branch 16 is opened to admit air to the interior of the retorts, after which the cover 13 is removed. The inner retort and tray are pulled out of the outer retort; the tray is removed, and the condensed calcium is scraped off and separately recovered. The residues are advantageously removed by washing the inner retort with water.

It will be clear to those skilled in this art that the invention lends itself to numerous modifications. Strontium and barium may be similarly treated to remove sodium and potassium, and to convert these explosive alkali metals into harmless compounds. Instead of titanium oxide, other suitable refractory metallic oxides, such as zirconium oxide and chromium oxide, may be employed, either separately or admixed.

In the practice of the invention, advantage is taken of the relative boiling points of the metals. The boiling points of sodium and potassium are substantially below those of calcium, strontium and barium. The temperature of the metal to be purified is therefore gradually elevated to a point where the metal impurity of lower boiling point is distilled. By heating its bottom, the retort is caused to yield a graduated temperature range. Since the sodium and potassium have the lower boiling points, their vapors tend selectively to rise highest in the retort. Since the calcium, strontium and barium have the higher boiling points, their vapors tend not to rise as high in the retort. They soon meet a temperature environment conducive to condensation. In other words, the alkaline earth metals may be made to condense in an intermediate section of the retort where the temperature is high enough to keep the alkali metals in vapor form. The alkali metal vapors, on the other hand, tend to rise to a cooler portion of the retort, where they were heretofore condensed, but where they are now converted into harmless compounds in accordance with the present invention.

I claim:

1. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium to a temperature at which the metal impurity of lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity vapor in a zone removed from the main body of calcium, and collecting the oxidized metal impurity as a solid separate from the calcium.

2. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium in the absence of air to a temperature at which the metal impurity of lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity vapor in a zone removed from the main body of calcium, and collecting the oxidized metal impurity as a solid separate from the calcium.

3. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium while under vacuum to a temperature at which the metal impurity of lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity vapor in a zone removed from the main body of calcium, and collecting the oxidized metal impurity as a solid separate from the calcium.

4. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium to a temperature at which the metal impurity of lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity vapor by bringing it in reactive contact with a refractory oxide in a zone removed from the main body of calcium, and collecting the oxidized metal impurity as a solid separate from the calcium.

5. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium in the absence of air to a temperature at which the metal impurity of lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity by bringing it in reactive contact with titanium oxide in a zone removed from the main body of calcium, and collecting the oxidized metal impurity as a solid separate from the calcium.

6. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium in the absence of air to a temperature at which the metal impurity of

lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity vapor in a zone removed from the main body of calcium, collecting the oxidized metal impurity as a solid separate from the calcium, distilling the calcium, and condensing the resulting calcium vapor as a solid separate from the oxidized metal impurity in a zone intermediate that in which the metal impurity is oxidized and that from which the main body of calcium is distilled.

7. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with a refractory oxide in a zone removed from the main body of calcium, and collecting the oxidized sodium as a solid separate from the calcium.

8. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with titanium oxide in a zone removed from the main body of calcium, and collecting the oxidized sodium as a solid separate from the calcium.

9. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with a refractory oxide in a zone removed from the main body of calcium, distilling the calcium, and condensing the resulting calcium vapor as a solid separate from the oxidized sodium in a zone intermediate that in which the sodium is oxidized and that from which the main body of calcium is distilled.

10. In the method of purifying calcium contaminated with potassium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the potassium but not the calcium, selectively oxidizing the resulting potassium vapor by bringing it in reactive contact with a refractory oxide in a zone removed from the main body of calcium, and collecting the oxidized potassium as a solid separate from the calcium.

11. In the method of purifying calcium contaminated with potassium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the potassium but not the calcium, selectively oxidizing the resulting potassium vapor by bringing it in reactive contact with titanium oxide in a zone removed from the main body of calcium, and collecting the oxidized potassium as a solid separate from the calcium.

12. In the method of purifying calcium contaminated with potassium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the potassium but not the calcium, selectively oxidizing the resulting potassium vapor by bringing it in reactive contact with a refractory oxide in a zone removed from the main body of calcium, distilling the calcium, and condensing the resulting calcium vapor as a solid separate from the oxidized potassium in a zone intermediate that in which the potassium is oxidized and that from which the main body of calcium is distilled.

13. In the method of purifying calcium contaminated with sodium and potassium as impurities, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium and potassium but not the calcium, selectively oxidizing the resulting sodium and potassium vapors by bringing them in reactive contact with a refractory oxide in a zone removed from the main body of calcium, and collecting the oxidized sodium and potassium as solids separate from the calcium.

14. In the method of purifying calcium contaminated with sodium and potassium as impurities, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium and potassium but not the calcium, selectively oxidizing the resulting sodium and potassium vapors by bringing them in reactive contact with titanium oxide in a zone removed from the main body of calcium, and collecting the oxidized sodium and potassium as solids separate from the calcium.

15. In the method of purifying calcium contaminated with sodium and potassium as impurities, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium and potassium but not the calcium, selectively oxidizing the resulting sodium and potassium vapors by bringing them in reactive contact with a refractory oxide in a zone removed from the main body of calcium, distilling the calcium, and condensing the resulting calcium vapor as a solid separate from the oxidized sodium and potassium in a zone intermediate that in which the sodium and potassium are oxidized and that from which the main body of calcium is distilled.

16. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with titanium oxide in a zone removed from the main body of calcium, distilling the calcium, and condensing the resulting calcium vapor as a solid separate from the oxidized sodium in a zone intermediate that in which the sodium is oxidized and that from which the main body of calcium is distilled.

17. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium in the absence of air to a temperature at which the metal impurity of lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity by bringing it in reactive contact with zirconium oxide in a zone removed from the main body of calcium, and collecting the oxidized metal impurity as a solid separate from the calcium.

18. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with zirconium oxide in a zone removed from the main body of

calcium, and collecting the oxidized sodium as a solid separate from the calcium.

19. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with zirconium oxide in a zone removed from the main body of calcium, distilling the calcium, and condensing the resulting calcium vapor as a solid separate from the oxidized sodium in a zone intermediate that in which the sodium is oxidized and that from which the main body of calcium is distilled.

20. In the method of purifying calcium contaminated with a metal impurity of lower boiling point, the improvement which comprises heating the calcium in the absence of air to a temperature at which the metal impurity of lower boiling point but not the calcium is distilled, selectively oxidizing the resulting metal impurity by bringing it in reactive contact with chromium oxide in a zone removed from the main body of calcium, and collecting the oxidized metal impurity as a solid separate from the calcium.

21. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with chromium oxide in a zone removed from the main body of calcium, and collecting the oxidized sodium as a solid separate from the calcium.

22. In the method of purifying calcium contaminated with sodium as an impurity, the improvement which comprises heating the calcium in the absence of air to a temperature sufficiently high to distill the sodium but not the calcium, selectively oxidizing the resulting sodium vapor by bringing it in reactive contact with chromium oxide in a zone removed from the main body of calcium, distilling the calcium, and condensing the resulting calcium vapor as a solid separate from the oxidized sodium in a zone intermediate that in which the sodium is oxidized and that from which the main body of calcium is distilled.

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