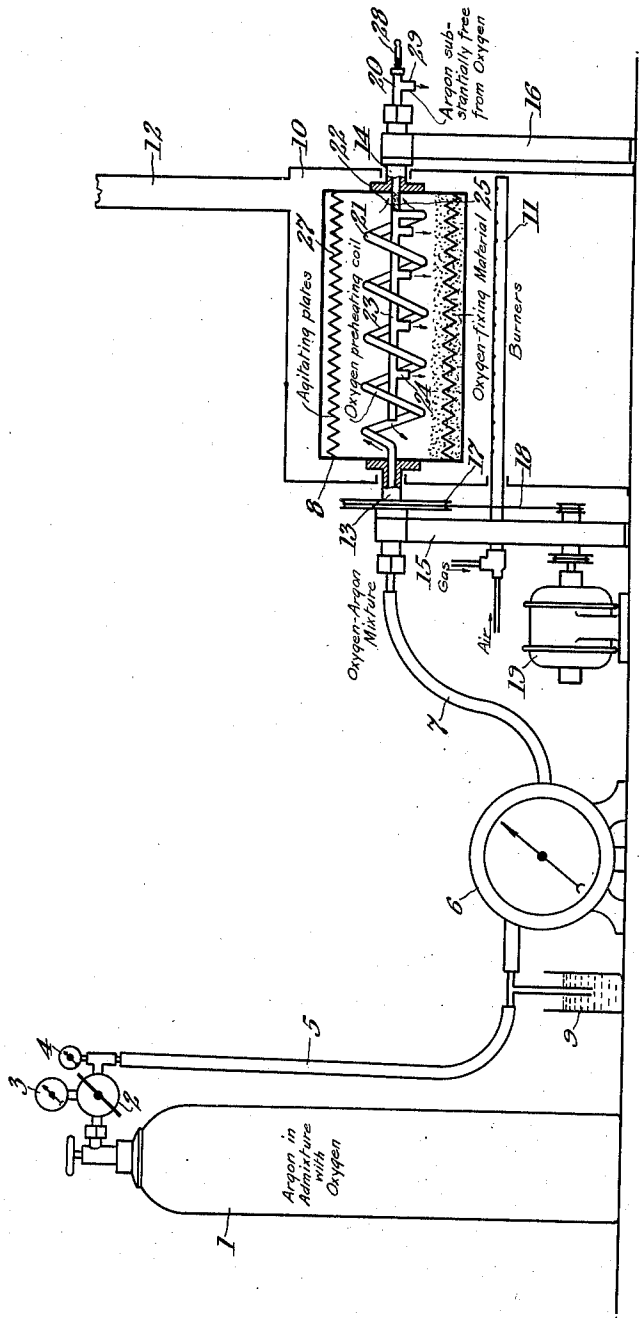
Sept. 29, 1925. 1,555,570

P. E. HAYNES

PROCESS OF PURIFYING ARGON AND PREPARING OXIDIZED PRODUCTS

Filed May 3, 1922



Inventor:
Pierre E. Haynes,
by Byrnes, Townsend & Brickenstein,
Attorneys.

Patented Sept. 29, 1925. 1,555,570

UNITED STATES PATENT OFFICE.

PIERRE E. HAYNES, OF BUFFALO, NEW YORK, ASSIGNOR TO THE LINDE AIR PRODUCTS COMPANY, A CORPORATION OF OHIO.

PROCESS OF PURIFYING ARGON AND PREPARING OXIDIZED PRODUCTS.

Application filed May 3, 1922. Serial No. 558,247.

To all whom it may concern:

Be it known that I, PIERRE E. HAYNES, a citizen of the United States, residing at Buffalo, in the county of Erie and State of New York, have invented certain new and useful Improvements in Processes of Purifying Argon and Preparing Oxidized Products, of which the following is a specification.

This invention relates to the production of argon, or argon-nitrogen mixtures, and to the manufacture of lead oxids. More particularly, the invention comprises the fixation of the oxygen content of mixtures of the atmospheric gases in the form of an oxid of lead, the process being preferably so regulated as to obtain a product containing a desired percentage of minium. The term "minium" is used herein to designate a definite chemical compound of the composition Pb_3O_4, while the term "red lead" is reserved for commercial products having oxygen contents intermediate those of PbO and Pb_3O_4, and probably comprising mixtures of minium with relatively small amounts of lower oxids.

According to the present invention, air may be treated for the production of argon, either directly or after suitable modification of its composition by physical or chemical means. For most industrial purposes, argon should be completely free from oxygen, carbon dioxid, and water vapor, and should contain not more than a small percentage of nitrogen. A product of this degree of purity can be conveniently obtained by operating upon commercial compressed oxygen, prepared by fractional distillation of liquid air, and I shall describe my process as applied to this as the source of the gaseous mixture to be deoxidized. The average composition of commercial oxygen is about 98% oxygen, 1% argon and 1% nitrogen. The argon percentage of course includes the other inert atmospheric gases, which are inseparable except by complicated physical processes. Where "argon" is mentioned in the succeeding description and in the claims, it should be understood to mean argon in admixture with the other inert gases, as I do not contemplate their removal.

The invention will be described in connection with the accompanying drawing, in which the figure is a diagrammatic, partly sectional, illustration of an apparatus for carrying out the process.

Referring to the drawing, reference numeral 1 denotes a container for a compressed gaseous mixture containing oxygen and argon. A valve 2, pressure gage 3, and pressure regulator 4, of suitable type, are provided on the container. A pipe 5 conducts the gas mixture to a meter 6, through which it passes into pipe 7 leading into a rotary tube furnace 8. A safety seal 9 is interposed in the line between the container and meter.

The tube 8 is enclosed in a furnace chamber 10 heated by burners 11 and having a stack 12 for escape of combustion gases. Hollow shafts 13 and 14 are fixed upon the ends of tube 8 and are journalled in standards 15 and 16. A pulley 17 is rigidly secured to shaft 13, and is rotated by belt 18 which is driven by motor 19.

Hollow shafts 13 and 14 receive pipes 7 and 20, respectively. The former pipe is bent into a helical coil 21 which extends substantially the entire length of the furnace tube. Pipe 20 is welded or otherwise secured to pipe 7 at 22, the pipe extends in a straight length 23, in alinement with pipe 20, and is provided with nozzles 24. This arrangement of pipes 7, 21, and 23, causes the oxygen to traverse a circuitous path in which its temperature is raised to a suitable degree before it is discharged into the furnace. Perforations 25 in that part of pipe 20 which lies within the furnace tube permit the exit of gases which have escaped combination in the furnace. The tube is provided with baffles 27 to assist in the agitation of the charge.

A thermometer 28 is inserted in the end of pipe 20, in contact with the effluent gases. Such gases may be drawn off through branch pipe 29 and stored or utilized as desired.

The preferred procedure for preparing argon and red lead is as follows: The furnace tube 8 is charged with pig lead through a charging door (not shown) and the temperature of the interior of the tube is raised to at least 340° C. to melt the lead. The oxygen-argon gas mixture is then admitted and the tube rotated. The rate of flow of gas is so adjusted that the oxygen is substantially completely fixed by reaction with the lead. The oxygen absorption is very

rapid at first, but a lower, substantially constant absorption rate is soon established, which is maintained until the greater portion of the lead has been oxidized. The operating conditions largely determine the permissible rate, but in any case a simple test of the effluent gas will indicate whether oxygen is being fed in at a higher rate than that at which it can be absorbed. The pressure may be controlled by the regulator 4, but it is advisable to insert the safety seal 9 to permit the escape of gas should it be supplied under excess pressure.

The temperature of the furnace is maintained approximately constant by adjustment of the burners. When the process has continued for a sufficient time to secure the desired amount of oxidation, the burners are extinguished and the oxygen supply discontinued. After the furnace has cooled, the oxidized product is removed, ground and sifted. The effluent gas, from which oxygen has been largely or wholly removed, is collected during the course of the operation and stored or subjected to further treatment, more fully discussed hereinafter.

The following specific example is illustrative of the improved process: A gas consisting of 98.25% oxygen, 0.80% argon, and 0.95% nitrogen is passed at a rate insuring satisfactory oxygen absorption over a charge of molten lead in a rotating furnace. The temperature is maintained around 350° C. The effluent gas has an oxygen content below 1%. The process is continued for about 24 hours. The oxidation of the lead at this time is substantially complete, the oxid produced corresponding in composition to a mixture containing approximately 50% minium and 50% massicot. This is a desirable mixture for certain industrial purposes, such as the manufacture of storage battery plates, and I prefer to arrest the process at this stage.

In an application Serial No. 558,246 filed of even date herewith by J. B. Huffard and P. E. Haynes; there is described the regulation of the process of oxidizing metallic lead with oxygen so as to obtain the desired percentage of minium. Such methods may be utilized in connection with the preparation of argon, as well as the specific oxidation process described herein.

Where argon of higher purity than that obtained as described above is desired, the effluent gas may be passed through ammoniacal copper solutions, over red hot copper, or treated with other reagents capable of removing the last traces of oxygen. Oxygen together with part or all of the nitrogen may be eliminated by treatment with metallic magnesium at elevated temperatures, or in other suitable ways.

I have found that the removal of oxygen is satisfactory not only when a relatively large proportion of metallic lead is present, but also when a stage of incomplete oxidation has been reached in the process of producing red lead. The lower oxids of lead may therefore be used to deoxidize the oxygen-argon mixture. In some cases, it is desirable to pass the gas remaining after the treatment with the lower oxids, over lead in a less oxidized condition, or over fused metallic lead, to remove oxygen which may have escaped combination.

Argon-nitrogen mixtures have been prepared on a small scale for experimental purposes by passing commercial compressed oxygen, containing a small percentage of argon and nitrogen, over red hot copper or iron. Also, oxygen has been removed from argon-containing gases by passing them into contact with molten sodium or potassium. My invention as distinguished from such methods, resides in the described process for eliminating oxygen from gas mixtures containing argon by causing the gas to come into intimate contact with a body of molten heavy metal undergoing agitation. Fresh surfaces for oxidation are constantly exposed and the process may therefore be conducted continuously for long periods with a large production of argon substantially free from oxygen. From the commercial point of view, it is obviously of importance to fix the oxygen in the form of a salable compound, but so far as I am aware, it has not heretofore been realized that argon could be obtained with the simultaneous production of a valuable oxidized product. As pointed out in my application above referred to, important technical advantages result from the use of a gas rich in oxygen for the manufacture of red lead, and as shown herein, such process is admirably adapted also for the production of argon.

While in the preferred form of my invention the separation of argon is combined with the production of lead oxids, it will be understood that other readily oxidizable metals or alloys fusible at a temperature sufficiently low to be used in an apparatus of the kind described, or metal oxids capable of being raised to a higher stage of oxidation, are suitable for the fixation of the oxygen. As examples, zinc, tin, or a low oxid of iron may be mentioned. Commercial compressed oxygen is not necessarily selected as the oxidizing gas, as other argon-containing gases, including argon partly freed from oxygen or nitrogen by a preliminary treatment, may be utilized in my process. Further modifications of the process as described may be made within the scope of the appended claims.

I claim:

1. Process of separating a reactive gas from argon, comprising passing the mixed gases over a molten metal capable of fixing

such reactive gas and continuously agitated in contact therewith.

2. Process of removing oxygen from admixture with small amounts of nitrogen and argon, comprising passing the mixed gases into intimate contact with molten lead, and collecting the effluent gas.

3. The invention according to claim 2, in which the metal is contained in a furnace which is continuously rotated during the passage of the gas.

4. Process of purifying argon and preparing an oxid of lead, comprising passing a gaseous mixture containing oxygen and argon, in proportions greater than in atmospheric air, into contact with lead maintained at a temperature above its melting point, and collecting the effluent gas.

5. Process of purifying argon and preparing an oxid of lead, comprising melting lead and agitating the same in a stream of gas containing oxygen and argon in proportions greater than in atmospheric air, and collecting the effluent gas.

6. The invention according to claim 5, in which the effluent gas is treated with agents adapted to absorb the oxygen which may have escaped reaction with the lead.

7. Process of preparing argon-nitrogen mixtures, comprising passing commercial oxygen containing approximately 1% argon and 1% nitrogen into contact with lead maintained at a temperature above its melting point, the rate of flow of the gases being such that substantially all the oxygen reacts with the lead.

8. Process according to claim 7, in which the process is continued until substantially all the lead is oxidized.

9. Process of preparing lead oxids, including minium, which comprises charging lead into a rotary furnace, melting and continuously heating the lead, rotating the furnace to agitate the lead, passing into the furnace a gas containing oxygen in admixture with a small amount of argon, until the desired percentage of minium is formed, and collecting the effluent gas containing argon substantially free from oxygen.

10. Process of removing oxygen from an oxygen-argon gas mixture, comprising passing said mixture over a metallic oxid capable of reacting with oxygen.

11. Process of removing oxygen from an oxygen-argon gas mixture, and preparing a commercially valuable oxid, comprising passing said mixture over a lower oxid of lead heated to a temperature above 340° C., whereby the oxygen is absorbed with the formation of an oxid of lead having a high oxygen content.

In testimony whereof I affix my signature.

PIERRE E. HAYNES.