March 10, 1970 P. J. PORTES ET AL 3,499,730
PROCESS FOR PRODUCING TITANIUM DIOXIDE BY THE VAPOR PHASE OXIDATION OF TITANIUM TETRACHLORIDE
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FIG.1

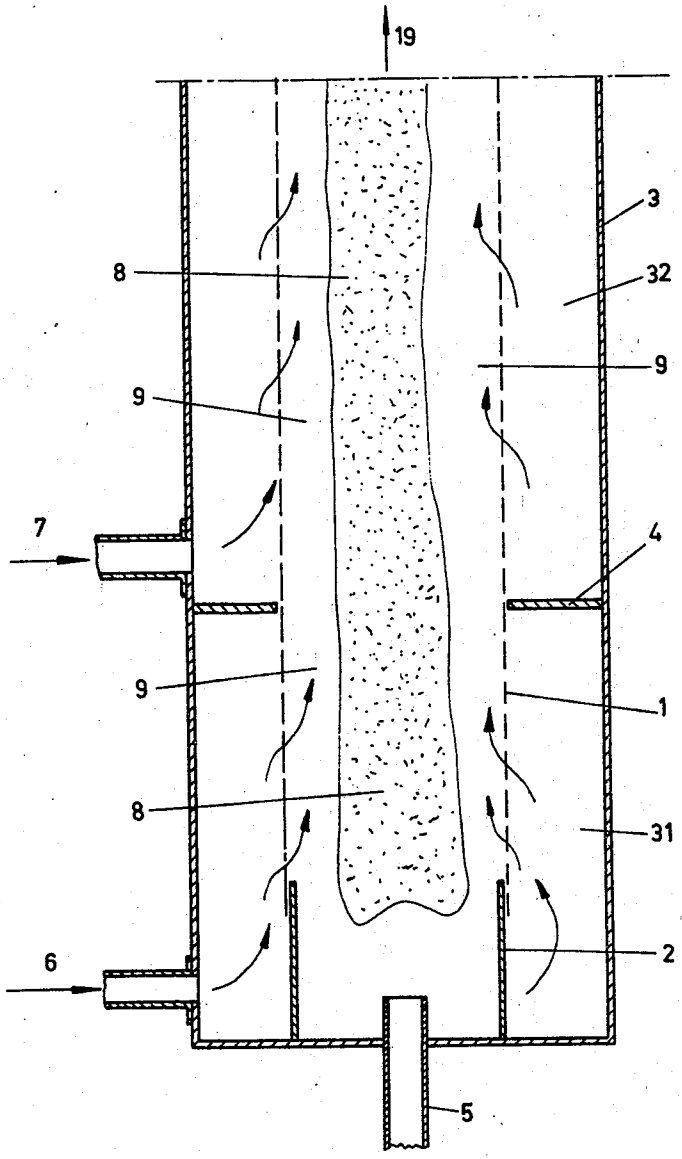

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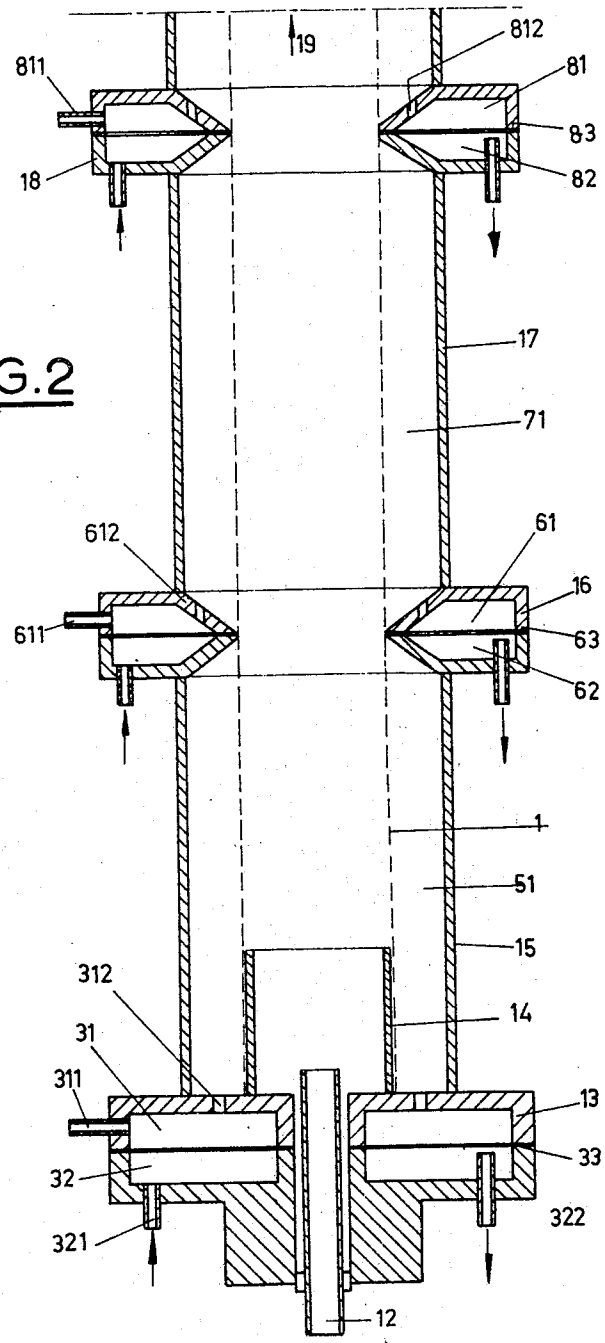
FIG.2



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3,499,730

# PROCESS FOR PRODUCING TITANIUM DIOXIDE BY THE VAPOR PHASE OXIDATION OF TITANIUM TETRACHLORIDE

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U.S. Cl. 23—202 4 Claims

## ABSTRACT OF THE DISCLOSURE

Process for producing a metal oxide and which comprises oxidizing in the vapor phase a metal halide with an oxidizing gas and a combustible gas, surrounding a thin, foraminous walled zone having a wall from about 0.05 mm. to 4 mm. in thickness and restricting the resulting combustion reaction to a confined space containing a central flame by surrounding said space with a thick barrier layer of gas and sustaining the combustion reaction flame by means of an auxiliary flame invariably laterally opposing the central flame but keeping the auxiliary flame away from the foraminous wall. Apparatus for carrying out this product is also disclosed.

The present invention is concerned with a process and apparatus for the vapor phase oxidation of metallic halides and is more particularly concerned with the production of pigmentary titanium dioxide by the combustion of titanium tetrachloride in the presence of an auxiliary flame.

The present process and apparatus can be used with all metallic halides, with the exception of fluorides, the volatility of which is sufficient at the selected oxidation temperature and which can form pigment oxides.

Various processes exist for producing metal oxides by oxidising vaporized metal halides. In these processes, the volatile chlorides, bromides or iodides are reacted with oxygen, air, or like suitable oxygen-containing gas to yield the respective oxide of the metal and the corresponding halogen. These processes are particularly suitable for the production of titanium, zirconium, silicon, aluminum and iron oxides.

In most instances, particularly in the case of the oxidation of titanium tetrachloride, such reactions require the feed of additional heat to maintain the reactants at a temperature such that ther reacion speed is sufficient. At present there are two principal processes for supplying the additional heat in question. In one, one or all the reactants are preheated separately to a temperature such that during their mixing the reactions can take place at high speed. In the second, recourse is had to the use of an auxiliary flame in which are introduced the reactants, pre-mixed, or not, and, sometimes, partially pre-heated.

These processes, requiring various apparatus, which distinguish them, all lead to the oxidation of the metallic halides within a flame limited of necessity by an enclosure at a temperature near that of the flame, and, on the walls of which can occur various phenomena. Thus halides which have not had the time to react in the principal reaction zone react with oxygen on the walls or on formed oxide deposited on the walls thus forming oxide crystals which are structurally very different from those which form in the reaction zone. These formed crystals can either come off mechanically and objectionably contaminate the desired products recovered from the operation, or, they may tenaciously remain on the internal surfaces



of the reactor causing an undesired alteration in the configuration of the dimensions of the reactor susceptible to modify the quality of the produced oxide and even completely block or plug the reactor requiring the shut down or dismantling and cleaning thereof. The same problems can arise where the halide is oxidized in the reaction zone to form particles which stick on the hot wall of the reaction chamber or agglomerate to an undesired particle size rendering the product unfit for its intended or pigmentary use.

To obviate these problems, it has been suggested to build the reactor walls of porous refractory materials and to force a gas through the reforactory wall in order to remove the crystals of oxide formed thereon or deposited on the wall. Repeated experiments have indicated that the efficiency of this expedient is limited and very uncertain. The pressure loss of gas blown through the porous refractory walls is very high owing to the fact that the pores are of small diameter and follow tortuous paths in such a way that gas penetrates into the reaction chamber with a velocity which is almost nil and in various non-uniform directions, since the pores terminate on the walls at various angles.

As a result, the combustion flame remains in contact with the wall of the reactor which is thus made very hot; the formation and the deposition of oxide on the wall are not therefore uniformly prevented but only in those areas where the flame is actually and effectively spaced from the wall. Additionally, the warping of the porous wall is frequent at the temperatures encountered.

It is also noteworthy to remark that the reaction chambers when at high temperature lose an appreciable quality of calories, a factor which is detrimental to the economics of the process. In the case of processes using an auxiliary flame, these thermal losses can be compensated by an increase in the quantity of the combustible gas used for the auxiliary flame. This, however, results in increasing the dilution of the halide obtained with the metallic oxide, which also is detrimental to the economics of the process.

It is, accordingly, the main object of this invention to overcome the above outlined disadvantages of prior art processes and to provide a novel and effective process and an apparatus for producing metal-oxides in the vapor phase, in which the oxidation is very rapid and extremely complete.

This and other related objects, features, and advantages of the present invention will be more fully understood as the description thereof proceeds, particularly when taken together with the accompanying drawing, wherein:

FIGURE 1 is a schematic view of the apparatus for carrying out the process and

FIGURE 2 is a cross-sectional view of a preferred apparatus according to the invention.

To summarize the invention, the same resides in a process for producing a metal oxide which comprises oxidizing in the vapor phase a metal halide with an oxidizing gas and a combustible gas surrounding a thin foraminous walled zone having a wall (0.05 mm. to 4 mm. thick) and restricting the resulting combustion reaction to a confined space containing a central flame by surrounding said space with a thick barrier layer of gas and sustaining the combustion reaction flame by means of and auxiliary flame invariably laterally opposing said central flame but keepjng said auxiliary flame away from the said foraminous wall. By providing a barrier layer of gas having a thickness ranging from about $\frac{1}{10}$ to about $\frac{1}{2}$ of the radius of the foraminous walled zone between the situs of the oxidizing reaction radius and the wall of the reaction zone depending on the diameter of the zone, it is not possible for the oxide which forms to reach the wall and accordingly the prior art problems are avoided by eliminating the source of their occurrence.

According to various embodiments of the invention, the gas which is used to maintain the reaction zone away from the wall can either be a combustible gas or an inert gas or a re-cycling gas. The confined space in the process is a circular reaction chamber and the central flame of the metal halide is a brilliant and stable flame suitably of titanium tetrachloride maintained and defined by the inflow of oxygen and titanium tetrachloride through a central tube; the inflow of auxiliary combustion gases by a suitable inlet in the reactor; and a gaseous layer located between the flame and the foraminous wall. The rate of introduction of gas forming the layer through the foraminous walled zone preferably ranges from 0.06 l./cm.$^2$/min. to 2 l./cm.$^2$/min. The ambient gas surrounding the flame preferably is formed by a mixture of reactive gases or inert gases, the precise nature of which varies depending upon whether the mixture is introduced by one or the other of the three zones of the reactor as defined below. The zones of the reactor above referred to are as follows: when the ambient gas surrounds the flame in its lower part, the mixture of reactive gases limits a reaction zone; when the ambient gas surrounds the flame in its middle part, it becomes a mixture of inert gases limiting a cooling zone; when the ambient gas surrounds the flame in its upper part, it is a mixture of re-cycling gas which defines a re-cycling zone.

The outer area surrounding the foraminous wall is common to all the zones of the reactor and the passage of gas from one to the other takes place without discontinuity while inside the zones, the gases follow first a horizontal direction, then a vertical direction, the flame thus being always spaced apart from the wall surrounding the reaction zone.

The foraminous wall permitting the passage and the uniform distribution of the reactive gases can be formed by one of the following means; a porous metallic wall permitting a large amount of gas to pass through perpendicularly even if these gases have been pre-heated; or a perforated metal sheet having a maximum number of holes to permit a large quantity of reactive gas to pass through. The surface of the walls should be perforated with holes spaced closely enough and small enough so that for a given input the speed of passage therethrough by the gas be sufficiently high. Also suitable is any metallic wall the free surface of which is perpendicular to the speed of the gas with respect to the total surface and having porosities ranging from 2 to 40%.

Referring now to the drawing, at FIGURE 1, it will be noted that according to the invention the gaseous reaction mixture such as a mixture of $TiCl_4$ and oxygen enters in the reaction chamber through an inlet **5** and burns in a flame **8** localised axially and centrally owing to the presence of a thick gaseous barrier layer **9** interposed between the outer wall **3** and the flame.

This gaseous envelope **9** can be formed either by the feed of a combustible gas such as carbon monoxide entering through inlet **6** between wall **3** and support **2** on which is mounted the foraminous tubular wall **1** and also by a feed of inert gas **7** entering above a dividing wall **4**. The combustible gas fed in at **6** goes through the perforations of the wall **1** as shown by the arrows and ensure combustion by combining itself with the oxygen fed in axially through inlet **5** together with the halide and also localises the flame or central oxidizing zone as shown. By feeding the gases laterally through **6** and **7** there are produced lateral auxiliary flames opposing the central flame.

Particles of metal oxide form rapidly in flame **8**, which is kept away from the foraminous wall by the barrier layer of gas. The recycling gases fed in through tube **7** into chamber **32** serve to maintain the temperature of said wall at a value substantially lower than that of the temperature of the reaction zone, for example as low as room temperature. At the outlet of this second zone, the gaseous mixture containing suspended therein the oxide is directed by outlets **19** toward a conventional recovery system from the metal oxide (not shown).

The process thus outlined can be effected in various ways. Thus one of the reactive gases or a mixture of partially or totally reactive gases can be brought in between the space comprised between the impervious outer wall **3** and the foraminous wall **1**, the remainder of the reactants being introduced with the metal halide inside the reaction chamber through one of the extremities of the reactor. The reactants introduced between the external wall **3** and the foraminous wall **1** must form in the external enclave of the foraminous wall a mixture which cannot react in this area. The entire reaction thus takes place within the chamber but far from the cooled walls thereof such that these are protected by the thick cooled layer of gas.

The temperature of this thin wall **1** which is continuously and uniformly cooled as it is traversed by gas coming from the outside is not high, which makes possible the construction of the wall with a commercially available metallic material such as steels, steel alloys, nickel or aluminum. Foraminous uniformly perforated walls suitable for use in the invention can consist of various materials such as a perforated sheet, a grill network made of bars secured together or a woven sheet of linked warp wires thicker than the woof wires. Through experimentation it has been found that the surface of the perforation: that is, the surafce of the wall which can be passed in a uniform direction by the gas and without loss of velocity should be from about 2 to 40% of the total wall surface so that the pressure of the gas is not substantially diminished when passing therethrough.

In the case where the metallic halide is titanium tetrachloride, and the auxiliary gas is carbon monoxide, the oxidation of the halide takes place in the area where all the gases necessary to the reaction are present. This zone has no material support; neither the walls of the reaction chamber, nor the inlet which is axially disposed with respect to the chamber and through which are set the other reactants. Owing to this fact, the thermal exchanges with the outside of the reaction chamber are substantially reduced since they can only take place by radiation and not by conduction. The heat contributed by the oxidation reaction of the carbon monoxide and the halide is essentially employed to increase the temperature of the reactants which is an important advantage over the known processes wherein the reaction zone is defined by refractory walls.

A preferred variant of the invention consists in causing the carbon monoxide to react in the lower part of the reactor and to allow the formation of the metal oxide to finish in the upper part before rapidly cooling. The perforated part **1** of the second reactor zone is protected from the hot reaction gases by a small amount of recycling gas which does not reduce appreciably the temperature of the reaction gases.

In the apparatus suitable for this embodiment, the outer part of the reactor consists of two glass cylinders **15** and **17** having a diameter of about 60 millimeters. As shown on FIGURE 2, the lower part of cylinder **15** is fixed in a circular groove provided in aluminum base **13**. The assembly is made gas-tight by a gasket provided at the bottom of the groove which is not shown.

The upper part of the cylinder is also fixed in the same manner in a circular grove provided in separating member **16**.

Cylinder **17** also uses member **16** as its base and a similar member **18** as its upper part, a joining of these members being effected as above-described.

Inside the envelope, is located the cylindrical, foraminous wall or grill **1** which, in this example, is 34 mm. in diameter and 200 mm. in height. The same can be formed, for example, of a wire gauze of nickel force-fitted in its lower part on the glass cylindrical support **14** rigid with base **13**.

Grill or wall **1** passes through the inside of members

16 and 18, thus defining a lower chamber 51 and an upper chamber 71. Base 13 has an inner chamber divided in two parts by metallic plates 33. The upper chamber 31 communicates with the outside through tube 311, and also with chamber 51 by means of 12 holes of which one only is shown by reference character 312, suitably having a diameter of 2 mm. The lower chamber 32 serves for the cooling of base 13 by the circulation of water entering through tube 321 and going out through outlet 322. Base 13 is perforated axially so as to permit the passage of inlet tube 12.

Separating member 16 and cooling members 18 are built along the same principle as base 13 and have an annular shape. Their inner chambers are divided into two parts by metallic discs 63 and 83 respectively. The upper chambers thus formed 61 and 81 serve also to ensure the distribution of gas while the lower chambers serve to water-cool each member by the continuous passage of water. The components of the apparatus are in gas-tight relationship with the outside.

Combustible gas, such as carbon monoxide introduced through tube 311 is uniformly distributed in gas distribution zone 51 by means of the 12 holes 312. The gas passes wall 1 along a distance of 60 mm., limited at one end by the height of member 14 and by the point of contact of member 16 with wall 1.

A part of the recycling gases are introduced through inlet 611 and the twelve holes 612 (i.e. the mixture of gases remaining after removal of the metal oxide). The gases pass through wall 1 along a height of 120 mm. defined by members 16 and 18.

Through inlet 811 and the twelve holes 812 is fed a sufficient quantity of cold recycling gas to bring the temperature of the halogen metal oxide and carbon dioxide products to a temperature lower than 600° C. These gases containing the formed product are then directed toward a conventional recovery system for metal oxides, such as titanium dioxide, which is schematically represented by reference character 19.

The inlet tube 12 for the halide-oxygen mixture suitably can be a glass cylinder having an internal diameter of 6 mm., the upper end of which is located 40 mm. from the top of cylindrical support 14 for wall 1.

The process according to the invention and its carrying out in the above-described apparatus will now be explained in greater detail by way of non-limiting examples.

## EXAMPLE 1

The reactor shown on FIGURE 2 is employed. The amounts of fluid used measured at room temperature were the following:

| | |
|---|---|
| CO | 3 l./min. (liter/minute). |
| $N_2$ | 1.2 l./min. (to bring combustible gas total to 70%). |
| $O_2$ | 5.2 l./min. |
| $TiCl_4$ | 3 l./min. |
| $AlCl_3$ | 2.1% with respect to $TiCl_4$. |
| Recycling 1 | 3 l./min. |
| Recycling 2 | 15 l./min. |

The auxiliary flame is first lit and rapidly assumes the shape of a cylinder 25 mm. in diameter and 70 mm. high the base of which lies on the lower level of wall 1. The introduction of $TiCl_4$ in the flame results in the thinning and rising thereof. Above the brilliant hot zone where the $TiCl_4$ is oxidized, the $TiO_2$ formed is carried by the oxidizing gases in the shape of a cylindrical column which has low tendency to contact the grill firmly protected by a small amount of recycling gas at 20 to 50° C.

After cooling by a larger amount to recycling gas at 20 to 50° C., and then by a conventional cooler, the product is collected and examined. The oxide obtained consisted of more than 98% rutile and of particularly good granulometry, its average size ranging from 1700 to 2300 A. The colour, the colouring power, the opacifying power, and the dispersibility of the titanium oxide thus obtained renders it particularly valuable for use in paint, plastic materials, paper, rubber and other applications.

## EXAMPLE 2

The operating conditions were similar to those described in Example 1, except that carbon monoxide was introduced pre-mixed with a variable amount of oxygen not exceeding 10%. There was thus obtained a larger flame in which the temperature was more uniform.

## EXAMPLE 3

The titanium tetrachloride was pre-heated to a temperature not exceeding 700° C. and closer to 450° C. The amount of titanium tetrachloride thus oxidized in a flame obtained under conditions similar to that of Example 1 was about 20% greater than that obtained in Example 1.

The carbon monoxide employed herein can be modified by the addition of water, hydrogen, hydrogenated gases and nitrogen-oxides, the effects of which on the combustion of carbon monoxide are well known.

Similarly, the halide can be mixed with various additives which modify the characteristic of the metal-oxide obtained, such as aluminum halides, or silicon halides in a proportion ranging between 0.01 and 5% by weight of the halide employed.

The apparatus as above-described is also new. It can be modified with respect to its shape, its size, the type of its openings and their spacing. The height of the combustible gas inlet can be greater or less according to the desired flame temperature. All these modifications and adaptations of the burner to a particular application of the process fall within the scope of the present invention.

The main advantages of the present invention consist essentially in the complete absence of deposit on the cooled walls of the reaction chamber, a decrease in the amount of the combustible gas necessary to maintain a temperature suitable for the oxidation of the halide and the obtaining of a halogen much less diluated than that obtained by other processes using an auxiliary flame thereby facilitating its use for the chlorination of rutile.

Furthermore, the apparatus according to the invention is of simple structure and requires only inexpensive materials. Additionally, the present apparatus does not require pre-heating prior to oxidizing the metal halide and cools down very rapidly after the introduction of reactive gases has stopped.

With the use of the thin walled foraminous zone described herein the temperature of the gas on the inner surface of the wall is not substantially higher than that of the gases on the outer surface so that the barrier layer of gas itself is relatively cool. This beneficial effect cannot be obtained with the thick porous walls described in the prior art because such thick walls have a considerable heat capacity providing a reheating gradient for the passing therethrough of gases so that even if such gases are introduced at a relatively low temperature they are hot when they reach the reaction chamber. With the present construction it becomes much less expensive to cool down the wall. Similarly the pressure of the gas can be low since the gas can pass straight through the openings which are not tortuous paths as in the prior art and provide a uniform direction for the gas at a substantially undiminished velocity.

Through the present process can be obtained metal oxides having a very uniform granulometry, which are particularly useful as pigments.

While the present invention has been described mainly with reference to the production of $TiO_2$ by the conversion of $TiCl_4$, the same has been successful in the production of the same oxide using other titanium halides and mixtures thereof. Similarly, the process of the invention can be used with not only chlorides of titanium but also bromides and iodides thereof, and of zirconium, antimony, aluminium, tin, zinc and iron.

What is claimed is:

1. Process for producing titanium dioxide comprising introducing $TiCl_4$ and an oxidizing gas to the lower part of an oxidizing zone, reacting $TiCl_4$ with said oxidizing gas and a combustible gas in a foraminous metallic walled zone having a thickness ranging from 0.05 mm. to 4 mm. and a porosity of 2 to 40% said titanium halide and said oxidizing gas being introduced in the lower part of an oxidizing zone, restricting said reaction to a central oxidizing zone containing a central flame by providing a cold barrier layer of combustible gas inwardly of said oxidizing zone and surrounding said central oxidizing zone of a thickness ranging from $\frac{1}{10}$ to $\frac{1}{2}$ of the radius of said foraminous zone, said layer being formed by continuously and uniformly passing gas at a temperature substantially lower than that of said central oxidizing zone temperature under undiminished slight pressure through said foraminous walled zone, sustaining said flame by an auxiliary lateral flame, passing a cooling gas through the upper part of the foraminous walled zone, recovering the metal oxide thus formed from the reaction products in the upper part of said oxidizing zone, and recycling gas remaining after removal of the metal oxide from the reaction products to form said barrier layer.



2. Process according to claim 1, wherein said barrier layer of gas consists of a recycling gas containing chlorine and carbon dioxide.

3. Process according to claim 1, wherein the gas fed through said foraminous-walled zone is carbon monoxide.

4. Process according to claim 1, wherein said barrier layer of gas is composed of a mixture of inert and reactive gases.


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