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PURIFICATION OF HYDROGEN UTILIZING HYDROGEN-PERMEABLE MEMBRANES

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Figure 1

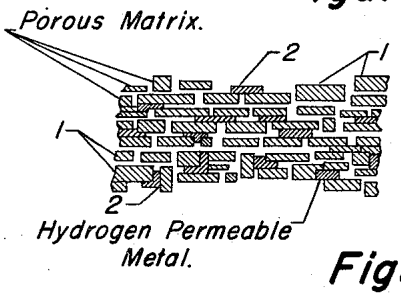


Figure 2

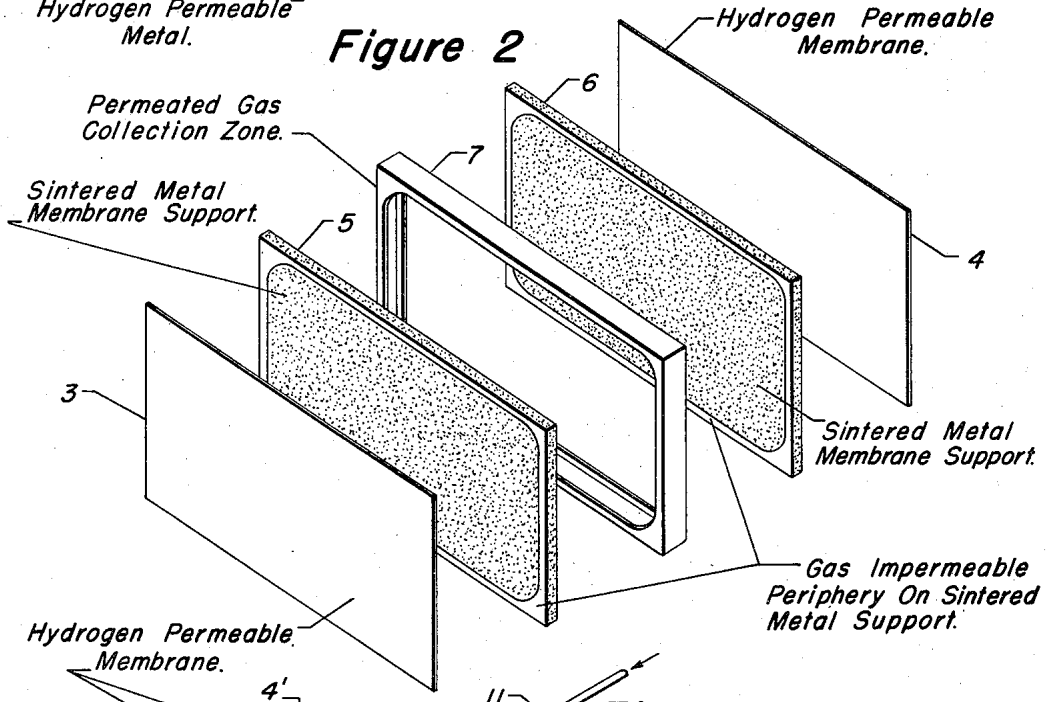
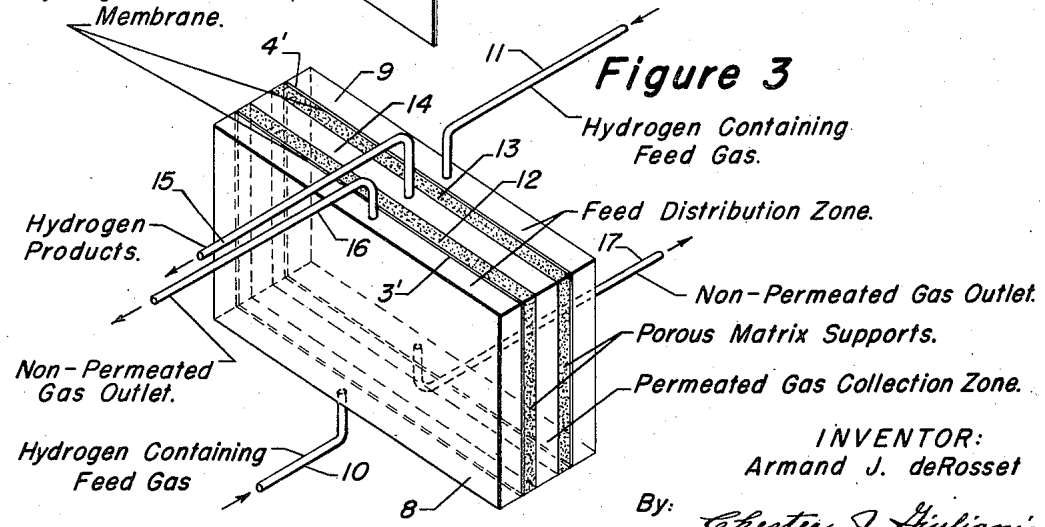


Figure 3



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PURIFICATION OF HYDROGEN UTILIZING HYDROGEN-PERMEABLE MEMBRANES

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This invention relates to the means for and the method of separating hydrogen from a mixture of gases which involves the diffusion of the hydrogen component of the gas mixture through a hydrogen-permeable membrane. More specifically, the invention relates to an apparatus

other diverse gases. However, it has been found that the use of such thin metallic membranes such as palladium foil for this method of separation are limited in their application to low pressures at a rate of hydrogen production because of the tendency of such thin membranes to rupture upon the application of even slight pressures on the upstream side of the hydrogen-permeable foil. Although palladium has been found to be one of the preferred hydrogen-permeable elements from which to fabricate such gas diffusion elements, other metals such as certain alloys of palladium, and the metals: iron, nickel, copper, platinum aud molybdenum, including certain alloys of the latter metals, may be employed to improve the permeablilty of the membrane to hydrogen without sacrificing purity of the gaseous product or without weakening the structural properties of the membrane. Thus, silver-palladium alloys containing from small amounts up to about 60% of silver, and preferably from about 25% to 40 atom percent of silver will in-

sintered metal particles, is generally manufactured by partially fusing a mass of the metal in powdered or finely divided condition, accompanied by heating and

however, being impermeable to the non-hydrogen of the gas mixture. This may be provided essentially by the method of at least partially filling or sealing off the pores

levels in a porous matrix, and which, taken together, over the tranverse area of the matrix presents an impervious barrier to the non-permeable gaseous components. The term "porous" as utilized herein, indicates a structural condition in which spaced voids are dispersed throughout a solid mass and in sufficient number and continuity to permit fluid flow through the mass, while the term "permeable" is intended to characterize a condition which permits diffusion through the mechanism of dissolution, followed by displacement.

A number of methods may be utilized to form the hydrogen-permeable membrane comprising the diffusion apparatus of this invention. Thus, a relatively thick hydrogen-permeable foil, for example a foil of from 0.5 to about 20 microns in thickness may be placed upon the surface of a porous plate constituting the membrane support and the resulting combination placed in the diffusion cell as the hydrogen-permeable element of the apparatus. The thickness of the foil in this modification of the present apparatus should be only sufficient to withstand the pressure differential between the upstream and downstream sides of the foil without yielding to the pressure and forming a fissure or aperture through which the gaseous mixture may flow. The required thickness of foil, will, in general, depend upon the size of the pores in the matrix background and will also be determined by the desired rate of diffusion, which is inversely proportional to the thickness of the foil and varies directly with the pressure and temperature of the gaseous mixture impressed on the upstream surface of the foil. Since these are mutually dependent factors, each must be determined by trial and error methods of the particular system involved.

One of the preferred methods of preparing the hydrogen-permeable membrane comprises depositing a thin foil on the surface of the matrix and subjecting the resulting combination to fluid pressure, such as to the pressure of the feed stock gaseous mixture at a pressure level at least as great as the pressure to be employed in the gas diffusion process and thereafter determining the purity of the hydrogen diffused through the membrane to the downstream side thereof. If the resulting hydrogen product is not of the desired purity, another layer of the hydrogen-permeable foil may be placed over the layer previously deposited and the procedure again repeated until the continuity of the resulting membrane is sufficient to yield a diffused product of the desired purity. The thin foil from which the ultimate membrane is fabricated through the repeated applications of the foil to the porous plate may, for example, be a foil having a thickness of from 4×10^{-6} to about 4×10^{-4} inches in thickness (approximately 1.0×10^{-1} to about 10 microns). When it is desired that the thickness of the membrane be increased gradually by the application of successive layers of foil to the upstream surface of the plate, the foil is preferably thin, such as foil of 0.1 micron thickness. Instead of applying the foil by the application of fluid pressure to a subadjacent layer of foil previously applied, the

two hydrogen-permeable membranes and two membrane supports comprising the porous matrices therefor, the apparatus providing for two upstream inlets, with the hydrogen product diffusing into an intermediate hydrogen-collecting zone. The permeable membrane on the two upstream sides is indicated in Figure 2 by the numerals **3** and **4** and the adjacent porous matrices therefor by the numerals **5** and **6** for said permeable membranes, respectively. The hydrogen collection zone which is placed between the downstream sides of two opposing porous matrices **5** and **6** is indicated in Figure 2 by numeral **7**. These may be clamped or bolted together into a unit, each of the pieces comprising the unit being sealed around their perimeters to prevent leakage of gas from the unit by means of a gasket, not shown, or by polishing the peripheral edges of the pieces to provide an hermetically sealed union between the individual portions of the apparatus. Figure 3 illustrates one form of a typical gas diffusion apparatus embodying the elements of this invention, above described, together with feed distribution zones **8** and **9** on the upstream sides of the hydrogen-permeable membrane on each end of the apparatus which also have their peripheral edges sealed against the hydrogen-permeable membrane, as shown in Figure 3. The feed distribution zones **8** and **9** are connected to feed lines **10** and **11**, respectively, which supply the respective zones with the hydrogen-containing gas mixture to be separated. The feed gas mixture is preferably heated to an elevated temperature within the range of from about 150° to about 1500° F., preferably to a temperature above about 200° F., up to about 1000° F., in order to increase the rate of hydrogen diffusion. The hydrogen component of the gas mixture, which, under the temperature and pressure conditions maintained within the feed distribution zones, diffuses through hydrogen-permeable membranes **3'** and **4'**, respectively, flows under the pressure existing within zones **8** and **9** through the porous membrane supports **12** and **13**, respectively, into hydrogen-collection zone **14**, the pressure differential between the feed-distribution zone and the hydrogen-collection zone being at least 10 pounds per square inch, and preferably from 20 to about 1500 pounds per square inch, in order to obtain a positive flow of hydrogen from the upstream side of the hydrogen-permeable membrane into the hydrogen-collecting zone. As hydrogen accumulates in zone **14**, it is desirably withdrawn therefrom through line **15** into storage or for disposition to other uses. The flow of hydrogen-containing feed gas into feed distribution zones **8** and **9**, respectively, is preferably countercurrent in order to take advantage of the concentration gradient effect inherent in gaseous diffusion; thus, the non-permeated gas outlets are desirably located on the feed-collection zone on the side opposite to the feed gas inlet. This arrangement is illustrated in Figure 3 by pipes **16** and **17** which connect with the feed-distribution zones **8** and **9**, respectively, through openings on the side opposite to the feed inlet openings **10** and **11**, repectively.

Although the foil-type membrane constitutes one of

matrix and thereafter burnished or polished to form a more continuous film over the pores of the supporting matrix. Another convenient method of placing a hydrogen-permeable metal film on the surface of the porous support, the method being one of the preferred means for fabricating the hydrogen-permeable membrane when a sintered metal powder plate is utilized in the apparatus, comprises electroplating the desired hydrogen-permeable metal or alloy on the upstream side of the porous support. Thus, palladium may be readily electroplated on the surface of a sintered stainless steel powder plate by methods and procedures well-known in the electroplating art. The electroplating process may be continued and the continuity of the hydrogen-permeable metal layer on the porous support developed to a degree sufficient to reduce the perviousness of the resulting membrane to the non-hydrogen components of the feed gas to the desired level. An alloy of the hydrogen-permeable metal, such as a platinum-silver alloy, may also be electroplated directly upon the porous plate.

Another method of applying a superficial layer or modified foil of the hydrogen-permeable metal on the upstream side of the porous matrix comprises permitting vapors of the metal to impinge on the surface of the matrix, usually by heating the metal in a high temperature electric arc (for example, electrodes fabricated from carbon) and allowing the vapors to rise to the flat surface of the matrix held above the metal being vaporized, as for example above the electrodes. The vaporization may

and if the latter is not sufficiently pure, repeating the above series of steps until a product of the desired purity is obtained. A suitable class of salts for this purpose are the nitrates which may be readily reduced by hydrogen or the metal precipitated therefrom with hydrogen sulfide, followed by oxidation of the metal sulfide with air or oxygen.

Still another method for incorporating the hydrogen-permeable metal into the matrix of the porous support comprises mixing the hydrogen-permeable metal in powdered form with the matrix-forming material before the latter is compacted and/or sintered, thereby preparing the matrix and the membrane in the same operation. This method is particularly suitable when the supporting matrix is a sintered metal powder, such as a sintered stainless steel powder. In this method, the perviousness of the resulting membrane, in combination with the desired porous matrix is directly proportional to the amount of powdered hydrogen-permeable metal incorporated into the matrix-forming material or by varying the mechanical and thermal treatment of the formed matrix-membrane combination to provide a membrane of the desired perviousness. Thus, the perviousness of the combined matrix and membrane may be reduced by sintering the metal powder at a higher temperature, thereby at least partially sealing the porous structure of the matrix while not substantially affecting the permeability of the membrane to hydrogen diffusion.

It is evident that other methods of incorporating the

obtainable thereby in the following examples, the examples being intended merely for illustrative purposes only and not as a limitation on the scope of the invention.

Example I

A hydrogen diffusion cell in simplified form is fabricated in accordance with the following procedure. A porous plate measuring 12" x 12" x 1" in dimension is utilized as a supporting porous matrix, the plate consisting of sintered particles of stainless steel powder (18% chromium, 8% nickel steel) molded into a structurally rigid form by heating and compressing the stainless steel powder of 10 microns average diameter at or near the melting point of the stainless steel. The plate is fitted into a housing which hermetically seals the peripheral edge of the plate against the walls of the housing, the plate dividing the housing approximately through its mid-section, thereby providing an enclosure on each side of the plate sealed on each side against the leakage of gases from the enclosure on one side of the plate into the enclosure on the other side of the plate. The apparatus is so designed and fabricated that different plates of 1" thickness may be substituted into the mid-section of the housing for test purposes. In the following example, the plate of sintered stainless steel particles which weighs approximately 8.57 kg. has pore diameters which average in diameter from about 2 microns to about 10 microns. When placed in the gas diffusion cell the plate allows approximately 100 cubic feet per minute of a mixture of 25% hydrogen and 75% nitrogen to pass through the plate per minute at an upstream pressure of 10 p. s. i. The porous stainless steel plate indicated above is thereafter soaked in a 0.9% solution of palladium dinitrate placed in a shallow pan, the solution being maintained at a level of ½ inch depth as the solution enters the porous structure of the upstream side of the sintered stainless steel plate. The plate containing the solution of palladium dinitrate is thereafter slowly dried in an oven of 110° C. for 10 hours, followed by heating the impregnated plate in an oven maintained at 900° C. for an additional 12 hours to decompose the palladium dinitrate salt to metallic palladium. The weight of porous plate, after the above treatment increased an additional 4.87 grams and when tested in the gas diffusion cell, the plate permits the passage of 50 cubic feet per minute of a mixture of 25% of hydrogen and 75% nitrogen at an upstream pressure of 10 p. s. i. and at a temperature of 115° C. The diffused gas withdrawn from the chamber on the downstream side of the sintered plate is enriched in hydrogen, containing 45% by volume of hydrogen and 55% by volume of nitrogen. The plate is thereafter removed from the gas diffusion apparatus and placed in a pan containing a 0.045% aqueous solution of palladium dinitrate to a depth of ½" from the top edge of the sintered metal plate. After soaking in the latter solution for 3 hours the plate is again dried and heated for 12 hours at 900° C. and thereafter replaced in the gas diffusion cell for determining the rate of diffusion and the concentration of hydrogen in the diffused gas. At 10 p. s. i. pressure, and with the gas mixture at 115° C. the plate permits the passage of 41 cubic feet per minute of gas enriched in hydrogen, the collected gas containing 93% by volume of hydrogen and 7% by volume of nitrogen.

The plate as prepared by the second impregnation of palladium metal is again placed in the shallow pan containing a hydrogen concentrate containing 99.5% hydrogen and 0.5% nitrogen. Utilizing a pressure of 100 p. s. i. on the upstream side of the sintered plate containing the palladium membrane, 123 cubic feet per minute of hydrogen concentrate are collected in the diffused gas collection compartment, the concentrate containing 98.4% by volume of hydrogen and 1.6% by volume of nitrogen. At 100 p. s. i. pressure and 300° C., 408 cubic feet per minute of hydrogen concentrate containing 97.5% by volume of hydrogen passes through the cell.

Example II

In a similar method of preparing a sintered plate of powdered stainless steel as described in the above Example I, except that in each case the aqueous solution of impregnating salt solution contains 50 mol percent of the palladium dinitrate salt and 50 mol percent of silver nitrate of the total salt concentration of the aqueous solution is utilized to prepare the hydrogen-permeable membrane. Following each impregnation with the above solutions of mixed palladium and silver nitrate, the impregnated plates are dried and the salts contained in the plate decomposed at temperatures of 1000° C. in order to form an alloy of the silver-palladium metals contained in the porous plate. At 100 p. s. i. pressure, a mixture of 75% nitrogen and 25% hydrogen permits the passage of 98 cubic feet per minute of a gas diffusate containing 99.5% hydrogen and 0.5% nitrogen.

I claim as my invention:

1. A process for increasing the concentration of hydrogen in a mixture of gases which comprises passing said mixture at an elevated pressure and temperature through a diffusion zone separated into an upstream portion and a downstream portion by a continuous, hydrogen-permeable membrane comprising a metal of group VIII of the periodic table, said membrane being supported on the downstream side by a porous matrix of compressed sintered metal particles and having sufficient structural rigidity to maintain the continuity of said membrane against the upstream pressure, collecting hydrogen on the downstream side of said membrane and the non-hydrogen components of said mixture on the upstream side of said matrix.

2. The process of claim 1 further characterized in that said metal particles comprise stainless steel powder of from 1 to about 100 microns in thickness.

3. The process of claim 1 further characterized in that said upstream pressure is at least 10 p. s. i.

4. The process of claim 1 further characterized in that the metal of said membrane is seelcted from series 4 and 6 of group VIII.

5. The process of claim 4 further characterized in that said metal is palladium.

6. An apparatus for increasing the concentration of hydrogen in a hydrogen-containing mixture of gases which comprises in combination: a housing comprising an upstream gaseous feed distribution zone and a downstream permeated-hydrogen collection zone, a hydrogen-permeable membrane supported by a porous matrix of compressed sintered metal particles and having sufficient structural rigidity to retain its structure against the upstream pressure of the gaseous feed, said membrane being sealed into said housing between said feed distribution zone and said hydrogen collection zone and comprising a metal of group VIII of the periodic table, said feed distribution zone containing an inlet for said gaseous feed.

hydrogen-permeable membrane placed on opposing sides of said permeated hydrogen collection zone.

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