April 12, 1966 R. E. BONNET 3,245,206

DIFFUSION PURIFICATION APPARATUS

Filed Aug. 2, 1963

FIG. 1

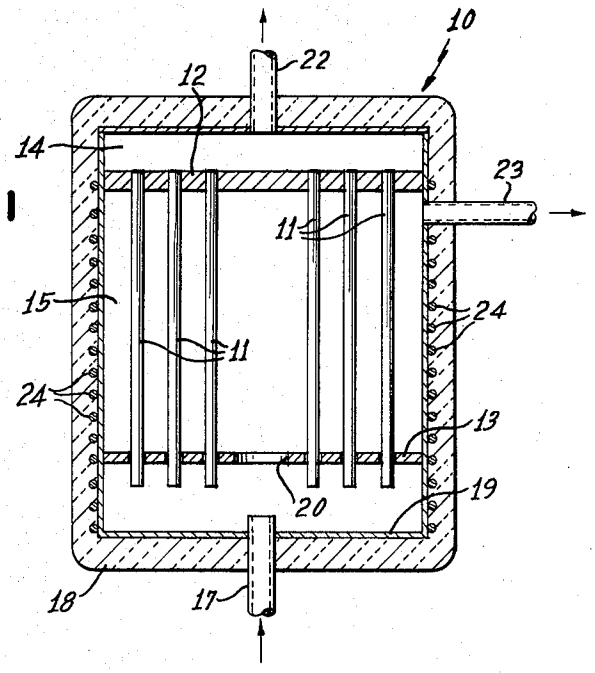


FIG. 2

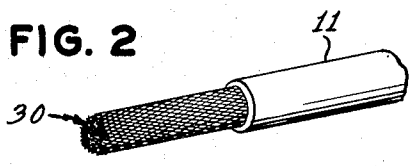
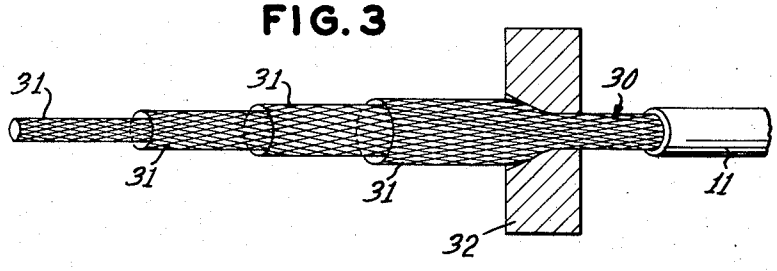


FIG. 3



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DIFFUSION PURIFICATION APPARATUS

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The present invention relates to improved apparatus for purifying gases, such as hydrogen and oxygen, and particularly relates to the construction of tubular elements through the walls of which a gas diffuses in the purifying apparatus.

It is a well known phenomenon that certain gases such as oxygen and hydrogen permeate and diffuse through certain metals. For example oxygen diffuses through silver and hydrogen will diffuse through palladium and palladium alloys such as palladium-silver, palladium-boron, and palladium-gold. A particularly suitable alloy for hydrogen diffusion is 75% palladium and 25% silver by weight.

This phenomenon is made use of in apparatus for purifying gases such as hydrogen or oxygen by bringing a gas mixture containing the gas to be purified into contact under heat and pressure with a thin non-porous wall of the metal through which the gas to be separated from the mixture will diffuse.

The present invention relates to diffusion purification apparatus in which the gas permeable metal walls are provided in the form of tubes. For convenience, the apparatus will be described with reference to apparatus having palladium alloy tubes for the purification of hydrogen, but it is to be understood that the tubes may be made of other metals for purifying hydrogen or other gases without departing from the spirit and scope of the present invention.

The rate of diffusion of the gas through the metal is increased by increasing the temperature and the pressure differential across the wall. With sufficiently high temperatures and pressure differentials the rate of diffusion of hydrogen through palladium or its alloys is rapid enough for this diffusion method of purifying gases to be commercially practical. The temperature is usually raised to the range of about 300 to 800° C. The pressure which can be applied is dependent on the strength of the diffusion wall. The thicker the wall the stronger it is but the rate of diffusion varies inversely with the thickness of the wall and the lower rate of diffusion resulting from increasing the thickness of the wall is not compensated for by increasing the pressure to the limit permitted by the strength of the wall. A continuing effort is therefore being made to develop efficient and economical hydrogen purification apparatus within the structural limitations imposed by the nature of the diffusion process.

Diffusion walls are frequently provided in the form of palladium alloy tubing and it has been found that to obtain a reasonable rate of diffusion, the tubing may be made with a maximum wall thickness of about 8 mils. The minimum wall thickness is about 3 mils which is determined by the state of the art of making non-porous metal tubing. The pressure such tubing can withstand depends not only on the dimensions and material of the tubing, but also on the direction of the pressure since tubing of a given wall thickness will withstand greater internal than external pressure.

In one general type of apparatus a plurality of tubes of palladium alloy extend into a chamber. The bores of the tubes open outside the chamber and the tubes are sealed in the chamber so that gas can only pass between the chamber and bores of the tubes by diffusion through the walls of the tubes. The impure gas is forced into the apparatus under pressure and means is provided

for heating the tubes and the impure gas in order to increase the rate of diffusion.

The impure gas containing hydrogen may be fed into either the chamber or the bores of the tubes. Apparatus in which the impure gas is fed into the chamber is referred to as "out-in" apparatus since the hydrogen diffuses from outside the tubes into the bores of the tubes. If the operation is in the opposite direction, i.e. by feeding the impure gas into the bores of the tubes so that the hydrogen diffuses out through the tube walls into the chamber, the apparatus is referred to as "in-out" apparatus.

The "out-in" and "in-out" types of diffusion purification apparatus each has particular advantages the other type does not. For example, if both types were built with tubes of the same dimensions, the "in-out" type would be operated under higher pressure than the "out-in" type since the tubes withstand greater internal than external pressure. In some other respects, however, the construction and operation of the "out-in" type apparatus is more economical and efficient.

In both types, the space in the bores of the tubes is more costly per unit of volume than the space in the chamber around the tubes but the "out-in" type permits more economical use of the spaces since in this type the greater volume of impure gas enters the chamber and the smaller volume of purified hydrogen diffuses into the bores of the tubes.

Also in the "out-in" type the tubes may be dead-ended in the chamber since the gas flow is in only one direction—out of the tubes. In "in-out" apparatus the tubes must for practical operation be open at both ends outside the chamber to permit entry of impure gas in one end and withdrawal of the undiffused gas from the other. Consequently, each tube requires only one seal through the chamber wall in "out-in" apparatus, but requires two in the "in-out" type. Reduction of the number of seals is an obvious advantage since sealing the tubes through the header and assuring that the seals are leak tight is a major part of the apparatus construction cost.

Heat to increase the rate of diffusion is also used more efficiently in "out-in" apparatus. In both types, heat is most conveniently supplied by resistance coils around the periphery of the chamber. In the "in-out" type the heat from the coils must first heat and penetrate the purified hydrogen in the chamber before it reaches the tubes and the impure gas in the tubes and some of the heat is lost before it reaches the tubes by the continual removal of the purified hydrogen from the chamber. With "out-in" apparatus, however, the impure gas is in the chamber and is heated directly by the coils and carries heat to tubes in the course of its normal flow so that the heating is more direct and less heat is lost.

Although the "out-in" type diffusion purification apparatus has a number of advantages, the limited external pressure which conventional diffusion tubes are able to withstand limits the practical commercial use of this apparatus. It is therefore a principal object of the present invention to provide a diffusion tube element which has greatly increased resistance to external pressure as compared with conventional diffusion tubing and which thus makes it possible to utilize the advantages inherent in the mode of operation of "out-in" type gas diffusion purification apparatus to provide a practical and efficient "out-in" type apparatus.

In accordance with the present invention a diffusion tube of palladium alloy, or non-porous metal through which a gas will diffuse, is given support to resist external pressure by inserting in the tube a mass of filaments which buttress the walls of the tubes without blocking the tube. In practice, the filaments are metal wire and the mass is in the form of a cylinder of knitted wire. The mass could be a jumble of filaments or wires in the nature of steel

wool but by knitting the metal filaments into a cylindrical shape, a firmer more evenly distributed support is provided with fewer filaments. Normally, the cylinder is made up of several superposed layers of knitted wire for added support.

The filaments in the tube do not seriously effect the permeability of the tube and the internal back pressure created does not significantly reduce the advantage resulting from the supporting action of the filaments.

The mass of filaments in the tube should, of course, be of material which will not react with or contaminate the purified hydrogen which diffuses into the tube and should be able to withstand high operating temperatures without damage to the filaments. Alloys from the group referred to as "high temperature" or "heat resistant" alloys would be suitable and alloys which have been tested and proved satisfactory for the mass of filaments are 304 stainless steel wire, "Inconel" alloy wire and "Inconel" alloy wire plated or coated with chromium, ceria, or alumina. The plating or coating tends to minimize the tendency of the wire to weld to the tubing.

Further objects and advantages of the present invention will be apparent from the following description and accompanying drawings in which:

FIGURE 1 is a side view of a vertical section through the center of a hydrogen purification unit in accordance with the present invention.

FIGURE 2 is a perspective view, partly broken away, looking at the end of a tubular diffusion element of the present invention; and

FIGURE 3 is a diagram illustrating the formation of the internal support for tubes in accordance with the present invention.

Referring to FIGURE 1 of the drawings, a hydrogen purification unit in accordance with the present invention comprises a stainless steel pressure vessel **10** in which a plurality of tubular diffusion elements or tubes **11** of the present invention are supported. The tubes **11** are sealed through a header **12** across the vessel **10** near the top and extend down into the vessel. The lower ends of the tubes **11** extend loosely down through holes in a plate **13** which is attached across the interior of the vessel. The plate **13** thus holds the lower ends of the tubes **11** in alignment and prevents excessive lateral movement of the tubes which might weaken the seals through the header **12**.

The header **12** extends across the diameter of the vessel **10** and is welded or otherwise attached to the walls to form a sealed barrier across the vessel near its upper end. The header **12** thus divides the interior of the vessel **10** into a collection chamber **14** at the top of the vessel above the header and a larger inlet chamber **15** into which the tubes **11** extend below the header. The bottom ends of the tubes **11** in the inlet chamber **15** are closed and their upper ends which are sealed through the header **12** open into the collection chamber **14**.

Impure feed gas from outside is fed into the inlet chamber **15** under pressure through an inlet tube **17**. As shown, the inlet tube **17** passes through a layer of insulation **18** which is around the outside of the vessel **10** and is fixed through the bottom wall **19** of the vessel to open into the inlet chamber **15**. The central portion of the alignment plate **13** is open as indicated at **20** to permit the feed gas from the inlet **17** to circulate freely up through the plate and among the tubes **11**. Hydrogen from the feed gas in the inlet chamber **15** diffuses into the bores of the tubes **11** and flows into the collection chamber **14** from which it flows out through an outlet tube **22** through the top of the vessel. The undiffused gas, the off gas, passes out of the inlet chamber **15** through an outlet tube **23** which is fixed through the side of the vessel **10** below the header **12**.

As previously mentioned, the rate of diffusion of hydrogen through the walls of diffusion tubes is increased by increasing the temperature and the pressure differential between the insides and outsides of the tubes. Accordingly the feed gas containing hydrogen may be pumped into the inlet chamber **15** under pressure by any conventional means. Heat is applied by resistance wires **24** around the outside of the vessel **10** and embedded in the insulation **18** which is around the outside of the vessel.

The tubes **11** are made of a metal through which hydrogen will diffuse from a mixture of gases without permitting the other gases of the mixture to pass through. A suitable metal for the tubes **11** is an alloy of 75% palladium and 25% silver by weight. Hydrogen will diffuse at a reasonable rate through a palladium silver alloy wall 3 to 8 mils thick and in practice, the tubes **11** have 4 mil thick walls and an outside diameter of ⅛ of an inch. These dimensions provide a balance of strength and diffusion characteristics which it is believed are particularly adapted to give an optimum rate of diffusion in apparatus of the present invention.

The hydrogen purification apparatus described herein is adapted to be operated at temperatures ranging up to about 800° C. in the inlet chamber **15** with a pressure differential up to about 250 p.s.i.g. between the outsides and insides of the tubes **11**.

Referring to FIGURES 2 and 3 the tubes **11** are strengthened against external pressure in accordance with the invention by inserting a mass **30** of filaments of metal wires which fit against the walls of the tubes. The filaments may be made of any heat-resistant material which will maintain its supporting strength at temperatures in a range up to about 800° C. and which will not combine with or contaminate the pure hydrogen which has diffused into the bores of the tubes. In practice 304 stainless steel wire and "Inconel" "nickel-chromium iron" alloy wire have been found suitable.

The wire which has been used for the mass **30** of filaments in the practice of the invention has had certain characteristics which it is felt may be significant for the successful practice of the invention. Specifically, the wire has been annealed, has had an elongation factor of 15–30%, a breaking load of between 150–400 grams, and tensile strength of 50,000–100,000 p.s.i.

The mass **30** of filaments is preferably made in the form of cylinder **31** of knitted wires. The cylinder **31** may be formed by feeding .003 inch wire through a 10 needle knitting cylinder to produce a ½ inch diameter cylinder of the knitted wire. Looking at FIGURE 3, the cylinder is then drawn through a die **32** to compress the mesh and reduce the outside diameter to fit in the tube **11**. To increase the strength of the cylinder **31** successive cylinders **31** of knitted wire are drawn over the previously knitted and compressed cylinders and the mass **30** composed of superposed cylinders **31** is drawn through the die **32** to compress the composite cylinder **31** for insertion in the tube.

Increasing the number of layers of cylinders **31** increases the supporting strength of the mass **30** but presumably a point would be reached at which the mass would become essentially solid and prevent the flow of hydrogen from the tube. In practice, good results are achieved with a 12 layer cylindrical mass of .003 inch diameter wire knitted on a 10 needle knitting cylinder and drawn through a die **32** to fit snugly into the tubes. The compressed knitted wire cylindrical mass **30** formed in this manner is somewhat resilient before being subjected to the high temperatures during the operation of the apparatus. This initial resiliency enables the cylinders **31** to be inserted into the tubes easily and seat firmly against the walls of the tubes. While this resiliency is lost due to the continual high temperatures the cylinders **31** are firmly in position and continue to support the walls against external pressure.

An alternative method of forming the knitted cylinders **31** which has been used successfully is to knit four wires simultaneously on a 10 needle knitting cylinder. Then the first knitted cylinder **31** is fed through the center of the knitting cylinder and a second cylinder is knitted

around the first. In similar fashion a third cylinder is knitted around the first and second to produce a three layer cylinder **31** of four wire mesh in each layer.

Knitted wire cylinders **31** as described above do not reduce the permeability of the tubing. They do, however, cause a slight back pressure in the tubes but this back pressure is more than compensated for by the greatly increased external pressure the tubing is able to withstand as a result of the supporting action of the masses **30** of filaments.

When the knitted wire cylinder **31** has been formed with the desired number of layers and reduced to a size to fit snugly into the bore of a diffusion tube **11**, the cylinder is inserted to a depth of about ¼ inch from the bottom of the tube. In practice the bottom end of the tube is open at this time and a nickel plug is inserted and welded in to seal the bottom of the tube.

In operation the tubes tend to flatten and in order to prevent creasing of the tube and dislocation of the wire cylinder **31** due to this flattening it has been found helpful to preform the tubes to have an oval cross-section by passing them between parallel rollers after the cylinders **31** are inserted. The open ends of the tubes are then swaged round to fit appropriate holes through the header **12**. The cylinders are made slightly shorter than the internal length of the tubes so that the upper ends of the cylinders will not interfere with the welding by which the open upper end of the tubes **11** are secured to the header **12**.

In comparing the operation of "out-in" hydrogen diffusion purification apparatus having conventional diffusion tubing and apparatus having tubing in accordance with the present invention it has been found that, as a result of the increased external pressure tubing of the present invention is able to withstand, the production of purified hydrogen is about 2½ times the production rate of the same size apparatus having conventional tubing and operated at the same temperature.

Specifically, in a comparison test apparatus included ⅛ inch outside diameter 75% palladium, 25% silver tubes with 4 mil thick walls. The comparison apparatus included the same number and size tubes and made of the same alloy from the same batch of tubes but the tubes were supported internally with knitted wire cylinders in accordance with the present invention. Both were operated at 800° C. The apparatus having the conventional tubing was operated with a pressure differential of 50 p.s.i. between the insides and outsides of the tubes, but the tubes fractured and collapsed after about 3 hours of operation.

The comparison apparatus was operated at a pressure differential of 200 p.s.i. and after about 100 hours of operation the tubes did not show any signs of leaks, fractures or collapsing.

It will be appreciated that the above description is of a preferred embodiment of the tubular element and "out-in" type purification apparatus of the present invention and that certain modifications may be made in the structure and arrangements without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

1. A tubular element for diffusion purification of a gas comprising in combination a thin-walled non-porous tube of metal through which the gas to be purified diffuses and means to internally support the tube walls, said means comprising a cylindrical member composed of a plurality of individual cylinders made of knitted metal filaments with the cylinders being in coaxial compressed nested relationship one within another, and the cylindrical member being seated in the tube snugly against the walls of the tube, with the filaments on the outside of the cylindrical member being coated with material from the group consisting of alumina, ceria and chromium.

2. An element as set forth in claim **1** in which the metal filaments are of metal from the group consisting of stainless steel and nickel-chromium iron alloy.

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