HYDROGEN PROCESSING MULTIPLE LAYER PRESSURE VESSELS

Filed March 15, 1963

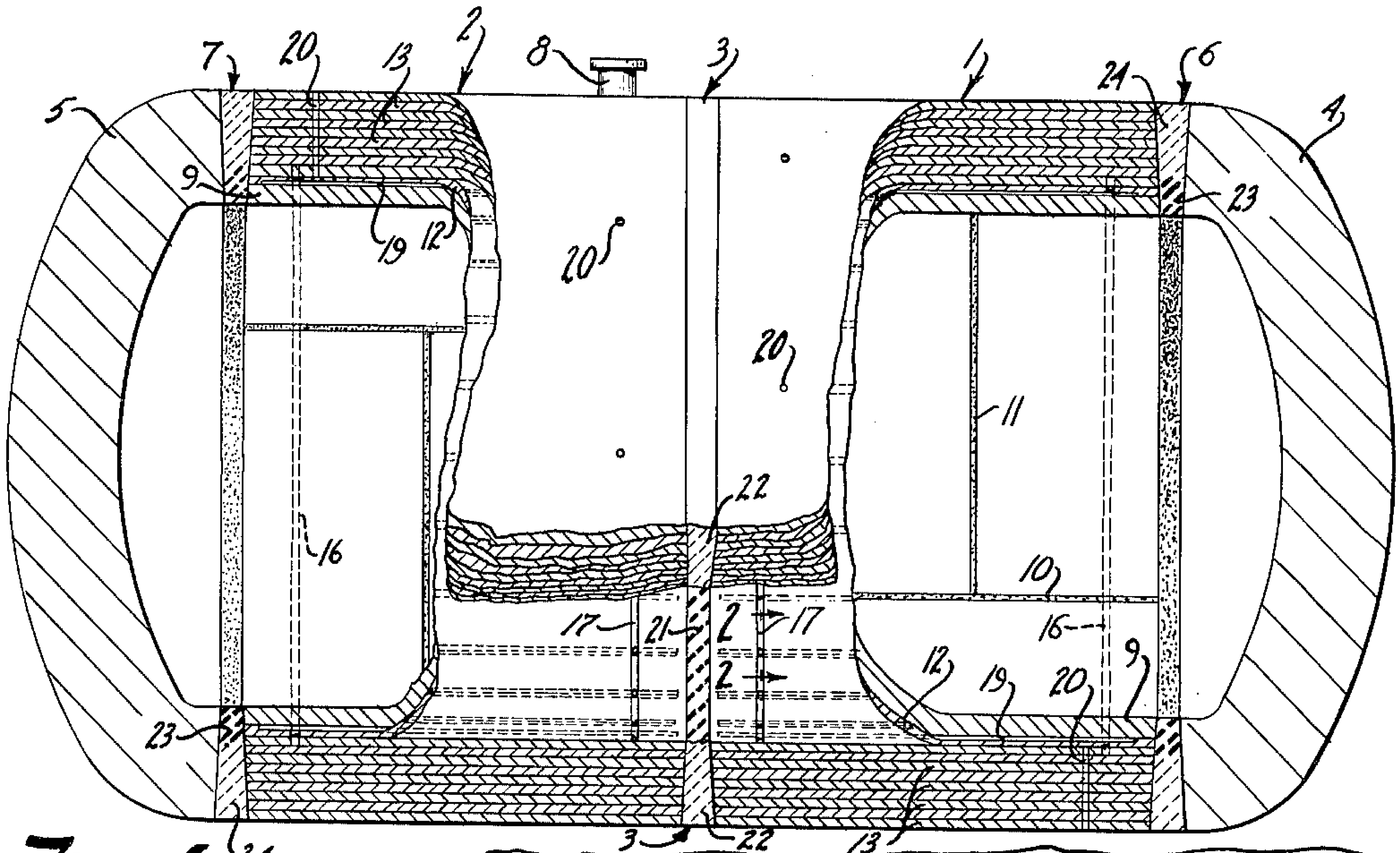

Fig. 1

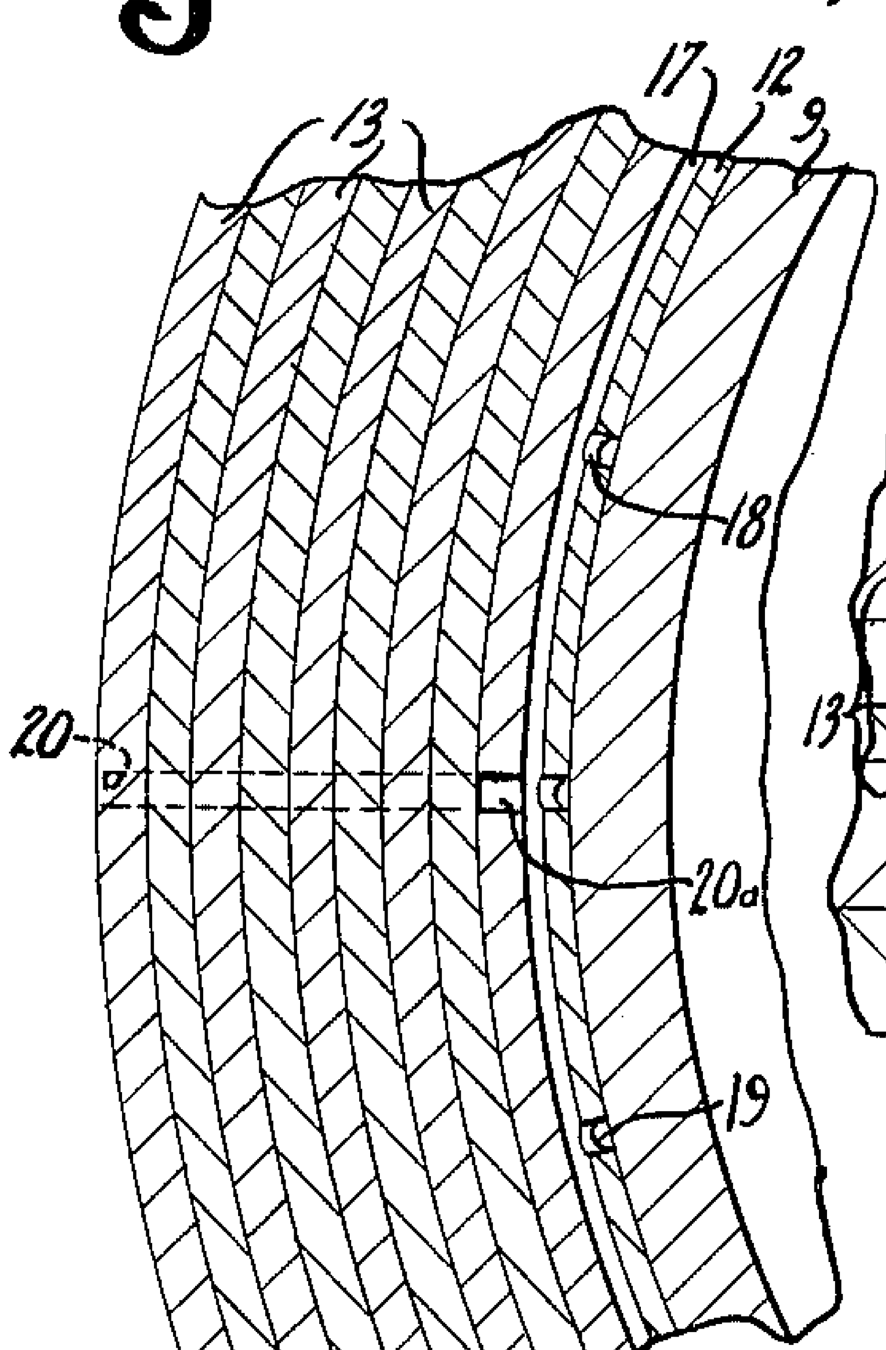

Fig. 2

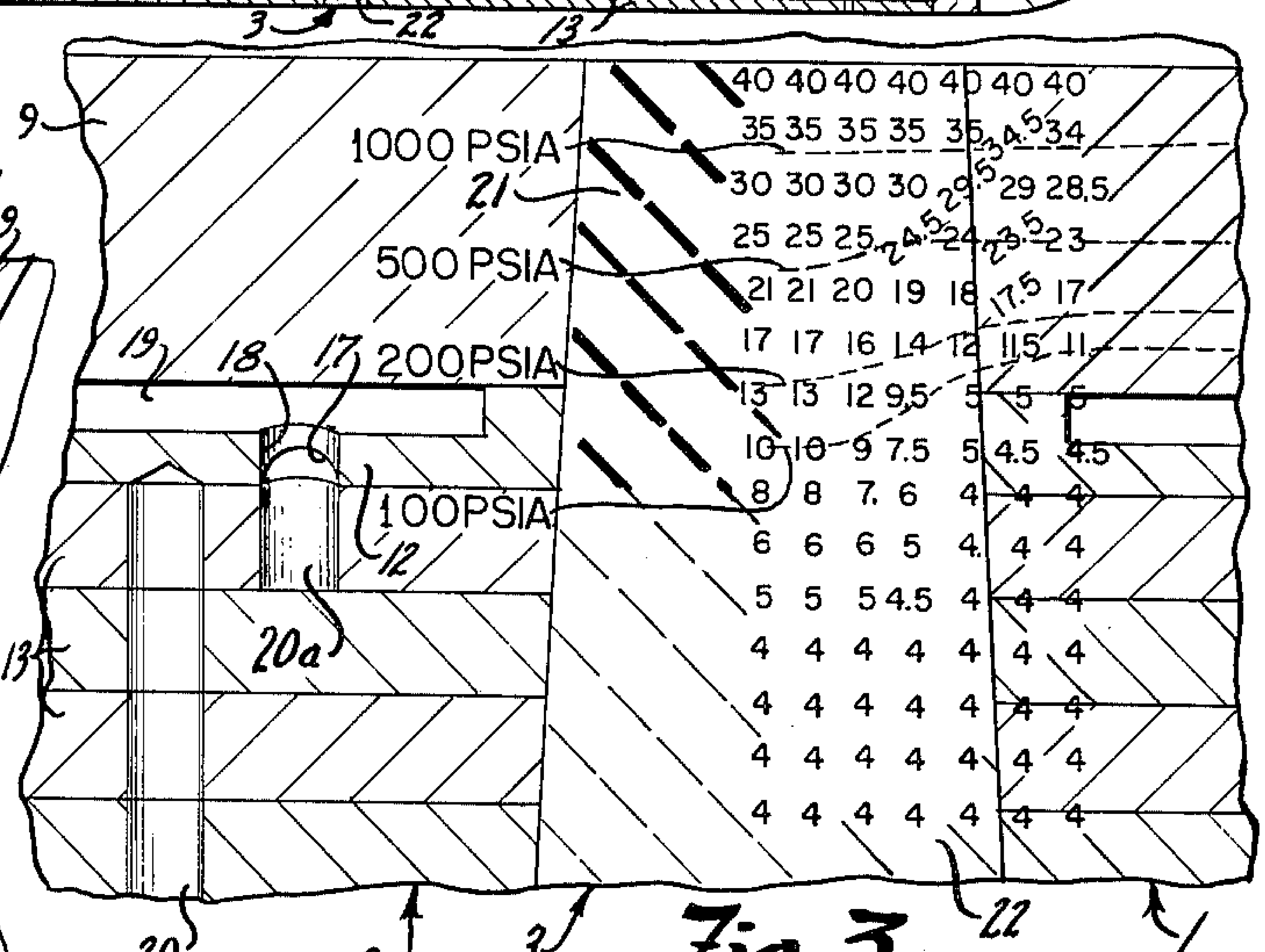

Fig. 3

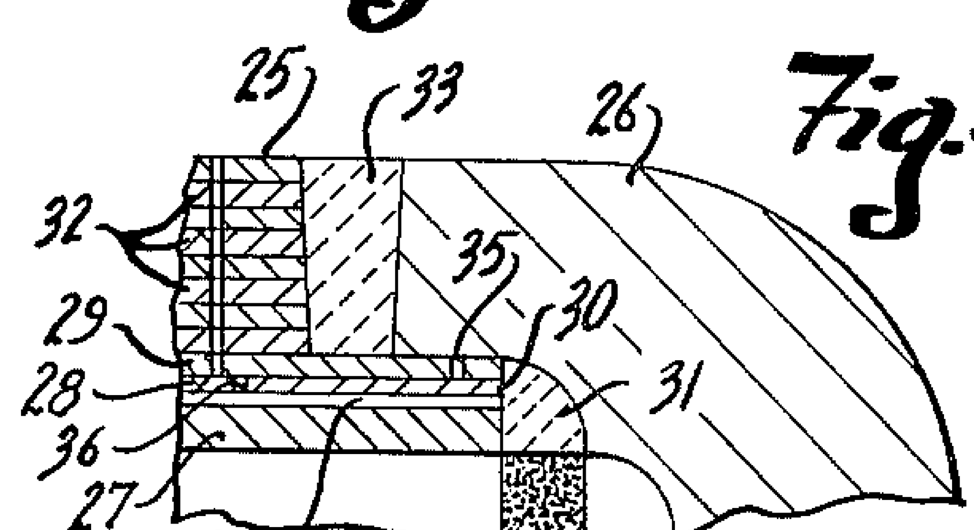

Fig. 5

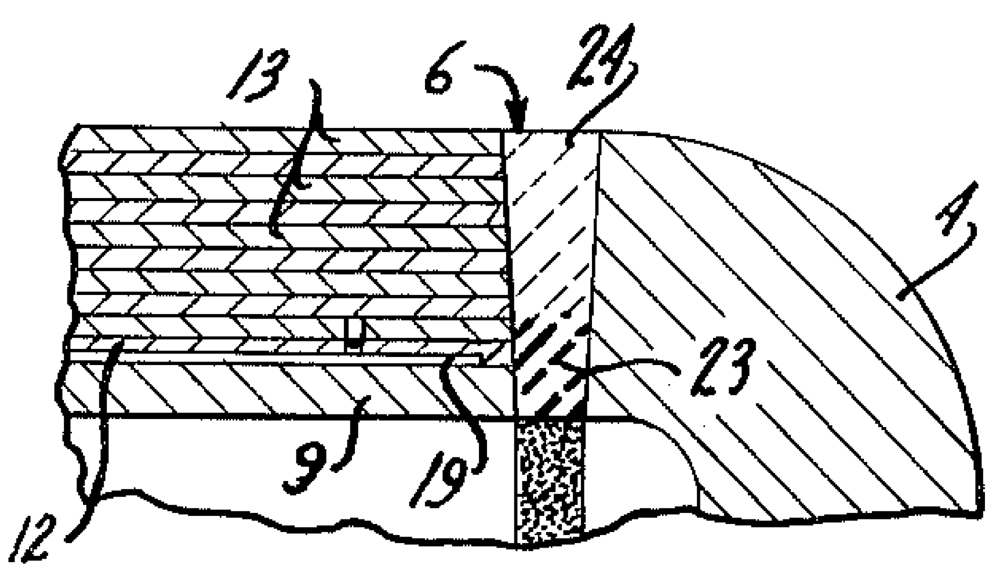

Fig. 4

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3,224,619

Patented Dec. 21, 1965

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3,224,619

HYDROGEN PROCESSING MULTIPLE LAYER PRESSURE VESSELS

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Filed Mar. 15, 1963, Ser. No. 264,746
1 Claim. (Cl. 220—3)

This invention relates to multiple layer pressure vessels employed in hydrogenation processes and particularly to a multi-layer vessel having circumferential girth welds within the vessel interconnecting an inner shell and a multiplicity of outer strengthening layers.

Multiple layer vessels as shown in United States Patent 2,243,240 to F. K. Zerbe have been employed successfully in high pressure and temperature hydrogenation of hydrocarbons and the like. As more fully set forth in the above patent, a multiple layer vessel provides increased resistance to pressure and heat as well as advantages of ease of manufacture and relatively low cost. Vessels for hydrogenation processes must however also be designed with proper consideration to the effects of nascent hydrogen which enters the metal of the vessel and tends to cause hydrogen embrittlement which results in eventual cracking and splitting of the vessel. As a result, special materials, alloys of steel such as chromium, molybdenum, tungsten, vanadium and manganese steel having a low carbon content are required. In accordance with the Zerbe patent, an improved venting system is provided which substantially reduces the transmission of hydrogen into the outer layers of the vessel. As a result, only the inner layer or layers must be provided with a special metal having a high resistance to hydrogen embrittlement and the outer layers can be formed of less resistant materials because of the protection afforded by the inner shell and/or layers and the venting.

Such structures have been found to provide relatively satisfactory service at 650 to 700° F. with pressures ranging from 1050 to 5500 p.s.i.

However, as more fully discussed in the copending application of Orrin F. Andrus, entitled Multi-Layer Pressure Vessel for High Temperature Hydrogenation Process, which was filed on April 19, 1962, with Serial No. 188,733 and which is assigned to a common assignee herewith, with the recent advent of new hydrogenation processes requiring very high hydrogen partial pressures at high temperatures, the problems of hydrogen transmission and hydrogen embrittlement of the walls of the processing vessels and particularly the welds interconnecting the various portions thereof have been severely increased. In particular, the welding of the various sections as disclosed in the Zerbe patent presented areas particularly subject to hydrogen damage, and reduced the life of the vessel when used in the new hydrogenation processes. The above-identified Andrus application provides as a solution the provision of an inner protective layer or layers welded to form a part of the innermost layer and to overlie the innermost portions of the weld. Venting openings are incorporated in the weld protective layer for releasing hydrogen gas and preventing or eliminating the concentration of atomic or nascent hydrogen within the welds. This essentially prevents damage to the welds as a result of chemical reaction of atomic hydrogen at high temperatures with the iron carbides in the welds. Although this structure has many advantages and reduces the problem of hydrogen concentration within the weld areas, it has certain disadvantages from the standpoint of economy and practicality of construction.

The present invention is particularly directed to a simplification and improvement in the construction of multi-layer vessels for use in hydrogenation processes and the like.

The present invention is based on an unusual analysis and realization of the various hydrogen concentrations in multi-layer welded vessel construction and is based on the concept that with suitable venting of the outer layers a completely satisfactory vessel for high temperature and pressure hydrogenation processes can include girth welds extending substantially throughout the vessel without any special diverting of the hydrogen from the weld area and with a minimal amount of special weld metal. Applicants have determined that only the innermost portions of the weld to a selected depth as hereinafter described need be formed of a material which is not subjected to hydrogen embrittlement. This is true because applicants have by acute analysis realized that the hydrogen concentration in a weld drops rapidly outwardly of the inner shell and that the problem of hydrogen embrittlement is sufficiently reduced to allow the use of a conventional inexpensive low carbon steel or the like. Further, the transfer of hydrogen through the weld into the adjacent or outer layers is minimal compared with the diffusion through the shell and consequently does not substantially increase the gas pressure in the outer layers which can be protected by the venting system of the Zerbe patent.

Thus, in accordance with the present invention, the vessel is formed of an inner shell or layer of material which is resistant to hydrogen embrittlement and with a dummy layer immediately adjacent to this inner shell. A plurality of strengthening layers of the girth welds are formed of a suitable alloy to a depth required to reduce the hydrogen concentration to a safe level. This depth generally corresponds to the depth of the inner shell and the dummy layer in a practical and economic structure. The outer portion of the girth weld is completed with inexpensive carbon steel having a good hydrogen resistance characteristic.

The weld construction of the present invention eliminates the necessity of post heat treatment of the girth seams as in the previous structure. The present invention thus provides an inexpensive method and structure for producing a multi-layer pressure vessel of exceptionally high quality and substantially avoids the hydrogen embrittlement problems heretofore encountered.

The drawing furnished herewith illustrates the best mode presently contemplated for carrying out the invention.

In the drawing:

FIG. 1 is a vertical longitudinal section through a multi-layer vessel constructed in accordance with the present invention;

FIG. 2 is a fragmentary vertical section taken on line 2—2 of FIG. 1;

FIG. 3 is an enlarged fragmentary view of the connection of a pair of adjacent multiple layer body sections in accordance with this invention;

FIG. 4 is an enlarged fragmentary view of the connection between the multiple layer body section and a solid head section; and

FIG. 5 is an enlarged fragmentary view of an alternative connection to a solid head.

Referring to the drawing and particularly to FIG. 1, a multiple layer vessel is illustrated including a pair of side-by-side tubular similar body sections 1 and 2 having the adjacent ends interconnected by a girth weld 3. Solid end sections 4 and 5 are secured to the opposite ends of the vessel and to the body sections 1 and 2 respectively by girth welds 6 and 7. A nozzle 8 is shown secured welded within an appropriate opening in the tubular body section 2.

Each of the tubular body sections 1 and 2 is similarly preformed prior to connection by weld 3 and the attachment of the heads 4 and 5. Body section 1 will be specifically described for purposes of clearly setting forth the present invention.

The tubular body section 1 includes a relatively thick tubular inner shell 9 formed of a multiple of continuous curved metal plates interconnected by longitudinal welds 10 and girth welds 11 such as heretofore employed in the manufacture of pressure vessels. The inner layer 9 and the interconnecting welds 10 and 11 therein are formed of a special alloy such as a stainless or chromium alloy steel which does not deteriorate when subjected to hydrogen gas at high temperatures and pressures. Generally, this inner shell construction is similar to that described more fully in the previously referred to copending application of Orrin E. Andrus.

The tubular body section 1 is completed by a dummy layer 12 immediately concentrically located adjacent the exterior of the shell 9 and a plurality of concentrically located tubular outer layers 13. The dummy layer 12 is fitted about the shell 9 or may be formed with a plurality of sections secured together by tack or spot welding on the outer surface and without penetration into the shell 9. The outer layers 13 may be constructed, generally in accordance with the method of constructing of the inner shell 9, of a plurality of arcuate sections interconnected by longitudinal welds which may penetrate the layer and extend into the adjacent layer. The dummy layer 12 and the outer layers 13 are formed of a suitable carbon steel interconnected by welds of a suitable carbon steel in accordance with the strength requirements of the material.

In accordance with the present invention, the dummy layer 12 is designed to permit the hydrogen which has diffused through the inner wall of the vessel to flow to the vents with a minimal pressure drop, as hereinafter described. The dummy layer 12 therefore serves only to transmit the pressure but is not employed or considered as part of the thickness of the wall for purposes of determining the strength of the vessel.

As clearly illustrated in FIGS. 1 and 2, circular grooves 16 and 17 are formed on the exterior surface of layer 12 and one each is spaced slightly inwardly from the opposite ends of the dummy layer 12. A plurality of radial openings 18 are provided in the layer circumferentially distributed in alignment with the circular grooves 16 and 17. A plurality of circumferentially distributed longitudinal grooves 19 are formed on the inner surface of dummy layer 12 joining the aligned radial openings 18. Each groove 19 extends beyond the groove 16 and 17 but terminates inwardly of the edge of layer 12. Several radial vent openings 20 extend through the outer strengthening layers 13 adjacent the circular grooves 16 and 17.

The hydrogen which passes through the inner shell 9 is diverted or carried through the longitudinal grooves 19 to the circular grooves 16 and 17 and then outwardly through the radial vent openings 20. The pressure of the hydrogen between the outer layers is thereby readily held below the pressure at which hydrogen embrittlement of an adverse character occurs.

Ideally, vent openings would be aligned with the grooves 17 and holes 18. Practically, precise alignment is not readily obtainable. By proper design, as hereinafter described, only approximate alignment is required. In practical construction, the dummy layer 12 is secured about shell 9 by exterior tacking of a plurality of dummy layer sections, the first strengthening layer 13 is then secured about the dummy layer 12 and vent openings 20*a* provided in relatively close alignment with grooves 17 and holes 18. The other strengthening layers 13 are then applied and the vent openings 20 are drilled through all the strengthening layers.

The head sections are of suitable material constructed in accordance with known methods.

In accordance with the present invention, the girth welds 3, 6 and 7 are solid continuous welds for the complete thickness or depth of the wall of the vessel. Weld 3 includes an inner layer or deposit 21 of special hydrogen embrittlement resistant weld metal and an outer deposit 22 of carbon steel or other suitable metal. Welds 6 and 7 are similarly formed of an inner deposit 23 and an outer deposit 24, except that deposit 23 is somewhat deeper than the corresponding deposit 21 of weld 3 for reasons subsequently developed.

The hydrogen diffusion can be rather readily determined for solid wall members with known formulas and assumptions. Thus, the hydrogen diffusion can be calculated from Fick's law of diffusion.

$$Nx = D\frac{dc}{dx}$$

where:

Nx=the local diffusion flux in the x direction.
D=diffusion coefficient
$\frac{dc}{dx}$=the concentration gradient in the x direction

That hydrogen diffusion in iron obeys Fick's law of diffusion and that the diffusivity coefficient is constant at any given temperature have been shown to be valid. An article in Transactions Metal Society AIME, vol. 218 (October 1960) at page 826 by Carmichael et al., and a book published by the University of Chicago Press in 1948 entitled Hydrogen in Metals by D. P. Smith and particularly at pages 58 and 73 therein shows that hydrogen diffusion follows Fick's law for metals in general and nickel in particular.

The steady state concentration distribution of hydrogen in the solid girth weld of the multi-layer vessel can be calculated from the same Fick's law of diffusion by providing proper allowance for the venting effects of the layers on the hydrogen concentration. Fick's law is completely analogous for this analysis to Fourier's heat conduction law, and, the relaxation method, as described for example, by McAdams Heat Transmission (1954), page 21, can be used to determine the hydrogen concentration distribution. For simplification of computation, the vessel wall may be treated as a slab rather than a cylinder. Although this introduces a very slight error, the calculation is proper because the ratio of the outside diameter to the inside diameter is generally close to one and because the calculated hydrogen concentration will be higher than would actually exist. From this information, the hydrogen pressure in equilibrium with hydrogen at known concentration can be readily determined from the "square root law" such as described in the previously referred to book of D. P. Smith at page 28.

For example, in FIG. 3, a fragmentary portion of the vessel shown in FIGS. 1 and 2 is given showing the attachment of the tubular body sections 1 and 2 and the girth weld 3. Based on the analysis of laws of diffusion, discussed above, if the vessel is formed of an inner shell 9 of approximately ¾ inch thickness and layers 12 and 13 of ¼ inch thickness with girth weld 3 one inch wide, the relative hydrogen concentrations will be generally such as shown in FIG. 3 with an internal hydrogen partial pressure of 1600 p.s.i.

The hydrogen concentration diagram of FIG. 3 is obtained generally as follows. The hydrogen partial pressure at the inner surface of shell 9 is known to be 1600 p.s.i.a. and from the square root law, the relative hydrogen concentration is 40, as shown. Further, the venting system will establish a pressure somewhat greater than atmospheric at the interface of the shell 9 and dummy layer 12 which can be selected as 25 p.s.i.a. The relative hydrogen concentration is therefore 5. The total flow of hydrogen diffusing through girth seam 3 and flowing between the layers 12 and layers 13 to the vents will be very small. This will give rise to an extremely small pressure differential between any portion of the layer spaces and the vent holes which are at atmospheric pressure. The partial pressure of hydrogen between the layers will therefore be nearly atmospheric and the concentration is shown by the corresponding square root value of 4. Further, for one-dimensional diffusion in a slab, the concentration varies linearly with distance from the boundary and the several partial pressures within the solid shell **9** at a sufficient distance from the weld can be determined directly. The distribution pattern within the weld **3** and the surrounding area can be arbitrarily set forth and revised to the actual distribution by the relaxation method wherein the average of four equidistributed concentrations about any given concentration must equal the given concentration.

The relative hydrogen concentration drops rapidly from a value of 40 at the internal diameter of shell **9** to a value of 5 at the inner face of the dummy layer **12** and drops to a value of 4 between the dummy layer **12** and the adjacent layer **13**. This plot of relative concentration is independent of the temperature.

From the plot of the concentrations, the pressure lines can be drawn in as shown. Hydrogen concentration in the weld drops to a value of 4 in the second strengthening layer **13** and therefore the hydrogen partial pressure, which is equal to the square of the concentration, is 16 p.s.i.a. At the inside diameter of the vessel, the hydrogen pressure is 1600 p.s.i.a. However, the pressure drops rapidly below 100 p.s.i.a. in the weld opposite the dummy layer **12**. It is known that even carbon steel is suitable for hydrogen service at 850° F. at pressures below 100 p.s.i.a. Experience charts are known giving the pressures and temperatures at which various metals may be used without danger of hydrogen embrittlement. For example, the Nelson chart, published in Welding Research Supplement, January 1955, pages 12–S to 21–S, "Blistering and Embrittlement of Pressure Vessel Steels by Hydrogen," by Nelson and Effinger.

In the illustrated embodiment of the invention and for the assumed operating conditions, the weld **3** is formed with deposit **21** joining the adjacent inner shells **9** and dummy layers **12** of sections **1** and **2** to each other. Deposit **21** is formed of a suitable weld metal which can be employed at the operating pressure and temperature in accordance with the experience reflected in Nelson's chart or the like. Under different operating conditions, deposit **21** may extend outwardly to include one or more of the strengthening layers **13**. The strengthening layers **13** of sections **1** and **2** are joined by the outer deposit **22** which is a continuous extension of deposit **21** but of a suitable carbon steel or the like.

The welds **6** joining the body section **1** to the solid head **4** are similarly analyzed. In the head **4**, or any solid wall vessel having 1600 p.s.i. of hydrogen partial pressure, the pressure of hydrogen drops to 100 p.s.i.a. at approximately 83% of the thickness measured from the inside. As a result, the solid wall head **4** must be formed of a suitable alloy material fully resistant to hydrogen attack.

The portion of weld **6** adjacent head **4** does not have the same concentration as weld **3** and dangerous hydrogen concentrations exist out to the outer face of the second strengthening layer **13** adjacent the dummy layer **12** and may extend further depending on operating conditions. Consequently, in weld **6**, the inner deposit **23** of a metal not subject to hydrogen damage extends from the internal diameter of the vessel outwardly to include the inner shell **9**, the dummy layer **12** and the first two strengthening layers **13** and more if analysis under a different set of operating conditions so indicates. The outer deposit **24** of weld **6** is formed of any suitable carbon steel.

For operations at much higher temperatures and at greater pressures, the weld adjacent the head section can be redesigned to provide further protection for the outer weld material, as shown in FIG. 5. A tubular multiple layer body section **25** is generally formed, as heretofore described, for welding to a solid head **26**. However, the inner shell **27**, the dummy layer **28** and the first stress carrying layer **29** is extended into a suitable recess or notch **30** on the inner edge of the head **26** and secured thereto by a weld **31** of suitable material which is insensitive to hydrogen attack. The balance of the outer layers **32** are secured to the adjacent edge of the head **26** by a suitable carbon steel weld **33**. A longitudinal vent groove **34** extends along one face of the dummy layer **28** and radial vent openings **35** and **36** are provided in layers **29** and **28** respectively on opposite sides of weld **33**. In effect the invention provides venting adjacent the main outer portion of carbon steel weld **33** to divert any hydrogen gas therefrom as suggested by the previously referred to copending application of O. E. Andrus.

The present invention thus provides a multiple layer vessel construction particularly suited for high temperature hydrogenation processes and the like and which is relatively simple and economical to fabricate.

Various modes of carrying out the invention are contemplated as being within the scope of the following claim particularly pointing out and distinctly claiming the subject matter which is regarded as the invention.

We claim:

A welded pressure vessel adapted to contain hydrogen bearing substances at elevated temperatures and pressures, comprising an inner liner fabricated from a metallic material resistant to hydrogen embrittlement, a dummy layer disposed intimately around said inner liner and having a series of passageways at the interface of the liner and said dummy layer, a plurality of stress-bearing layers disposed intimately and concentrically around the dummy layer, said stress-bearing layers having a network of radially extending vent openings providing communication between said passageways and the exterior for releasing hydrogen to the atmosphere, and a girth weld joining said liner and layers to a wall of the vessel, said girth weld consisting of a metal resistant to hydrogen embrittlement in a first weld zone extending coextensively with at least the inner shell and the dummy layer and extending outwardly beyond said passageways and of a high strength metal subject to hydrogen embrittlement in a second weld zone extending outwardly of said first zone and coextensive with said stress-bearing layers.

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