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HYDRIDE COMPOSITIONS

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HYDRIDE COMPOSITIONS

5 BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to hydride compositions for use in storing hydrogen. In particular, the present invention relates to metal
10 hydride compositions made so that hydrogen is absorbed as a preselected function of pressure. The United States Government has rights in this invention pursuant to Contract No. DE-AC09-89SR18035 between the U.S. Department of Energy and Westinghouse Savannah River Company.

15 2. Discussion of Background:

Hydride formers (sometimes simply referred to as "hydrides") are capable of absorbing hydrogen which can then be desorbed under the appropriate temperature and pressure conditions. These materials have many applications, particularly in the hydrogen processing and
20 energy conversion fields where they are used for hydrogen storage, hydrogen pumping and compression, heat pumps, batteries, and fuel cells. Many hydrides absorb the three isotopes of hydrogen (protium, deuterium, tritium) at different rates. These hydrides are useful in hydrogen isotopic purification and separation processes.

25 Known hydrides include many pure metals (Mg, Ti, V, Nb, Pt, Pd, and so forth), alloys (La-, Mg-, Ti-, and Co- alloys, Ti-Fe alloys, and rare earth-Ni alloys), and hydride compositions including those

described in commonly-assigned patent applications Serial Nos. 07/933,152, filed 08/21/92 (Palladium/Kieselguhr Composition and Method), 07/952,931, filed 09/29/92 (Dimensionally Stable Metallic Hydride Composition), 07/967,653, filed 10/28/92 (Composition For
5 Catalyzing Hydrogen Isotope Exchange), and 07/999,338, filed 12/31/92 (Tetraethyl Orthosilicate-Based Glass Composition and Method), the disclosures of which are incorporated herein by reference. The hydrogen absorption/desorption capacity of a particular hydride depends on its composition, temperature and surface area, and on the
10 external hydrogen gas pressure. To maximize the available surface area and the absorption/desorption efficiency, hydrides are often supplied in the form of small-grained particles or pellets.

The hydrogen-storage capacity of a hydride may be determined by plotting isotherms of the hydrogen equilibrium pressure (P_{H_2} , P_{eq})
15 versus the hydrogen content of the hydride at a predetermined temperature. At the equilibrium pressure, the partial pressure of hydrogen outside the hydride equals the pressure of the hydrogen absorbed by the hydride. The hydrogen content may be measured in any convenient units, including weight (grams H_2 /grams hydride),
20 atomic weight (mols H_2 /mols hydride), or the ratio of hydrogen atoms to metal atoms in the hydride (H/M).

A series of hydrogen sorption isotherms is illustrated schematically in Fig. 1. Each isotherm 10a, 10b, 10c, 10d has a plateau region -- a region of approximately constant pressure (the "plateau
25 pressure") where the hydride absorbs or releases large quantities of hydrogen with relatively small changes in pressure. The plateau pressures for absorption and desorption may be different, a

phenomenon known as hysteresis. Useful hydrides have low hysteresis, that is, absorption and desorption pressures are close and long, approximately flat plateaus.

In typical hydrides, the plateau pressure increases with
5 temperature over the useful operating range of the material. Thus, isotherms 10a, 10b, . . . represent the hydrogen equilibrium pressure versus the hydrogen content of a single hydride, with each isotherm measured at a different temperature. The isotherms are also
10 characteristic of the particular hydride, thus, different hydrides have isotherms with different plateau pressures and different H/M ratios. The plateaus may occur at different pressure levels and may start and end at different H/M ratios.

Hydrides with well-defined plateaus include quaternary alloys having the formula $Zr_{1-x}Ti_xCr_{1-y}Fe_{1+y}$, where $0.05 \leq x \leq 0.2$ and $0 \leq y \leq 0.4$ (Lee, et al., U.S. Patent No. 5,028,389); alloys of the formula
15 $Fe_{1-x}Mn_xTi_{1-y}V_y$, where $0 \leq x \leq 0.2$ and $0.005 \leq y \leq 0.08$ (Liu, et al., U.S. Patent No. 4,358,316); and ZrMn₂-type alloys (Van Essen, et al., U.S. Patent No. 4,489,050). Alloys that contain lanthanum and/or
20 nickel may also have well-defined plateaus (Sasai, et al., U.S. Patent No. 4,744,946; Sandrock, U.S. Patent No. 4,668,424; Sandrock, et al., U.S. Patent No. 4,409,180; Bruning, et al., 4,378,331).

For many applications, it is desirable to be able to measure the hydrogen content of a hydride with a reasonable degree of accuracy in order to determine whether the hydride is saturated or whether it can
25 absorb more hydrogen. However, it is difficult to measure the hydrogen content directly, for example, by measuring the pressure and determining the hydrogen content from the appropriate isotherm. In

the useful operating range of the hydride -- the plateau region -- data derived from pressure measurements are unreliable since very small pressure changes are associated with large changes in H/M. The inaccuracy in pressure measurement corresponds to a large variation in

5 hydrogen content. Instead of using pressure as a measure of hydrogen content, hydrogen is desorbed from the hydride to a container having a known volume, and the quantity of hydrogen calculated from temperature and pressure measurements using the ideal gas law. There is a need for a way to determine hydrogen content of a hydride

10 accurately and directly, without desorbing stored hydrogen from the composition.

SUMMARY OF THE INVENTION

15 According to its major aspects and broadly stated, the present invention is a composition for use in storing hydrogen and a method for making the composition where there is no plateau region, and where pressure increases significantly with hydrogen content, preferably linearly, so that measurement of pressure provides a good indication of

20 hydrogen content. The composition comprises a mixture of hydrides each of which has a different isotherm. When the mixture is formed, the resultant isotherm has no plateau but increases in a well-behaved, controlled way so that pressure and hydrogen content can be correlated. Preferably, the individual hydrides are chosen so that their composite

25 isotherm is a linear function for ease in determining the hydrogen content from the pressure and, thus, in controlling the absorption and desorption of hydrogen.

This result is achieved by comparing the locations of plateau regions of several hydrides and selecting more than one so that each has a different plateau region. To prepare the composition, the selected hydride particles, in the desired size (preferably less than 100 microns) are mixed, activated by degassing, saturated with hydrogen, and heated to remove the absorbed hydrogen. Processing temperatures are lower than the melting or softening points of the individual hydrides in order to maintain the chemical and structural integrity of the individual hydride types.

When the composition is used for hydrogen storage, the amount of stored hydrogen can be found simply by measuring the equilibrium pressure and determining the hydrogen content from the appropriate isotherm without the need for desorbing the stored hydrogen. Thus, it can be more readily determined whether the composition is capable of absorbing more hydrogen, or whether all hydrogen has indeed been desorbed. The composition can be used to store hydrogen, separate hydrogen from a gaseous mixture, or, with a suitable choice of hydrides, separate the three hydrogen isotopes (protium, deuterium, tritium) from each other.

An important feature of the invention is the selecting of hydrides for making the mixture that do not have plateaus at the same region. By selecting hydrides to avoid having the same plateaus, the isotherm of the composite mixture will have a continuously rising hydrogen/metal atom content with increasing pressure. Selecting the types of hydride and amounts of each will determine the shape of the composite isotherm. Thus, by choosing suitable hydrides, a mixture can be provided that exhibits a readily measurable change in equilibrium pressure over any

Fig. 2 shows a series of schematic hydrogen sorption isotherms for a hydride family according to a preferred embodiment of the present invention;

5 Fig. 3 shows a hydrogen sorption isotherm for a hydride composition according to a preferred embodiment of the present invention;

Fig. 4 shows a hydrogen sorption isotherm for a hydride composition according to another preferred embodiment of the invention;

10 Fig. 5a is a partially cut-away view of an apparatus for storing and releasing hydrogen using a composition according to a preferred embodiment of the invention; and

Fig. 5b is a partially cut-away view of an alternative embodiment of an apparatus for storing and releasing hydrogen using a composition
15 according to a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

It has been found that the hydrogen sorption isotherm of a
20 mixture of several hydrides can have an hydrogen equilibrium pressure (P_{H_2}) that varies in a well-behaved, steadily increasing manner with increasing absorbed hydrogen (H/M). When such a mixture is used in a hydride bed, the measured pressure indicates accurately and directly the quantity of absorbed hydrogen and the overall fraction of the bed's
25 capacity that is used. Preferably, the mixture is made up of hydrides selected from those that have sorption isotherms with substantially flat plateaus, particularly, mixtures containing hydrides of a single group or

family of alloys. As used herein, the term "family" refers to an alloy containing two or more constituent metals whose proportions can be varied, where the "members" of the family are hydrides with slightly different proportions of those constituents. Each hydride belonging to
5 this family will have a set of sorption isotherm depending on the temperature of operation and, at a specified operating temperature, each will have a different isotherm. If properly mixed in accordance with the present invention, the hydrogen isotherm of the alloy mixture can have a preselected shape. Most preferably, the isotherms of the mixture
10 have regions where $\ln P_{H_2}$ varies in an approximately linear manner with H/M.

A series of sorption isotherms of a hydride family according to a preferred embodiment of the present invention is shown in Fig. 2. Isotherms 12a, 12b, 12c, 12d show the equilibrium pressure (P_{H_2})
15 versus the hydrogen content (H/M) of the composition, each isotherm measured at the same operating temperature. The family contains a plurality of hydrides, each hydride having a series of isotherms similar to that shown in Fig. 1. Each isotherm 12a, 12b, . . . of the family has at least one distinct plateau.

20 When a composition is formed from two or more of these hydrides, its isotherm may be used to determine its hydrogen content to a high degree of accuracy simply by measuring the temperature and pressure. Knowing the pressure and the available hydride storage capacity of the composition, one can determine accurately how much
25 hydrogen is contained in the composition. The greater the number of hydrides present in the mixture, each in the same amount, the more

uniformly the isotherm will change with hydrogen content of the composition.

Metal hydrides that can be used in the composition include Zr, Ti, V, Nb, Pd; binary, tertiary, and more complex alloys of La, Al, Cu, Ti, 5 Co, Ni, Fe, Zr, Mg, Ca, Mn, the rare earth's, and so forth; and mixtures thereof. For example, the hydridable $AB_{5-x}C_x$ alloy families, where $0.1 \leq x \leq 1$ and the letters A, B, and C represent elements, can be used in the composition. In particular, the lanthanum-nickel-aluminum alloys represented by the formula $LaNi_{5-x}Al_x$ ($0.1 \leq x \leq 1$) are usable in the 10 composition. Other suitable hydrides with well-defined plateau regions include the Zr-Ti-Cr-Fe alloys and the Fe-Mn-Ti-V alloys.

For many applications, it is desirable to use hydrides with low hysteresis. Such hydrides may be used with the invention, however, hysteresis effects are minimized by the step-wise isotherms of the 15 composition. Therefore, the invention is not limited to use with low-hysteresis hydrides.

By way of example, a composition may be made with three hydrides with different, distinct plateaus. The hydrides may be three different alloys of a family or any combination of three hydrides that 20 have different plateaus. The amount of each hydride to be in the composite can be selected based on the length of each plateau and the pressure difference between adjacent plateaus. The optimum constituents of the composition are best found by a modest degree of experimentation for each particular application.

25 Compositions containing 2-3 hydrides may still have step-wise isotherms. Compositions containing at least four hydrides have

isotherms with regions where the pressure P_{H_2} is related to the hydrogen content H/M by the equation:

$$\ln P_{H_2} = a + b(H/M) + c(H/M)^2 + \dots,$$

5

where a, b, c, \dots are constants for each isotherm. With a suitable choice of hydrides, the isotherms have regions where the contribution of second-order and higher-order polynomials is sufficiently small that $\ln P_{H_2}$ varies approximately linearly with H/M , so that:

10

$$\ln P_{H_2} = a + b(H/M).$$

The constants a and b may be adjusted by varying the relative proportions of the various hydrides of the same family or different hydrides in the mixture. For example, where the mixture contains hydrides with well-defined plateau regions, a and b depend on the lengths of the individual plateaus and the pressure differences between adjacent plateaus.

Since the isotherms of the individual hydrides in the mixture contribute to the overall isotherm, the constants a and b are best determined empirically for each particular hydride mixture. Once a and b are known, the hydrogen content of the mixture can be found by measuring P_{H_2} and computing $H/M = (\ln P_{H_2} - a)/b$ using the appropriate isotherm.

25 To obtain a composition having approximately linear isotherms, the mixture preferably can be made by selecting equimolar amounts of different hydrides from a family of alloys such as the $\text{LaNi}_{5-x}\text{Al}_x$ ($0.1 \leq$

x \leq 1) alloys. As noted above, the isotherms of composition can be varied by varying the proportions of the constituent metals. Depending on the choice of hydrides, different proportions may be needed to obtain a mixture having approximate linear isotherms. If desired, the constituents of the mixture may be chosen to provide a nonlinear relationship between P_{H_2} and H/M.

Alloys suitable for use with the invention are made by mixing together the proper amounts of granules, powder or small ingots of the constituent pure metals. The constituents of each alloy are melted in an arc or induction furnace to form the alloy, in an inert atmosphere or under vacuum, then cooled to room temperature. The alloys may be melted and cooled several times to ensure their homogeneity. After cooling, the alloys are ground and sifted to obtain the desired particle size for use with the invention.

Before combining, the particles of the alloys are activated by degassing, then saturated with hydrogen and heated to remove the absorbed hydrogen.

The properties of the composition depend upon the properties of its constituent hydrides. Therefore, care must be taken to maintain the chemical and structural integrity of the hydrides during processing and use. For example, if the hydrides are metals or alloys, temperatures exceeding the softening point could change the lattice structure of the composition. Temperatures exceeding the melting point could form a new alloy with different hydrogen-absorption properties.

The following non limiting examples further illustrate a hydride composition according to a preferred embodiment of the present invention.

EXAMPLE 1

A hydride composition containing equimolar amounts of two
5 $\text{LaNi}_{5-x}\text{Al}_x$ alloys was prepared. The mixture contained 52.14 wt.%
 $\text{LaNi}_{4.51}\text{Al}_{0.49}$ (molecular wt. 416.9 g) and 47.86 wt.% $\text{LaNi}_{4.20}\text{Al}_{0.80}$
(molecular wt. 407.0 g). A 0.0075-liter hydride bed containing 5.277 g
of the mixture was maintained at a temperature of approximately 120°
C. The bed was in fluid communication with a calibration volume of
10 0.0327 L.

To obtain an isotherm, a known quantity of hydrogen (H_0) was
admitted into the hydride bed and allowed to equilibrate. The
equilibrium pressure (i.e., the partial pressure of hydrogen above the
bed) was measured, then the free hydrogen was transferred to the
15 calibration volume. The quantity of free hydrogen (H_f) was computed
from the ideal gas law, using measurements of the temperature and
pressure in the calibration volume. The hydrogen content of the
mixture was found by subtracting H_f from H_0 and expressing the result
in terms of H/M , that is, the number of hydrogen atoms per metal atom.
20 As seen in Fig. 3, the isotherm had two plateaus, at hydrogen pressures
of approximately 2 atm ($H/M \approx 0.1 - 0.3$) and 6 atm ($H/M \approx 0.4 - 0.7$).

EXAMPLE 2

25 A hydride composition containing equimolar amounts of five
 $\text{LaNi}_{5-x}\text{Al}_x$ alloys was prepared. The mixture contained the following
alloys:

	x	alloy	molecular wt. (g)
	0.74	LaNi _{4.26} Al _{0.74}	408.9
5	0.80	LaNi _{4.20} Al _{0.80}	407.0
	0.86	LaNi _{4.14} Al _{0.86}	405.1
	0.91	LaNi _{4.09} Al _{0.91}	403.5
	0.96	LaNi _{4.04} Al _{0.96}	402.3

10 The molecular weight of the mixture was 405.4 g.

A 0.010-liter hydride bed containing 5.629 g of the mixture was maintained at a temperature of approximately 120° C. The bed was in fluid communication with a calibration volume of 0.185 L. The composition was maintained at approximately 120° C, and an isotherm

15 was obtained as described above.

When the hydrogen equilibrium pressure was plotted on a logarithmic scale, the step-wise plateaus of the individual hydrides merged into an approximately linear, sloping plateau region between $P_{H_2} \approx 0.6 \text{ atm} - 3 \text{ atm}$ ($H/M \approx 0.10 - 0.65$) (Fig. 4).

20 A hydride composition according to the present invention may be used in an apparatus for absorbing, storing and releasing hydrogen. A partially cut-away, perspective view of such an apparatus is shown in Fig. 5a. An apparatus 20 includes a housing 22 with an inlet conduit 24 and an outlet conduit 26. Conduit 26 carries a screen 28, positioned
 25 generally as shown. Conduit 24 carries a similar screen (not shown). Valves 32, 34 and pressure sensors 36, 38 are disposed in conduits 24,

26, respectively. Apparatus 20 is provided with means for controlling temperature, such as a heating/cooling jacket or coil 40.

Housing 22 contains a hydride composition 42 according to the present invention. With valve 32 open and valve 34 closed, hydrogen
5 gas is passed into housing 22 through inlet 24. When valves 32 and 34 are closed, the quantity of hydrogen in the interior of housing 22 is constant and the hydrogen gas pressure above composition 42 will adjust itself to an equilibrium pressure as composition 42 absorbs hydrogen. If composition 42 is saturated with hydrogen, the equilibrium pressure
10 is approximately equal to the plateau pressure at the temperature concerned. If composition 42 contains less hydrogen, the equilibrium pressure is less than the plateau pressure.

An alternative embodiment of an apparatus according to the invention is shown in Fig. 5b. An apparatus 50 includes a housing 52,
15 and a conduit 54 in fluid communication with the interior of housing 52. Conduit 54 carries a screen 56, similar to screen 28 of apparatus 20. A valve 58 and a pressure sensor 60 are disposed in conduit 54, generally as shown. Coil 62 contains a heating/cooling fluid for controlling the temperature in the interior of housing 52. Housing 52
20 contains a quantity of a hydride composition 42 as described above.

The components of apparatus 20 (and apparatus 50) have sufficient mechanical strength to withstand the pressure inside housing 22 (and housing 52). The components of apparatus 20 are preferably made of stainless steel or other materials that are compatible with
25 composition 42 and the operating environment of the apparatus. When apparatus 20 is in use, the pressure inside housing 22 may range from a few atmospheres to 100 atm. or higher, depending on the choice of

hydride, the temperature, and the amount of hydrogen absorbed by composition 42.

5 The quantity of hydrogen that can be absorbed by composition 42 depends on the choice of hydrides used in the mixture. It is well known that hydrides are capable of absorbing very large amounts of hydrogen, so that when saturated with hydrogen, a hydride may have a hydrogen density equivalent to that of liquid hydrogen.

10 For composition 42 to absorb hydrogen, the hydrogen gas pressure inside housing 22 (or housing 52) must be higher than the plateau pressure. At any given temperature, when the pressure is at the plateau pressure, composition 42 is in equilibrium with the surrounding atmosphere and neither absorbs nor releases hydrogen. When the hydrogen pressure is increased above the plateau pressure, the temperature of composition 42 rises as the composition absorbs
15 hydrogen, until a new equilibrium state is reached. If the increased hydrogen pressure is maintained by supplying hydrogen to housing 22 via inlet 24, composition 42 eventually becomes saturated with hydrogen. Conversely, when the hydrogen pressure is lowered, the temperature of composition 42 decreases as it desorbs hydrogen until
20 equilibrium is reached.

Hydrogen absorption is an exothermic process, that is, the temperature of composition 42 rises as it absorbs hydrogen. For any hydride, the higher the temperature, the higher the pressure that is needed for the material to absorb a predetermined quantity of
25 hydrogen. As the temperature rises, composition 42 absorbs less and less hydrogen until a new equilibrium state is reached. Therefore, to maintain absorption, composition 42 may be cooled by pumping a

cooling fluid from a source (not shown) through coil 40. Hydrogen desorption is an endothermic process, therefore, composition 42 is warmed to release hydrogen therefrom.

Whether apparatus 20 is operated in the hydrogen-absorption or
5 hydrogen-desorption mode is determined by regulating its temperature: cooling composition 42 for absorption and warming composition 42 for desorption. The operating temperature range of apparatus 20 depends on the choice of hydrides for composition 42. If the temperature of composition 42 is known, its hydrogen content may be determined
10 simply by measuring the hydrogen pressure P_{H_2} and computing H/M from the appropriate isotherm.

To increase the efficiency of hydrogen absorption/desorption, the surface area of composition 42 is maximized by supplying the composition in the form of small particles. For many hydrides, the
15 particle size is reduced with each absorption/desorption cycle until eventually the particles disintegrate into a fine-grained powder. Furthermore, the powder can readily become entrained in the gas stream, migrating with it and causing contamination of downstream piping and equipment. Screens 28 have sufficient porosity to allow the
20 flow of gas therethrough, but a fine mesh to substantially prevent escape of hydride fines from housing 22.

Apparatus 20 may be used to store hydrogen, separate hydrogen from a gaseous mixture, and separate the three hydrogen isotopes (protium, deuterium, tritium) from each other. For example, to
25 separate hydrogen from a gaseous mixture, the mixture is pumped into housing 22 through inlet 24. As the mixture passes through housing 22, it contacts hydride composition 42 where at least a portion, and

preferably most of the hydrogen in the mixture is absorbed.

Substantially hydrogen-free gas exits housing 22 via outlet 26. Housing 22 is then heated to recover the stored hydrogen.

To separate hydrogen isotopes from each other, composition 42
5 contains one of two types of hydride. The first type, such as palladium, absorbs the lighter hydrogen isotopes better than the heavier isotopes, that is, it absorbs protium better than deuterium and tritium, and deuterium better than tritium. The second type of hydride, such as
10 vanadium, absorbs the heavier isotopes better than the lighter isotopes, that is, it absorbs tritium better than deuterium and protium, and deuterium better than protium.

Composition 42 is any suitable hydride mixture according to the present invention. Composition 42 may comprise a mixture of hydride compositions (other than metals or alloys), as long as the constituents of
15 composition 42 have a suitable range of hydrogen equilibrium pressures for the practice of the invention.

Composition 42 preferably has a series of hydrogen sorption isotherms with regions that are approximately described by the equation
 $\ln P_{H_2} = a + b(H/M)$. However, other hydride mixtures having
20 isotherms where P_{H_2} varies in a readily measurable manner with H/M over the operating range of apparatus 20 may be used. Thus, the hydrogen content H/M of composition 42 can be determined from measurements of P_{H_2} without the necessity for desorbing the hydrogen into a standard volume.

25 It will be apparent to those skilled in the art that many changes and substitutions can be made to the preferred embodiment herein

described without departing from the spirit and scope of the present invention as defined by the appended claims.

ABSTRACT OF THE DISCLOSURE

A composition for use in storing hydrogen, and a method for making the composition. The composition comprises a mixture of two
5 or more hydrides, each hydride having a different series of hydrogen sorption isotherms that contribute to the overall isotherms of the mixture. The hydrides are chosen so that the isotherms of the mixture have regions wherein the hydrogen equilibrium pressure increases with increasing hydrogen, preferably linearly. The isotherms of the mixture
10 can be adjusted by selecting hydrides with different isotherms and by varying the amounts of the individual hydrides, or both. Preferably, the mixture is made up of hydrides that have isotherms with substantially flat plateaus and in nearly equimolar amounts. The composition is activated by degassing, exposing to hydrogen and then
15 heating at a temperature below the softening temperature of any of the constituents so that their chemical and structural integrity is preserved. When the composition is used to store hydrogen, its hydrogen content can be found simply by measuring P_{H_2} and determining H/M from the isothermic function of the composition.

Fig 1-

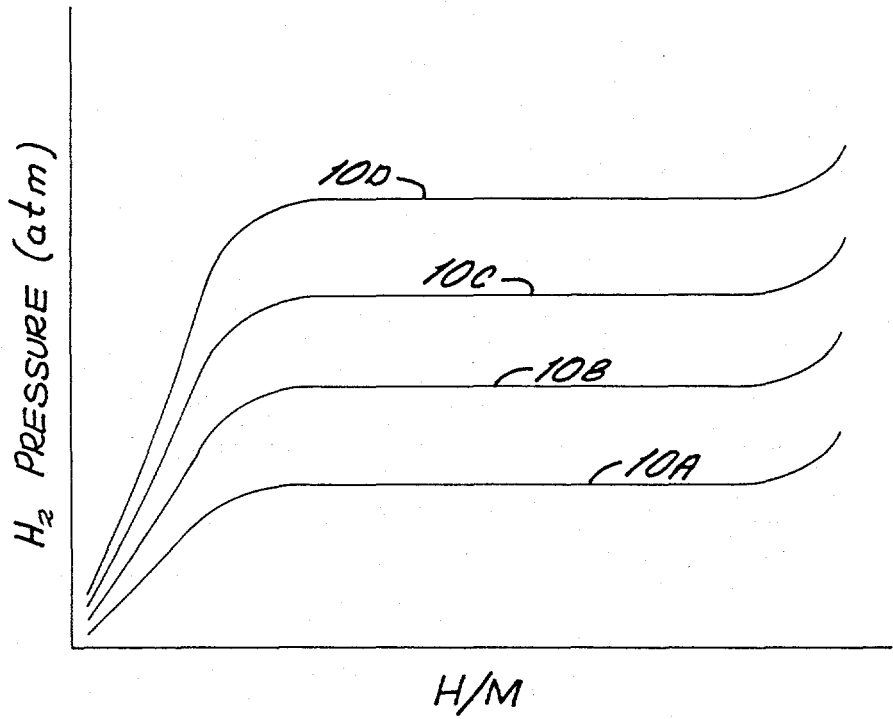


Fig 2-

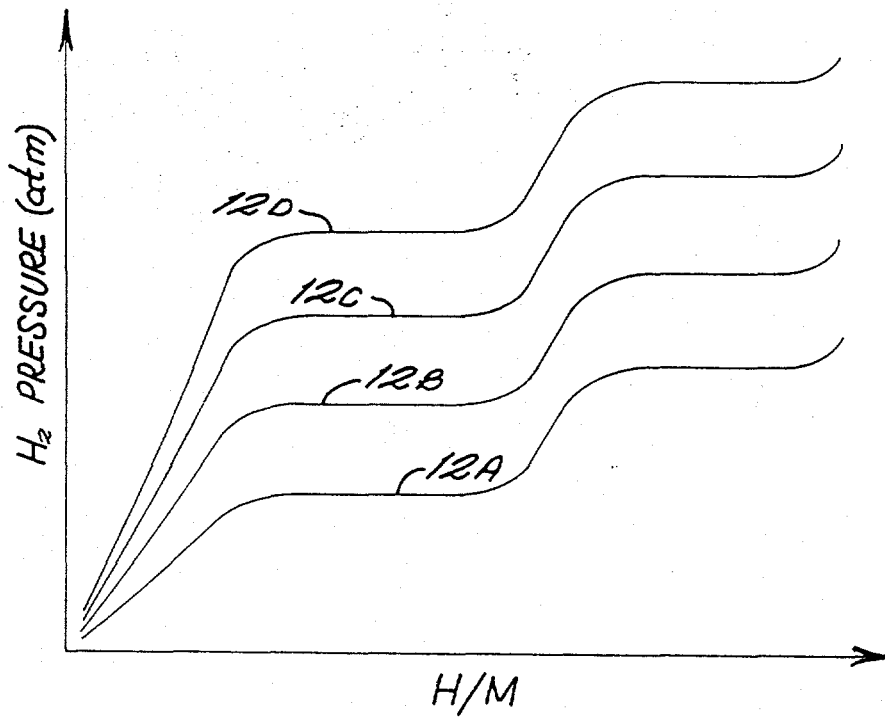


Fig 3

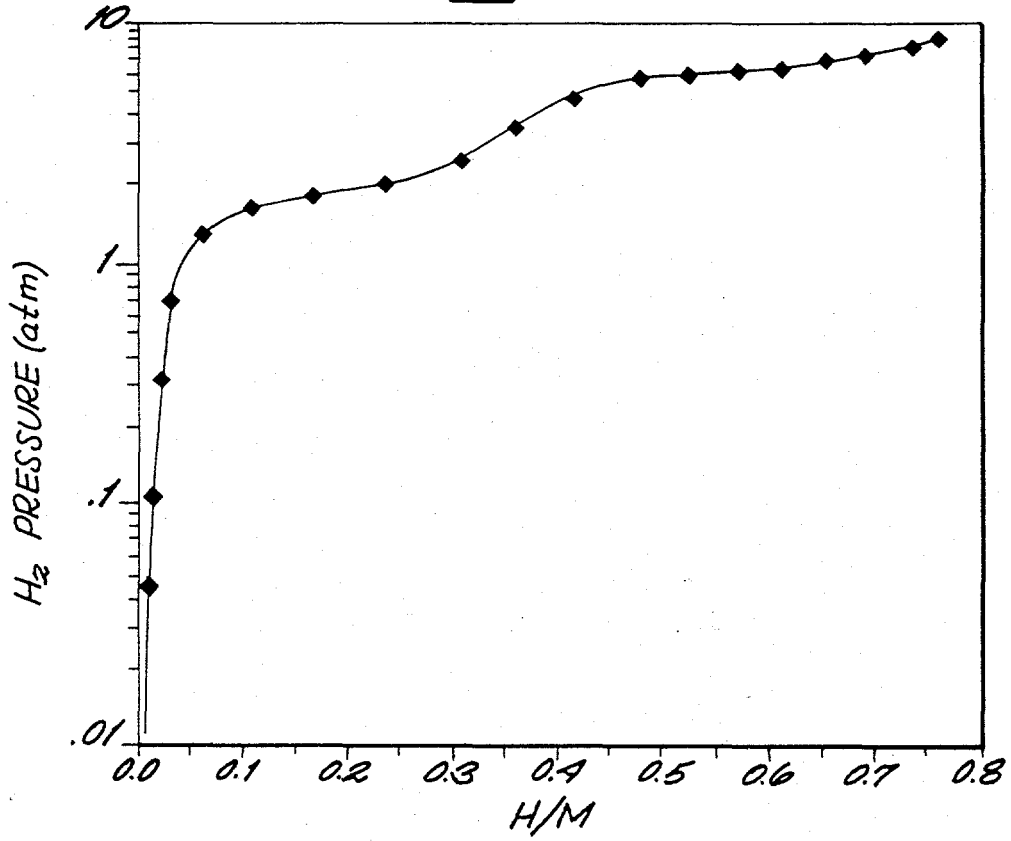


Fig 4

