

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
30 January 2003 (30.01.2003)

PCT

(10) International Publication Number  
**WO 03/008664 A2**

(51) International Patent Classification<sup>7</sup>: **C23C 16/40**

(21) International Application Number: PCT/IB02/02770

(22) International Filing Date: 15 July 2002 (15.07.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/306,014 17 July 2001 (17.07.2001) US  
10/157,466 29 May 2002 (29.05.2002) US

(71) Applicant: L'AIR LIQUIDE-SOCIETE ANONYME A DIRECTOIRE ET CONSEIL DE SURVEILLANCE POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE [FR/FR]; 75, quai d'Orsay, Paris (FR).

(72) Inventors: JACKSIER, Tracey; 6199 Hinterlong Court, Lile, IL 60532 (US). BENESCH, Robert; 16 W 486 Lake Drive, Apt 103, Clarendon Hills, IL 60514 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declaration under Rule 4.17:**

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

**Published:**

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 03/008664 A2**

(54) Title: INCREASED STABILITY LOW CONCENTRATION GASES, PRODUCTS COMPRISING SAME, AND METHODS OF MAKING SAME

(57) Abstract: Methods of passivating a metal surface are described, the methods comprising the step of i) exposing the metal surface to a silicon-containing passivation material; ii) evacuating the metal surface, iii) exposing the treated surface to a gas composition having a concentration of reactive gas that is greater than an intended reactive gas concentration of gas to be transported by the metal surface; iv) evacuating the metal surface to remove substantially all of the gas composition to enable maintenance of an increased shelf-life, low concentration reactive gas at an intended concentration; and v) exposing the metal surface to the reactive gas at the intended reactive gas concentration. Manufactured products, high stability fluids, and methods of making same are also described.

**INCREASED STABILITY LOW CONCENTRATION GASES, PRODUCTS  
COMPRISING SAME, AND METHODS OF MAKING SAME**

5

**Background of the Invention**

**1. Field of the Invention**

[0002] The invention is generally related to the field of gases and packaging  
10 and using same. More specifically, the invention relates to increased stability, low  
concentration reactive gases, products including same, and methods of making same.

**2. Related Art**

[0003] Moisture is known to react with so-called "acid gases", such as  
15 hydrogen sulfide, carbonylsulfide, carbondisulfide and mercaptans (mercaptans are  
also referred to as thiols) to form a complex compound. (The term "acid gas" is used  
herein to denote either gas phase, liquid phase, or mixture of gas and liquid phases,  
unless the phase is specifically mentioned.)

[0004] One problem presents itself: if one is interested in producing acid gas  
20 standard compositions, in other words acid gases having a known concentration of  
one of these gases in a matrix or carrier fluid, then one must consider how to reduce  
or remove the moisture. Gas standards may have to have, and preferably do have, a  
long shelf life, since the standard acid gas may not be required immediately after  
25 production. A source of acid gas and/or matrix gas may contain a considerable  
amount of moisture. Therefore, the reduction or removal of moisture from the acid  
gas is of primary importance if the stability of the acid gas in the standard gas is to be  
maintained.

[0005] U.S. Pat. Nos. 5,255,445 and 5,480,677 describe processes for  
30 drying and passivating a metal surface to enhance the stability of gas mixtures  
containing one or more gaseous hydrides in low concentrations in contact therewith.  
The process comprises purging gas in contact with the metal surface with inert gas to  
remove the purged gas, exposing the metal surface to an amount of a gaseous  
35 passivating or drying agent comprising an effective amount of a gaseous hydride of

silicon, germanium, tin or lead and for a time sufficient to passivate the metal surface, and purging the gaseous passivating agent using inert gas. Optionally, an oxidizing agent is applied after the third step to stabilize the adsorbed stabilizing agent. The patent also mentions prior known processes, such as saturation passivation, where the container is subjected to several cycles of evacuating and filling with a much higher concentration of the same gaseous hydride, prior to being filled with the low concentration hydride mixture of interest. The two patents do not mention or describe processes to passivate containers adapted to store sulfur-containing gases, nor do they mention passivation techniques in which a first passivating agent is applied to the surface, followed by contacting with a higher concentration of the gas to be stored.

[0006] Co-pending application serial number 10/\_\_\_\_\_, filed on even date herewith, (serie 5718) describes the use of certain acid gas resistant molecular sieves to reduce or remove moisture from fluid compositions comprising a sulfur-containing compound. There is no disclosure or suggestion, however, for the passivation of containers adapted to contain the moisture-reduced compositions. Such containers may have moisture adhered to the internal surfaces, which can and does react with acid gases, reducing their stability and shelf-life.

[0007] Given the problem of moisture reacting with acid gases and reactive gases in general, it would be advantageous if passivation methods could be provided which increase the shelf-life during the storage of these compounds.

#### Summary of the Invention

[0008] In accordance with the present invention, methods of passivating internal surfaces of containers that have been cleaned are employed to increase the shelf-life of gas compositions, especially low concentration gas products. As used herein the term "shelf-life" means that time during which the initial concentration of a gas stored in a container is substantially maintained at the intended or desired concentration. In this context, the phrase "substantially maintained" means that for concentrations of about 1000 parts per billion (ppb), the concentration does not vary by more than +/- 10 percent; for concentrations of about 500 ppb, the concentration does not vary by more than +/- 15 percent; for concentrations of about 100 ppb, the

concentration does not vary by more than +/- 20 percent. "Low concentration" means gases having a concentration in another gas, such as inert gas, of 1000 ppb or less.

[0009] Gases which benefit for the passivation techniques of the present invention include nitrous oxide, nitric oxide, hydrogen chloride, chlorine, boron trichloride, and any acid gases except those that would react with a silicon-containing compound.

[0010] As used herein the term "acid gas" means sulfur-containing compounds, including carbon disulfide, carbonylsulfide, and compounds within formula (I):



wherein S is sulfur,  
X and Y are the same or different and are independently selected from the group consisting of hydrogen, alkyl, aryl, oxygen, hydroxyl, amine, aminosilane, oxygen, and alcohol.

Examples of preferred sulfur-containing compounds within formula (I) include hydrogen sulfide, methylthiol, ethylthiol, n-propylthiol, i-propylthiol, benzylthiol, and the like.

[0011] A first aspect of the invention relates to a manufactured product comprising:

- a) a container having an internal space and a passivated internal metal surface;
- b) a composition comprising a reactive gas contained within the internal space and in contact with the passivated internal metal surface, the reactive gas having an intended concentration that is substantially maintained; and
- c) the passivated internal metal surface comprising:
  - 1) the reaction product of a silicon-containing material and an oxygen-containing material (preferably selected from the group

consisting of moisture, molecular oxygen, metal oxides, and mixtures thereof), and

- 2) an effective amount of the reactive gas, the effective amount being many times the intended concentration of reactive gas that is to be substantially maintained.

5  
10  
15  
[0012] Preferred manufactured products of the invention are those wherein the reactive gas is selected from the group consisting of chlorine and an acid as selected from the group consisting of carbondisulfide, carbonylsulfide, and compounds within formula (I). Other preferred manufactured products include products wherein the passivated internal surface is a passivated metal. Preferably the metal is selected from the group consisting of aluminum, aluminum alloys, steel, iron and combinations thereof. Yet other preferred manufactured products of the invention are those wherein the silicon-containing material is selected from the group consisting of compounds within the general formula (II):



20  
wherein R1, R2, R3, and R4 are the same or different and are independently selected from the group consisting of hydrogen, halogen, amine, alkyl, aryl, halogenated alkyl, and halogenated aryl; and manufactured products wherein the compound is silane or a methyl-containing silane, more preferably wherein the methyl-containing silane is selected from the group consisting of methylsilane, dimethylsilane, trimethylsilane and tetramethylsilane.

25  
30  
[0013] Preferred manufactured products of the invention are those wherein the composition comprises a reactive gas having a concentration of about 1000 ppb and that does not vary by more than +/- 10 percent; products wherein the composition comprises a reactive gas having a concentration of about 500 ppb and that does not vary by more than +/- 15 percent; products wherein the composition comprises a reactive gas having a concentration of about 100 ppb and that does not vary by more than +/- 20 percent;. Products wherein the composition comprises higher or lower concentration of reactive gas, and correspondingly larger or smaller variation in concentration, are considered within the invention.

[0014] Preferred manufactured products of the invention comprise only a single reactive gas with an inert gas like nitrogen, argon, helium, and the like. The composition may comprise a mixture of two or more reactive gases. Also, the balance of the fluid composition is, in some preferred embodiments, a hydrocarbon, such as ethylene, propylene, and the like.

[0015] A second aspect of the invention is a method of making a manufactured product of the invention, the method comprising the steps of:

i) exposing an internal metal surface of a container to a first fluid composition comprising a silicon-containing compound for a time sufficient to allow at least some of the silicon-containing compound to react with oxygen-containing compounds (preferably selected from the group consisting of moisture, molecular oxygen, metal oxides, and mixtures thereof) present to form a silicon-treated surface on at least some of the internal metal surface, the silicon-containing compound selected from the group consisting of compounds within the general formula (II):



wherein R1, R2, R3, and R4 are the same or different and are independently selected from the group consisting of hydrogen, halogen, alkyl, aryl, amine, halogenated alkyl, and halogenated aryl;

ii) evacuating the container for a time sufficient to remove substantially all of the silicon-containing compound(s) that has not reacted with the oxygen-containing compound to form the silicon-treated surface;

iii) exposing the silicon-treated surface to a second fluid composition, the second fluid composition comprising a reactive gas having a concentration that is greater than an intended reactive gas concentration of the manufactured product;

iv) evacuating the container for a time sufficient to remove just enough of the second fluid composition to enable maintenance of an increased shelf-life, low concentration reactive gas at the intended concentration in the container; and

v) filling the container with a third fluid composition having the intended reactive gas concentration for the manufactured product.

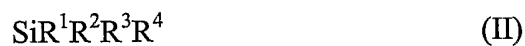
[0016] Preferred methods in this aspect of the invention are those wherein the silicon-containing compound is silane or a methyl-containing organosilane;

particularly those wherein the methyl-containing organosilane is selected from the group consisting of silane, methylsilane, dimethylsilane, trimethylsilane and tetramethylsilane. Also preferred are methods wherein the second fluid composition has a concentration of reactive gas at least 10 times the intended reactive gas concentration of the manufactured product; methods wherein steps i) and ii) are repeated prior to step iii); methods wherein the metal surface is cleaned prior to step i); methods wherein the concentration of the silicon-containing compound used in step i) ranges from about 100 ppm to 100 percent; methods wherein during step i) the silicon-containing compound is heated to a temperature of not more than 74°C, and methods wherein during step iii) the second composition is heated to a temperature of not more than 74°C. Other preferred methods are those wherein the container is a gas cylinder having an attached cylinder valve, and the cylinder valve is removed prior to step i). After all the steps are completed, preferably at very high temperatures for steps i) and iii), the cylinder valve is reattached, and the process steps i) – v) are repeated, but steps i) and iii) take place at not more than 74°C.

[0018] A third aspect of the invention is a method of passivating a metal surface, the method comprising the steps of:

i) exposing the metal surface to a first composition comprising a silicon-containing compound for a time sufficient to allow at least some of the silicon-containing compound to react with oxygen-containing compounds present to form a silicon-treated surface on at least some of the metal surface, the silicon-containing compound selected from the group consisting of compounds within the general formula (II):

25



wherein R1, R2, R3, and R4 are the same or different and are independently selected from the group consisting of hydrogen, halogen, amine, alkyl, aryl, halogenated alkyl, and halogenated aryl;

30

ii) evacuating the surface for a time sufficient to remove substantially all silicon-containing compound that has not reacted with the oxygen-containing compound to form the silicon-treated surface;

iii) exposing the silicon-treated surface to a second fluid composition, the second fluid composition comprising a reactive gas having a concentration that is greater than an intended reactive gas concentration to be in contact with the silicon-treated surface;

5 iv) evacuating the surface for a time sufficient to remove just enough of the second fluid composition to enable maintenance of a low concentration of reactive gas at an intended concentration; and

v) exposing the metal treated surface to a third fluid composition having concentration of reactive gas at the intended reactive gas concentration.

10

[0019] Preferably, the metal surface is part of a pipe, piping manifold, tubing, tubing manifold, ton unit, tube trailer, tank trailer, cylinder, flow regulator, pressure regulator, valve, cylinder valve, or other pressure-reducing device. The metal surface is preferably cleaned prior to step i) as disclosed further herein.

15

[0020] Further aspects and advantages of the invention will become apparent by reviewing the description of preferred embodiments that follow.

#### **Brief Description of the Drawing**

20

[0021] FIG. 1 is a logic diagram illustrating the methods of the invention

25

[0022] FIG. 2 illustrates that a prior art process of "vacuum baking" an aluminum cylinder at 65°C to vacuum of 1 micrometer Hg for 3 days was not sufficient to provide stability of a 150 ppb H<sub>2</sub>S balance nitrogen mixture for a cylinder which was previously exposed to moisture;

30

[0023] FIG. 3 illustrates that a prior art process of passivation of a cylinder and valve after vacuum baking with a high concentration of the gas mixture to be prepared, which had also been used to extend shelf life of a high purity mixture, did not prove successful; and

[0024] FIGs. 4 and 5 illustrate stability of gas products made in accordance with the invention.



### Description of Preferred Embodiments

[0025] While the following discussion focuses on a container which has a metal internal surface, the description is not limited thereto, and could apply to a piping or tubing system, a manifold, a gas cylinder having a cylinder valve, ton unit, and the like.

[0026] Silicon-containing compounds within the general formula (II) are known to react with oxygen-containing compounds, such as  $H_2O$ ,  $N_2O$ ,  $CO_2$ , and the like, to produce  $SiO_2$ , especially when the silicon-containing compounds are in the gaseous or vapor state. This fact is taken advantage of in the practice of the various aspects of the invention. The reaction product of a silicon-containing compound and an oxygen-containing compound such as water forms an amorphous or crystalline glassy material on the surfaces on which it is deposited. The amorphous or crystalline glassy material may include aluminum silicide, if the container or surface being treated comprises aluminum. Although the deposited material is referred to herein as a "coating", it shall be readily understood that in fact the material may deposit non-uniformly, or not at all on certain areas of the surface being treated. This coating then serves the function of deactivating a surface for the adsorption of molecules of the gas that is ultimately to be contained in the container or piping system at low concentration. In other words, the coating serves to decrease the number of reactive sites on the metal surface being treated. For simplicity, silicon-containing compounds within formula (II) shall be referred to as organosilanes, although their formal name under IUPAC convention may differ.

[0027] The reaction of an organosilane within general formula (II) with oxygen-containing materials such as water proceeds without catalyst at room temperature ( $25^\circ C$ ); however, it is preferred to carry out the reaction at moderately elevated temperatures, such as temperature ranging from  $25^\circ C$  up to  $100^\circ C$ , in order to produce the coatings in reasonable time. The pressure of the reaction of an organosilane with water vapor will generally also proceed at atmospheric pressure, however, the pressure in the container, or near the surface being treated, may either be in vacuum or above atmospheric pressure. This will of course depend on the rates of reaction of the organosilane with the oxygen-containing compound, the desired

coating deposition rate, and desired thickness of the coating. It is of course within the invention to make layered coatings of two or more organosilane/oxygen-containing compound reaction products. It is also considered within the invention to employ two or more organosilanes simultaneously to make a "mixed" coating. Indeed, it is possible that the organosilane may be employed in conjunction with a non-organosilane to form either layered or mixed coatings.

[0028] Silane and organosilanes are toxic materials, and, depending on the organosilane, pyrophoric. Special care in handling these materials is warranted, preferably well-ventilated hoods. Electronic grade silane ( $\text{SiH}_4$ ) is available commercially in cylinders from Air Liquide America Corporation, Houston, Texas. Trimethylsilane is available commercially from Dow Corning Corporation.

[0029] Preferred silicon-containing compounds include silane, and methyl-containing organosilanes; particularly those wherein the methyl-containing organosilane is selected from the group consisting of methylsilane, dimethylsilane, trimethylsilane and tetramethylsilane. Preferred organosilane compounds include methylsilane compounds having the structure  $\text{SiH}_n(\text{CH}_3)_{4-n}$ , where  $n=1$  to  $3$ , i.e. methylsilane, dimethylsilane, or trimethylsilane or the structure  $\text{Si}_2\text{H}_m(\text{CH}_3)_{6-m}$ , where  $m=1$  to  $5$ . The most preferred organosilane compound is methylsilane,  $\text{CH}_3\text{SiH}_3$ . The organosilane compounds are hydrolyzed by reaction with water, oxygen or water-containing gases such as humid air and/or other oxygen-containing gases, such that the carbon content of the deposited film is from 1 to 50% by atomic weight, preferably about 20%.

[0030] It is conceivable to employ adjuvants during the reaction of an organosilane with water. In the practice of the invention, "adjuvant" includes physical and chemical adjuvants, and combinations thereof. Suitable physical adjuvants include electrostatic discharge, plasma discharge, laser excitation, and the like, under temperatures and pressures suitable for each of these processes. For example, plasmas are preferably best employed in moderate vacuum. A chemical adjuvant might include an oxidant gas such as oxygen, ozone, chlorine dioxide, combinations thereof, and the like. When a combination of physical and chemical adjuvants is employed, for example ozone and plasma discharge, the reaction product

may be described as similar to the films produced by the process described in U.S. Pat. No. 6,054,379, which is incorporated herein by reference for its teaching of the production of such films.

5           **[0031]** The container or surface to be treated may be selected from the group consisting of iron, stainless steel (for example 301, 316, 401), aluminum, aluminum alloy, steel alloys and the like. The internal surface of the container, or the surface to be treated, may be subject to abrasion prior to reaction of the organosilane with water vapor in order to improve adhesion of the reaction product to the metal. Residues  
10 may be removed by a variety of mechanical means such as scrubbing, grinding, and peening. Scrubbing may be performed with non-woven abrasives. The use of lofty, fibrous, nonwoven abrasive products for scouring surfaces such as the soiled surfaces of pots and pans is well known. These products are typically lofty, nonwoven, open mats formed of staple fibers which are bonded together at points where they intersect  
15 and contact each other. The staple fibers of low-density abrasive products of this type can be, and typically are, bonded together at points of contact with a binder that may or may not contain abrasive particles. The staple fibers are typically crimped, have a length of about 3.8 cm, a diameter ranging from about 25 to about 250 micrometers, and are formed into lofty open webs by equipment such as "Rando-Webber" and  
20 "Rando-Feeder" equipment (marketed by the Curlator Corporation, of Rochester, N.Y. and described in U.S. Pat. Nos. 2,451,915; 2,700,188; 2,703,441 and 2,744,294). One very successful commercial embodiment of such an abrasive product is that sold under the trade designation "Scotch-Brite" by Minnesota Mining and Manufacturing Company of St. Paul, Minn. ("3M"). Low-density abrasive products of this type can  
25 be prepared by the method disclosed by Hoover et al. in U.S. Pat. No. 2,958,593, incorporated herein by reference.

**[0032]** Low-density, lofty abrasive products may also be formed of webs or mats of continuous filaments. For example, in U.S. Pat. No. 4,227,350, Fitzer,  
30 incorporated herein by reference, discloses a low-density abrasive product comprising a uniform cross-section, generally flat-surfaced, open, porous, lofty web of autogenously bonded, continuous, undulated, interengaged filaments. The web of Fitzer is formed by downwardly extruding a plurality of thermoplastic organic (e.g. polyamide, polyester) filaments from a spinneret into a quench bath. As the filaments

enter the quench bath, they begin to coil and undulate, thereby setting up a degree of resistance to the flow of the molten filaments, causing the molten filaments to oscillate just above the bath surface. The spacing of the extrusion openings from which the filaments are formed is such that, as the molten filaments coil and undulate at the bath surface, adjacent filaments touch one another. The coiling and undulating filaments are still sufficiently tacky as this occurs, and, where the filaments touch, most adhere to one another to cause autogenous bonding to produce a lofty, open, porous, handlable filament web. The web, so formed, is then impregnated with a tough binder resin which adherently bonds the filaments of the web together and also bonds a multitude of abrasive granules, uniformly dispersed throughout the web, to the surface of the filaments. Fibrous polishing and/or abrading materials can be prepared from continuous or substantially continuous synthetic filaments by the method disclosed by Zimmer et al., in U.S. Pat. No. 3,260,582, incorporated herein by reference. In this method crimped or curled continuous filaments are straightened out under tension into a substantially parallel relationship with one another, uniformly coated while under tension with an adhesive which may or may not contain abrasive particles, interlocked with one another by release of such tension and then set in a permanently interlocked and lofty, open, 3-dimensional state by curing or setting up the adhesive. Low-density, lofty, open, porous, nonwoven scouring articles have been more easily and economically manufactured from continuous filaments by the method disclosed by Heyer et al., in U.S. Pat. Nos. 4,991,362, and 5,025,596, both incorporated herein by reference. The scouring pads described in these patents comprise a multiplicity of crimped or undulated, continuous, thermoplastic organic filaments that are bonded together (e.g., by fusion or an adhesive) at opposite ends. The pad is made by arranging a multiplicity of continuous, crimped or undulated, thermoplastic organic filaments in an open lofty array, with one point of each filament in the array corresponding to a first filament bonding site and a second point of each filament, distant from the first point, corresponding to a second filament bonding site. A pad is formed in the filament array by bonding substantially all of the thermoplastic organic filaments together at the first and second bonding sites. When a pad having greater abrasiveness is desired, abrasive particles may be adherently bonded to the filaments of the pad, preferably before the individual pad is cut from the filament array. These pads have also enjoyed commercial success and are economical to make. U.S Pat. No. 5,363,604, incorporated by reference, describes nonwoven scouring

articles comprising a low-density, lofty, open, porous, nonwoven web, the web comprising a multiplicity of crimped or undulated, continuous, preformed thermoplastic organic filaments, at least partially coated with an organic thermoset binder which binds the filaments at least at a portion of points where they contact. The continuous thermoplastic organic filaments, preferably in the form of tow, are entangled together at a multiplicity of points along their length to provide a cross-direction tensile strength the web of at least about 0.02 kg/cm, more preferably at least about 0.03 kg/cm, before coating the web with a thermosetting binder precursor solution. The continuous filaments are "entangled", preferably by needlepunching from a plurality of directions perpendicular to the machine direction. Other background references include U.S. Pat. Nos. 3,688,453; 4,622,253; 4,669,163; 4,902,561; 4,927,432; 4,931,358; and 4,935,295; World Patent Application No. WO 92/01536, published Feb. 6, 1992; European Patent Application number 0 492 868 A1, published Jul. 1, 1992, the disclosures of which are incorporated herein by reference.

**[0033]** Other means of removing residues from metal surfaces include grinding, such as by using so-called bonded abrasives. Bonded abrasives typically consist of a shaped mass of abrasive grains held together by a binder. The shaped mass can be in any number of conventional forms such as wheels, points, discs, and cylinders, but is preferably in the form of a grinding wheel. A preferred bonded abrasive product useful in the present invention comprises between about 50 to about 90 weight percent abrasive grains dispersed and adhered within a binder. Bonded abrasives products are preferably manufactured by a molding process, and are made with varying degrees of porosity to control the breakdown. Bonded abrasives which may be used for this purpose are such as those described in U.S. Pat. Nos. 5,250,085; 5,269,821; and 5,273,558, all incorporated herein by reference. Abrasive products comprising a solid or foamed organic polymeric matrix having abrasive granules dispersed throughout and bonded therein are well known and widely used. Typically, the polymeric matrix is composed of either a hard, thermoset resin, such as a catalyzed phenol-formaldehyde, or resilient elastomer, such as a polyurethane or a vulcanized rubber.

[0034] Bonded abrasives are to be distinguished from coated abrasives in their construction and mode of operation. Bonded abrasives (e.g., grinding wheels) are three-dimensional structures of binder and abrasive grains which rely upon the continual breakdown and removal of the abrasive grains on the cutting surface to  
5 continually present sharp cutting points to the material being ground. Coated abrasives, on the other hand, typically have only a single layer of abrasive grains. See, for example, U.S. Pat. No. 5,011,512, incorporated herein by reference.

[0035] When elastomeric binder matrices are used in bonded abrasives they  
10 generally produce an abrasive article having some degree of flexibility and resiliency. These abrasive articles typically provide a smoother abrasive action and a finer surface finish than that provided by a bonded abrasive article made with hard, thermoset resin. As a result of this, elastomeric bonded abrasive articles have found a wide range of industrial applications, such as deburring, finishing, and sanding in the  
15 metal and wood-working industries. However, often these elastomeric bonded abrasive articles have shown premature loss of abrasive particles and, in some cases, undesirable smearing or transfer of portions of the elastomeric binder to the surface of the workpiece.

[0036] Conventional flexible bonded abrasive articles typically employ an  
20 elastomeric polyurethane as the binder matrix. The polyurethane binder matrix may be a foam, as disclosed in U.S. Pat. Nos. 4,613,345, 4,459,779, 2,972,527, 3,850,589; UK Patent Specification No. 1,245,373 (published Sep. 8, 1971); or the polyurethane binder may be a solid, as disclosed in U.S. Pat. Nos. 3,982,359, 4,049,396, 4,221,572,  
25 and 4,933,373, all incorporated herein by reference.

[0037] For very large containers, such as ton units, bullets, and spheres, peening may be used with success to remove residues, scales and other deposits on internal surfaces of these containers. U.S. Pat. Nos. 3,638,464 and 3,834,200  
30 (incorporated herein by reference) disclose a high-intensity peening flap construction which includes an elongate strap of a flexible, tear-resistant material, and at least one metal peening particle support base fastened to the elongate strap. A plurality of refractory-hard, impact fracture-resistant peening particles are metallurgically joined to an exposed face of the support base. In use, one or more of the flaps are mounted

on a hub, and the hub is rotated while the flaps are forced against the workpiece to be peened. The peening particles on each support base strike the workpiece in turn, thereby causing the peening particles to perform their normal peening function, but preventing the normal uncontrolled scattering which occurs in conventional shot  
5 peening. Improvements to these articles are described in U.S Pat. Nos. 5,179,852 and 5,203,189, incorporated herein by reference where necessary to understand their use in removing residues.

[0038] Once the metal container inner surface, or metal surface to be treated  
10 is cleaned, and the reaction of organosilane with oxygen-containing compounds completed, either with or without adjuvants, to form a coating, the processes of the invention comprise evacuating the container for a time and vacuum sufficient to remove substantially all organosilane that has not reacted with oxygen-containing compounds. This first evacuation step preferably includes evacuation down to a  
15 vacuum of about 1 torr, more preferably down to 0.01 torr. The temperature during this evacuation process is not critical, but higher temperatures may tend to increase the removal rate of organosilane. This will be balanced by safety issues, in that higher temperatures may be more hazardous. Therefore, room temperature (about 25°C), or slightly lower or slightly higher than room temperature is preferred.

20 [0039] Subsequent to this first evacuation step, the next step is exposing the coating to a gas composition, the gas composition having a concentration of reactive gas that is greater than an intended reactive gas concentration of a manufactured product. The reactive gas is caused to contact the coating and deactivate the surface  
25 even further. The reactive gas preferably has a concentration of at least 10 times the concentration of the reactive gas that is to be ultimately stored in the container or exposed to the surface, and more preferably has a concentration 500 times greater than the ultimate concentration, even more preferably 50,000 times the concentration of the reactive gas to be stored in the container or exposed to the surface.

30 [0040] The degree of adsorption of the reactive gas onto the coating depends in a complicated way on the composition and physical properties of the coating, the temperature and pressure employed during this step, as well as on the chemical and physical properties of the particular reactive gas that is being adsorbed thereon. These

parameters are in turn dictated by the final concentration of reactive gas that is to be stored in the container. A discussion of adsorption of gaseous species onto surfaces that is helpful in this respect is included in Daniels, F. et al., "Experimental Physical Chemistry", Seventh Edition, McGraw-Hill, pages 369-374 (1970). While the

5 inventors are not certain, it is believed that the attraction of the reactive gas to the coating is physical in nature, involving an interaction of dipoles or induced dipoles, but may be chemical in nature involving chemical bonds, as when oxygen is adsorbed on charcoal. A combination of physical and chemical forces may be at work as well. Thus, the surface area of a coating produced by the practice of the present invention

10 may be determined by the B.E.T. method, and preferably is at least about 1 m<sup>2</sup>/gram, more preferably at least 10 m<sup>2</sup>/gram. If the coating is somewhat porous, the pore volume may be determined by nitrogen adsorption isotherm methods, and is preferably at least 0.1 ml/gram. The B.E.T. method is described in detail in Brunauer, S. Emmet, P. H., and Teller, E., J.Am.Chem.Soc., 60, 309-16 (1938). The nitrogen

15 adsorption isotherm method is described in detail in Barrett, E. P., Joyner, L. G. and Helenda, P. P., J.Am.Chem.Soc., 73, 373-80 (1951), incorporated by reference herein. In general, if the concentration of reactive gas to be stored in the container is 100 ppb, then for the same reactive gas, same temperature and pressure, and same coating, the concentration of reactive gas used in this step will be higher than if the ultimate

20 concentration of reactive gas is to be only 50 ppb, assuming adsorption is the governing pathway. An increase in temperature will tend to require an increase in concentration of reactive gas, an increase in pressure, or both, to achieve the same degree of adsorption. In contrast, a decrease in temperature will tend to require a decreased concentration of reactive gas, a decrease in pressure, or both to achieve the

25 same level of adsorption.

[0041] After the surface has been further deactivated by exposure to the reactive gas at high concentration, a second evacuation step is carried out to remove excess reactive gas. In this step, evacuation of the container is carried out for a time

30 sufficient to remove substantially all of non-adsorbed reactive gas, leaving reactive gas adsorbed on the coating. The container is then filled with a gas composition comprising the intended low concentration of reactive gas.



[0042] Referring now to FIG. 1, there is illustrated schematically a logic diagram for carrying out processes of the invention. A container having a metal internal surface is selected at 12. The metal surface is exposed to a silicon-containing passivation material, 14, for a time and at a temperature and pressure sufficient to react most of the silicon-containing material with oxygen-containing compounds present on the metal surface. The container is then evacuated for a time sufficient to remove the bulk of the non-reacted silicon-containing material, at 16. Next, the metal surface is exposed to high concentration of reactive gas or liquid of the desired end product to be contained in the container, at 18. The container is again evacuated at 20 for a time sufficient to remove substantially all of the non-adsorbed reactive gas, then the container is filled with the composition having the desired material at the desired concentration, at 22. At this point, the container is allowed to equilibrate and the concentration of the gas in the container is tested at various times to determine the concentration of reactive gas in the container. If the shelf life is acceptable at 24, the product is made in accordance with the procedure followed, at 26. If the concentration of the gas increases or decreases beyond the accepted tolerances, then the process of steps 20, 22, and 24 are repeated. Optionally, steps 14 and 16 may be repeated, as indicated at 26.

#### 1. Examples

[0043] In the following examples, hydrogen sulfide concentrations were measured using a chemiluminescence detector.

[0044] Comparative Example 1. Vacuum baking has long been employed to reduce moisture in cylinders to prevent and/or decrease corrosion due to acid as reactions with moisture and the cylinder wall (and cylinder valve). However, as illustrated in FIG. 2, vacuum baking an aluminum cylinder at 65°C to vacuum of 1 micrometer of Hg for 3 days was not sufficient to provide stability of a 150 ppb H<sub>2</sub>S balance nitrogen mixture for a cylinder which was previously exposed to moisture.

30

[0045] Comparative Example 2. Passivation of the cylinder and valve after vacuum baking with a high concentration of the gas mixture to be prepared has also been used to extend shelf life of high purity mixtures. However, this has not proved

successful. After an initial vacuum baking as in Comparative Example 1, the cylinder was subsequently filled with 5000 ppm of H<sub>2</sub>S balance nitrogen and heated at 80°C for 3 days. After 3 days the contents were emptied and a vacuum pulled on the cylinder in order to remove all residual H<sub>2</sub>S. The cylinder was subsequently filled  
5 with 150 ppb H<sub>2</sub>S balance nitrogen. As illustrated in FIG. 3, although the stability of the mixture was enhanced, a fast decay was still observed.

[0046] Example 1. Silane, a silicon-containing material having the formula SiH<sub>4</sub>, is known to react with moisture and other oxygen-containing compounds and  
10 hydrogen. It has also been reported that SiO<sub>2</sub> can bind to aluminum, and we have data indicating formation of weak Si-Al bonds when treating an aluminum alloy cylinder known under the trade designation "Calgaz 3003". In this example, a 1 percent silane balance nitrogen mixture was introduced into an aluminum cylinder (note: this was not a cylinder known under the trade designation "Calgaz 3003") and left in the  
15 cylinder overnight. Subsequently the balance was vacuumed out and the cylinder was filled with a 250 ppb H<sub>2</sub>S balance nitrogen mixture. As illustrated in FIG. 4, the signal decay for the curve labeled "No H<sub>2</sub>S Passiv" was slower than observed previously, indicating that the reaction of moisture with the H<sub>2</sub>S was not solely responsible for the loss of stability of the H<sub>2</sub>S. The cylinder was subsequently  
20 evacuated and passivated with a 5000 ppm mixture of H<sub>2</sub>S at 62°C. The cylinder was evacuated and filled with 150 ppb H<sub>2</sub>S. The signal was observed to increase with time, indicating that substantially all of the passivation mixture had not been removed prior to filling.

25 [0047] Example 2. Applying the same silane treatment followed by H<sub>2</sub>S passivation as in Example 1, but using a longer vacuum time period to remove extraneous silane, it was possible to achieve a stable H<sub>2</sub>S mixture, as illustrated in FIG. 5 by the curve labelled "H<sub>2</sub>S Passivated."

30 [0048] Although the description herein is intended to be representative of the invention, it is not intended to limit the scope of the appended claims.

**CLAIMS:**

1. A manufactured product comprising a gas having an extended shelf-life, the product comprising:

- 5 a) a container having an internal space and a clean and passivated internal metal surface;
- b) a composition comprising a reactive gas contained within the internal space and in contact with the clean passivated internal metal surface, the reactive gas having a concentration that is substantially maintained; and
- 10 c) the clean and passivated internal metal surface comprising:
- 1) the reaction product of a silicon-containing material and an oxygen-containing material, and
- 2) an effective amount of the reactive gas to form the passivated internal metal surface, the effective amount being many times
- 15 the intended concentration of reactive gas that is substantially maintained.

2. The product of claim 1 wherein said reactive gas is selected from the group consisting of nitrous oxide, nitric oxide, hydrogen chloride, chlorine, boron

20 trichloride, and acid gases that will not react with a silicon-containing material.

3. The product of claim 2 wherein said acid gas is selected from the group consisting of carbondisulfide, carbonylsulfide, and compounds within formula (I):

25 
$$Y-S-X \quad (I)$$

wherein S is sulfur, and

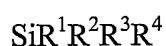
X and Y are the same or different and are independently selected from the group consisting of hydrogen, alkyl, aryl, oxygen, hydroxyl, amino,

30 and aminosilane.

4. The product of claim 1 wherein said passivated internal surface is a passivated metal.

5. The product of claim 4 wherein said metal is selected from the group consisting of aluminum, aluminum alloys, steel, iron and combinations thereof.

6. The product of claim 1 wherein said silicon-containing material is selected  
5 from the group consisting of compounds within the general formula:



wherein R1, R2, R3, and R4 are independently selected from the group consisting of  
10 hydrogen, halogen, alkyl, aryl, amine, halogenated alkyl, and halogenated aryl.

7. The product of claim 6 wherein said compound is a methyl-containing silane.

15 8. The product of claim 7 wherein said methyl-containing silane is selected from the group consisting of methylsilane, dimethylsilane, trimethylsilane and tetramethylsilane.

9. The product of claim 1 wherein the composition has a reactive gas concentration of about 1000 ppb and which does not vary  
20 by more than +/- 10 percent.

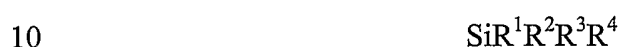
10. The product of claim 1 wherein the composition has a reactive gas concentration of about 500 ppb and does not vary by more than +/-15 percent.

25 11. The product of claim 1 wherein the composition has a reactive gas concentration of about 100 ppb and does not vary by more than +/-20 percent.

12. The product of claim 1 wherein the composition comprises a single reactive gas mixed with a gas selected from the group  
30 consisting of an inert gas, a hydrocarbon gas, and mixtures thereof.

13. A method of making the manufactured product of claim 1 from a clean container, the method comprising the steps of:

5 i) exposing an internal metal surface of a container to a first fluid composition comprising a silicon-containing compound for a time sufficient to allow at least some of the silicon-containing compound to react with an oxygen-containing compound present to form a silicon-treated surface on at least some of the internal metal surface, the silicon-containing compound selected from the group consisting of compounds within the general formula:



wherein R1, R2, R3, and R4 are the same or different and are independently selected from the group consisting of hydrogen, halogen, alkyl, aryl, amine, halogenated alkyl, and halogenated aryl;

15 ii) evacuating the container for a time sufficient to remove substantially all silicon-containing compound that has not reacted with the oxygen-containing compound to form the silicon-treated surface;

iii) exposing the silicon-treated surface to a second fluid composition, the second fluid composition comprising a reactive gas having a concentration that is greater than an intended reactive gas concentration of the manufactured product;

20 iv) evacuating the container for a time sufficient to remove substantially all of the second fluid composition, thus forming said passivated internal metal surface in the container; and

v) filling the container with a third fluid composition having the intended reactive gas concentration for the manufactured product.

25

14. The method of claim 13 wherein the silicon-containing compound is selected from the group consisting of silane and a methyl-containing silane.

30 15. The method of claim 14 wherein said methyl-containing silane is selected from the group consisting of methylsilane, dimethylsilane, trimethylsilane and tetramethylsilane.

16. The method of claim 13 wherein the second fluid composition has a concentration of reactive gas at least 10 times the intended reactive gas concentration.

17. The method of claim 13 wherein steps i) and ii) are repeated prior to step  
5 iii).

18. The method of claim 13 wherein the composition of the silicon-containing gas used in step iii) ranges from about 100 ppm to 100 percent.

19. The method of claim 13 wherein during step i) the first fluid composition  
10 is heated to a temperature of not more than 74°C.

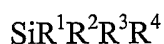
20. The method of claim 13 wherein during step iii) the second fluid composition is heated to a temperature of not more than 74°C.

15

21. A method of making a device having a passivated metal surface, the method comprising the steps of:

i) exposing a metal surface to a silicon-containing compound selected from the group consisting of compounds within the general formula:

20

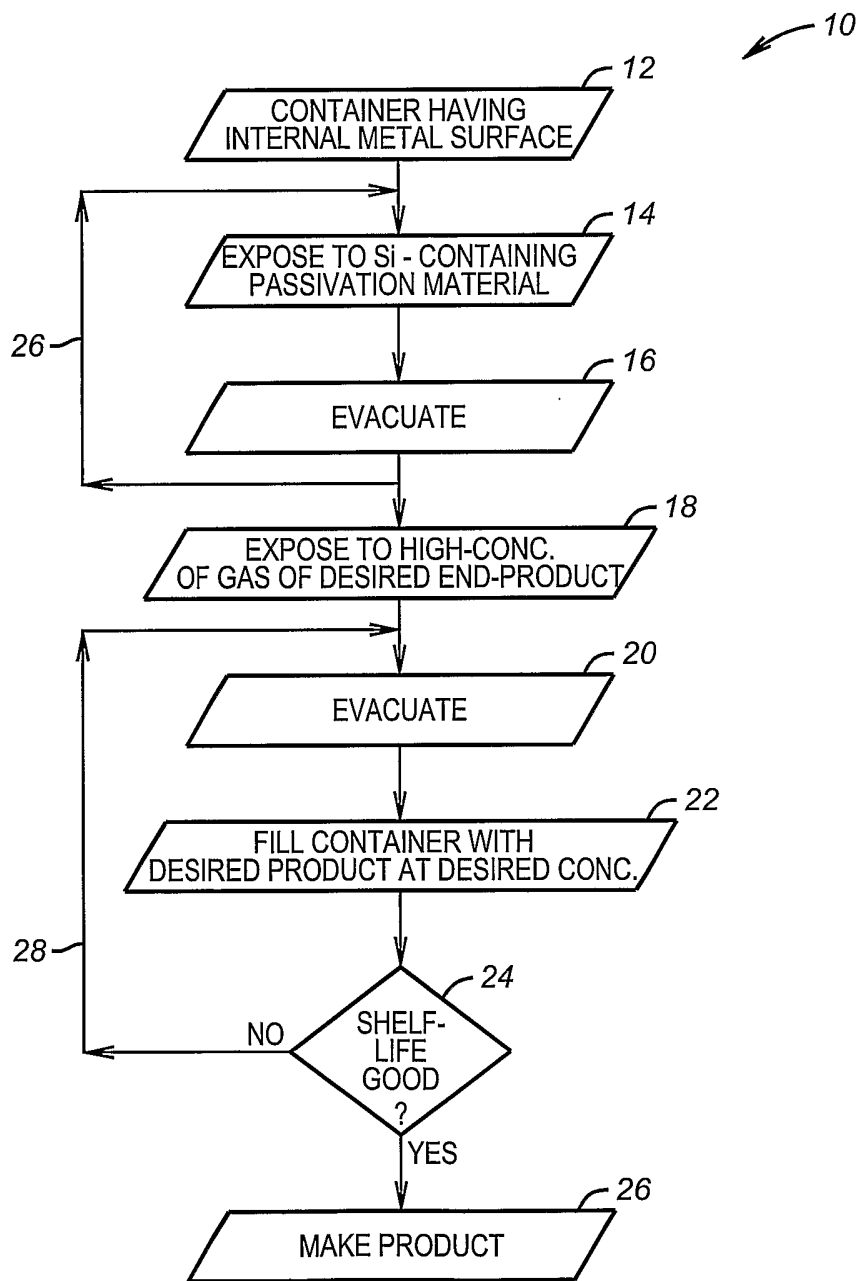


wherein R1, R2, R3, and R4 are independently selected from the group consisting of hydrogen, halogen, amine, alkyl, aryl, halogenated alkyl, and halogenated aryl, for a  
25 time sufficient to form a silicon treated surface on at least some of the metal surface;

ii) evacuating the metal surface for a time sufficient to remove silicon-containing material that has not reacted with oxygen-containing compounds to form a silicon-treated surface;

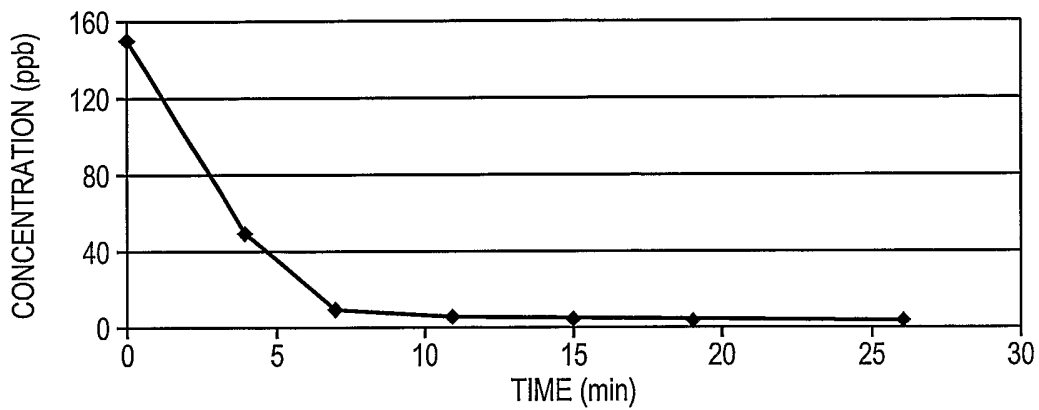
iii) exposing the silicon-treated surface to a gas composition, the gas  
30 composition having a concentration of reactive gas that is greater than an intended reactive gas concentration of gas to be transported by the metal surface; and

iv) evacuating the silicon-treated surface for a time sufficient to remove substantially all of said gas composition and thus form a passivated metal surface. A

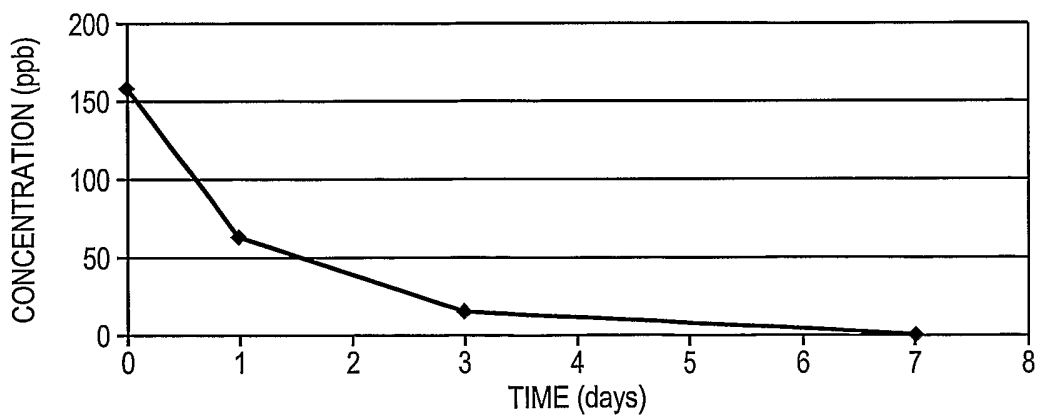


**FIG. 1**

2/3

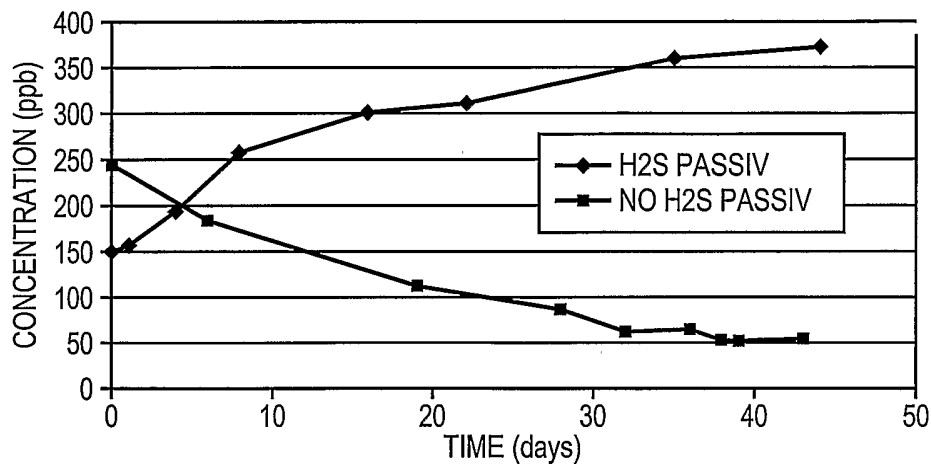


**FIG. 2**

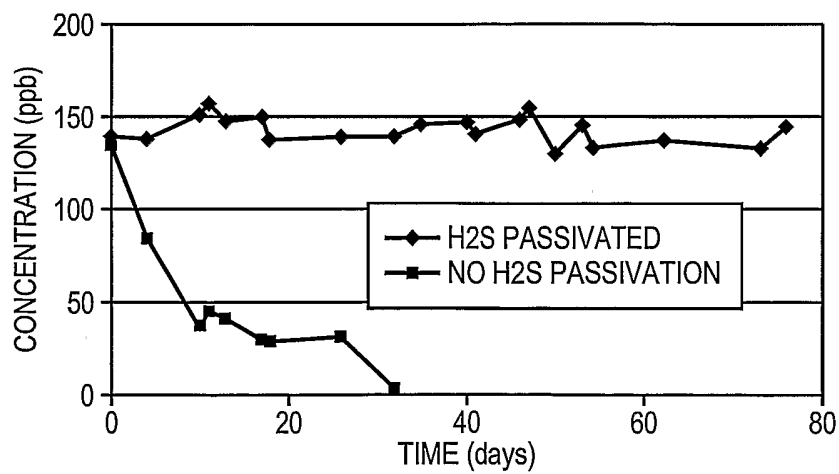


**FIG. 3**





**FIG. 4**



**FIG. 5**