PLASMA DRYING AND PASSIVATION OF COMPRESSED GAS CYLINDERS

FIELD OF THE INVENTION

The present invention provides for a process for cleaning and passivating a compressed gas cylinder using a cleaning gas and a power supply to create a plasma in the cylinder.

BACKGROUND OF THE INVENTION

The cleanliness standards for gases continue to rise yearly. This is particularly true for those gases used in the electronics industry. The delivery systems for these gases are primarily gas cylinders and the focus is primarily upon gas cylinder cleaning and preparation.

Moisture contamination is a major source of contamination of clean electronic gases. Cylinder bake-out is employed in vacuum to remove residual water and is currently the last cleaning step employed in present cleaning procedures. The water removal by bake-out to very low water vapor pressures requires a long time, typically 2 to 3 hours. This adds to the expense of cylinder cleaning as higher concentrations of water will require longer bake-out times at higher temperatures.

After the bake-out step, post-treatment cleaning is performed. This is typically passivation of the interior surface of the gas cylinder with a reactive gas. Again this adds to the expense of cleaning and preparing the cylinders for use.

The present inventors have discovered that the use of a plasma generated inside the gas cylinder provides improved removal of moisture. The further

backfilling with an inert gas eliminates the need for additional treatment and aids in reducing the loss of cleaning and preparing gas cylinders for use in the electronics gas industry.

SUMMARY OF THE INVENTION

The present invention provides for a process for plasma drying and for passivation of compressed gas cylinders which have been discharged of their appropriate gas. The process comprises applying a plasma gas to the inside of the cylinder to be cleaned and applying a current to the gas for a time sufficient to clean and/or passivate the interior cylinder surface. The process further comprises the steps of connecting the empty cylinder to a flange which has a center opening which allows for insertion of a metal tube through the flange and into the cylinder; connecting a vacuum source to the flange; attaching a source of plasma gas to the metal tube; inserting an anode electrode through said metal tube and connecting a power supply to the anode electrode; starting the flow of plasma gas into the cylinder and applying current to the anode electrode; continuing the flow of gas and current until the cylinder is free of moisture.

This process offers advantages over the traditional bake-out method of drying a cylinder. Since the plasma concentrates on the surface of the cylinder, as opposed to heating the bulk of the cylinder, it is a more efficient process. Additional energy can be supplied to the surface by bombarding molecules such as argon or by using chemical reactions such as with hydrogen in removing the oxides on the surface. This chemistry cannot occur using a bake-out process.

By using DC or AC type plasma methods, customized plasmas can be designed to remove specific impurities, as opposed to a bake-out process which can only remove volatile impurities. For example, organics can be removed by oxygen plasma and hydrogen or fluorine plasmas can remove oxygen. Further, the metal

surface can be sputtered away to expose a fresh surface of metal which cannot be done in a bake-out process.

Further efficiencies are realized in that a plasma system can operate around 1 torr while vacuum levels during bake-out need to be on the order of 10^{-4} torr to remove moisture. The steady flow of the high purity gas through the cylinder from top to bottom allows impurities to be swept effectively from the cylinder and accelerates cleaning.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 represents an overview of the plasma gas process.

Fig. 2 is a graph of amount of water present versus time for plasma treatment of a cylinder and bake-out treatment of a cylinder.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A plasma treatment system 1 is described in further detail. A pump package 10 connects through a valve 11 to a tube 12. This tube connects to control valve 20. This control valve is suitably sized to handle flow rates and pressures encountered in the process. The control valve 20 attaches to tube 21 which connects flange 22 to a four-way cross 23.

The cylinder 70 that is to be dried and/or passivated connects via a flange assembly 80 to the four-way cross assembly 23. When the flange is engaged to the cylinder, a vacuum can be drawn on the cylinder. Typically, a vacuum in the range of 10 torr to about 0.1 torr is employed in the drying and for passivation of the cylinder.

An anode electrode 60 is introduced through the vacuum feed-through flange 24 and through the flange assembly 80 into the cylinder 70. An insulator 50 surrounds the anode electrode within the four-way cross assembly 23 so that no plasma energy is released within the four-way valve assembly.

Vacuum feed-throughs 30 and 31 attach to the anode electrode 60 so as to electrically isolate the anode electrode from the entire plasma treatment systems and the gas feed tube 33. The plasma power supply 90 which can be either AC or DC connects to the anode electrode at 91 and to the four-way cross assembly at 92. Connection can be made by a clamping device or soldering of the power leads to the respective connection points.

Feed tube 33 connects to the anode electrode at fitting 32. The feed tube 33 further connects to a valve 40 which connects via line 41 to the gas supply Mass Flow Controller (MFC) 42. Feed tube 33 also connects to manifold 43 which connects to tube 44 which connects further with valve 46 and further through line 47 to the gas supply MFC 48. Several other feed gas supply lines can be connected to this manifold in a like manner. The gas cylinder will typically contain a gas selected from the group consisting of argon, helium, hydrogen, nitrogen, oxygen, neon, krypton or mixtures thereof. The gases that can be employed as the plasma gas include but are not limited to oxygen, hydrogen bromide, bromine, chlorine, ClF_3, nitrogen trifluoride, freons, sulfur hexafluoride, BCl_3, HCl and mixtures thereof.

The plasma treatment system operates by establishing a vacuum in the system and a flow of the plasma gas into the cylinder. The power is then supplied to the anode electrode and a plasma is created within the cylinder. The plasma can be controlled to provide a variety of conditions. For example, argon can be employed and a sputtering condition created so that the cylinder is bombarded with inert atoms to clean off specific impurities. Other conditions can be created where the surface of the cylinder is chemically modified by the introduction of NF_3, hydrogen bromide,

bromine, chlorine, BCl_3 or other reactive gases to chemically convert the surface of the cylinder to a chemical condition appropriate for the gas to be placed in the cylinder later. Typically, flow rates for these gases into the center of the tube ranges from about 0.5 to about 5.0 slm.

In one embodiment of the described process, a fiber optic probe 100 is employed to look at the emissions coming from the plasma in the cylinder. The spectrum of this emission can be analyzed to look for the presence of moisture and other gases being generated during the plasma process and to monitor the progress of the passivation and/or drying of the cylinder using the spectrum analyzer 110. Based on the spectrum analyzer data, once a specific condition has been achieved, the plasma process can be discontinued.

In another implementation of the process, the low pressure exhaust gas from the process is passed through an FT-IR, moisture analyzer, laser ringdown analyzer, tunable diode laser analyzer, Residual Gas Analyzer (RGA), intracavity laser analyzer or other spectroscopic analyzer before going to the pumping system and the progress and completion of the drying and/or passivation process is determined based on this spectral information.

An experiment was performed with the plasma process using argon for the removal of moisture from cylinders. 400 cc per minute of argon were passed through the system and the vacuum pump established a 1 torr pressure in the cylinder. Plasma was struck using a DC plasma power supply with 2.5 ampere and 250 volt settings. The plasma process was operated for approximately 2 hours on the cylinder.

Once the plasma was completed, the cylinder was then filled with high purity nitrogen at a rate of one liter per minute. An Atmospheric Pressure Ionization Mass Spectrometer (APIMS) was used to measure the moisture levels coming from the cylinder. Comparatively, a cylinder was baked-out using a turbo molecular vacuum

pump and a heating blanket at a temperature of 130° F and 10^{-6} torr pressure and the moisture levels of dry N2 passing through the cylinder were checked with the APIMS.

The cylinder cleaning and test protocol that was employed for both the plasma cleaning and bake-out cleaning is outlined below. Those steps designated with an "a" are for the plasma and those steps designated with a "b" are for the bake-out.

1. Cylinder dried to 10 ppb with 2 slm N_2
2. Evacuated briefly with a roots blower for 15 seconds at 2 mTorr
3. Filled with wet N_2 (dew point 3.4C = 7700 ppm H_2O) to 800 torr and let sit for 1 hour
4. Evacuated briefly

5a. Filled and maintained with Ar at 1 torr and 200 sccm

5b. Pumping switched to turbo pump

6a. Plasma treated for 2 hours

6b. Heated to 110° C and held for 2 hours

7a. Evacuated briefly

7b. Pumping switched to roots blower

8. Filled with dry N_2 to 800 torr
9. Evacuated briefly
10. Filled with dry N_2 to 900 torr
11. Maintained at 900 torr and 2 slm N_2 stream analyzed by APIMS

Fig. 2 shows that the moisture leaving the cylinder after plasma treatment was considerably lower than that of the bake-out treatment. As seen in Fig. 2, the amount of moisture coming out of the plasma process treated cylinder was less than one tenth the total amount of moisture coming out of the baked-out cylinder. The dry-out curve was also much steeper for the plasma process, which indicates that residual moisture was depleted in the cylinder treated by the plasma process much more rapidly.

Based on the treatment times for the two processes, the plasma process produced a much lower moisture level. It is anticipated that a shorter period of time using the plasma process would be sufficient for removing significant levels of moisture compared to the bake-out process.

Once the plasma process is completed, the system is back-filled with an ultra-dry inert gas to ensure that the modified chemistry is not affected by the introduction of air. The valve is inserted into the neck by several possible means. A glove box can be attached to the system to allow for insertion of the valve under an inert environment. A mechanical manipulator within the vacuum system can be used to insert the valve and/or inert gas environment can be established around the exit of the cylinder so that a valve can be inserted externally while maintaining the purity of the cylinder's contents. Once a valve is inserted, it will be tightened by standard means and subject to standard leak test procedures. The cylinder is then fully removed and is ready for filling with an appropriate gas.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

CLAIMS:

1. A process for drying a compressed gas cylinder comprising introducing a gas into said cylinder and applying a current to said gas to create a plasma in the cylinder for a sufficient time to remove any moisture from said cylinder.

2. The process as claimed in claim 1 wherein said gas is selected from the group consisting of argon, helium, hydrogen, nitrogen, oxygen, neon, krypton or mixtures thereof.

3. The process as claimed in claim 1 wherein said current is alternating or direct.

4. The process as claimed in claim 1 wherein said cylinder is under vacuum.

5. The process as claimed in claim 1 wherein the flow rate of said gas ranges from about 0.5 slm to about 5.0 slm.

6. The process as claimed in claim 1 wherein said cylinder is back-filled with an inert gas subsequent to the removal of moisture.

7. The process as claimed in claim 1 further comprising passivating the interior surface of said cylinder.

8. The process as claimed in claim 7 wherein said passivating is performed with a gas selected from the group consisting of oxygen, hydrogen bromide, bromine, chlorine, ClF_3, nitrogen trifluoride, freon, sulfur hexachloride, BCl_3, HCl or mixtures thereof.

9. The process as claimed in claim 1 further comprising sputtering the interior surface of said cylinder.

10. A process for plasma drying a compressed gas cylinder comprising the steps of:

a) connecting said cylinder to a flange having a center opening;

b) inserting a metal tube through said central opening and into said cylinder;

c) connecting a vacuum source to said flange;

d) inserting an anode electrode through said metal tube;

e) connecting a power supply to said anode electrode;

f) starting a flow of a gas through said metal tube and into said cylinder;

g) applying current to said anode electrode to create a plasma in the cylinder for a time sufficient to remove moisture from said cylinder.

11. The process as claimed in claim 10 wherein said vacuum source provides from about 10 torr to about 0.1 torr vacuum to said cylinder.

12. The process as claimed in claim 10 wherein said vacuum source is a pump.

13. The process as claimed in claim 10 wherein said power supply is direct current or alternating current.

14. The process as claimed in claim 10 wherein said gas is selected from the group consisting of , argon, helium, nitrogen, hydrogen, oxygen, hydrogen bromide, bromine, chlorine, $C1F_3$, nitrogen trifluoride, freon, sulfur hexafluoride, $BC1_3$, neon, krypton and HC1 of combinations thereof.

15. The process as claimed in claim 14 wherein the flow of said gas ranges from about 0.5 to about 5.0 slm.

16. The process as claimed in claim 10 further comprising a spectrum and/or chemical analyzer wherein the exhaust gas from said cylinder is analyzed for moisture content.

17. The process as claimed in claim 10 further comprising and FT-IR, moisture analyzer, laser ringdown analyzer, tunable diode laser analyzer, Residual Gas Analyzer (RGA), intracavity laser analyzer or other spectroscopic analyzer for analyzing the low pressure exhaust gas.

18. A process for passivating a compressed gas cylinder comprising the steps of:

a) connecting said cylinder to a flange having a center opening;

b) inserting a metal tube through said central opening and into said cylinder;

c) connecting a vacuum source to said flange;

d) inserting an anode electrode through said metal tube;

e) connecting a power supply to said anode electrode;

f) starting a flow of a gas through said metal tube and into said cylinder;

g) applying current to said anode electrode to create a plasma in the cylinder for a time sufficient to passivate said cylinder.

19. The process as claimed in claim 18 wherein said vacuum source provides from about 10 torr to about 0.1 torr vacuum to said cylinder.

20. The process as claimed in claim 18 wherein said vacuum source is a pump.

21. The process as claimed in claim 18 wherein said power supply is direct current or alternating current.

22. The process as claimed in claim 18 wherein said gas is selected from the group consisting of , argon, helium, nitrogen, hydrogen, oxygen, hydrogen bromide, bromine, chlorine, $C1F_3$, nitrogen trifluoride, freon, sulfur hexafluoride, $BC1_3$, neon, krypton and HC1 of combinations thereof.

23. The process as claimed in claim 22 wherein the flow of said gas ranges from about 0.5 to about 5.0 slm.

24. The process as claimed in claim 18 further comprising a spectrum and/or chemical analyzer wherein the exhaust gas from said cylinder is analyzed for moisture content.

25. The process as claimed in claim 18 further comprising and FT-IR, moisture analyzer, laser ringdown analyzer, tunable diode laser analyzer, Residual Gas Analyzer (RGA), intracavity laser analyzer or other spectroscopic analyzer for analyzing the low pressure exhaust gas.