

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 824 970 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.02.1998 Bulletin 1998/09

(51) Int Cl.⁶: **B05D 7/22, B05D 7/14**

(21) Application number: **97306321.7**

(22) Date of filing: **19.08.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**

(30) Priority: **19.08.1996 GB 9617368**

(71) Applicant: **AIR PRODUCTS AND CHEMICALS,
INC.
Allentown, PA 18195-1501 (US)**

(72) Inventors:
• **Paterson, Alan John Francis
Crewe, Cheshire CW3 0LB (GB)**

• **Irven, John
High Wycombe,
Buckinghamshire HP15 6JS (GB)**
• **Obadun, Segun Lateef
Birmingham, West Midlands B21 8BU (GB)**

(74) Representative: **Burford, Anthony Frederick
W.H. Beck, Greener & Co.
7 Stone Buildings
Lincoln's Inn
London WC2A 3SZ (GB)**

(54) **Coated gas cylinders**

(57) A gas cylinder is coated on its internal, gas-con-
tacting surface with a polar film-forming polymer, such
as poly(vinyl alcohol), whereby non-polar organic mol-

ecules will not adhere to the polymer film. The coating
greatly increases the stability of gases stored in the cyl-
inder, which is particularly useful in storing gas mixtures
used for gas calibration methods.

EP 0 824 970 A2

Description

The present invention relates to coating gas cylinders to improve the stability of gas mixtures contained therein.

It is known that the concentration of active constituents within a gas cylinder can decay over time. This is a particular problem in the pollution monitoring market, which requires calibration standards of parts per billion concentrations of, for example, benzene, toluene, xylene or oxides of nitrogen or sulphur. This can happen even with aluminium gas cylinders, which are generally regarded as the best available technology. It is understood that this is due to the constituent gases reacting with or sticking to or condensing on the cylinder wall. As health-related information is deduced from analyses taken using calibration mixtures of reactive or condensible gases, it is extremely important for the gas mixtures within the cylinder to be stable and reliable over periods of say six to twenty-four months.

GB-A-2075366 disclosed the use of a layer of an inert water-insoluble organic polymeric material with at least 75% of the layer formed from a monomer containing hydrophilic chemical groups to reduce carbon dioxide bubble nucleation on the internal walls of a container for liquid carbonated beverages. There is no teaching that the coatings would be of use, if applied to the internal surface of a metal gas cylinder, to maintain the standard of a calibration gas mixture within the cylinder. It refers to the use of poly(vinyl alcohol) ("PVA") as a suitable hydrophilic polymer but states that PVA must be insolubilized by, for example, cross-linking before it is suitable for use.

JP-A-55115694 discloses the coating of internal surfaces of gas cylinders with poly(trifluorochloroethylene) ("PCTFE") to stabilize calibration gas mixtures and JP-A-54134070 discloses the coating of the internal surfaces of gas cylinders with a wax also to stabilize calibration gas mixtures. The exemplified waxes are Japan wax, ceresin wax, paraffin wax and silicon wax. PCTFE and the exemplified waxes are hydrophobic and are non-polar (i.e. non-water-wettable) and were used only to prevent contact between the gas and cylinder walls.

The present invention is directed to stabilizing gas mixtures in a gas cylinder and has particular, but not exclusive, application to the storage of calibration gases. It has been found that stability of gas mixtures is significantly improved by coating the internal surfaces of gas cylinders with a film of a polar (i.e. water-wettable) film-forming polymer whereby non-polar organic molecules will not adhere to the polymer film.

According to a first aspect of the present invention, there is provided a metal gas cylinder, the cylinder having an internal, gas-contacting surface coated with a film of a polar film-forming polymer, whereby non-polar organic molecules will not adhere to the polymer film.

For reasons which will be explained below, the polar polymer prevents, or at least tends to inhibit, condensation of polar organic compounds and nitrogen oxides on, or reaction of compounds with, the internal, gas-contacting surface of the cylinder.

Preferably, the polar polymer is water-soluble, whereby it can be applied to the internal cylinder wall by contacting the wall surface with an aqueous solution of the polymer to coat the wall with the solution, and drying the coating to evaporate water from therefrom to leave a film on the wall surface. This process may be repeated to build up a second layer, or even more layers, on the gas-contacting surface.

Preferably, the water-soluble polymer has multiple hydroxyl groups and suitably is a polymer of an alcohol, a glycol, or a polyhydroxyalcohol, for example poly(ethylene glycol) or, especially, (uncrosslinked) PVA.

The metal of the cylinder usually will be aluminium but may be, for example, steel.

The present invention also includes a metal gas cylinder, the cylinder having an internal, gas-contacting surface coated with a film of a polar film-forming polymer, and the cylinder containing a calibration-gas mixture.

The present invention also includes the use of a polar polymer to coat the internal, gas-contacting surface of a gas cylinder in a gas-calibration method.

The following is a description by way of example only and without limitation of a presently preferred embodiment of the invention.

Polyvinyl alcohol ("PVA") having a molecular weight of 25,000 in the form of chips was dissolved in hot water and allowed to cool. It is preferable to make the solution as concentrated as possible as the water has to be dried off later. It was found to be possible to dissolve 15% by weight (w/w) of PVA in water.

A quantity of the cooled solution was poured into a standard high quality aluminium gas cylinder in an amount sufficient to wet the entire internal, gas-contacting surface of the cylinder. A torch was used to inspect the inside of the cylinder to ensure that the whole surface has been fully coated with the solution. The gas cylinder was then be inverted to allow the excess solution to drain off and dry gas gently blown through the gas cylinder in order to evaporate water from the coating. This resulted in a gas cylinder which has a complete polymer film over the whole of its internal, gas-contacting surface.

The whole process may be repeated in order to build up a second coating layer. Of course, further layers may be applied if desired.

Those parts of the gas cylinder valve that are in contact with the gas inside the cylinder were also coated using the same solution. The parts include the base of the valve and the bore which leads to the valve seat.

Gas cylinders coated as described above provide for extremely stable storage of mixtures within the gas cylinder.

This is particularly important where the gas mixture is used in a calibration method and is therefore stored for a considerable period of time.

Without wishing to be bound by any particular theory, it is believed that the present invention derives its improved properties as follows. An uncoated metal cylinder is covered with oxygen atoms at its surface and the surface may be slightly polar, especially if the oxide layer is thin and new. In an untreated cylinder, larger organic molecules such as xylene tend to stick to, or condense on, the surface, thereby reducing the concentration of the molecules in the gas space in the cylinder. The use of a polar polymer coating as proposed in the present invention, and particularly one which has multiple OH groups, causes the organic molecules to be repelled and thus prevents or inhibits the loss of the organic molecules from the gas space in the cylinder.

The benefit obtained with nitric oxide mixtures is attributed to a different mechanism. Nitric oxide mixtures are present in nitrogen because, in air, the nitric oxide reacts to form nitrogen dioxide. However, the problem is that there are still traces of oxygen in nitrogen and the aluminium surface of the gas cylinder can promote a reaction. Nitric oxide can be lost in two ways from an uncoated gas cylinder. In one mechanism, the nitric oxide reacts with gaseous oxygen, in which case the concentration of NO is lowered but the total NO_x remains constant. In the second mechanism, the NO seems to react with the aluminium surface of an aluminium cylinder, but is retained so that the levels of NO and NO_x both fall. In both of these mechanisms, however, the metal surface of the gas cylinder either acts directly or as a catalyst in the mechanism, particularly in the case of an aluminium cylinder. Coating the surface of the cylinder with a substance which is not an oxide allows the concentration of NO to be stabilised.

It is also believed that OH groups can form a useful key to which other reactive compounds such as silanols could attach. This facilitates the provision of water-repellant coatings or other tailor made coatings for particular applications.

The present invention, whilst described above with particular reference to aluminium gas cylinders, can also be applied to gas cylinders of other materials, for example steel.

The results of experiments to determine the effectiveness of standard high quality aluminum gas cylinders having a PVA coating applied as described above compared with identical but uncoated (prior art) cylinders are described in the following two Examples with reference to the data shown in Tables 1 and 2 which follow.

Example 1

In Table 1, the concentrations (ppb) of NO and NO_x in gas mixtures stored the coated cylinders are compared with the concentrations (ppb) of NO and NO_x in gas mixtures from the same source stored in the uncoated cylinders. NO loss in the uncoated cylinders was between 15 and 30% within 2½ months. In contrast, the gas mixture stored in the coated (invention) cylinders was stable to ± 1.5% over a period of up to 1½ years.

TABLE 1 -

Nitric Oxide Mixture Stability			
Nitric Oxide Mixtures in PVA Coated Cylinders			
Cylinder #	Days After Fill	NO Analysis	NO _x Analysis
6732	0	520	520
	6	518	518
	20	520	520
	140	520	520
2413	0	497	not measured
	4	503	not measured
	13	504	503
	164	504	504
	197	494	501
	555	493	494
Nitric Oxide Mixtures in Uncoated Cylinders			
Cylinder #	Days After Fill	NO Analysis	NO _x Analysis
2331	0	520	not measured
	26	422	not measured

TABLE 1 - (continued)

Nitric Oxide Mixture Stability			
Nitric Oxide Mixtures in PVA Coated Cylinders			
Nitric Oxide Mixtures in Uncoated Cylinders			
Cylinder #	Days After Fill	NO Analysis	NO _x Analysis
2333	64	355	not measured
	69	349	349
	0	805	not measured
	7	750	not measured
	29	704	not measured
	58	673	not measured
	67	680	not measured
	72	682	808

Example 2

Hydrocarbons are often unstable and sometimes lost either when transfilled from one cylinder to another or when stored over a long period in a gas cylinder, especially at very low concentration. Component loss could be due to physical absorption onto metal surfaces or through chemical reaction and decomposition. The four hydrocarbons the results for which are shown in Table 2 are chosen to be a fair representation of those that are often stable (e.g. propane) and those that are often unstable (e.g. isoprene and the C₈ and C₉ compounds).

In Table 2, the "Stability Ratio" is the quotient of the chromatographic peak area of a master cylinder component on day 0 and the chromatographic peak area of a target cylinder component on day x. The "Reference Component" is a component that may be regarded as stable (such as propane). The "Normalised Stability Ratio" is the quotient of the Stability Ratio of a component on day x and the stability ratio of the Reference Component on day x. In an ideal cylinder all the values would be 1.00. Because of the decay shown by gas stored in the uncoated cylinders, no further measurements were made for those cylinders after 35 days. However, measurements were made for the coated cylinders for 394 days.

Table 2 - Hydrocarbon Mixture Stability**Hydrocarbon Mixtures in PVA Coated Cylinders**

Cylinder # 2505	NORMALISED STABILITY RATIO					
	DAYS					
	0	34	106	188	272	394
Propane	1.00	1.00	1.00	1.00	1.00	1.00
Methylbenzene	0.99	0.98	0.99	1.00	1.00	0.98
1,3-dimethylbenzene	0.99	0.96	0.98	1.01	0.98	0.99
isoprene	0.97	0.97	0.99	1.00	0.97	0.98
1,2,4-trimethylbenzene	1.03	0.93	0.98	1.04	0.95	1.02

Cylinder # 2503	NORMALISED STABILITY RATIO					
	DAYS					
	0	34	106	188	272	394
Propane	1.00	1.00	1.00	1.00	1.00	1.00
Methylbenzene	0.99	0.99	1.00	1.01	1.01	1.00
1,3-dimethylbenzene	0.98	0.98	0.98	0.99	1.00	0.97
isoprene	0.97	0.98	1.00	1.00	0.97	0.97
1,2,4-trimethylbenzene	0.97	0.97	0.98	0.98	0.99	0.91

Hydrocarbon Mixtures in Uncoated Cylinders

Cylinder # 6981	NORMALISED STABILITY RATIO					
	DAYS					
	0	6	26	35		
Propane	1.00			1.00		
Methylbenzene	0.98			1.01		
1,3-dimethylbenzene	1.01			1.27		
isoprene	1.06			4.21		
1,2,4-trimethylbenzene	1.10			2.63		

Cylinder # 6977	NORMALISED STABILITY RATIO					
	DAYS					
	0	6	26	35		
Propane	1.00	1.00	1.00	1.00		
Methylbenzene	1.50	1.49	1.36	1.21		
1,3-dimethylbenzene	3.62	3.45	2.85	2.18		
isoprene	1.22	1.26	1.48	1.55		
1,2,4-trimethylbenzene	17.53	16.11	10.70	6.97		

The following is clear from the Table 2:

(i) for the coated cylinders, analysis on day 0 is very close to the analysis of the Master Cylinder (i.e. the Normalised Stability Ratio substantially 1.0) whereas, in contrast, several of the unstable components are reduced in transfill (i.e. the Normalised Stability Ratio are greater than 1.05) in otherwise identical uncoated cylinders;

(ii) after 35 days storage, the Normalised Stability Ratio of the unstable components in the uncoated cylinders is substantially greater than it is after 394 days storage in the coated cylinders;

(iii) the measurements for the uncoated cylinders indicate that some unstable components are progressively lost to the wall, whereas others are initially lost but then appear to desorb from the surface back into the gas space; and

(iv) there is no evidence of decay in the coated cylinders of the present invention; the small variations can be accounted for by analytical inaccuracy, since no clear trend can be seen.

It will be appreciated that the invention is not restricted to the particular embodiment described above but the numerous variations and modifications may be made without departing from the scope or spirit of the present invention.

Claims

1. A metal gas cylinder having a coated internal, gas-contacting surface, characterized in that said surface is coated with a film of a polar film-forming polymer, whereby non-polar organic molecules will not adhere to the polymer film.
2. A cylinder as claimed in Claim 1, wherein the polar polymer is water-soluble.
3. A cylinder as claimed in Claim 2, wherein the water-soluble polymer contains multiple hydroxyl groups.
4. A cylinder as claimed in Claim 3, wherein the water-soluble polymer is a polymer of an alcohol, a glycol or a polyhydroxyalcohol.
5. A cylinder as claimed in Claim 4, wherein the polymer is poly(vinyl alcohol).
6. A cylinder as claimed in Claim 4, wherein the polymer is poly(ethylene glycol).
7. A cylinder as claimed in any one of the preceding claims, wherein the gas cylinder is made of aluminium.
8. A cylinder as claimed in any one of Claims 1 to 6, wherein the gas cylinder is made of steel.
9. A cylinder as claimed in any one of the preceding claims containing a calibration gas mixture.
10. A cylinder as claimed in Claim 9, wherein the gas mixture contains calibrated trace amounts of nitric oxide.
11. A cylinder as claimed in Claim 9, wherein the gas mixture contains trace amounts of hydrocarbons.
12. The use of a polar film-forming polymer to form on an internal gas-contacting surface of a metal gas cylinder a film to which non-polar organic molecules will not adhere to stabilize a gas mixture contained within the cylinder.
13. A use as claimed in Claim 12, wherein the polymer and/or cylinder is as defined in any one of Claims 2 to 8.
14. A use as claimed in Claim 12 or Claim 13, wherein the calibration gas mixture is as defined in Claim 10 or Claim 11.