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Subject: Fill Density for Germane and Nitric Oxide

As discussed at the Specialty Gas Committee meeting June 6, 2005, I have some concerns with the fill densities being proposed for Germane and Nitric Oxide. Due to my travel schedule, I was not able to make the Task Force meeting of March 31, 2005 where this was discussed

The fill densities for both were reduced after incidents which caused a fatality and serious injuries when the cylinders ruptured due to a decomposition reaction. Both gases had subsequent incidents.

Germane

Matheson manufactured and filled pure Germane for many years to a density of 0.227 kg/liter. On Nov. 26, 1984, a 44 liter cylinder filled to 10 kg ruptured violently as a worker at the Nippon Sanso Kawasaki Japan facility was removing it from the delivery truck. He and a second worker were seriously injured. This cylinder was shipped from the Matheson, Gloucester, MA facility.

Hazards Research Corporation was contracted by Matheson to test pure Germane. They determined that pure germane can deflagrate when ignited with a spark in the absence of air, decomposing to Ge metal and hydrogen, exothermically. It is estimated that the cylinder reached a pressure >9000 psig in 100 milliseconds. Immediately after this report, Matheson changed the fill density to 0.062 kg/lter based on theoretical calculations assuming full adiabatic decomposition and the test pressure of the cylinder.

Additional testing by Hazards Research in 1986 for Voltaix Inc and Horiguchi, Urano and Kondo

- **"Decomposition explosion hazards of semiconductor manufacturing gases"**, *Journal of High Pressure Gas Safety Institute of Japan*, 28(3), pg 270-284, 1991
- **"Decomposition explosion hazards of semiconductor manufacturing gases"**, *Journal of High Pressure Gas Safety Institute of Japan*, 28(5), pg 351-363, 1991

confirmed that pure Germane will deflagrate. They also determined that mixing the Germane with a high concentration of Helium or Hydrogen would reduce the hazard by reducing the propagation. At high enough concentrations it will eliminate it.

One test by Horiguchi at a fill density of 0.225 kg/liter had a pressure increase to 9775 psig confirming the earlier theoretical calculations.

Based on this testing Voltaix Inc. established a maximum fill density of 0.045 kg/liter assuming the working pressure of the cylinder.

T. Hirano in his article **"Accidental explosions of semicondcutor manufacturing gases in Japan"**, Journal of Loss Prevention in the Process Industries, 17, pg 29-34, 2004 (see attached) reported a second Germane explosion in a process collector in Japan. The company and date of the incident was not given.

Nitric Oxide

At the Matheson Nitric Oxide manufacturing facility in East Rutherford facility lecture bottles were filled directly from a source cylinder pressurized to 800 psig. On Feb 1, 1963 when the valve to the 44 liter source cylinder was opened it violently ruptured killing the operator. The investigation determined that the lecture bottle valve was not open which caused the gas in the small volume to heat up significantly from the rapid compression. This may have ignited some oil contamination in the valve/line. This was enough energy for the Nitric Oxide decomposition to be initiated. It propagated back into the source cylinder, rupturing it into 4 pieces.

The Matheson investigation highlighted DuPont test data (do not have report) that reported theoretical decomposition of Nitric Oxide can cause a 15 fold increase in pressure. The decomposition reaction however requires significant energy to initiate it. A blasting cap triggered the decomposition in a test cylinder which had a 12 fold pressure increase. At the 800 psig fill pressure the final pressure in the source cylinder may have reached 9600 psig.

As a result of this incident, Matheson reduced the fill pressure to 500 psig (max decomposition pressure of 6000 psig). With one exception, the other gas suppliers have follow this limitation.

On Oct 9, 1972, Big Three Industries (now Air Liquide) had a similar incident except at a considerably lower pressure of 200 psig. The cylinder and the system contained the pressure of 2400 psig.

I hope that this answers the question as to what the safe maximum fill should be for Germane and Nitric Oxide.

I have not had the time to investigate the other exceptions in the proposed table but will do so over the next month.

I'm sorry that I cannot make the meeting in Germany to participate but am on the way to Taiwan.

Sincerely,

Eugene Ngai
Dir. Of ER & Disposal Technology