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Solkatronic Chemicals Silane CG-4 PRD Incidents

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To: CGA G-13 Task Force

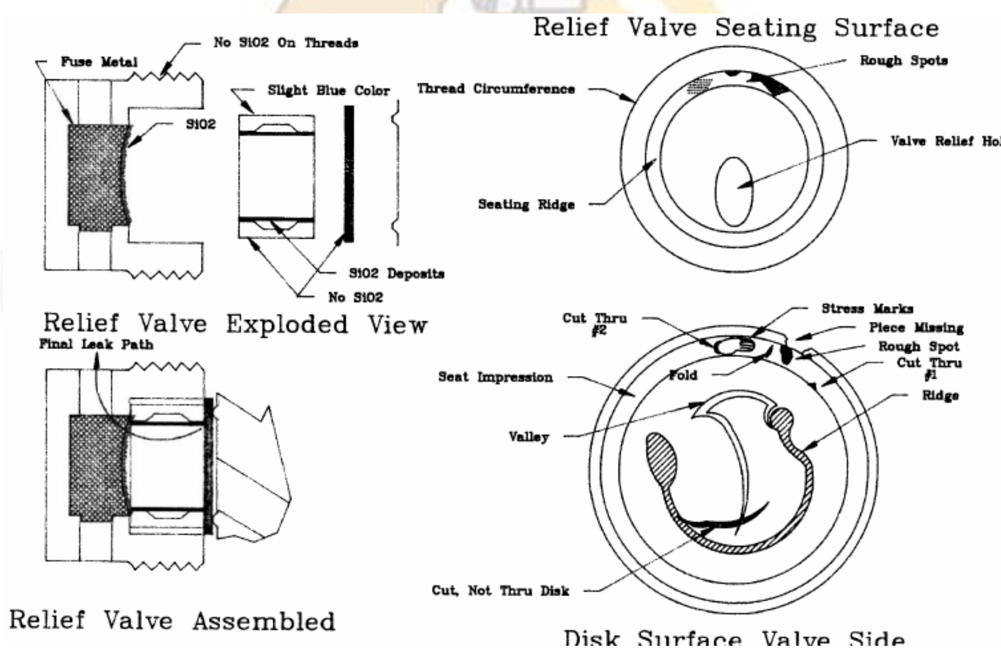
The following is a summary of CG-4 PRD incidents involving silane and other gases which I investigated in the period between 1987-1999 for Solkatronic Chemicals Inc. Neither PRD design is similar to what is used today for bulk silane packages

Pure Silane Cylinder PRD Leak, 1989 (New Pneumatic Valve Design)

On April 17, 1989 a pure silane cylinder at a customer site in Phoenix, AZ started to leak at the PRD when the valve shrink wrap was removed. This ignited, producing a small flame. The site ER team quickly vented and inerted the cylinder. This was a new cylinder and valve that was filled on Jan 13, 1989. The valve was a pneumatic valve which was of a new design. It had a unique PRD assembly which compressed the metal rupture disk against a polished bead (seating ridge) machined into the valve body.

This valve was taken apart at the valve manufacturer and visually examined. It was concluded by the investigation team that the polished bead was poorly polished and inspected. As the rupture disk was being compressed against the valve body, the disk rotated against this rough surface causing 2 tears. The fuse metal held back any gas leakage for a number of months. It started to cold flow and slowly pushed the fuse metal out of the PRD collar and then continued extruding at the vent holes until it started to leak.

Other valves from this batch were removed from other filled silane cylinders and examined, none had the same bead damage. The valve manufacturer modified his design and inspection procedures and there were no further PRD problems. This valve design is no longer being made.



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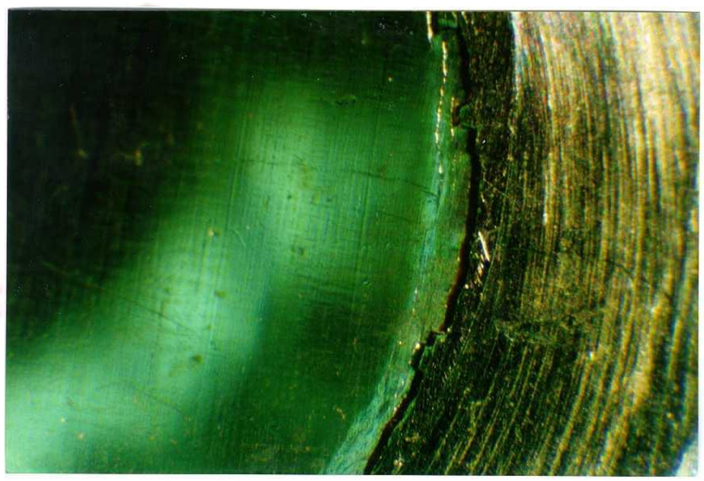
20% Silane/Hydrogen Fire 1998 (As reported at 1998 CGA Specialty Gas Safety Seminar)

24 new cylinders and valves were filled on August 1991 with a 20% silane/hydrogen mixture. 5 were never used and returned by the customer to Morrisville, PA where they were stored on an open dock. On July 6, 1998 one of these cylinders was reported to be smoking at the cylinder cap. This quickly developed a 6” flame at the cylinder cap vent hole. As the ER team approached the cylinder 10 minutes later, the PRD fully activated, releasing the contents of the cylinder in <2 minutes. The flames impinged on 2 adjacent cylinders and the dock roof. It did not cause any other cylinders to leak. The PRD was removed from the cylinder and a visual inspection revealed that the rupture disk had fully ruptured

This was a manual valve was made by a different valve manufacturer. It had a CG-4 PRD which consisted of a Platinum clad copper rupture disk and 165ºF fuse metal. The other 4 cylinders were immediately vented and the valves taken apart for visual inspection. One cylinder was found to be empty, a visual inspection revealed that the rupture disk was fully cracked through (see picture). Other than extruded fuse metal, there was no other visual



evidence of a leak, e.g. SiO_2, fire damage. A second cylinder also had a crack through the rupture disk and the fuse metal was extruded but it had not started to leak. The remaining 2 had cracks only in the platinum layer.

This caused a further examination of all cylinders with CG-4 PRD’s at the Morrisville, PA and Lone Butte, AZ facilities, with the following results

Silane and Mixtures

A number of PRDs in Mixture and Pure service had cracks fully through the rupture disk. Many others had a crack only in the platinum layer

Disilane Mixture

55 ppm Disilane/Hydrogen crack in platinum layer and extruded fuse metal

10% Disilane/Helium mixture had no evidence of a crack

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Diborane mixtures

3 Diborane mixture leaks at customer sites which triggered emergency responses in 1993 & 1995 were all examined by the valve manufacturer. All had extruded fuse metal (see picture) and fully cracked rupture disks. The engineering report suggested that the cause of the cracks was due to fatigue.

4 Diborane/Hydrogen mixture cylinders had a crack only in the platinum layer.

2 Diborane/Silane mixture cylinders had no evidence of cracks

Hydrogen Chloride

No PRD in pure HCl service had cracks

1 of 2 cylinders in HCl/Hydrogen mixture service had a crack in the platinum layer

Hydrogen

Only 2 cylinders filled with pure hydrogen used a stainless steel valve with a platinum clad copper PRD. Most had the traditional bronze rupture disks. The 2 platinum clad PRD's had a crack in the platinum layer.

Hydrogen Sulfide

3 Hydrogen Sulfide/Hydrogen mixture PRDs were inspected. Two were cracked fully through the rupture disk and had extruded fuse metal. One was cracked only in the platinum layer. A valve manufacturer conducted testing in 1988 which demonstrated the potential for corrosive attack by Hydrogen Chloride or Hydrogen Sulfide of the platinum clad copper disk, recommending that other metals should be used in this service.

Boron Trifluoride and Silicon Tetrafluoride

Neither BF_3 or SiF_4 PRDs had cracks in the rupture disk. There was however a subsequent problem in 2000 with the use of a stainless steel rupture disk in BF_3 service. 4 cylinders developed leaks at a customer site. These were inspected by the valve supplier and determined to have stress cracking due to corrosive attack of the stainless steel.

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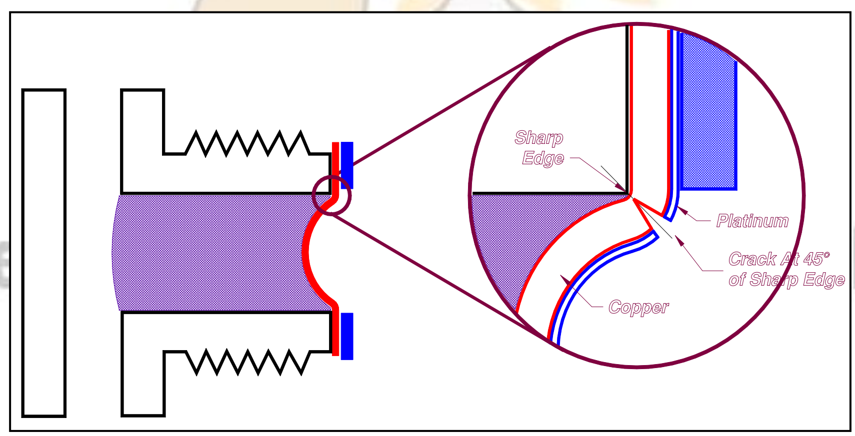
A further review of all prior ER incidents revealed that besides the 3 Diborane mixture leaks reported above, there were also a Disilane mixture and a 2% silane/Hydrogen in 1995 that were leaking at the PRD at a customer site. These triggered an emergency response. Based on the findings above, these were also likely to have been caused by a fully cracked rupture disk.

Discussion

Based on the tests, analysis and discussions with materials and valve experts, it is believed that the leaks have occurred due to an unusual combination of factors, all of which had to occur at the same time for the leaks to develop. In outdoor storage or during shipment in a closed cargo container, a cylinder can experience significant temperature changes from night to day of >60ºF. Testing has shown that cylinder skin temperatures in the summer if exposed directly to the sun can reach 150ºF. This in turn will cause significant pressure swings in a full cylinder. In the extreme case of a pure Silane filled to the industry fill density of 0.313 kg/l, the pressure swing can be approximately 1000 psig. This change in pressure flexes the rupture disk against the sharp edge of the PRD. (see figure)

It has been theorized that crasking is occurring as a result of hydrogen migrating into the platinum layer. One company during their investigation found evidence of embrittlement of the Pt-Cu alloy by hydrogen. They theorize that the platinum was cracking the metal hydride gas or hydrogen to form atomic hydrogen which diffuses thru the platinum layer and embrittles the alloy (Pt-Cu) in the middle of the disk.

With the repeated flexing that can occur over a period of a few years, the disk will start to crack. Based on discussions with a valve expert, cracks if they are to initiate will occur immediately above the discontinuity caused by the sharp edge of the housing. SEM scans indicate that the crack was at a 45º angle to the initiation point, which is indicative of tension failure around a sharp edge. The bond of the Platinum to the Copper is so strong that the crack will continue to propagate into the Copper bottom layer with time.



With the corrosive gases such as Hydrogen Sulfide, Hydrogen Chloride and Hydrogen Selenide, once the platinum layer cracks the gas will immediately attack the copper, penetrating the copper layer fairly quickly. It has been reported that this could be as short as a few days. With the non-corrosive gases such as silane, the flexing will continue and the crack will continue to grow until it completely breaks through the rupture disk. Many PRDs had the beginnings of a crack which would have fully cracked the rupture disk in time.

The fuse metal will hold back the gas pressure for some period of time but will start to cold flow of the pressure is >500 psig. Bench testing of a typical 165ºF fuse metal by a valve manufacturer has demonstrated that it can take over 100 hours at a pressure of 2000 psig to push the fuse metal far enough before it starts to leak at even at a temperature of 120ºF.

Based on our findings, we initiated a worldwide recall for all cylinders with platinum clad copper CG4 devices containing metal hydride gases or as a hydrogen mixture. We also immediately alerted the CGA community to the problem by filing an incident report and asked to make a last minute presentation at the 1998 CGA Specialty Gas Safety Seminar about the incident and findings

Other Gas Supplier Experience

After my 1998 CGA presentation, a number of the gas suppliers provided me with information that suggested that they had experienced a similar problem. All have changed from the platinum clad copper disk to stainless steel or nickel

One supplier in 1993 had a release similar to the Morrisville event at a US location. They had a second one outside of the US shortly after. Their metallurgist indicated that the problem was due to a convergence of a number of factors which caused the disc to mechanically fail. The primary causes due to the repeated flexing of the disc due to high differential pressures caused by daily temperature swings between night and day and bending against a sharp edge.

One supplier did a spot check of returned cylinders. A disilane cylinder had a diaphragm crack 180º around but did not leak because of the low vapor pressure. It was significantly less than the 500 psig required for fuse metal to cold flow. It was filled 10 years earlier.

One supplier in May of 1993 had a full 49 liter cylinder containing a 23% Silane/Hydrogen mixture completely leak through the PRD at a US facility. The flames impinged on adjacent cylinders triggering the release from two additional cylinders

One supplier had two major Silane fires in the US involving multiple cylinders of pure silane stored outdoors. It is believed that at least one was caused by a Pt clad copper PRD

One supplier had 6 cylinders of Hydrogen leak from the PRD at a customer site. They all had a platinum clad copper PRD and were in service for 18 months. In January 1998 they initiated a worldwide recall for these cylinders numbering in the thousands. They also had a number of cylinders in Hydrogen Selenide mixture service leak in the early 1980's. They attributed this to corrosive attack of the copper, similar to the Hydrogen Sulfide problem described above.

One supplier had a 12 kg cylinder of silane cylinder fully vent from the PRD on the loading dock. I have seen a spectacular picture of this with 5-6' flames from the top of the cylinder. This happened in the early 1980's or late 1970's and was probably a brass valve. The PRD material is unknown.

Since the platinum clad copper rupture disks were replaced in 1998 with other metal types, I am not aware of any additional issues with CG-4 devices however my involvement with valves and PRD's has been limited since 1999 when my responsibilities were transferred into other groups within the AP Electronics Division.

Eugene Y. Ngai