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PHOSPHORUS TRIFLUORIDE CYLINDER FAILURE

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Printed in the United States of America. Available from Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

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Date of Issue: April 3, 1969

Report Number: K-1772

Subject Category: Health
and Safety

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A B S T R A C T

A mild steel, high pressure gas cylinder containing phosphorus trifluoride failed in storage about 15 months after filling. Microscopic and metallographic examinations of the failed cylinder have shown the failure to have probably been the result of stress corrosion of the mild steel. The similarity to failure of carbon monoxide gas cylinders is pointed out. Specific recommendations for future use and storage of phosphorus trifluoride cylinders are presented. These include among others limiting the filling pressure to less than 1000 psia and a maximum period of storage not to exceed one year.

PHOSPHORUS TRIFLUORIDE CYLINDER FAILURE

On the morning of September 23, 1968 a small leak was discovered in the wall of a high pressure gas cylinder containing phosphorus trifluoride, PF_3 . Since PF_3 is a highly toxic material with a maximum allowable concentration in air of $\frac{1}{2}$ ppm, the cylinder was placed in a bucket which was then packed with soda lime to react with the phosphorus trifluoride. Later the packed bucket containing the cylinder was moved to the pier of the Hazardous Material Disposal Facility while arrangements were being made for the safe disposal of the material. Shortly after being moved, billows of white smoke, presumably hydrolyzed PF_3 , were observed coming from the cylinder and bucket, indicating that the leak had increased greatly in size. Arrangements were then made through the Shift Superintendent's Office with the Guard Department to put a bullet hole in the cylinder; this was done on September 25, 1968. Only a small amount of gas was released by the bullet penetration, indicating that most of the PF_3 had escaped previously through the leak. The cylinder was then dropped into the holding pond. On October 3, 1968 the cylinder was retrieved for examination after having been under water for a period of about 8 days.

The cylinder, which originally contained five pounds of PF_3 , was received on July 25, 1967. The vendor had indicated that the PF_3 was contaminated by appreciable amounts of phosphorus pentafluoride, PF_5 , and phosphorus oxytrifluoride, POF_3 . Calculations indicate that the pressure must have been in excess of 2000 psia. The gas was employed in experimental studies in December, 1967, but the quantity used would not have reduced the cylinder pressure significantly. The cylinder was then placed in a metal storage box on the back porch of building K-1006 where it remained until the leak was discovered.

Cylinder Examination

Following recovery of the cylinder from the holding pond, it was leak tested to determine the exact location of the leak. Figure 1 is a photograph of the cylinder; the leak was located within the chalk rectangle. The large hole was the result of shooting the cylinder, as described above. The leak is clearly visible in the photograph shown in figure 2, where air bubbles are seen to form along the leak when a slight positive pressure (less than 1 psig) was applied to the cylinder and water was applied to the leaking area.

The cylinder was then sectioned through the leak, and the light micrographs shown in figures 3 and 4 were obtained; the inside surface of the cylinder is at the top of each figure. Figure 3 is a cross section of the leak itself at 50X magnification. The large cracks have the characteristic jagged pattern of intergranular cracking, which, in turn, is characteristic of stress corrosion cracking. Many smaller cracks could be seen near the inner surface of the cylinder; two of these are clearly

Figure 1

PHOSPHORUS TRIFLUORIDE GAS CYLINDER WITH
LOCATION OF LEAK INDICATED

Figure 2

AIR BUBBLES SHOWING LEAK IN PHOSPHORUS TRIFLUORIDE CYLINDER

Figure 3

CROSS SECTION OF CYLINDER WALL SHOWING CRACK THROUGH
WHICH LEAK OCCURRED (50X)

Figure 4

SMALL CRACK ON INNER SURFACE OF CYLINDER (500X)

visible in figure 3. One of these smaller cracks is shown in figure 4, magnified 500X. The intergranular nature of the cracking is even more apparent, again indicative of stress corrosion cracking.

Samples of the cylinder wall were deliberately fractured, with the fracture occurring at the weakest point, i.e., at one of the sites where a small crack had begun to form. A scanning electron micrograph of such a fracture is shown in figure 5 at a magnification of 100X. The light area at the top of the figure is the inner surface of the cylinder, while the gray area is the wall of the fracture. Two areas can be identified on the fracture wall. Near the surface is a rough, oxidized area, apparently the wall of a crack which was already present in the cylinder, similar to those shown in the preceding light micrographs. The remainder of the fracture wall has the pattern characteristic of a ductile fracture and is attributed to the newly, intentionally fractured area. The wall of the old crack is shown in figure 6, which is a scanning electron micrograph at a magnification of 1000X. The metal grains are clearly visible, again indicating the brittle or intergranular nature of the crack, characteristic of stress corrosion cracking.

The area around one of the small cracks was examined by electron probe analysis in an attempt to identify the corroding agent and/or corrosion products. The cylinder metal was apparently the usual mild steel containing chromium and manganese. No phosphorus or fluorides could be detected. This was probably due to the fact that the cylinder had been in water, and as a result of hydrolysis and dissolution, compounds containing the elements phosphorus and fluorine no longer remained on the surface.

Conclusion and Recommendations

The main crack in the cylinder through which the leak occurred, and many smaller cracks on the inner surface of the cylinder, have been found to be intergranular in nature, strongly indicative that the cylinder failure was caused by stress corrosion cracking.

Carbon monoxide is known to cause failure of gas cylinders by stress corrosion cracking, especially at pressures of 2000 psig and in the presence of impurities such as moisture and/or sulfides. It has also been suggested that carbon monoxide directly attacks the iron with the formation of iron pentacarbonyl, $\text{Fe}(\text{CO})_5$. Phosphorus trifluoride has an electronic structure similar to that of carbon monoxide and therefore would be expected to enter into similar chemical reactions. It is therefore recommended that precautions similar to those currently employed with carbon monoxide cylinders be observed in any future employment of phosphorus trifluoride cylinders. These include the following specific recommendations:

Figure 5

SCANNING ELECTRON MICROGRAPH OF CYLINDER FRACTURE (100X)

Figure 6

SCANNING ELECTRON MICROGRAPH OF WALL OF CYLINDER CRACK (1000X)

1. The phosphorus trifluoride pressure should not exceed 1000 psia.
2. The phosphorus trifluoride should be as free of impurities as possible, since impurities can promote stress corrosion.
3. Phosphorus trifluoride cylinders should be kept on hand for the minimum possible time and in no case for greater than one year.
4. If storage is necessary, phosphorus trifluoride cylinders should be kept in a well-marked area away from active work locations and buildings. The cylinder should be stored in a heavy-walled metal container.
5. When in use, phosphorus trifluoride cylinders should be mounted in a well-ventilated box or hood to insure against release of the PF_3 in the working area.