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Hydrocarbon contamination of an air separation plant

Here's a practical example of a safe shutdown, decontamination, and derime of an oxygen unit in an ammonia plant.

A HYDROCARBON CONTAMINATION incident, which occurred in the air separation plant at Dow Chemical of Canada Ltd. in Sarnia, Ont., is the subject of this case study. On January 14th, 1959 an underground propane storage well located 600 ft. south of the ammonia plant overflowed allowing a mixture of propane and propylene with small quantities of other hydrocarbons to vent to atmosphere.

The pilot light arrangement on the vent pipe which was supposed to ignite the mixture under such emergency conditions failed to operate and the hydrocarbon vapors from the resulting spill were directed towards the air intake of the air separation plant by a south wind. This air pollution necessitated the shutdown of the air separation plant for nearly 5½ days in order to safely purge the oxygen and hydrocarbons from the cold box and to carry out a normal derime and start-up.

The first indication the ammonia plant operators had of the spill was the strong odor of hydrocarbons in the atmosphere. Adjacent hydrocarbon plants and plant security guards were immediately requested to try to determine the source of the hydrocarbon spill. As the odor of hydrocarbons became stronger the Johnson Williams gas detectors located on the ceiling above the compressors in the ammonia plant triggered. These detectors are calibrated to sound an alarm when the combustible gas concentration surrounding the detector exceeds 20% of the lower explosive limit. Gas tests with an M.S.A. gas tester in the area immediately to the south of the ammonia plant also gave results of 20 to 30% of the lower explosive limit.

Ammonia plant supervision were advised of the situation and instructions were given to purge the liquid oxygen from the air separation plant immediately and to prepare for a plant shutdown. The plant was completely shut down within 35 min. from the time the odor of hydrocarbons was first noticed by the operators. However, purge of the liquid oxygen from the cold box took several hours as the liquid drained from the trays of the columns. In the meantime, plant security guards had located the source of the spill and appropriate steps were taken to stop it.

Most of the hydrocarbons that had concentrated in the liquid pools in the air separation plant were probably removed when the liquid was drained from the cold box. However, it was felt that there was still sufficient liquid oxygen and possibly liquid or solid hydrocarbons still on the trays of the columns or trapped in low points in the cold box to represent an explosion hazard of considerable magnitude. Several precautionary measures were taken to minimize the possibility of an explosion and to protect personnel. Such measures included:

(a) No work or footwear which would produce static sparking was allowed in the area.
(b) Care was taken in the operation of ferrous purge valves which might have induced internal sparks.
(c) A minimum of personnel was allowed in the area of the cold box following the shutdown and throughout the entire purging operation that followed.

The importance of these precautions was emphasized by an occurrence during the analysis of a sample of liquid oxygen that had been withdrawn from the vaporizer of the air separation plant shortly after the shutdown. An attempt was being made to determine the hydrocarbon content of the sample. During the analytical procedure a small explosion occurred in the glass absorption train of the apparatus as the hydrocarbons that had been in the oxygen were being desorbed from silica gel prior to passing through the combustion furnace which converts the hydrocarbons to carbon dioxide.

The concentration of hydrocarbons in the air used to desorb them from the silica gel apparently exceeded the lower explosive limit and when the mixture reached the furnace it flashed back to the absorption train and exploded. To achieve this concentration

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in the desorbing air the concentration of hydrocarbons in the original liquid oxygen sample must have been extremely high.

Proposed safety plans

The problems and hazards of removing the oxygen and hydrocarbons from the air separation plant were thoroughly discussed before any corrective measures other than draining the liquid oxygen from the cold box were taken. Initially, consideration was given to the purge procedure suggested by other air plants that had undergone hydrocarbon contamination to some degree. Most of these procedures suggested that the equipment located ahead of the air separation plant, *i.e.* the caustic scrubber, air chiller, air drier, and knock-out pots, be purged free of hydrocarbons with air from the air compressor.

When all hydrocarbons had been removed from the system the air could be admitted to the air separation plant via the normal air inlet and used to systematically flush the exchangers, columns, and filters of the air separation plant until there were no traces of hydrocarbons in the effluent air. The cold box could then be started up and when oxygen and oxygen-rich liquids were obtained in the columns, this too would be purged until analyses indicated that there were no hydrocarbons present in the liquids. The air separation plant could then be brought back into production. However, recognizing the fact that an explosion hazard still existed, at least during the initial stages of purging the air separation plant with air in this manner, further information and recommendations as to the handling of the problem were sought from the Dow Chemical Co., Midland and L'Air Liquide Society in Montreal.

After several consultations with representatives of both companies a procedure was developed for the safe purge and derime of the air separation plant. This procedure had three main phases:

(a) **To dilute the oxygen concentration** in the air separation plant to a low order with nitrogen while maintaining temperatures low enough to keep the vapor pressure of the hydrocarbons present in the cold box as low as possible, *i.e.* to keep the concentration of hydrocarbons below the lower explosive limit.

(b) **To slowly raise the temperatures** in the air separation plant with warm nitrogen to gradually vaporize the remaining oxygen and solid or liquid hydrocarbons in the columns and purge them from the cold box.

(c) **To carry out a complete and thorough derime** of the air separation plant.

Safe decontamination

Under the initial phases of the procedure the oxygen and hydrocarbons were to be purged with N_2 introduced through the nitrogen pass of the air separation plant. It was reasoned that since all of the hydrocarbons that had entered the cold box should have been trapped out in the air feed side of the exchangers or in the columns or hydrocarbon filter, it would be extremely unlikely that there would be any hydrocarbons present in the nitrogen pass out of the cold box. By introducing N_2 back through the nitrogen pass it would be cooled down to temperatures close to those existing in the columns before it came in contact with any hydrocarbons, thereby reducing the risk of thermal shocks which might conceivably cause an explosion.

During this phase of the purge procedure the velocity of the effluents from the various purges were to be kept very low and the temperatures in the air separation plant were to be raised very slowly so that the concentration of hydrocarbons in the effluent purge gases could be kept below the lower explosive limit at all times. The temperatures in the air separation plant were to be gradually raised in this manner until they were all above $-100°F$ at which time it was considered that a complete and thorough derime could be started.

Approximately 150,000 std. cu. ft. of N_2 was used to purge the air separation plant. To conserve N_2 as much as possible the once-through method of purging was discontinued as soon as the first phase of the purge procedure had been completed, *i.e.* to dilute the oxygen concentration to a low order. At this point the concentration of oxygen in the air separation plant had been reduced to less than 2%.

For the second phase of the purge procedure, namely to raise the temperatures with warm nitrogen, the N_2 was passed through a steam heated exchanger and then introduced to the cold box via the normal air inlet where it passed through the shell side of the exchangers to the columns of the cold box. The effluent N_2 was taken from the tube side of the exchangers and recycled through the steam heater and back into the air inlet. Sufficient purges were maintained to ensure that the warm nitrogen reached all sections of the cold box. Continuous make-up nitrogen was added to the recycled nitrogen to make up for losses.

Analyses carried out on the effluent purge gas indicated that the oxygen content was reduced to the order of 2% over a period of 24 hours. The hydrocarbon content during this phase of the purge procedure was kept to less than 0.1%. Temperatures in the cold box were gradually raised to $-100°F$. Analyses carried out on samples drawn from medium pressure column and vaporizer and from the hydrocarbon filter showed no increase in hydrocarbon concentration as the temperatures were raised.

From vapor pressure curves it was established that at a temperature of $-100°F$ the vapor pressure of liquid propane, if present in the air separation plant, would have been 2.94 lb./sq. in. which would have been sufficient to show a detectable concentration of hydrocarbons in the effluent purge gas, (approximately 15% from the vaporizer). Since the analytical results showed no trace of hydrocarbons it was contended that all hydrocarbons had been purged from the air separation plant. At this point the derime of the air separation plant using recycled nitrogen was discontinued and a normal air derime was started.

Following the completion of the derime the air separation plant was started up and brought on stream with no further trouble. #