

## EXPLOSION IN FEED-GAS SECTION

Where there is a hazardous condition because of impurities in a feed stream, analyzers should be provided on the incoming stream with the means to shut down the operation if necessary.

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The purpose of this article is to present a description of the cause and events surrounding an explosion that occurred in the Diamond Shamrock 100 ton/day ammonia plant in Deer Park, Texas on February 18, 1970. This explosion occurred in equipment that handles the mixed hydrogen and nitrogen synthesis gas, as a result of oxygen entering with the nitrogen stream.

The hydrogen to the operation was supplied from our electrolytic chlorine cells. These cells are of the diaphragm type as well as mercury cells. Our normal hydrogen supply contained about 100- to 200 ppm oxygen, some carbon dioxide, and traces of mercury. The average hydrogen purity supplied to the plant was 99.5%. The nitrogen supply to this facility was from an off-site air separation plant, and compression was supplied by two Ingersoll Rand reciprocating eight cylinder HHE compressors. Each compressor was capable of carrying 1/2 the load of the entire plant.

### Gas compression and purification

The purpose of the feed gas section was to mix the hydrogen and nitrogen feed gases, purify them, and compress them to 3,000 lb./sq. in. gauge for addition into the synthesis loop. There were four stages of compression required in this section. In the first stage, each of the feed gases was compressed separately and combined through the use of appropriate ratio control instrumentation on the discharge of the first stage. The combined gases were then compressed in the second stage. It should be kept in mind that there were two compressors and both were equipped with a cylinder for each stage. After the discharge of the second stage, the mixed synthesis gas entered the purification train. The deoiler, the first vessel in this train, was a sacrificial activated carbon bed. Its purpose was to remove the bulk of the entrained compressor oil before the gas passed to the other units in the purification train. It also served to remove a large percentage of the mercury vapor from the gas. The next pieces of equipment in the train were two regenerable activated carbon absorbers which operated in parallel to remove chlorides from the gas. One unit was removed from service each week and regenerated with 150 lb./sq. in. gauge steam. At the time of the explosion, one of these adsorbers was being regenerated.

The next piece of equipment in this train was a Deoxo unit, which contained a platinum based catalyst. The purpose of this bed was to remove trace amounts of oxygen by catalytically reacting the oxygen with hydrogen to form water. Following the Deoxo bed, the next piece of purification equipment was another activated carbon bed to remove final traces of mercury from the gas. The last piece of equipment was a caustic wash tower in which the gas was scrubbed with a 10% solution of caustic soda to remove carbon dioxide. Following this column, the purified synthesis gas entered the third and fourth stages of compression before addition to the loop.

### Critical instrumentation

The first item of critical instrumentation was a purity analyzer on the incoming hydrogen stream set to shut down both compressors if the hydrogen purity fell below 95%. The second piece of instrumentation was a Beckman Model 80 trace oxygen analyzer. This analyzer was connected so that it could monitor the oxygen content of either the incoming nitrogen or hydrogen stream, or the synthesis gas leaving the purification train. Normally the analyzer was left on this latter stream. It was wired to shut down both compressors if the oxygen content of the purified gas was above 20 ppm. The last piece of instrumentation that we will be concerned with was an intermittent temperature recorder in the Deoxo catalyst bed. A high temperature in this bed indicated an excessive amount of oxygen reaction in the bed, and it too could shut down both compressors.

Due to the size, simplicity and compactness of this plant, only one operator per shift was required for the entire ammonia operation.

The explosion occurred at 4:50 p.m. in the only operating carbon absorber. This vessel was 5 ft. in dia., and 13 ft. tall, with a 6 ft. skirt. The shell was 7/8 in. thick ASTM-121B steel with two 3/4 in. thick 2:1 ASME elliptical heads.

Its design pressure-rating was 364 lb./sq. in. gauge at 650° F. The vessel, which weighed 16,000 lb., was torn into three large sections, plus fragments. The largest section came to rest some 10 yards from the original location. The second section, weighing 1,400 lb., was projected over some adjacent storage tanks, and landed about 90 yards away. The third section, which weighed about 600 lb., did extensive

damage to piping and pipe supports as it flew north underneath the adjacent compressor building. The relief valve from the top of the vessel was blown some 90 yards away. The entire charge of activated carbon inside the vessel was pulverized to dust and scattered into the wind by the explosion. As a result of the explosion, the escaping hydrogen gas burned for some 10- to 15 min. before the system was blocked out, depressured, and purged. There was some fire in the area due to torn electrical wiring and the small amount of combustible material in the control room. The operator on duty was about 10 yards away from the vessel at the time of the explosion. He received severe burns to the trunk of his body as well as minor burns over most of his body. Thankfully, due to prompt attention by the plant first aid team and excellent subsequent medical treatment, he has recovered from these burns.

In our estimation the most probable cause of the explosion was the ignition of a mixture of hydrogen, oxygen, and nitrogen present in the system. The presence of an unusually large concentration of oxygen in this case was indicated by several things. First, the recorded Deoxo bed temperature had just started to rise at the time of the explosion. This indicates an increase in the rate of the catalytic reaction in the bed due to the presence of an increased amount of oxygen. Second, there was oxygen present in two mixed gas samples that were taken downstream of the Deoxo bed immediately after the explosion. These samples contained 4,200- and 7,600 ppm of oxygen. As pointed out earlier, the concentration of oxygen at this point is normally less than 20 ppm. This breakthrough of oxygen before the Deoxo temperature indicator could respond is highly indicative of a rapid increase in oxygen concentration rather than a gradual increase. The capacity of the catalyst was exceeded before the temperature instrument had time to respond. Obviously, it must be concluded, that the provision for shutting down the plant by high temperature in the Deoxo bed was not adequate protection against hazardous concentration of oxygen in the feed gas.

#### Source of ignition

As a result of our investigation following the explosion, we feel that the most probable source of ignition was the Deoxo catalyst. Immediately preceding the explosion, a multi-point temperature recorder on the gas stream entering the Deoxo bed indicated a temperature rise from 300- to 720°F during the last 32 sec. interval between imprints. This, we feel, indicates a fire inside the piping at that point prior to the time of the explosion.

The minimum ignition temperature for hydrogen in air is 1,065°F. Due to the effect of mixture composition, pressure, and temperature, the actual ignition temperature could have been possibly as high as 1,200°F. Assuming this as an ignition temperature, the gas composition would have to contain approximately 3% oxygen in order to release sufficient heat of reaction to create the temperature of 720°F observed in the piping on the inlet to the Deoxo bed. Here 3% oxygen would be equivalent to 10% oxygen in the feed nitrogen, or 44% air in the feed nitrogen. In any event, if the minimum ignition temperature of 1,065°F is assumed, the level of oxygen in the feed nitrogen would be 8.7%. If the Deoxo catalyst was the source of ignition, then we must conclude that the flame traveled from the source of ignition backwards to the carbon ad-

sorber vessel which exploded. The oxygen concentration in the gas mixture may have gradually increased toward the adsorber vessel, causing it to explode as the mixture entered the explosive range. On the other hand, the induction time, which is often observed between the time of ignition and the time of explosion for gas mixtures, may have caused the delay.

#### Safety measures

We observed other indications that the oxygen entered the process along with the nitrogen feed. A fire inside the nitrogen first stage suction drum burned the paint off the lower part of the vessel. The combustible at this location was probably oil mist which enters the vessel with the flow controlled recycle nitrogen from the first stage nitrogen cylinder discharge. In addition, the effects of an internal fire in the piping was seen from the tee where the two gases mix up to a second stage suction. If the oxygen had come from the hydrogen stream, we would have expected the fire to have continued to back into the hydrogen line ahead of the tee.

For economic reasons, Diamond Shamrock has decided to discontinue the production of ammonia at this location. Therefore, the ammonia plant will not be rebuilt. However, we did reach some definite conclusions as to safety policies as a result of this incident. First, we believe that where there is a possibility of a hazardous condition existing because of impurities in a feed stream, continuous analyzers must be provided on the incoming streams. These analyzers should also be provided with the means to shut down the operation in the event of a hazardous concentration of contaminants. Further, we feel that it is a must that we know, and continually check, the response time of any analyzers used in this safety application. This response time must be short enough so that a shut down of the operation can be effected before the impurities have reached a point in the process where hazardous conditions result.

Second, we feel that when our operations are closely integrated with the operation of outside suppliers, particularly in the case of a gas process where low residence time is involved, a sense of understanding and good communications between supplier and customer are a must. We feel that in such situations the customer has the right, and should make it his business, to be made aware of potential upsets that can occur in his supplier's plant - and to evaluate the effect of these upsets on the customer's operation. We feel that in such cases, with the proper attitude and understanding, joint loss prevention audits by both customer and supplier can be of immeasurable mutual benefit.



SANDERS

#### DISCUSSION

**Q.** What happens to platinum catalyst in the presence of mercury? Does it become poisoned or lose its activity?

**SANDERS:** We have been concerned about this since the beginning of our operation in 1962. We had these activated

carbon beds ahead of the Deoxo catalyst that removed the traces of mercury to the part per billion range entering the Deoxo bed, and during the some 8 years of operation we showed no decline in the Deoxo bed activity.