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Oxygen plant reboiler explosion

Laboratory study of plant clues indicate a co-crystal of acetylene and nitrous oxide, which built up over a six month period at the bottom of the reboiler, caused plant mishap.

ON JANUARY 11, 1956, A REBOILER explosion occurred in the large tonnage oxygen plant of Monsanto Chemical Company at Texas City, Texas. There were no personnel injuries and no ruptures of lines or vessels. Reboiler tubes were extensively damaged, however, and trays in the associated distillation column were displaced. Repairs required several weeks.

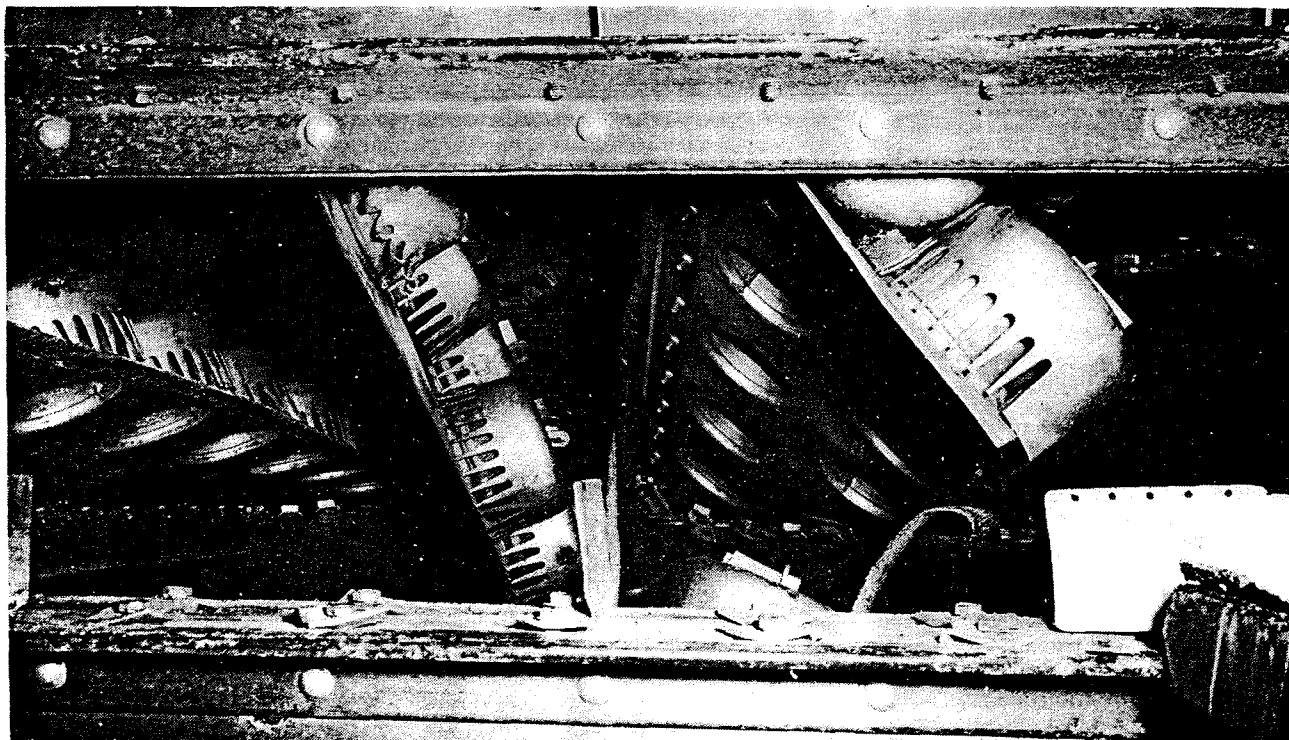
The oxygen unit produces gaseous oxygen at .95% purity plus a relatively small stream of high pressure nitrogen. The oxygen is used principally

for the partial oxidation of natural gas to acetylene, which in turn goes to adjacent acrylonitrile and vinyl chloride units. The nitrogen is used throughout the plant as an inert gas for purging.

The process employs a low pressure cycle. A simplified flow diagram is shown in Figure 1. Incoming filtered air is compressed with centrifugal machines and cooled in reversing exchangers. Fractionation is carried out in the conventional double column; the two columns and the reboiler-condenser between them are built as

an integral unit. Liquid rich air from the high pressure column, after sub-cooling, passes through a silica gel bed on its way to the low pressure column. Refrigeration is provided by an expansion turbine operating on uncondensed overhead from the high pressure column.

The unit first went into operation in 1952. At the time of the explosion it had been in operation for about 9 months since the last complete warm-up and cooldown. Six months before the explosion, however, it was shut down in a cold condition for me-



View of displaced trays in low pressure distillation column immediately above reboiler where explosion occurred.

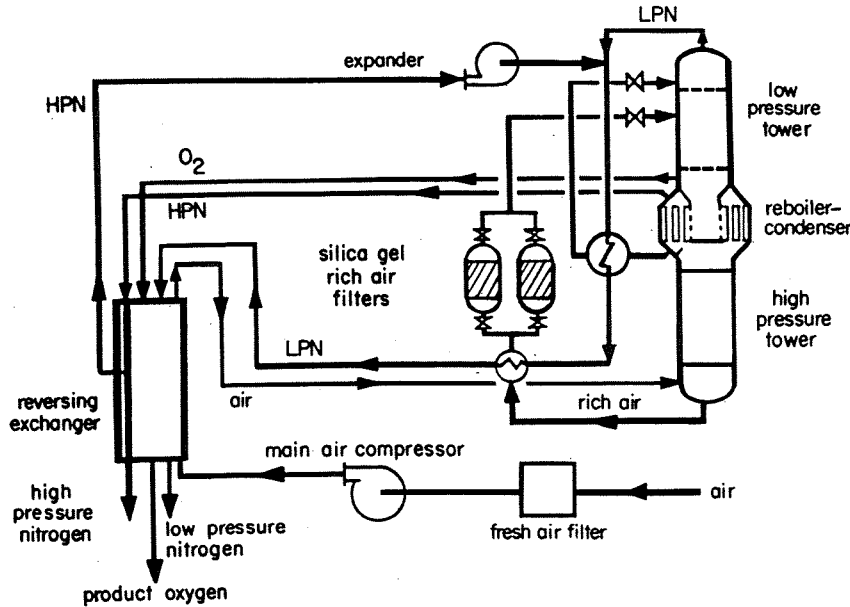


Figure 1. Simplified flow diagram of the oxygen plant.



Figure 2. Typical example of tube from reboiler that had been crushed by explosion.

chanical repairs and restarted 5 days later without rewarming.

Operation in the days immediately preceding the explosion was completely normal. The silica gel filter was in service and acetylene content of the reboiler by routine sample taken the day of the explosion was several orders of magnitude below the saturation limit. The adjacent acetylene unit, the most likely source of dangerous air contamination, was completely shut down at the time and had been for the preceding 24 hr.

Reboiler explosion

The explosion was evidenced by a rumbling sound. Pressure pens on recording instruments swiped the chart and oxygen purity decreased sharply and considerably. Paint on the tower foundation bolts was cracked, but there was no external evidence of damage. The plant continued to operate at reduced purity until shut down in an orderly procedure.

Detailed examination of the equipment after warmup showed the most extensive damage to have been sustained by the reboiler tubes. About 70% of the approximately 25,000 tubes showed some damage; about 31% showed severe damage. All tubes affected showed the same deformation pattern, which varied only in de-

gree; they were crushed by extreme external pressures, highly localized, just above the bottom tube sheet (Figure 2). Damage was generally more pronounced near the periphery of the tube bank (Figure 3).

About half the pressed-metal trays in the low pressure column were wholly or partly displaced (see introductory figure). Displacement severity decreased in a regular pattern upward through the column.

The reboiler tube sheets, the reboiler, and tower shells were not detectably deformed.

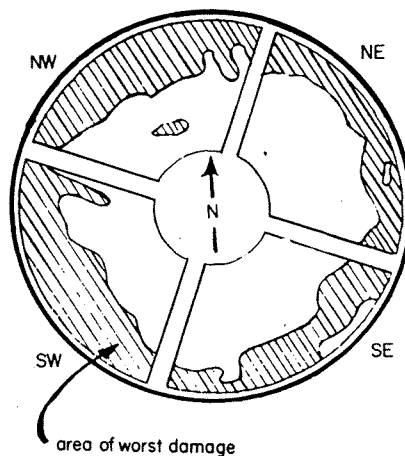


Figure 3. Horizontal cross-sectional diagram of reboiler showing areas of severest damage.

From the over-all damage picture, it was concluded that the total explosive force was equivalent to that of about 2 lb. of TNT (or 1 lb. of acetylene). The local pressures of several hundred thousand lb./sq. in. necessary to deform the tubes in the way described could only have been produced by the detonation of a condensed (liquid or solid) material. Consideration of the location of the tube damage, the great number of tubes involved, and the relatively small weight of explosive, leads to the conclusion that the material was distributed in a very thin layer that lay quiescently on the bottom tube sheet. Only a very sensitive explosive material would be expected to detonate in this manner. Tray damage is thought to be a secondary effect resulting from sudden vaporization of liquid oxygen.

Investigation of possible causes was facilitated by the fact that the plant was still more or less intact. Residue found on the bottom of the reboiler was analyzed, as was the silica gel bed for absorbed materials. During normal operation after the explosion, various plant streams were extensively analyzed for contaminants, which were detected in fractions of a part per million.

As various clues were picked up from the plant studies, laboratory studies were undertaken to test the

low temperature physical and explosive properties of various materials revealed by the plant investigation. Operating procedures prior to the explosion were examined to determine how the various materials might be brought into the reboiler.

Basically, the investigation had to answer three questions:

- 1) What was the explosive fuel?
- 2) How did it get to the reboiler?
- 3) Why did it explode when it did?

Explosive fuel investigation

It was concluded that co-crystals of acetylene and nitrous oxide (N_2O) formed the fuel.

Acetylene was suspected from the first. It is an ever-present contaminant in air plant inlets, even without an acetylene unit next door, and was, of course, found in the silica gel bed just after the explosion. Solid acetylene in liquid oxygen meets the requirements set for sensitivity and violence. However, solid acetylene tends to float in liquid oxygen. It was necessary to find an anchor for the acetylene that would hold it on bottom of the reboiler (and thus keep it from getting into the regular reboiler sample for acetylene analysis) without appreciably affecting its explosive sensitivity.

Nitrous oxide (solid) provides such an anchor. It was found unexpectedly in the silica gel bed just after the explosion, and its regular presence in rich air and reboiler blowdown has been confirmed during plant operations since. It may arise from the

flaring of nitrogenous wastes in the adjacent acrylonitrile unit or from more normal combustion processes.

In the laboratory, co-crystals of acetylene and nitrous oxide were found to sink in liquid oxygen (at its normal boiling point) if they contain less than 50 mol % acetylene. Co-crystals containing more than 25 mol % acetylene were found to be easily detonated. Thus crystals with between 25% and 50% acetylene both sink and detonate.

To carry out the tests, gaseous mixtures of various ratios of acetylene and nitrous oxide were made up at room temperature and blown through a glass tube onto the surface of liquid oxygen in a test tube which was surrounded by liquid oxygen in a Dewar (Figure 4). Cautious shaking overcame surface effects, and rather clearly defined limits of sinking or floating were obtained.

The equipment was modified slightly for the explosibility tests. The entrance tube dipped below the surface of the liquid oxygen. A 4-grain pyrotechnic squib was inserted loosely into the lower end of the entrance tube. After the gaseous mixture was introduced, the deposited solids were tamped lightly with a wooden rod (Figure 5). Tamping was necessary to get effective results. The Dewar was removed and the squib fired immediately. Both sets of experiments were safely carried out in a steel safety chamber with observation ports.

Similar results were obtained in drop-weight tests. The anvil of the drop-weight tester was cooled with liquid oxygen; the various gaseous mixtures were deposited on the anvil; and the anvil was then flooded with liquid oxygen. A 3000-gm. weight and 100 cm. drop height were used. These conditions were sufficient to detonate solid acetylene in liquid oxygen in the drop-weight apparatus used. Solid mixtures containing up to 75 mol % nitrous oxide in acetylene showed the same sensitivity to detonation as did pure acetylene.

To more closely approach plant conditions, a further test was made with a reboiler mock-up. Twenty one tubes similar to those used in the plant were set in holes in a brass plate (same spacing as in the plant) and held there with plaster of Paris. This assembly was placed in a 12-in. diam. can, which in turn was set in a 24-in. diam. can in a hole in the ground. The outer can was filled with liquid nitrogen. A layer of 60 mol-% nitrous oxide and 40 mol-% acetylene, about 1 mm. thick, was condensed on

the "tube sheet" in the small can and tamped lightly. Several inches of liquid oxygen were added to the inner can, and the mixture was fired with a No. 6 detonator cap. Results were surprisingly violent and gave a damage pattern similar to that in the plant explosion (Figures 6 and 7).

Other fuel potentials

Carbon dioxide, which also sinks in liquid oxygen and is regularly present in the reboiler beyond saturation limits, was also considered as a possible anchor for acetylene. Using lab techniques similar to those described above, it was found that acetylene-carbon dioxide co-crystals sink if they contain less than 50 mol % acetylene. Co-crystals detonate only if they contain more than 60 mol % acetylene, however. Thus, no mixtures were found which both sink and detonate.

Soot was also an early suspect as a fuel. Small quantities were found in the reboiler residue after the explosion. Laboratory tests indicated that soot-liquid oxygen mixtures will indeed detonate, but these mixtures are considerably less sensitive than the acetylene-nitrous oxide-liquid oxygen mixtures. Soot saturated with acetylene showed the same sensitivity as soot alone. Although soot represents a real hazard in an oxygen plant reboiler, tests showed it to be a much less likely fuel for the explosion being investigated than did acetylene-nitrous oxide.

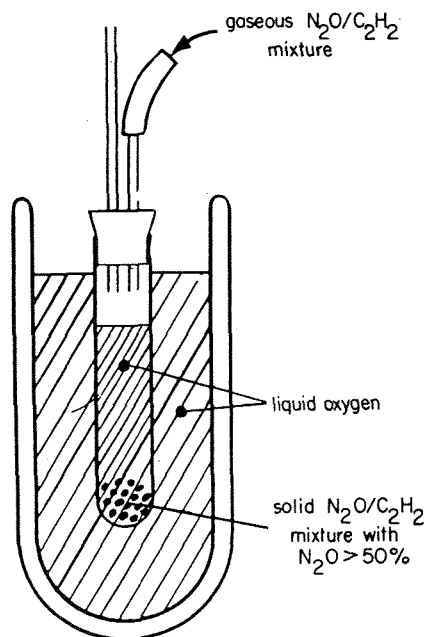


Figure 4. Laboratory apparatus for determining the density of mixtures of acetylene and nitrous oxide in liquid oxygen.

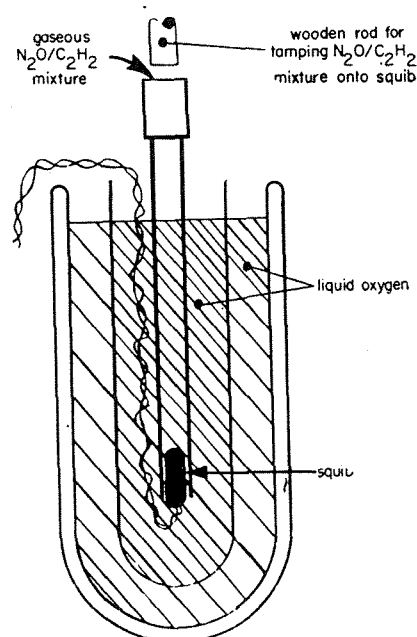


Figure 5. Laboratory apparatus used to experimentally determine the explosibility of mixtures of acetylene and nitrous oxide in liquid oxygen.

Silica gel dust was also found in the reboiler residue and the possibility of this dust saturated with acetylene as a fuel was considered. Russian workers have established that gel beads saturated with acetylene will not explode in liquid oxygen (1). Laboratory tests were run using a finer (28-200 mesh) gel. No explosions were obtained, either with a detonator cap or in drop-weight tests.

The question of a secondary role of nitrous oxide—as oxidant or explosive in its own right, rather than mere diluent—remains open. Previous work (2) produced explosions of pure gaseous nitrous oxide at ambient temperature, but failed to produce an explosion of the solid in liquid oxygen. In the drop-weight tests, no explosion was obtained with solid nitrous oxide at liquid oxygen temperatures in the absence of liquid oxygen. Similarly, a 50-50 mixture of solid nitrous oxide and acetylene without liquid oxygen failed to explode, although it exploded readily in liquid oxygen. However, in view of the narrower range of explosibility for carbon dioxide-acetylene solid mixtures, a secondary role for nitrous oxide cannot be ruled out.

The nature of the co-crystal is also a question. It is thought to be a simple physical mixture resulting from crystallization of both substances on the same nuclei, not a solid solution. At any rate, acetylene shows the same solubility in liquid oxygen whether the solid phase is pure acetylene or a co-crystallized mixture.

Fuel path to reboiler

The conclusion about the fuel would be more credible if a reasonable explanation could be made of how it got to the reboiler.

It was concluded that acetylene and nitrous oxide were introduced into the reboiler together by partial regeneration of the silica gel bed during start-up following the cold shutdown 6 months before the explosion.

A clue strongly associating these events, even though they were separated by 6 months, was the history of reboiler acetylene analyses during this period. During normal start-ups, the silica gel bed is bypassed until a liquid inventory is obtained. As a consequence, the first reboiler analyses are high in acetylene (up to 2 ppm). This concentration falls rapidly after

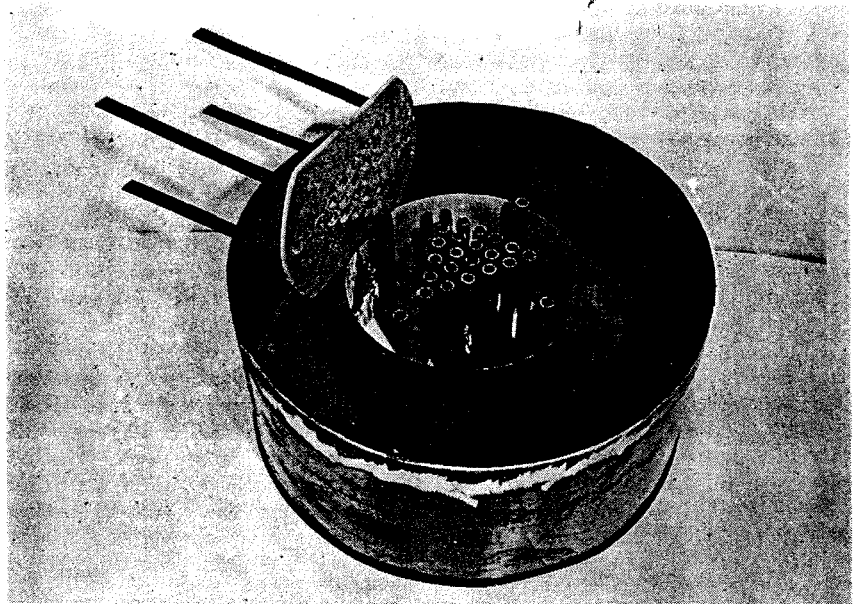


Figure 6. Reboiler mock-up used to simulate actual conditions in explosion tests.

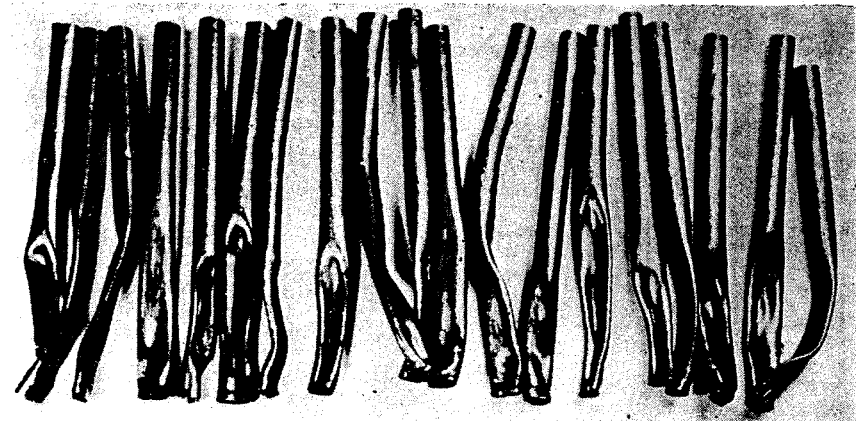
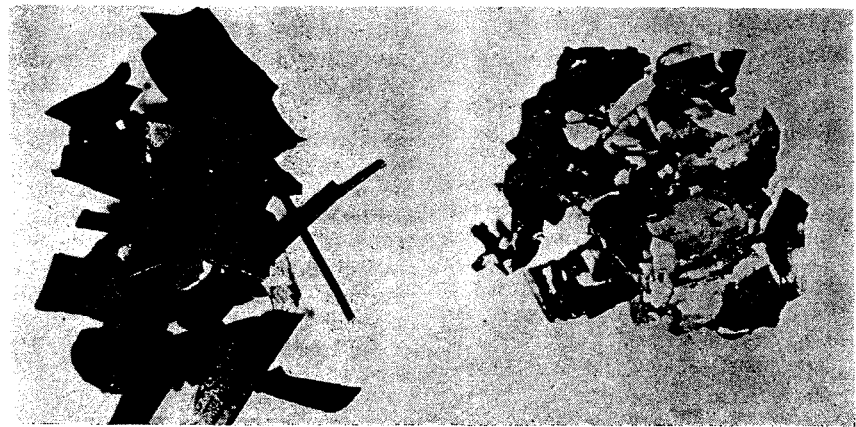


Figure 7. Damage to tubes and plate in reboiler mock-up test. The upper part of the picture shows fragments of the outside (left) and inside (right) cans.

the bed is put in service, both because of the reboiler liquid inventory build-up and because there is essentially no acetylene input; within one to two days it reaches a stable level of 0.003 to 0.005 ppm.

However, following the cold shutdown the pattern was different. Analyses of 0.005 ppm were not reached for 8-10 days. Even thereafter, results were erratic; during the following month some showed as much as 0.070 ppm. The variations gradually decreased, both in magnitude and frequency during the next two months.

In the light of present conclusions, this behavior is reasonable. The sample point was near, but not right on the bottom of the reboiler. The settled crystals were probably not densely packed at first and were more apt to be stirred up by normal motion in the reboiler and carried into the sample stream.

The start-up procedure following the cold shutdown suggests the source of contaminant. Part way through the cold shutdown, the columns were drained of liquid to prevent excessive acetylene build-up. The silica gel bed remained full (except for normal evaporation), and its liquid inventory was used as the source of refrigeration during start-up

to cool the reversing exchangers before air flow was begun and the expander started. The liquid was pressured (backwards) into the high pressure column using nitrogen from an external source. The nitrogen flow was continued after the bed was empty, bubbled through the liquid now in the bottom of the column, up through the column, through the reflux line into the low pressure column, overhead through the low pressure nitrogen line, and finally through the reversing exchanger (refer to Figure 1). Gas flow through the bed continued in this way for about 10 hr. Although sufficient data are not available for complete analysis, it is believed that partial regeneration of the gel took place. The bottom of the bed remained cold, but warming necessarily occurred in the upper part.

Plant studies since the explosion show that the silica gel bed absorbs considerable nitrous oxide in typical runs and that breakthrough occurs well before the bed is saturated with acetylene. Analyses of the bed outlet gas during a number of regenerations showed small concentrations of nitrous oxide as soon as the regeneration was started. Acetylene appeared in considerably smaller but still measurable quantities somewhat later, but before the cold end of the bed showed detectable increase in temperature. Peak concentrations of both materials occurred considerably later, as did the first appearance of carbon dioxide.

Thus, it seems reasonable that in the start-up following the cold shutdown, a mixture of nitrous oxide and acetylene (predominantly nitrous oxide) was carried as a gas into the high pressure tower, where it was condensed in the liquid pool, ultimately exceeding the solubility limit. Subsequent operation carried it into the reboiler.

Only a small fraction of the acetylene capacity of the bed would need to have been desorbed to account for the quantity of explosive believed to have detonated.

The possibility of precipitation of solid acetylene (and nitrous oxide) in the reboiler during the cold shutdown, before residual liquid was drained, was also considered. Even assuming the reboiler contents saturated with acetylene at the time of shutdown, and all this acetylene retained in spite of the draining, the quantity of fuel is entirely inadequate to explain the damage caused by the explosion.

It also seems unlikely that the necessary quantity of fuel could have

accumulated during normal operations without detection in the frequent routine reboiler analyses.

Residence time

There is still the question of timing—how the acetylene-nitrous oxide mixture remained 6 months in the reboiler without redissolving. If it be established that it did remain, a further question is how it stayed so long without exploding. The answer to the first question gives a clue to that of the second.

It was concluded that the rate of solution of solid acetylene in liquid oxygen is extremely slow because of its very limited solubility, which is the driving force for diffusion through the liquid film surrounding the solid. Nitrous oxide is about 27 times as soluble as acetylene, on a mol basis, according to literature values (3, 4); by the same reasoning, it dissolves proportionately faster. The solids when first laid down were predominantly nitrous oxide; an estimate is 90 mol %. They were therefore nonexplosive. As both components slowly redissolved, but at markedly different rates, the composition of the remaining solid changed to become richer in acetylene, until it reached the explosive range. Thus, a substantial delay after original deposition of solids was not only possible, but also necessary.

A mathematical approach to rate of solution indicated something like 6 months would be required to dissolve a solid layer of acetylene 1 mm. thick (liquid oxygen flowing slowly past one side). By comparison, ten days would be required for nitrous oxide, and copper sulfate in water would take only 30 min.

A number of laboratory experiments were run to check this conclusion in principle. Acetylene was deposited as a solid on the side of a Dewar containing liquid nitrogen. The nitrogen was drained off and liquid oxygen immediately added. After vigorous stirring for 1 hr. no acetylene was found dissolved in the oxygen, by Illosvay analysis.

If liquid oxygen contacts acetylene vapor, as in the crystal density experiments, or by letting the Dewar warm up partially before the liquid oxygen is added in the test just described, the oxygen is saturated with acetylene.

Other explanations for the delay are possible, such as time required for the crystals to reach a critical packing density, or lack of initiation. In any case, a very slow rate of solution of solid acetylene must be assumed. The conclusion given goes a step further in accounting for predominantly nitrous



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oxide crystals originally deposited, as evidenced by bed regeneration studies, changing composition to become explosive.

Initiation, of course, would time the instant of explosion. No investigation was made of possible sources of initiation. A number can be suggested, but the task of pinning down which particular one did this job appeared both near-impossible and singularly unrewarding.

Conclusion

The theory presented is considered a probable cause of the Monsanto reboiler explosion and takes account of all pertinent facts uncovered in the investigation. It cannot be proved rigidly, however, without undue expense.

It would be interesting to know the

extent to which nitrous oxide is found as a contaminant in the inlet air to other oxygen plants. It is relatively easily detected during silica gel regeneration. If it is generally or occasionally present, it may help account for other explosions verbally reported to have occurred at the bottom of the reboiler.

Together with ever-present carbon dioxide, it may represent some measure of safety, since both compounds form co-crystals with acetylene which sink, if the acetylene content is not too great. A further necessary condition is that the reboiler (or column sump) be so designed that solids do not accumulate there, but may be regularly removed and disposed of outside the plant. The Monsanto unit has been modified in this way.

The slow rate of solution of acetylene has considerable significance in interpreting the results of reboiler analyses. A rise in acetylene concentration in the reboiler needs to be discovered and corrected before saturation is reached. Once acetylene crystals are formed, they may continue to exist without appreciably affecting the concentration of dissolved acetylene after this concentration has returned to normal.

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