

the operators
report on
SAFETY
in air
and ammonia
plants

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The fourth and final
part of CEP's
exclusive report on
the informal
roundtable session
takes up, in detail,
the direct problems
involved in actual
explosions experienced
by the companies
represented at
the session.

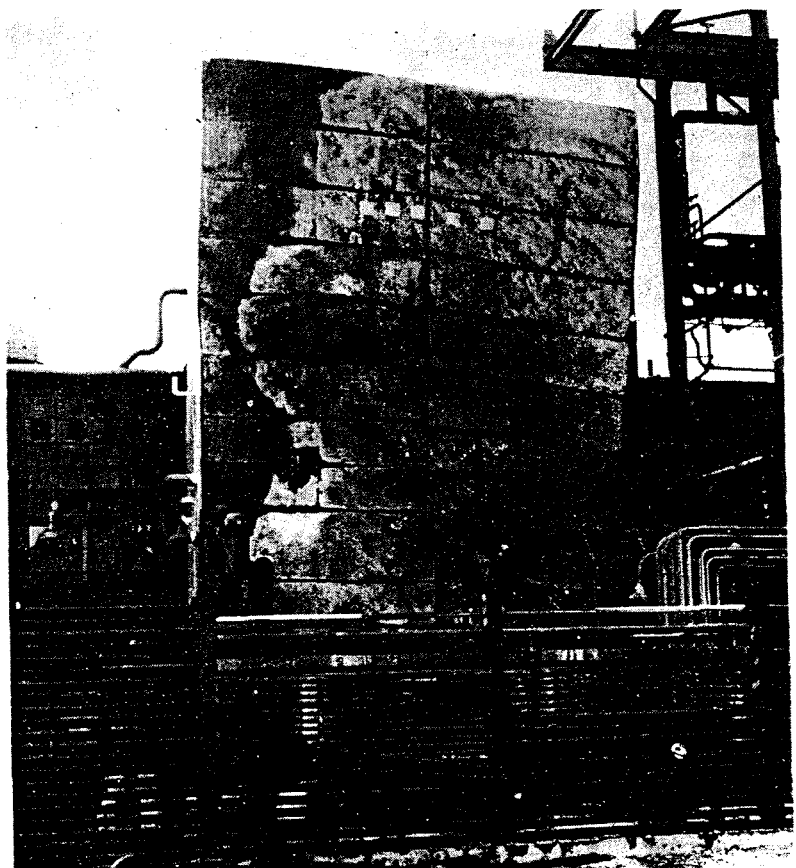
BOLLEN, Dow (Canada): On December 13, 1957 at about 4:15 p.m. an explosion and fire occurred at the ammonia plant of the Dow Chemical of Canada Ltd., in Sarnia, Ont., which destroyed the hydrogen purification unit. Two men were fatally injured and one man was seriously burned.

The Dow Emergency Plan (a pre-conceived plan designed to train and coordinate plant personnel in the performance of specific duties in the event of major disasters) was put into effect immediately. The value of this plan was evident by the lack of panic and the smoothness with which the plant was shut down and isolated by operating personnel, and in the effectiveness of the fire fighting force and various supporting operations. It was possible to confine the fire to the area of the hydrogen purification unit. The fire, fought entirely by Dow personnel, was brought under control by approximately 5:00 p.m. and was completely extinguished by approximately 8:00 p.m. The large inventory of liquid hydrocarbons in the various vessels and exchangers which had to burn off

made it almost impossible, and in fact undesirable, to extinguish the fire any earlier.

The hydrogen purification unit, in which the explosion occurred, was located on the north side of the compressor building so that the south side of the unit formed part of the building wall near the main control area of the plant. This arrangement permitted a great part of the blast to pass directly into the building. Extensive damage was done to most of the piping and a large percentage of all the equipment in the hydrogen purification unit. General damage was done to nearby piping and control panel instrumentation of the ammonia plant, and some damage to structural steel, roof, and windows of the ammonia plant building.

The hydrogen purification unit, in operation since early 1955, was designed to process hydrogen-rich streams from two nearby oil refineries and a demethanizer overhead stream from the adjacent Dow ethylene plant. Hydrogen content of the refinery streams may vary from
continued



General view of the cold box from the north side after the fire had been extinguished.



Close-up of cold box from the north side, showing extent of damage to the lower section.

continued

70 to 93 volume percent. The remainder is essentially saturated hydrocarbons, predominately methane. The ethylene plant stream contains from 30 to 35% hydrogen and the rest is mostly methane with about 2 to 4% ethylene and ethane, 0.5% CO, and a trace of acetylene.

At the time of the explosion, the ammonia plant (air separation unit, hydrogen purification unit, and ammonia synthesis system) was operating normally at about 60% capacity. The hydrogen purification unit, the "cold box," consisted of low temperature processing equipment, fabricated of stainless steel and copper, most of which was inside the cold box casing and completely embedded in rock wool insulation packed at a density of 10 to 12 lb./cu. ft. Processing consisted of successive cooling of the raw gas by heat interchange, condensing out the hydrocarbons and their expansion to vapor to recover refrigeration, followed by a liquid nitrogen scrub in a plate column.

All of the equipment used, except the ethylene precooler, the ammonia-refrigerated ethylene condenser and the ethylene receiver and connecting piping, were inside the cold box casing. The combined hydrogen-rich gas streams, compressed to approximately 180 lb./sq. in. ga., free of CO, moisture, dust and other impurities entered the first heat exchanger at about +40°F. In this exchanger, the combined feed gas was cooled by countercurrent heat exchange with the product streams leaving the unit. The heavier hydrocarbons were condensed in this element and were withdrawn as liquid at about 40°F.

The gas proceeded through an ethylene cooled exchanger and on into the second heat exchanger where the ethane and the remaining propane and propylene in the feed gas were liquefied. The gas, leaving the second exchanger was further cooled in the third exchanger, where it was submitted to the reflux action of liquid ethane, which was designed to dissolve an appreciable amount

of the acetylene present in the feed gas. The liquid fractions withdrawn from the lower parts of the second and third exchangers were expanded to near atmospheric pressure and were passed back through the tube bundles of the exchangers. The combined fraction from these made up the C₂-rich stream delivered as a gas at the outlet.

The remainder of the feed gas was further cooled in a fourth exchanger where the main part of its methane content was condensed, with a small amount of nitrogen and CO. Further methane removal was carried out in the reflux condenser where the feed gas was cooled by the refrigerating action of residual CO and liquid nitrogen boiling in the low pressure shell of this exchanger. Free from most of its original methane content, the gas entered the liquid nitrogen scrubbing column, a plate column in which the gas rose through the plates countercurrent to a stream of liquid nitrogen which absorbed the CO and the balance of the methane.

The gas, now free of all hydrocarbons and most of the CO, came out the top of the column where it was mixed with an additional amount of nitrogen. The composition of the gas mixture at this point was approximately the stoichiometric necessary for ammonia synthesis. This gas mixture proceeded back through the heat exchangers to the inlet of the synthesis gas compressors. The refrigeration necessary to run the hydrogen purification unit was supplied by a cascade system in which high pressure nitrogen was cooled by a closed ethylene refrigeration system, cooled in turn by an ammonia refrigeration system.

After the fire in the hydrogen purification unit had been extinguished, the unit and the surrounding area were roped off and left undisturbed until personnel investigating the accident had had an opportunity to view the wreckage. The rock wool and loose debris were then cleared away to expose the vessels and the piping.

All evidence indicated that the explosion had been inside the cold box casing, but outside the equipment. Careful examination of all the pipe and vessels revealed no evidence of rupture by internal pressure or explosion, or any

evidence of mechanical failure. The center of force, although not too clearly defined, was in the general area of the liquid nitrogen scrubbing column at an elevation of approximately 13 feet. The force of the explosion tore the top head off the cold exchanger and collapsed and tore loose the bottom head of the reflux condenser. Support legs under other nearby units were shattered allowing the vessels to drop, causing separation of numerous lines.

The liquid and gaseous hydrocarbons released from the broken lines supplied more fuel for the fire. Many lines were so badly melted where the liquid and gaseous hydrocarbons, present in the lines and vessels, had ignited at the open fractures of the lines that it was impossible to determine which of the line separations were at joints. Other lines were torn and severely crushed. All copper lines, near what was believed to be the center of the blast, showed evidence of having been subjected to severe external force. These lines were badly mangled and crushed flat. There was also evidence of external forces applied to the units whose legs had collapsed.

Experts familiar with the investigation of explosions were of the opinion that the general nature of the explosion and the limited extent of the damage suggested that the explosive force was characterized by high velocity and relatively low total energy. The nearly flat trajectory followed by pieces of valves, clods of rock wool, and other debris which were hurled completely across the compressor building and out through the windows on the opposite side of the building with sufficient force to strike and plaster against vessels outside the building, supported the suggestion of a high velocity explosion. That the severest damage was limited to approximately one quarter of the cold box and adjacent equipment, provided further evidence. The effect compared to that to be expected from two or three sticks of dynamite.

Purging nitrogen was introduced to the cold box casing through a 1-in. perforated sparger pipe which ran along the concrete pad the length of the cold box. Inspection of the nitrogen purge valve after the explosion showed the valve, a 1-in. gate valve, to be open approximately $\frac{1}{4}$ of a turn. The valve normally operated with 200 lb./sq. in. gauge nitrogen on the upstream side.

The cold box casing was not air tight. It is quite probable that the nitrogen purge was insufficient to prevent air from entering the casing, permitting air and hydrocarbon mixtures.

In view of the concentrated nature of the damage it was agreed that it could not have been caused by a simple gas phase explosion, because this type of explosion would not have had sufficient energy to shatter equipment, provide the high velocity, nor exert the unequal blast force within the casing evidenced by the limiting of the explosion to the lower half of one end of the cold box.



Waiton

Bollen

Funk

A theory which fitted all the evidence proposed that a mixture of partially liquefied air with oxygen content possibly in excess of 40% to 50%, and hydrocarbons in either liquid or solid phase, accumulated in the vicinity of the bottom of the liquid nitrogen scrubbing column and the connecting line to the reflux condenser; that it was the ignition of this mixture which caused the explosion.

The waste nitrogen from the bottom of the nitrogen scrubbing column, at about 180 lbs./sq. in. ga. and -320°F . was expanded through a valve to nearly atmospheric pressure. This expansion cooled the waste nitrogen stream down to a temperature below -325°F so that this line was the coldest part of the cold box. Since the temperature for the liquefaction of air at atmospheric pressure is about -310 to -311°F , it would be possible for air to condense on the surfaces around the bottom of the column and along line, and, in fact, saturate a small volume of rock wool in the vicinity of these sections of equipment with oxygen-enriched liquid air. This oxygen concentration may have been further increased, to some extent, by a refluxing process around the bottom of the nitrogen scrubbing column and the line.

Hydrocarbons leaking into the casing of the cold box from flanges and/or line joints could be expected to dissolve in the partially liquefied air and (through a similar refluxing process to that of the air) could have been concentrated to the point where they exceeded their solubility, causing solid hydrocarbons to exist in the presence of oxygen-enriched liquid air. The presence of hydrocarbons either in the liquid or solid phase in oxygen-enriched liquid air would have made a highly explosive mixture, requiring only ignition to cause an explosion such as occurred in the casing of the hydrogen purification unit.

It was recognized that a large quantity of energy would be required to detonate a liquid mixture of air and hydrocarbons. However, hydrogen was also present in the cold box and a gaseous mixture of hydrogen and air would require only a small quantity of energy for ignition. It was considered that this could have served as a fuse to carry a flame to the liquid mixture of air and hydrocarbons.

The question of ignition is still open to speculation. In all probability it will never be answered to everyone's satisfaction. Some possible sources considered by the investigating team were:

1. **Internal explosion within pipe lines or vessels, or their mechanical failure.** There was no evidence that an explosion internal to the lines or vessels had occurred, nor of any mechanical failure preceding the explosion and fire.
2. **Static sparks from particles either inside or outside the cold box.** It was theorized that static charges could have been generated by drops of liquid air dripping from the pipes and vessels.
3. **Sparks from electrical equipment.** The nearest electrical equip-

ment was the instrument panel and those instruments containing electrical circuits were supplied with air purge, in use at the time of the explosion.

4. **Sparks from oxyacetylene cutting operation in the vicinity of the cold box.** This appeared to be the obvious source of ignition since the cutting was done on a steel structure approximately six to eight feet west of the cold box. However, the investigation revealed that the cutting had been completed before the explosion. The interval of time could not be definitely established, but it was believed to be between one-half and three or four minutes. The immediate area between the cold box and the location of the cutting operation had been carefully tested with an explosimeter and found to be free of combustible gases prior to the start of the job. Hot work permit had been issued for the cutting job which took about 20 minutes to complete.
5. **A secondary nonluminous hydrogen flame ignited by the welding might have burned unnoticed for some time before the exact conditions occurred for propagation of the flame into the box.**
6. **A steam hose was used to quench sparks from the cutting operation.** A static-free hose was used for this operation but tests subsequent to the explosion showed that the conductor embedded in the hose was open-circuited. This may have resulted from damage in the explosion and fire, since the hose was badly charred by the fire. This hose could have been the ignition source.
7. **Two men were working in the area at the time of the explosion.** A spark could have been caused by striking of metal tools or equipment.

Subsequent to the explosion, flame propagation through rock wool was investigated using flames produced by hydrogen-air, ethylene-air, and hydrogen-oxygen-nitrogen mixtures containing higher amounts of oxygen than found in air. These tests indicated that only the high-oxygen containing mixtures would propagate a flame through rock wool. While verifying the effectiveness of rock wool as a flame arrester, these tests did not eliminate the external sources of ignition from further consideration. All of the sample lines, purge lines, and deriming lines exited from the cold box at the west end. Inadequate sealing of these lines and possible voids or channelling of the rock wool along the lines inside the cold box could have permitted a flame to pass into the cold box. Thus, any source of energy either inside, or immediately outside, the cold box could have initiated the explosion.

The prime purpose of the investigation was to determine the cause of the explosion so the necessary steps could be taken to eliminate any possible fu-

SAFETY ROUNDTABLE

ture recurrence. On the basis of the investigation and the conclusions drawn by the investigating team, it was felt that this could be accomplished by eliminating the oxygen from the casing of the cold box and/or eliminating the gas leakage from vessels, flanges, and lines into the casing of the cold box.

Although it was practically impossible to eliminate all possibility of leakage of hydrogen and hydrocarbons from equipment at these operating temperatures, it was possible to redesign the equipment to reduce leakage to the absolute minimum. The elimination of the oxygen, however, was practical and feasible. The following changes were some of the major steps taken in connection with the reconstruction and operation of the new cold box.

1. The outer walls of the cold box were made as tight as possible. All panels and bolts in the casing of the box were carefully sealed in place and seals were provided around valve stems and pipe lines passing through the panels of the box. The inner surface of the panels was given a protective coating to prevent internal corrosion.
2. The nitrogen purge system was redesigned to give better distribution throughout the cold box. Instrumentation and necessary alarms were provided to assure a continuous flow of dry purge nitrogen to the cold box casing, to measure the pressure within the casing so that it could be maintained above atmospheric pressure at all times, and to sample the gas content of the cold box so that the oxygen content could be maintained below 2%.
3. Sample probes were installed at several locations in the cold box so that the gas content could be sampled and analyzed. Analyses for hydrogen, hydrocarbons, and oxygen are carried out regularly, in addition to the continuous oxygen-content indication provided by the oxygen analyzer.
4. A procedure was set up whereby the casing of the cold box is thoroughly flushed with dry nitrogen until the oxygen has been displaced each time the cold box is started up after a shutdown. This is assured by analyses of the vent gas from the various sample points.
5. To help minimize gas leakage from vessels and lines within the cold box, all vessels with flanged heads were replaced with vessels of all-welded construction, and all vessels and lines, formerly of copper, were replaced with stainless steel. The only flanged connections were

continued

those located at control valves. All other piping and vessel connections were made by Heliarc welding. All field welds were radiographed for flaws. Prior to start-up, the entire unit was pressure-tested then filled with Freon, and inspected for leaks with a halide detector.

6. All vessel legs which formerly were carbon steel, were replaced with stainless steel.
7. All vessels in the cold box were individually grounded to prevent build-up of static charges.
8. The previous location of the cold box had proved unsatisfactory for maintenance work due to the generally crowded nature of the plant in this area. Therefore, the cold box was rebuilt away from the building and operating area. It now is operated by remote control from the original control area.

The new hydrogen purification unit has now been in operation for approximately 3½ months and appears to be functioning well in all respects. Recent analysis of the gas content within the casing of the box showed it to be 99.7% N₂, 0.2% O₂, and 0.1% H₂. It is felt that the possibility of an explosion, like the one just described has definitely been eliminated.

This report of the explosion and subsequent investigation is given with the sincere hope that the information may help to prevent similar disasters. In closing, I would like to point out that the conclusions drawn and the theories formed are those of the Dow Chemical Company of Canada, Limited. As in most explosions, a lot of theorizing had to be

done. We don't pretend to have all the answers as to how and why the explosion occurred, but we have tried to the best of our ability to match theory with fact.

CHAIRMAN WALTON: To my way of thinking, this places a premium on tight cold boxes and good purge. The tight cold box has to be made pretty much in the original construction, or else in a major revamp of the equipment. I'm impressed by the 3-4,000 cu. ft. of purge. That certainly shows you did a great job of making a tight box.

FUNK, German Linde: I would like to read a note from Dr. Karwat which gives some explanations for explosions in hydrogen purification plants. More than 30 years ago our company learned about explosions in hydrogen purification cold boxes when the first units were built to recover pure hydrogen and to yield synthesis gas of 75% hydrogen and 25% nitrogen, by applying low temperature techniques for separating the components of coke oven gas. In some cross sections of exchangers in the ethylene fraction we observed deposits of brown resins which could ignite by themselves and decompose. These resins proved to be similar to deposits in city gas lines. These are the products of the reaction of NO and NO₂ with dienes, especially cyclopentadienes. The low temperature promotes NO molecules to form double molecules (NO)₂, their oxidation to 2(NO₂), and then the agglomeration of NO-NO₂ to the double bonds of dienes =C=C=. The dienes eventually polymerize to nitrosate and nitrosite complexes and to resins. These compounds are relatively soluble in liquid ethylene. However, the vapor pressure is so low that they cannot be completely evaporated with ethylene



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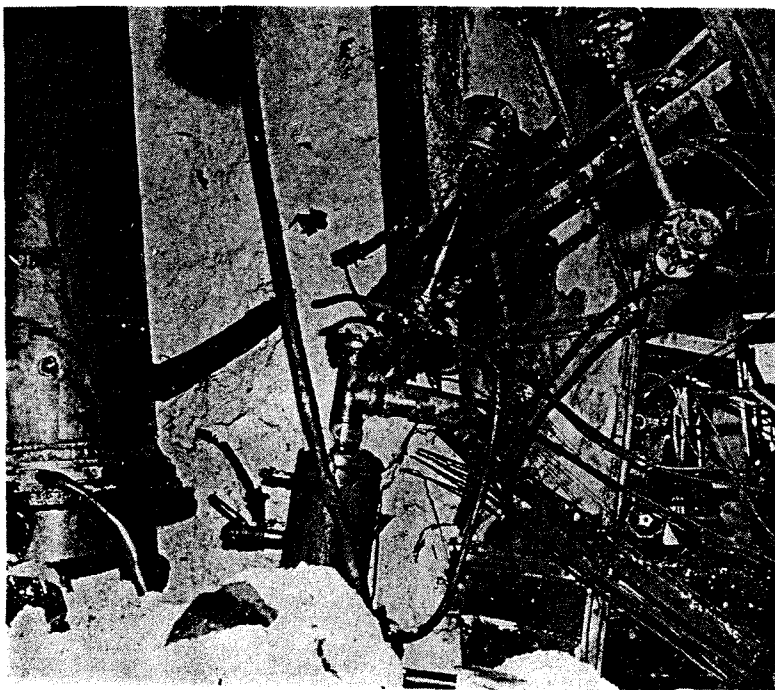
Jones

and they, therefore, accumulate in the heat exchangers, and very likely in blow-down lines, also. These resins decompose and explode at ambient temperatures. It, therefore, is essential to remove these deposits at low temperatures. This can be accomplished by washing the resin-covered surfaces with acetone or a solution of sodium with methanol. Only then can the heat exchangers be safely heated to ambient temperatures, and cleaned afterwards with caustic soda. Such a cleaning procedure is necessary after about one to two liters of NO have entered the cold box. Of course, we try to keep the NO content down by introducing as little smoke gas as possible into the gas chambers, when producing coke oven gas. About 80-90% of the NO can be removed by dry desulfurization. We have developed a process which lets NO react with chlorine dioxide, after which the gas is scrubbed by caustic-containing thiosulfate. Sometimes water-scrubbing under pressure is used. However, the water must test out as free from microorganisms which produce NO to avoid increasing this most undesired component. The danger of explosion related to NO must not be underestimated. For instance, the rupture of a ½-in. drain line caused the fire of escaping pressure-gas which destroyed the roof of the building and the down-pour of debris damaged the machinery.

Another point which I would like to mention is that if hydrogen is cooled to freeze out CO and nitrogen in boiling liquid nitrogen under vacuum, it is necessary to keep the oxygen content of the nitrogen very low, below 0.5%, to prevent infiltration of hydrocarbons into the circulating nitrogen through leaks in the exchangers. Check this by analytical methods. Otherwise, oxygen in the refrigeration liquid would enrich above the tolerable limit and react with hydrocarbons to initiate an explosion.

BRUNI, Sec Edison, (Italy): In February of 1957 there was a violent explosion in the hydrocarbon purification cold box in a plant in Porto Marghera, Italy. We considered that there were two explosions. The first was in the cold box and then an awful explosion outside the box. We think if the explosion had been only in the box the effect would have been small.

DePAUW, Carbochimique: I'll try to explain this story. A high pressure part of the equipment had been inadvertently connected to a low pressure part. Apparently there had been some leak from the high pressure part towards the low pressure part, so that a build-up of pressure occurred in a small heat exchanger,



Close-up of cold box from inside the building, showing extent of damage to lower southwest corner.

normally in low pressure service. The bottom was ripped off by the pressure and as a result of that, a small explosion resulted which damaged one of the nearby high pressure lines. This caused a terrible fire and explosion which killed, I believe, one man.

Materials and their inspection

WRIGHT, Standard Oil (Ind.): The subjects to be covered are:

1. Corrosion of a Brown-Boveri nitric acid plant air compressor.
2. Pressure-gauge bourdon-tube failures and new specifications.
3. Ammonium nitrate tank leaks and corrections.
4. Brass trim in valves in ammonia service.
5. High pressure valve stem failures.

Corrosion has been encountered in the last four stages of the 14,000 cu. ft./min. Brown-Boveri nitric acid plant air compressor. The corrosion product was identified as Mohr's Salt: $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. This corrosion was caused by condensation of moisture containing SO_2 from the saturated air in high pressure stages. The compressor has interstage cooling.

Arocoat, a coal-tar epoxy resin which has a relatively low moisture-vapor transmission and broad chemical resistance, was applied to the compressor case, diffusers, and rotating assembly after these parts were thoroughly sandblasted. The compressor has been run only a short period of time since this application, so it has not been possible to evaluate the results.

Vapor-phase inhibitors are being studied and may be used if the Arocoat is not satisfactory. Alloy diffuser sections have been ordered and will be installed at some later date. It may also be necessary to obtain alloy wheels for the last four stages of compression.

MEA and caustic systems were inspected after almost two years of service and appeared to be in excellent condition. Kontol 121 is used as a corrosion inhibitor in MEA solutions.

Numerous failures of bourdon tubes in high pressure gauges and transmitters (3000-9000 lb./sq. in.) have been encountered in synthesis gas service. All failures occurred in drawn tubes constructed of low alloy SAE-4130 or 4140 material. Examination of the failed surfaces disclosed that the failures were fatigue and appeared to have originated at fissures in the metal.

Replacement bourdon tubes are now being installed which have been constructed of Type 316 stainless steel. The tubes are bored instead of drawn. Type 316 stainless was chosen because it is less liable to have fissures as encountered in the SAE 4130 or 4140 material. Bored tubes are considered superior to drawn tubes, since the bore can be made smoother, the wall thickness is more uniform, and stresses due to drawing are not present. These features make the bored tube less liable to a fatigue failure than the drawn tube. Again, the bored Type 316 stainless steel tubes have not been in

service for a long-enough period of time to evaluate their worth.

A number of leaks have been encountered in ammonium nitrate storage tanks. The tanks are constructed of carbon steel clad plate. The cladding is 1/16 in. thick, Type 321 stainless steel. Nitrate of 80-92% strength is normally stored in these tanks. The leaks in the tank shells, in several instances, were serious enough to necessitate lowering the levels of the tank and making a temporary, bolted or patch, repair.

After one of the tanks was taken out of service and inspected, a number of leaks were found on the bottom. They all occurred at points where lifting lugs had been welded to the plates during construction, and later cut off. Apparently there was some diffusion of carbon steel through the stainless steel cladding. Repairs to the bottom were made by cutting out the affected metal, filling the voids with stainless steel weld metal, and then covering the area with an overlaid stainless steel patch.

The most serious leaks occurred at cracks in welds in the shell of the tank. Inspection revealed that faulty weld practice, during the deposition of the root pass of the carbon steel portion of the weld joint, resulted in a band of carbon steel being deposited on the edge of the stainless steel cladding. As a result, the stainless steel cover pass at this point had inadequate thickness and hot-cracked. The cracks opened to the inner surface and exposed the carbon steel to the hot nitrate. Stress corrosion of the carbon steel shell plates resulted in cracking of the shell plates from the inside out. The leaking ammonium nitrate caused local corrosion of the outer sur-



Swope

King

White

face metal and promoted stress corrosion cracks, which progressed from the outside of the shell inward. Cracks were discovered which were as much as eight inches long.

A complete inspection was made of all the tank seams by magnetic particle, dye check, and radiographic methods. All cracked areas and areas of suspected faulty welding were cut out. Inlaid patches of stainless steel clad material were welded in place. The entire inner surface of the tank was checked with CuSO_4 solution to determine if any carbon steel was present.

Failure of the yoke bushing in a drain valve in NH_3 service recently necessitated shutdown of all three synthesis loops. Inspection of the valve revealed the yoke bushing was made of brass. Galvanic action between the yoke bushing and the carbon steel bonnet caused the carbon threads to deteriorate. Con-



SAFETY ROUNDTABLE

sequently, the stem and threads lifted and the valve could not be shut off.

Inspection of all valves in NH_3 service throughout the unit disclosed that a number with brass yoke sleeves, yoke bushings, and brass packing glands had inadvertently been installed. Even though the brass in the valve that failed appeared to be in good condition, it was decided to replace all brass with either carbon or stainless steel to prevent galvanic action and also to prevent corrosion due to direct contact of ammonia with brass, as is possible in the case of the packing glands.

Several high pressure valve stems (9000 lb./sq. in.) were found to be broken in service, and many others were broken on disassembly of the valves at a recent shutdown. The valve stems were originally made of manganese, non-deforming tool steel, heat treated to 50-55 Rockwell "C." The stems were frozen in and had to be sledged to remove them, causing most of the breakage.

To alleviate this situation, several stems are being constructed of different materials; materials which are more ductile, therefore, more able to withstand shock. One material being tested is a high-carbon, high-chrome tool steel. It is being hardened to 61-62 Rockwell "C" and will be tempered at 775-800°F. The other material is tungsten-alloy chisel and punched steel, similar to the original steel, but is higher in chrome and tungsten. This material is being hardened to 50-55 Rockwell "C."

Molybdenum disulfide will also be used on the stem threads to help prevent them from becoming frozen, thereby eliminating the necessity of sledging them.

MASON, Dow: We had a gauge accident at Midland which might be of interest. It was standard practice to check the pressure on returned oxygen and argon cylinders. If the pressure was high, we assumed that the gas in them need not be removed from the cylinder. On oxygen cylinders we exclusively used an oxygen cylinder gauge made up especially for the purpose. One day this gauge assembly happened to be unusable. The operator used a gauge assembly that had been prepared for argon. The fittings for some argon cylinders were the same as for oxygen, although the standards are being changed and argon cylinders are being converted to a different type of fitting. The gauge was put on and the operator opened the valve to test the pressure. The gauge exploded. The operator was wearing safety glasses and leather gloves which limited the injuries to slight burns on the hands and minor damage to his face, nothing serious.



SAFETY ROUNDTABLE

Since the frangible discs on the valve were ruptured, we couldn't get reliable analyses of the gas inside the cylinder previous to the explosion. Thus, we could not determine definitely whether or not this gas had been explosive.

The assembly had been made up using Pipe-tite, a pipe stick dope. We found that this material would actually burn in air. Needless to say we are not using it any more. We are now using Key Absolute Sealing Material. The face and part of the Bourdon tube definitely show evidence of heat and they were probably the source of the sparks that were reported as the cylinder was depressuring.

CHAIRMAN WALTON: We have had four pressure gauge failures, all in hydrogen or synthesis gas service. In every case it was a failure of the Bourdon tubes. The pressure gauges were provided with two blowout plugs in the case, but these plugs did not do what they were supposed to do. The whole gauge shattered at the time of the explosion and flew all around the place. As a result, we have adopted a new standard for pressure gauges for 400 lb.-and higher service. We have gone to the Maxi-safe type gauge—a so-called turret case, a steel case with a complete blowout back. A particular example of this type gauge is the Ashcroft Maxi-Safe Duragauge type 1379, with a 316 stainless steel tube, and socket with bottom connection. The case is a steel casting and the whole back “relieves,” or blows out, in case of a failure. Since we used these gauges, we have had no gauge failures. We also use plexiglass instead of glass in the front of the gauges. Metallurgical examination showed there was poor grain structure in the Bourdon tubes that failed. In some cases it was thought to be due to notch-type failure, caused by insufficient finishing of the interior of the Bourdon. One of the items asked for was cold-service relief valves. We use 304 or 316 material in the valve, or brass, as the case may be. In the ammonia system, of course, we use stainless steel almost entirely.

We have found no evidence of hydrogen embrittlement in any of our piping. The hottest location that we examined was the discharge pipe from the final stage of the synthesis compressor. We cut out a piece of that pipe and checked it with bend tests and so on, and it was completely ductile. The operating temperature had been about 330°F, at about 400-lb. pressure. Over a period of about five years there was no evidence of hydrogen embrittlement.

The converter shell has a liner of 11½-13 chrome and a washer sample was cut of that to check for nitriding and grain structure. That showed no change from its original structure. We debated as to

what we should do in the way of proof-testing the high pressure vessels, the converter, the high pressure separator, and oil filter. We finally decided that since the interior looked so good, and that the washer sample cut out of the liner also looked good, that we would not subject it to a hydrostatic test at that time, although probably in another five years we feel that we will need to give a proof test to it, to the separator and to the oil filter.

JONES C.I.L.: Are your vessels forgings, or of laminated construction?

CHAIRMAN WALTON: Multilayer A. O. Smith type construction.

JONES, C.I.L.: You should be safe there. I think the main hazard in hydrostatic testing would arise with thick wall forgings, especially those containing side entry ports, or other stress-raising features. This is a case in which it is highly desirable to use warm water for hydrostatic testing. A thick wall forging may be notch brittle at temperatures as high as plus 70°F. I think that a company manufacturing ammonia had a brittle failure some years ago, when hydrostatically testing a converter forging. The fracture originated at a small crack caused by an electrical short circuit—the grounding of one of the starting heater electrodes to the vessel shell at the point of entry due to failure of the electrical insulation. The failure was certainly brittle, the converter shell shattered and fell apart. I don't think this is at all likely with either A. O. Smith type construction or strip wound vessels, and it would be just a question of convenience to test hydrostatically. Water above 70°F would be desirable for thick wall forgings.

CHAIRMAN WALTON: There were a number of tank failures a few years ago that were thought to have been caused by the use of very cold water in hydrostatic testing.

MASON, Dow: I would like to ask about the experience of this group in hydraulic testing of the high pressure cylinder storage for oxygen, nitrogen, or argon, that is, tube bank storage similar to the semitrailers used for transportation of these gases at high pressure. I believe the Interstate Commerce Commission recommends five year frequency for such hydraulic testing of this transporting equipment and I wondered: first, what is the consensus here as to how frequently this hydraulic testing should be done on stationary storage and second, if anyone had any experience in doing this without taking the horizontal tubes out of the rack. This gets to be quite a problem when you have 40 or 50 of these tubes to test.

One other question: What is the recommended frequency of changing the frangible discs in oxygen, argon, and nitrogen cylinders? Has anyone decided to go through an annual replacement of these discs? Has anyone had difficulty from their fatigue and breaking at a time

when the pressure is less than the normal test pressure?

SWOPE, Southern Oxygen: The regulations are quite clear as to what must be done in maintaining storage tubes when they are in transit. The ICC regulations stipulate they must be tested every five years. If they are fixed tubes, not in transit, and you are using them for storage, the ICC would not have jurisdiction. The local authority will recognize them as long as they are used and maintained in accordance with the ICC regulations. On the other hand, if you are using ASME containers as fixed storage vessels, no retest would be required. At the present time it's possible to purchase tubes that are stamped with both ICC and ASME markings. If you desire to use them as ASME containers, you must conform to the lower pressure limits permitted under the ASME code. However, the same tube may be used for higher pressures providing you maintain it as an ICC tube.

As to the method of testing, in general, you would have to remove the tube from any rack in which it was mounted because the ICC test requires a water jacket test. The ICC recognizes other test procedures, but, in general, they are not too satisfactory.

Regarding replacement of safety devices, I don't know that anyone has a standard procedure. We do not. We have no fixed replacement schedule as far as cylinders and storage vessels of this sort are concerned. The frequency of their pressure cycling would really be the determining factor.

CHAIRMAN WALTON: Mr. King, you spoke on this subject before and, as I recall, your feeling was for annual inspection. Have you changed your thoughts any since then?

KING, Sohio: Due to a variety of reasons we are having inspection this fall. We'll metal-inspect the major portion of the processing equipment. In particular, we will inspect the points where we may have had some high temperature operation at the converter outlet.

As to hydrostatic testing, we did retest the converter effluent coolers but only at operating pressures. We applied a formula.

CHAIRMAN WALTON: Has anyone else removed a set of internals in service five years or more, getting nitriding data on them?

WHITE, San Jacinto: If you are interested in anything less than five years, we recently had some converters made at 321 stainless. After a very short time they were very badly nitrided, in fact, they failed. It looks to us that at any temperature over 625°C, the nitriding is extensive, so we now operate considerably under that, and we are trying some 347 stainless on our next converter. We made some tests and found that 46 chrome comes out better than any of the stainless steels we were able to find. #