

OXIDIZING SALT EXPLOSION

W. A. Mason
The Dow Chemical Co.
Midland, Mich.

Although the incident which is under consideration did not occur in a plant closely associated with an air separation or ammonia plant, it did involve an explosion in which an oxidizing material and a reducing material reacted under somewhat unusual conditions. This incident does teach some lessons.

This incident involved a mixture of sodium bromate with lubricating grease and a felt bearing seal. Sodium or ammonium nitrates are not as dangerous as bromates. However, a similar reaction is possible with these materials, so it seems appropriate to discuss this incident.

Events preceding accident

To understand the nature of the explosion, let us review the events preceding the incident. A jaw crusher which was being used to crush chunks of sodium bromate had roller-type pillow block bearings on the movable jaw and eccentric shaft. These bearings which were lubricated with hydrocarbon grease and which were equipped with the usual type of felt seal became worn and were to be replaced. During the period of washing the jaw crusher with cold water, it is quite likely that the felt seals became saturated with strong sodium bromate solution. Also, during the operating period, some sodium bromate had worked through the felt seal and into the interior of the bearing housing and mixed with the grease.

When the crusher was being disassembled to replace the bearings, one of the bearings seemed frozen to the hinge shaft. The mechanic placed the jaw, shaft, and bearing in a vapor phase degreaser to clean it and loosen the bearing on the shaft. Subsequently, the jaw was removed from the degreaser and placed on the floor while it was still hot (about 125° C). When the mechanic tapped the bearing with a lead mallet to remove it, a violent explosion occurred. The explosion shattered the bearing, spreading the parts and pieces over the entire machine shop.

Violence of reaction

Subsequent investigation disclosed several pieces of information explaining the violence of the reactions.

1. The amount of oxygen contained in sodium bromate is nearly as great as in an equal volume of liquid oxygen.
2. The breakdown of sodium bromate to sodium bromide and free oxygen is exothermic, adding to the energy of oxidation of the reducing materials.

3. The heating of the bearing in the degreaser evaporated the water from the bromate solution leaving the bromate in intimate mixture with the felt fibers. It was probably crystallized into a solid structure rigidly attached to the bearing parts.
4. Apparently the energy of the mallet tap was enough to shock the hot mixture to the detonation point. And apparently the detonation of the felt-bromate mixture ignited the grease-bromate mixture which added to the destructive violence.

Corrective measures

It is believed that the lessons learned from this incident are worthy of passing on, hoping to prevent a similar occurrence under any similar circumstances. The corrective measures which were taken exemplify these lessons.

1. Since possible ignition sources are so varied and not completely controllable, it is believed that the most reliable approach to the problem is to prevent intimate mixtures of reducing materials and oxidizing materials, especially in confined spaces. Sometimes this is not easy or simple.
2. We have resorted to the use of highly fluorinated lubricants, in areas where oxidizing materials might accumulate. Such materials include Halocarbon lubricants, Fluorolubes and Kel-F lubricants. These lubricants are used in electric motor bearings as well as roller and ball bearings in other machinery.
3. Seals and gaskets are to be made of asbestos, Teflon, or similar noncombustible materials.
4. Sometimes speed reducers, gear boxes, or other machinery require large quantities of lubricating oils. Where the cost of such oil charges would be exorbitant, an alternate safeguard may be substituted. Such cavities can be protected from contamination by abundant ventilation with clean air between the equipment and the source of contamination or by maintaining a positive pressure in the cavity with clean air.

Of course, there are many variations of methods to prevent explosion hazards of mixtures of oxidizing and reducing materials. But there are two basic principles to follow:

1. Where possible, avoid the use of reducing material where oxidizing materials can be present.
2. Where oxidizing materials and reducing materials must be used in the same vicinity, prevent the possibility of mixtures of the two.

GENERAL DISCUSSION

Hydrogen blistering

Anonymous: I have a question regarding gas purification equipment, specifically hydrogen blistering. I wonder if any people here have experience with hydrogen blistering in their gas purification equipment?

TAYLOR—Northern Chemical Industries: We have a severe case of hydrogen blister in our water scrubber. We have corrected the problem, but we are questioning whether additional safeguards should be taken. The water scrubber is a 10-ft. diam. carbon steel vessel that operates about 375 psig. An area between the water line and about 10 ft. up the tower has been affected. The blisters penetrated, I would say, about one-sixteenth of an inch. We have punctured the blisters and beat the metal back and clad the whole area with 304 S. S. plates. The vessel wall thickness is about 1-1/2 inches. We question whether the affected areas will continue to blister and thus reduce the effective wall thickness of the vessel.

SIMMS—Phillips Petroleum: Mr. Taylor, have you determined that the hydrogen blistering is due to the process gas or could it be due to the bacterial action from the water?

TAYLOR: It is a combination of the two. The water scrubbing system includes a side stream that flows to a settling pond. This settles out small amounts of sulfur and sulfur compounds that tend to build up in the system caused by H₂S in the synthesis gas. We noticed over a period of 3 to 4 months a gradual drop in the pH. It has been concluded that this was due to bacterial action in the water, originating in the settling pond. The pH got down as low as 3.5 before we had the problem fully analyzed and were able to bring the pH under control. The system normally operates at a pH of 5.5. Of course, during this period, we did not realize that hydrogen blistering was occurring in the water scrubber. This condition was not discovered until our annual shut-down some months following the pH control program.

Monitoring penetration

Anonymous: We had hydrogen at 250 lb. pressure in a particular vessel, and we were wondering whether we would have hydrogen blistering, so we designed two special plants with an additional piece on the inside, the protruding ends of the main part of the column. This piece is inspected, taken off every year, and a piece is cut out of it and examined. This tells us how far the headers in penetration have been. In this way we think we will have some continuous idea of how bad it is.

TAYLOR: I believe the previous comment concerns hydrogen embrittlement, which is a somewhat different problem from hydrogen blister. One of the suggestions that has been made is that we take sample plugs of metal from the vessel wall and subject it to metallurgical examination.

HEPP—Sun Oil: We've only had a few isolated cases of hydrogen blistering and not in the application that you mentioned. In our case, at least; if it was an isolated blister, we never considered that this weakened the bulk structure of the vessel at all. We used to drill them to release the pressure; if you have a massive hydrogen blister, this may be something else. An occasional blister, we don't believe, it is anything to worry about structurally.

Mechanism of blistering

MASON—Dow Chemical: The mechanism by which Jess Taylor's blistering took place was probably different from that which occasionally caused blistering in a converter heater housing at Midland, Mich. For this housing, which operated at a pressure of about 5,000 lb./sq. in. and at temperatures of the order of 500 to 600° C, we believe the following mechanism explains the trouble. Hydrogen, either molecular or atomic or both, diffused into the steel and reacted with the carbon to form methane. This methane could not diffuse back through the steel but did accumulate at a high pressure within pockets in the steel. This caused the blisters. We changed to low carbon steel, or copper to eliminate the trouble.

Of course, one cannot believe that such a methane reaction would take place at 80 to 90° F which Taylor believed was the operating temperature where his trouble occurred. However, it seems possible that atomic hydrogen could diffuse rapidly into a fissure or cavity in the steel and then combine to form molecular hydrogen. This molecular hydrogen could not diffuse back out as rapidly and would tend to accumulate and build up internal pressures in the cavity.

TAYLOR: That is our understanding of the hydrogen blistering phenomena. Atomic hydrogen penetrates to those areas of discontinuity and concentrates and combines to molecular hydrogen. Molecular hydrogen then builds up pressure because it cannot get out as easily as the atomic hydrogen got in, and the blistering occurs. As I previously mentioned, the affected areas were covered with 304 ELC stainless plate rolled to the diameter of the vessel and made up in sections large enough to get through a manhole. The area in the shell behind each cladding section was drilled through, and each section was completely seal welded and tested. These holes were tapped, so we can check the cladding sections for leakage and also prevent the cladding from blowing off in the event of sudden depressuring of the vessel, should a gas leak occur in the seal weld.

A plug would give us assurance that we don't have another set of blisters building up on the areas already affected.

HEPP: Where that plug is?

TAYLOR: Where that plug is, yes. We're not going to be able to plug the whole vessel.

WHITE—Smith Douglas Co.: Could it be that a low pH might be the reason for the trouble? We have found that a low pH in water is often caused by nitric acid resulting from the oxidation of ammonia absorbed in the water.

X-ray or gamma ray inspection

SIMMS: Mr. Taylor, I still suggest that you contact Sohio and learn of their continuing success through the use of gamma ray inspection. They inspect the vessels in operation and through insulation as well as heat exchangers.

MASON: It may be dangerous to depend too much upon X-rays or gamma rays for detection of blisters. It might give a false sense of security because these X-rays or gamma rays indicate only differences in total thickness of the plate. A plate made up of many paper thin layers would appear the same as a solid plate of equivalent steel. So a radiograph of any kind might not give any indication of a blister. Some of the sonic methods would probably be more reliable to detect a blister.

JONES—Canadian Industries Ltd.: I believe that Mr. Mason is entirely correct in his analysis of the situation. It is interesting to conjecture on the formation of blisters. Generally, corrosion produces molecular hydrogen, but in some environments, the association of the monoatomic hydrogen first formed to molecular hydrogen is inhibited by the presence of specific elements, such as sulphur, selenium, antimony, and phosphorus. In these cases, the monoatomic hydrogen tends to diffuse into the lattice of the parent metal, which it can do quite readily in the case of steel. Eventually, this monoatomic hydrogen encounters discontinuities in the steel, at laminations and slag inclusions, and since it is now no longer subject to the influence of sulfur, etc., readily associates to form molecular hydrogen. However, molecular hydrogen cannot diffuse away as quickly as the new supply of monoatomic hydrogen arrives, forming more molecular hydrogen. This results in the accumulation of pressure, sufficiently large, eventually, to pop or round out laminations in the steel to form blisters.

Steel containing substantial quantities of hydrogen tends to lose ductility, in extreme cases becoming dangerously embrittled. The damage seems to be much more serious with high strength steels, or steels exposed to low temperatures. It is usually quite difficult to repair weld steel having a high hydrogen content.

In order to evaluate the damage to pressure vessels or such important process equipment, I imagine one would have to rely on a hydraulic proof test. One might supplement this by doing some mechanical testing on readily detachable parts of the equipment, i.e., by tensile and impact or notched bend testing.

It is unusual, I believe, to encounter blistering at temperatures close to ambient. It is much more frequent in oil refinery equipment operated at moderately elevated temperatures. To the best of my knowledge, such blistering rarely causes catastrophic failure, and blistering is most common with the weldable grades of carbon steel. On the other hand hydrogen embrittlement does cause dangerous failures with no warning in high strength steels.

WALTON—Sun Olin: I was associated with the petroleum industry for a good many years and a member of the Pressure Vessel and Corrosion Committee of the company for about 10 years. I saw a great deal of hydrogen blisters. Most of them were the ones that were

located in reflux drums, some of them in storage tanks, mostly in the 100° temperature range. The advent of catalytic cracking brought on a great increase in hydrogen blistering and in the reflux drums of the main columns.

It was thought that at about the time I left the petroleum industry that cyanides were responsible for the great increase in the amount of hydrogen blistering; cyanides along with the H₂S dissolved in the water phase separators. I've seen hydrogen blisters ranging from as small as a pencil point to 6-in. in diameter. I particularly remember the 6-in. one which was in the reflux drum of a gas plant where the water phase had quite a bit of dissolved H₂S in it. The metal inspection people, whenever they saw blisters, drilled them with a 1/16-in. drill, released the pressure and analyzed the gas to determine if it was hydrogen. In drilling them you also determine how deep is the location of the laminations and then watch this vessel for the development of other blisters.

When the shutdown came, the blistered areas were cut out and sectioned and if you couldn't replace the vessel at that time, a piece of plate was welded in the vessel. This is the attack which was made on this problem.

Incidentally, the thing which the industry, at that time, seemed to move toward to stop this hydrogen blistering was the use of these large amine molecules such as Kontol, which is marketed by Tretolite.

Corrosion—erosion

WALTON: On Wednesday, September 25th, at 7 P.M., a hydrogen line suddenly ruptured in our hydrogen plant. This was a line downstream of the reboiler on the MEA stripper. Let me outline the flow to orient you. This is a natural gas reforming unit for the production of hydrogen, and CO₂, and CO.

The hydrogen stream which has some CO₂ in it and some steam, coming from the shift converter goes through an exchanger, comes out at 365° F, and passes into the shell side of a reboiler on an MEA stripper in order to provide heat for the stripping of the MEA. The hydrogen stream leaves this reboiler at 260° F and still contains, of course, hydrogen, CO₂, and now more condensate and still some water vapor. Upstream of the reboiler, ammonia has been injected. This ammonia injection rate is controlled to give a neutral pH of the condensate which is condensed out further down the line at about 100 degrees.

A whole elbow blew out of this line about six feet downstream from the point where it comes out of the reboiler. Examination of the line, which is about 200 ft. long, indicated that every elbow in the line was extremely thin. This had been Schedule 80 carbon steel pipe. However, after the cooler, which is further downstream and where most of the steam is condensed, no corrosion was found. It is at this point that samples are taken for pH control by injection of amines, as noted before. It appears that the use of ammonia injection does not control corrosion in the higher temperature range where you have some condensate, but only partial condensation.

I'm interested in knowing if anybody else has experienced this and, if so, what they suggest to combat it. One of the things that occurs to me is the use of Kontol, but does this make the condensate unfit for use in the process again? Our condensate from this point is used in the process for quenching. I would be interested in any comments.

STRELZOFF—Chemical Construction Co.: I was wondering whether you were trying to make some carbam-

ide by combining ammonia and CO₂. It can be formed very rapidly.

WALTON: Our plant has two shift converters in it; the second was added in the revamp about a year and a half ago when a cold box was inserted in the middle of the plant to produce CO. The first shift is bypassed, partly, in order to have CO available for the cold box to remove. We had been using ammonia injection in the outlet hydrogen stream from the first shift for about 4 or 5 years. This controlled the corrosion condition there reasonably well, not completely satisfactorily but reasonably satisfactorily. No problem was encountered with ammonia carbonates or any deposition in the reboiler; the temperatures coming out of those reboilers are about 210°. What seemed to be satisfactory at a lower temperature is not at all satisfactory at this higher temperature reboiler outlet.

SIMMS: You mentioned that you used your condensate in the process for quenching. I would assume that this condensate might have a substantially high iron content. Does this create a problem?

WALTON: No. The iron content is quite low.

MASON: Nort, the fact that these thin places were at the elbows would lead one to conclude that the effect was due to erosion rather than corrosion. Was there any evidence of corrosion or erosion in straight lengths of pipe?

WALTON: No.

Preventing corrosion

MASON: This indicates that erosion at least contributes to your trouble. It might help to either increase the thickness of the elbows or provide internal baffles to prevent impingement of solid particles or drops of liquid on the inside of the elbow. Also, it is well known that CO₂ in the presence of water is very corrosive especially at elevated temperatures. If the gas mixture could be kept dry (free of liquid water) it would probably not be corrosive. Also the ammonium carbamate and carbonate salts are very corrosive.

WALTON: You can't dry it very well because the steam in there is required for the shift converter operation. I'm sure it's a mixture of erosion and corrosion; very few things are 100% one or the other. The elbows were Schedule 80. It would be undesirable for many reasons to go up to Schedule 160. The straight line piping does not show any evidence of thinning. The elbows were thinned rather than pitted. Perhaps the answer may be to go to 304 or 316 elbows. I think some people have done this.

MASON: Could long radius bends be used in place of the elbows?

WALTON: Well, that's another problem. Bill Mason suggests long radius bends instead of elbows. We have long radius elbows.

Sam Cavallaro mentioned that he lined the elbows with 304. Our elbows returning from the reboilers on the MEA side, the elbows going into the stripper tower corroded, eroded out deep grooves. We lined with 304 and that seemed to stop that on the MEA side. Cavallaro has a good suggestion on this other case.

Elbows lined with welding beads

CAVALLARO—Valley Nitrogen: We had the same experience about 6 or 8 months after our plant started up. We noticed it particularly on the gas-condensate line leaving the gas reboiler and leading into the condensate knockout pot. On investigation, we concluded that the pipe had thinned out more from erosion than corrosion. We noted that only the bottom surface of the ells were severely chewed out. We replaced the ells with carbon steel and lined the bottom surface with welding beads of Chomoloy #6. I am not sure of the number, but if anyone is interested I will find out from our maintenance department.

Every year we have checked these Chomoloy lined ells and they have held up terrifically. The same erosion-corrosion problem has shown up in other parts of the plant where we handle gas-condensate flows and we have solved the problem with stainless steel lining or Chomoloy lining, depending on severity of service.

On the MEA side we have either lined or installed stainless steel elbows, depending on severity of erosion-corrosion found. This latter problem is relatively new to us and so far, after 6 month's service, everything seems to be O. K.

GEIST—Air Products: Without getting involved in the details of the discussion of erosion versus corrosion, I'd like to add one comment concerning the injection of ammonia into a stream containing CO₂. Those who are familiar with plants in which aqueous ammonia is used to absorb CO₂ from either air or hydrogen, know that although only one or two theoretical trays are necessary to remove the CO₂ from the air or hydrogen, the absorbers require a fairly large number of actual trays in order to remove the CO₂. The mere injection of ammonia into a gas stream, which contains some CO₂, will not lead to a complete chemical reaction.

STRELZOFF: We have done that with the Claude ammonia synthesis process. We actually had to use cast iron instead of ordinary steel when we worked with this solution, in making ammonia carbonate solution, which sometimes leads to the formation of carbamate. The carbamate solution is certainly very corrosive. I will not argue about the process of CO₂ removal by ammonia, but you have a condition which might lead to a corrosion problem, particularly if you raise the temperature. That's why this problem of corrosion-erosion must be handled together and it is advisable to protect the elbows by using appropriate materials of construction.

Stainless steel elbows

BUDDENBERG—Collier Carbon and Chemical: You can have this corrosion-erosion problem whether you reboil or not, of course. That hasn't been brought out yet. I predict Sam Cavallaro is going to have failures because we've attempted the same remedies he is trying now. The lining at the elbow will eventually undercut and he'll be back right where he started. We've gone into completely stainless elbows. In addition, the straight runs of pipe will develop a groove at the bottom where the condensate travels. We are meeting that problem by going to heavier piping and rotating 120° every two or three years.

DU PUY—Monsanto Co.: As you probably know, we just finished building an ammonia plant at Muscatine, Iowa, and last month had our first turn around. This discus-

sion pertaining to corrosion around MEA reboiler systems is of great importance to us.

When we first built the plant, we did put in stainless ells, on the gas side, going into the stripping tower. This first turnaround showed no evidence of corrosion on the stainless ells; however, we did notice some corrosion on the straight piping, beginning on the bottom of the pipe, indicating the same thing happening here, as before.

We also had some corrosion problems adjacent to the MEA stripper, where we had carbon steel nozzles. We had to line these nozzles with stainless steel this time because of corrosion problems there. We also had corrosion problems on the opposite side of our towers. I'm sure this is not a new problem to most of you. Is there a better way of protecting the towers other than lining with stainless steel on the opposite side of these towers? Now this is true of any gas entering any tower; our contact cooler, absorbers, and MEA regenerator. We're protecting our towers with stainless plate. Is there a better way of protecting a tower from corrosion-erosion?

STOCKBRIDGE—Southern Nitrogen: Speaking to the question of corrosion opposite the gas entrance at the bottom of the stripping tower, we have a hot potassium carbonate system removing CO₂ from our gas in two stages. In the second stage, operating at 875 lb., we noticed some erosion opposite the gas inlet. We lined the inlet nozzle with a thin lining of stainless steel, and gave it a slight downward cant, about a 22 1/2°, so that the entering gas stream actually impinged on the liquid level in the bottom of the tower rather than on the opposite metal wall. Incidentally, we also installed an impingement plate of stainless steel on the tower wall opposite the inlet.

Monel as a protective medium

MCMAHON—Collier Carbon and Chemical: We've had a lot of difficulty with corrosion at the bottom of the rectifier columns also, and efforts to control it using stainless steel have been quite unsuccessful. We switched to using Monel as a protective medium and are having extremely good success with it.

Anonymous: I'd like to make a comment on this question of erosion versus corrosion. Based on a number of studies, we found that for pure erosion there is no difference between carbon and stainless. For this reason I think that we're primarily considering a corrosion problem which is perhaps aggravated by some erosion, but the principal problem is the corrosion.

WARREN—Du Pont: We have had some experience with corrosion in the MEA system; it may not be exactly specific to the original problem here but it's an observation. We found that a film builds up on the MEA side. With high velocity gas, this film is cut out very rapidly and again is redeposited and you cut out the end and pretty soon you go through your carbon steel.

The film on stainless steel does not seem to build up apparently as rapidly as on carbon steel. It seems to be a much more tightly adhering film and this can stand then a higher velocity of gas. I'm talking about a gas which does have CO₂ in it because you have to have a corrosion medium here of some sort.

SIMMS: I will relate our experience which is intermediate between Sam Cavallaro's and Mr. Buddenberg's.

We experienced this corrosion-erosion on the ells, particularly the outlet ells from our reboiler. The next area was the channel or reboiler head. We noticed

this corrosion by inspection, and also found considerable iron in our condensate.

We replaced the ells with stainless ells and laid down a stainless coating with welding rod on the inner surface of our channel cover. We suspect that it is possible for us to have continued corrosion, with less erosion, even in the straight run of pipe, and in the condensate receiver, particularly at the interface. We have been using, with some success, a filming amine to protect what you might call, the low velocity areas in the system, such as the straight pipe and the condensate separator. At least we've noted that the iron content of our condensate has dropped to near zero.

The other reboiler corrosion on the amine side is typical of corrosion-erosion which is a function of reboiler temperature and design. The higher the skin temperature, the more rapid this type of corrosion-erosion. The only two remedies we have found are, first, lowering the reboiler temperature as much as you can and, second, the continuous operation of your side-stream reclaimer.

Compressor rod failure

WHITE: With regard to rod fracture, we have set up procedures to inspect our rods every one or two years when the compressors are down for preventative maintenance overhauls.

One of the principal reasons we found for overstressing the rods on our synthesis recirculator was excessive heavy oil in our cylinder. This would cause heavy knocking at the end of each stroke because of low cylinder head clearances. By changing to a lighter grade oil on our ring lubrication, we were able to completely eliminate cylinder knocking.

JONES: I was talking to some compressor manufacturers, 18 months ago; they commented that the practice of induction hardening of the rod, in the packing area, to provide wear resistance in this region, had occasionally resulted in the formation of a quench crack in the region between the nonhardened rod and the hardened section, and this particular manufacturer had introduced magnaflux as a standard requirement on the rods in order to pick up this defect.

Now this particular manufacturer had some evidence that this had arisen, he had this situation on the rod which he was manufacturing, and he needed this sort of protection. It is possible that if a break occurs in a packing area, the region in which induction hardening has been done, that the nucleus of this break existed right from the time at which the rod was originally manufactured.

DEMINSKI—Cooper Bessemer: Fortunately we had very little experience with rod breakage. But the problem of circulators is one that we have been aware of for some time, and our answer to the problem of knocking as a result of excessive liquid, is simply to build as much as 100% fixed clearance in these cylinders. You're generally dealing with a ratio of the order of magnitude of 1.1 which yields a high volumetric efficiency that is virtually independent of the percentage of fixed clearance.

As of late we are building most of our cylinders so that they have at least 1 in. of end clearance; I am sure that some machines are being operated with as much as 3 in. of end clearance.

Vibration monitors

STOCKBRIDGE: In our new ammonia plant we have a centrifugal air compressor. We haven't had a lot of

trouble with vibration, but we are considering installation of vibration monitors. I wonder if anybody here might have experience they would like to comment on concerning vibration monitors.

HENDERSON—Dow Chemical: I went down to Spencer Chemical in Vicksburg, Miss., a couple of years ago to look at a Maulwurf centrifugal circulator. They had a vibration shutdown switch on the shell of the circulator. They don't know what they set it at, however, it never operated. I could see why it wouldn't because we have one of the same pumps in operation and there is no vibration of the pump or piping system. The entire high pressure structure used to dance like marionettes but there is no vibration now. As far as vibration is concerned, we have eliminated that one problem. We used to have a lot of leaks develop from the vibration of the system and since using the centrifugal pump instead of reciprocating machines we've eliminated all the vibration in the structure.

HEPP: On our cooling towers we have vibration monitors to shut down the fans if they get out of balance. It is simply a small mercury switch which is held down by a 1/4-in. metal ball sitting in a shallow depression on one end. If vibration starts, the ball is thrown out and the mercury switch tilts, shutting off the fan.

HENDERSON: To supplement the discussion regarding vibration in compressors I have made some measurements of movement of compressor foundations when running machines fully loaded.

We have five 4-stage compressors operating at the following pressures:

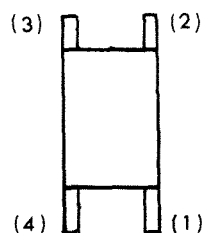
	Pressures, lb./sq. in. gauge	
	Suction	Discharge
1st stage	3	80
2nd stage	80	450
3rd stage	450	1650
4th stage	1650	5200

These machines are four cornered compressors driven by 350 hp. engine-type synchronous motors at 150 rev./min. Foundations are set on piling driven to refusal at about 40 ft. with two batter piles at each end and contain about 30 yards of concrete.

We also have two 5-stage compressors operating at the following pressures:

	Pressures lb./sq. in. gauge	
	Suction	Discharge
1st stage	3	45
2nd stage	45	230
3rd stage	230	800
4th stage	800	2200
5th stage	2200	5200

They are also 4 cornered with the 4th and 5th stages at one corner and are driven by 1,000 hp. engine-type synchronous motors at 138 rev./min. Foundations are similar to the 4-stage machines and contain 110 yards of concrete.



Movement of the foundations was measured by indicator and in all cases but one the movement was lengthwise of the machine and varied from 0.007 in. to 0.011 in. In one machine the movement was lateral and was about 0.017 in.

SOMMERS—Pennsalt Chemicals: I think it can be said that many of the strange things that have happened to compressors in general over the years, whether it be broken piston rods, broken shafts or bearings, or perhaps excessive trouble with valves in some specific location, or whatever it may be, can be traced to vibration problems. Harmonics can be set up in some particular part of a compressor due to the volume, length and configuration of the interstage coolers and piping, which seem to concentrate and hammer with destructive force at some particular part of the compressor.

It is rather common that for example, in the case of excessive valve breakage in some particular location, simply changing to a different type of valve will clear up the problem. It is not so simple in the case of piston rods. I think most everyone who has run compressors over a long period of time will have experienced peculiar rod breakage for which there appears to be no reason or solution. This is a problem which the compressor manufacturers have been unable to satisfactorily solve.

They do not seem to be able to specify a material which will not fracture in some locations. Rods have failed, flame hardened, stainless steel or carbon steel, nothing seems to be right but other identical rods on the same compressor last indefinitely. We have broken fifth stage rods on one of our syngas compressors at the rate of about one a year and we still do not know what the reason is. I do know that at least one compressor manufacturer has set up instrumentation to detect harmonics and by the simple expedient of changing the size, length or volume of the interstage piping; destructive harmonics have been eliminated.

We all know about the need, or probable need, for piston rod catchers, particularly for circulators, but this seems like "locking the door after the horse was stolen." It seems to me that much more work should be done in this area to really get at the cause and solution to rod breakage. If anyone has any thoughts on this general subject, I would be glad to have them.

DEMINSKI: There are several philosophies that go into cylinder support designs and the reason you see different types of supports is reflected by the size of the machinery. With every stress in metal you get a comparable strain that goes with it. As you start stacking up equipment that's absorbing as much as 5,000 hp. you are going to get into some sizable pieces of machinery that are going to stretch out to be quite long in over-all dimensions. Even with the moderate unit strains and stresses that are imposed upon this equipment, significant total strain will be experienced. It will appear as though the cylinder and adjacent equipment is moving as much as 1/4 of an inch. Actual measurements will indicate that this is not the case and that actually the amplitudes of movement are rather small. To absorb the lateral movement, but restrain the transverse movement we use what we term a web support.

We have other designs that accomplish the same effect and one of these is what we term a gib-type support. This support is basically a bearing that permits longitudinal sliding with restriction to lateral motion. When motions are small we can rely on the simple pipe-type support. This support, of course, will allow the cylinder to move in the transverse and longitudinal direction. These are generally employed when the

magnitude of movements are small enough so that they will not cause any adverse conditions during operation. Generally speaking, when we are operating at the higher pressures and subsequently the higher rod loadings, we must take a more sophisticated approach to the support problem.

WALTON: I recall that Atlantic had some difficulty with breaking synthesis rods, that metallurgical examination and studies were made and that the conclusion that the Atlantic metallurgists consultants came to, was that the rods which broke were ones where the grain size was rather large. They at that time wrote a purchase specification which limited or specified rather closely a small grain size.

Mr. Gibson says that this specification was agreed upon with Ingersoll Rand—controlling the grain size of these rods—and that he hasn't had any further difficulty.

Ammonium nitrate contaminated hardware

JONES: I'd like to comment on the disposition of ammonium nitrate contaminated hardware. Our explosives plants are manufacturing ammonium nitrate. They burn off parts contaminated with explosives as a consequence of making TNT, nitroglycerine or other such compounds. As a consequence we deal with ammonium nitrate piping in the same way. We would want to decontaminate piping or the like which contained ammonium nitrate in any quantity before putting it on the scrap pile, where a welder may conceivably want to salvage it. I would be interested to hear whether this is a wise precaution, or whether other people do the same sort of thing. Could we ask the people present whether they would indicate if they would do this or not?

SIMMS: All of you who decontaminate before you dispose of scrap please raise your hand. Apparently there are 2. Apparently all others do not. We are now talking about common rules that may benefit manufacturers, blenders, or users from a safety standpoint.

LAWRENCE—Central Nitrogen: A man put ammonium nitrate in an oil drum with a film of oil at the bottom. He began welding it and killed himself. This is only one case, and I could think of another case where a pipe was welded. I think we mentioned one of these last year. I didn't want to pass over the subject without emphasizing the point, that there are still a lot of farmers, customers, and people that treat ammonia nitrate a little too lightly. They store it in garages, around oil, and on wooden floors. They smoke around it and stamp out cigarettes on these wooden floors.

Molecular sieves

GLASS—Monsanto: I have a comment from one person concerning the use of molecular sieves but I'm afraid I'll have to keep him anonymous for the moment. They use molecular sieves in the high pressure circuit in their plant and they are quite happy with their results.

HOUSER—Navy Bureau of Ships: In the last five or six oxygen-nitrogen plants we bought for ship's service, small plants using high pressure air at 3,000 lb., the contractor used molecular sieve beds at the beginning of the plant for CO₂ and water removal. So far as I know these have been very successful.

Catalytic oxidation

HOUSER: During World War II there was much research done on catalytic oxidation of hydrocarbons using gels made by precipitating manganese oxide with copper oxide together with various other activators in these gels. There must have been 40 or 50 different compositions studied. As I recall, the best one was a manganese oxide-copper oxide, with certain activators which I do not know the identity of. At any rate, I know nothing of the composition that was used by the MSA. I assume that it's the composition that was developed during the war years.

GLASS: I believe this has been reported by MSA and previously as being basically manganese oxide type.

Silica gel adsorbers

DJUVIK—Rohm & Haas: We changed silica gel in our rich liquid filters after six years of operation and discovered that the material removed actually had slightly better absorption characteristics than the replacement material and there was very little attrition loss. The plant is fed by nonlube centrifugal compressors. Has any one else had this experience?

GLASS: We have checked our gels, I believe, at the end of five years and found no signs of oil absorption. We found no oil take up and the color was about the same as it was when it was put in. We plan to look at it again; the next opportunity we'll have will probably be somewhere in the order of seven years of service. The efficiency for hydrocarbon removal seems to be increasing if anything. This we attribute to the fact that it is in extremely dry service and, if anything, we are taking out moisture in the process of using it in this service. Unless we see something different the next time when we take a look at it, we intend to keep the same gel in service.

WARREN: We have a plant with about 3 years of comparable experience and no attrition or shrinkage due to attrition; there might be a little that we can't spot, however, there is no evidence of loss. What has been your past reported history on that silica gel life?

GLASS: With our own service at Monsanto, we had been in service about 3 years when we had an explosion in the plant. We changed the silica gel at that time but have not changed it since.

WARREN: We have silica gel for removing oil on the downstream side of the third stage at 1,500 lb. pressure. We noticed that when we get enough oil to move up in the beds, about half to 2/3 of the way up, you start to get oil seepage through the beds apparently travelling along the metal surface. You have to dump the bed or switch over to another unit. I was wondering if anybody had any suggestions on recovery of this gel—when you got that much oil in it?

GLASS: One thing that should be brought out is the type of service the gel is in and whether or not you have parallel beds for regeneration. We do have two beds and we alternate between them and we're on about a 2-week regeneration cycle, for our beds.

ADRIAEN—Brockville Chemicals: I would like to know if the silica gel used in liquid oxygen streams is supposed to absorb oil as well as light hydrocarbons.

GLASS: No, we don't really have them in there for that purpose. We don't see oil in our system; we have centrifugal compressors with seals on them and don't see any oil. We have inspected our system using a solvent after one of the runs, and saw no sign of oil. So the silica gel is really not there for the purpose of catching oil.

SIMMS: At one of our earlier meetings I believe there was an indication that an interruption in operation might result in adsorbers being partially regenerated during the startup. If I remember correctly, I think Monsanto perhaps had this experience. I'm wondering if everyone, who operates hydrocarbon adsorbers in parallel within their cold box, switches adsorbers every time they have an interruption in operation for one hour or two?

PAPENFUSS—Olin Mathieson: One point before I answer that. A 3 year history that I listed on our hydrocarbon traps includes one abuse of regeneration where wet air was used to regenerate them. We expected considerable scalding but we couldn't detect it. Our operating practice is, if we have parallel traps, both of them normally in service, to regenerate on a quarterly cycle. If we have any sort of failure where a shutdown occurs, we'll take one of the traps out, regenerate it and then switch and regenerate the second one. On our traps, we also go to the standby unit if we have any sort of a failure.

DJUVIK: We also switch rich liquid filters following a plant failure. It's a little effort but we feel the additional safety margin justifies it.

Trichloroethylene dangers

MASON: It would be well to warn anyone not to smoke in an area where chlorinated hydrocarbons are present. The passage of these materials through the temperature of the fire at the end of a cigarette converts these to phosgene and other halogenated chemicals.

DOYLE—Factory Insurance Association: We have paid for at least two losses involving explosions of trichloroethylene vapors set off by welders. So in addition to the health hazard with your trichloroethylene, there is an explosive hazard. A welding torch is a sufficiently high intensity ignition source to cause an explosion if the vapor concentration is right.

The trichloroethylene itself or a contaminant or decomposition product, I investigated quite a few years ago, was a degreaser for washing machine parts which had been machined from aluminum. There were aluminum chips with fresh surfaces. The liquid analyzed normal inhibitor content. There is no proof, however, there may have been some vinyl acetylene involved, there may not. It was a nasty loss; there was a lot of hydrochloric acid around and electric parts were etched; that type of thing.

Another incident which occurred recently in Florida, a year ago possibly, involved the use of trichloroethylene to wash fabrics. I didn't investigate this myself so I'm not too familiar with it. The drier or unit where the trichloroethylene was being driven off the fabrics was being welded and exploded. In this case it wouldn't be a question of contamination; it must have been the trichloroethylene.

Flame ionization detector

HOUSER: Mr. Glass, you have previously mentioned the hydrogen flame ionization detector on a chroma-

tograph; I do not know what it is and I think, possibly, others do not.

GLASS: Yes. What this device is: you pass your carrier stream from the chromatograph through a hydrogen flame—a little flame burning hydrogen—the flame itself will ionize the various components that are present and you pick up the variations and ionization with an ionization detector.

Nitrogen analysis

SIMMS: I have a question. We are about to erect a nitric acid plant within a matter of a few hundred feet of our air separation plant. Will the caustic wash preceding the air plant remove the nitrogen oxides? If not, how do you monitor them? Does anyone have a similar situation?

STRELZOFF: In that case I would use an air intake sufficiently long to eliminate any chance of contamination of the air by nitric oxides.

WARREN—Du Pont: First I wanted to ask, what oxide nitrogen Mr. Simms was specifically referring to, maybe then I could answer the question.

SIMMS: I would presume we could consider this a mixture of nitrogen oxides, in a typical tail gas from a nitric acid plant.

WARREN: We think that we have NO₂ in our tail gas in the neighborhood of about 0.2%. I think this is probably common to most nitric acid absorbers under pressure. The NO₂ will vary, depending on where you take your sample from; as it leaves the top of your tower, the NO₂ content will be very small but your NO content would be sizeable. As long as your're running with excess oxygen, your NO is going to oxidize NO₂, so that somewhere downstream you've got your caustic scrubber and you're going to remove both NO and NO₂. The efficiency of this removal is going to depend upon how much NO and NO₂ you have at that time. I'd like to go into another problem, slightly related to this. We have an Engelhard-Du Pont process which is scrubbing nitric acid off gases. The system is a caustic scrubber followed by a water scrubber to remove ammonia. Now the NO content of the gas leaving the oxide unit—you don't have to go into the unit—we recently measured and found in the neighborhood of 5 to 10 ppm NO in the nitrogen. Our oxygen content is nil and as far as we can determine it's less than 1 ppm of oxygen. In fact we have an excess of hydrogen at this point. This gas goes all the way down to compression equipment. It goes through drying equipment and goes into our cold box. It goes through activated char which is at -60°C and we find this NO is still present. We now feel that this NO is going into our liquid nitrogen wash column. The problem that I would like to discuss is: Is there any hazard? Does anybody feel that there is a hazard here of reaction with ethylene in our liquid nitrogen? We know that we have traces of ethylene; less than 1 ppm in the hydrogen, in the same wash column.

GLASS: I'd like to comment about the analysis for nitrous oxide in liquid oxygen. We do this with a pressure cell. We do it with infrared in a ten meter cell; infrared analysis, under pressure.

WARREN: We started analyzing for NO using a sampling bulb and taking it down to our analyzer and putting it on 10X magnification, which is the best our in-

strument has at the present time. Our analysts tell us that they cannot analyze any lower than 30 ppm, 30 ppm was our limit. Up to this year we were assuming that less than 30 meant zero, however, it may not.

Silver ammonium complexes

WARREN: We have found in a anhydrous ammonia storage tank, which had a silver rupture disc, that we had accumulated some solids on the underside of the rupture disc. We examined it and then sent it to our explosive lab for tests. They found that it was explosive, a fairly high explosive. We made a literature search and found that there are some silver ammonium complexes which are explosive. As a result, until we know further under what condition these are explosive, and what the compounds are, we are making sure that we don't have any silver in anhydrous ammonia usage. We also had a silver soldered joint on the electric

heater in the converter and we examined this. There was no evidence of an accumulation of this material so we're still in the dark as to exactly what we did find.

Fluorinated lubricants characteristics

DOYLE: Fluorocarbon lubricants are wonderful things but they mostly need an additive to prevent hydrolysis and acid etching of the lubricated surface. What these additives are are pretty much trade secrets but when you buy one you should explain the use so you will not leach out under conditions of normal use or of cleaning, otherwise, you will corrode your bearings very fast.

MASON: There is one other thing to remember about these fluorinated lubricants. As Mr. Doyle points out, they have some objectionable characteristics. At high temperatures they break down into toxic materials.