EXPLOSION IN NITROGEN GAS COMPRESSORS

Prepared by J. A. Rogers
The Best Fertilizer Co.
Lathrop, Calif.

Presented by F. W. Wilson
Consulting Engineer
St. Paul, Minn.

The California Ammonia Co. operates an air separation plant for the production of nitrogen gas as part of its ammonia plant facilities located at Lathrop, Calif.

Medium pressure steam reforming

The over-all process for ammonia production is medium pressure steam methane reforming (150 lb./sq. in.) followed by shift conversion, mono-ethanolamine scrubbing for CO_2 removal, and compression to 350 lb./sq. in. for the separation of carbon monoxide and residual methane in a liquid nitrogen wash unit. The hydrogen-rich synthesis gas is then compressed to 3,000 lb./sq. in., the operating pressure of the ammonia synthesis unit. Additional pure nitrogen is also compressed to 3,000 lb./sq. in. and the required hydrogen-nitrogen ratio is maintained by regulating the amount of 3,000 lb./sq. in. nitrogen added to the synthesis. The general system is illustrated in Figure 1. A simplified flow diagram of the air separation plant is shown in Figure 2. The air-nitrogen compressor flow sheet is shown in Figure 3.

Crude hydrogen is produced by reacting natural gas and steam over a nickel catalyst. The reformer furnace generates its steam supply in a waste heat boiler and is fed with natural gas through regulating valves direct from the high pressure transmission line. The reformed gas passes through the shift converter, MEA absorber and miscellaneous heat exchange to arrive at the suction (100 lb./sq. in. and 100°F.) of the multiservice, multistage compressors. The crude hydrogen (about 90% hydrogen, 2% nitrogen, (from the natural gas) 3% carbon monoxide and 5% methane), is compressed to 350 lb./sq. in., washed with caustic and dried before going to the nitrogen wash unit.

Moderate speed compressors

All of the compressors are of moderate speed (360 rev./min. × 12-in. stroke, and 300 rev./min. ×

14-in. stroke) driven by synchronous motors. The plant is basically a one train plant except that all compressor services are provided as two 50% units. 50% of the air (three stages to 250 lb./sq. in.) and 50% of the nitrogen (five stages to 3,000 lb./sq. in.) service are combined on each of the multiple service air-nitrogen compressors.

The plant is located in a rural area with minimum contamination of the feed air. The air is washed with caustic after compression, chilled, and dried over activated alumina. The cool dry air at about 40°F enters the main heat exchangers of the air plant. These exchangers are two identical units in parallel but are manifolded without isolation valves. There is a butterfly valve on the inlet air to each unit for flow distribution. All of the product gas streams pass counter-current to the incoming air. The major portion of the chilled air passes through turboexpanders to provide the necessary refrigeration of the system. A small portion of the air by-passes the expanders, and is further cooled and liquefied by the product streams in the liquefier exchanger. It is then subcooled in a reboiler coil in the base of the high pressure tower before being flashed through a control valve into the tower at the liquid feed tray.

Product purity

The rich liquid air from the bottom of the high pressure tower (containing 35 to 40% oxygen in nitrogen) is passed through a silica gel filter for hydrocarbon removal, then through the argon condenser of the argon side column, and on into the main feed tray of the low pressure column. Nitrogen reflux is drawn from the top of the high pressure column, subcooled by heat exchange with the product nitrogen gas and feed to the top of the low pressure column.

Pure nitrogen product gas (99.995%) is removed from the top of the low pressure column and 98% oxygen gas is removed from base just below the first tray. A waste gas stream is removed several trays down from the top to smooth out the variations and surges of the system.
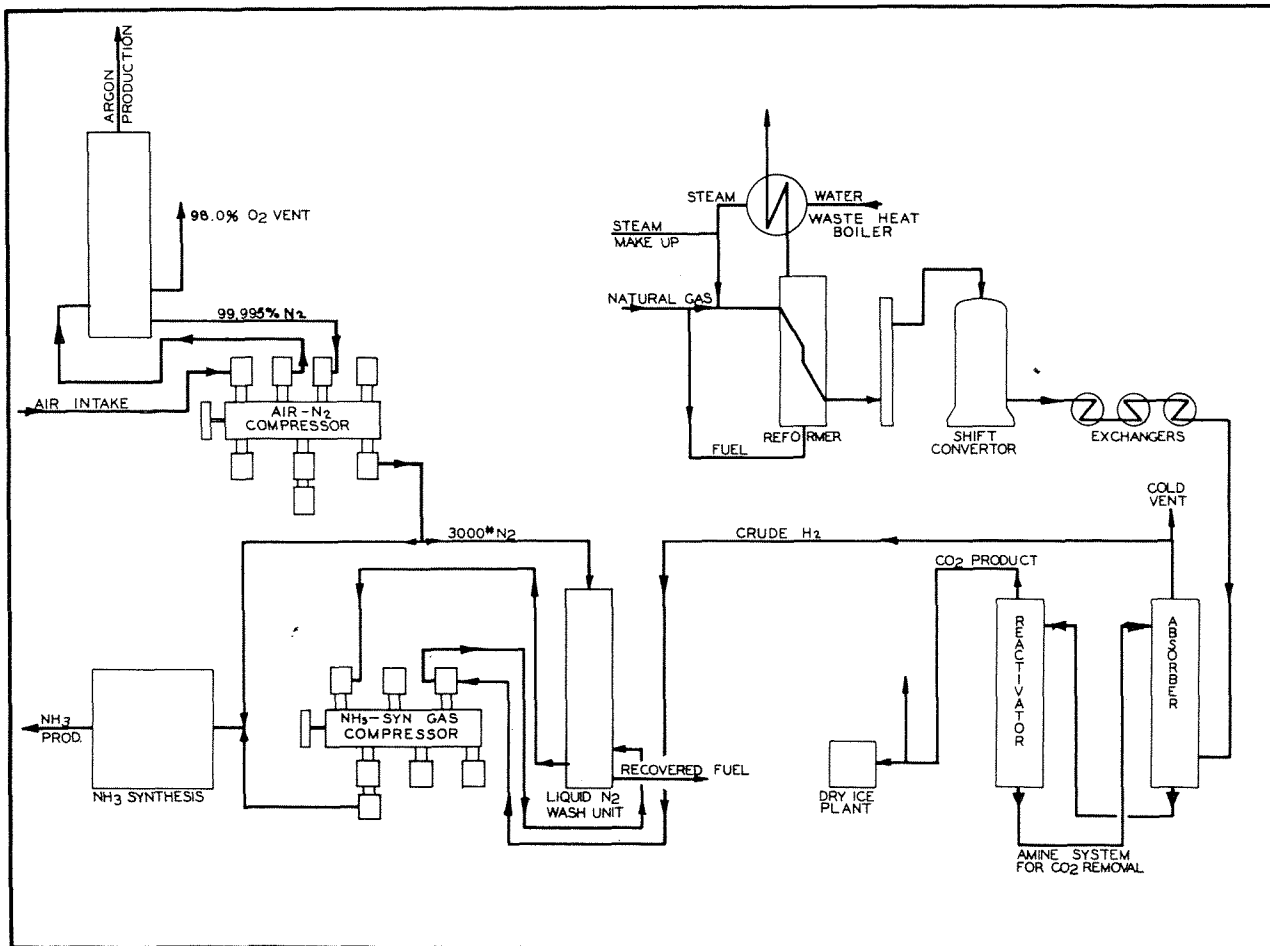
Figure 1. Simplified flow sheet of the ammonia plant of California Ammonia Co.

Repair of a leaking tube

On November 3, 1963, the ammonia production was stopped to repair a leaking tube in the waste heat boiler. The main exchanger of the air separation plant had been derimed the previous month so the air plant was kept running at a low rate during the shutdown to provide purge nitrogen. An attempt was made to derime two exchangers in the nitrogen wash unit which were showing a loss of exchange. During restarting operations on the morning of November 7th one of these exchangers showed evidence of plugging. A further derime operation was started in the nitrogen wash unit.

The reformer furnace was in operation at low rate. The crude hydrogen was being vented at the inlet of the compressor. No hydrogen was being compressed either to the 350 lb./sq. in. nitrogen wash level or to the 3,000 lb./sq. in. synthesis level.

The air plant has been in continuous operation and functioning normally. The output from the nitrogen compressors was running above 1,500 lb./sq. in. gauge. A small amount of the compressed nitrogen was being vented, the main part was recycled back to suction.

Temperature upset of inlet air

Shortly before 11:00 a.m. on November 7, 1963, the temperature of the inlet air to the air separation plant turboexpanders rose about 50°F in approximately 15 minutes. At the same time there was a rise in the air pressure to the air separation unit and a rise in the high pressure column pressure. Simultaneously the oxygen impurity in the product nitrogen started to rise. The oxygen analyzer on the product nitrogen had been running about 60 ppm oxygen. It rose to full scale of 200 ppm in about four minutes. The operator then switched to the secondary scale of 0 to 1,000 ppm. The analyzer then started indicating 400 ppm oxygen and continued to rise to full scale of 1,000 ppm over a period of about two minutes. At this point the operators isolated the nitrogen system from the ammonia synthesis unit and the nitrogen wash unit.

The limit of the analyzer was 1,000 ppm of oxygen. This was reached in approximately six minutes from the beginning of the upset. Eight minutes later, or a total of about 14 minutes from the initial indication of increasing oxygen by the analyzer, both of the nitrogen compressors were blown apart by an explosion.

The extent and type of damage would indicate that a detonation apparently took place simultaneously in the fourth stage cylinder and the fifth stage after-coolers and separators of both compressors. The nitrogen section of each compressor was almost a total loss. Four men were in the building, all of whom suffered shock, eardrum damage and varying degrees of cuts and abrasions. One of the four suffered a concussion and required hospitalization for a few days. All have recovered and are back to work.

Figures 4 to 10 show the extent of the damage.

N2A/B MAIN INLET EXCH.
N3 LIQUIFIER EXCH.
N6 N_2 SUBCOOLER
N39A/B EXPANSION TURBINES
N61 ARGON COLUMN
N62 ARGON CONDENSER
N63 COIL
N67 HP COLUMN
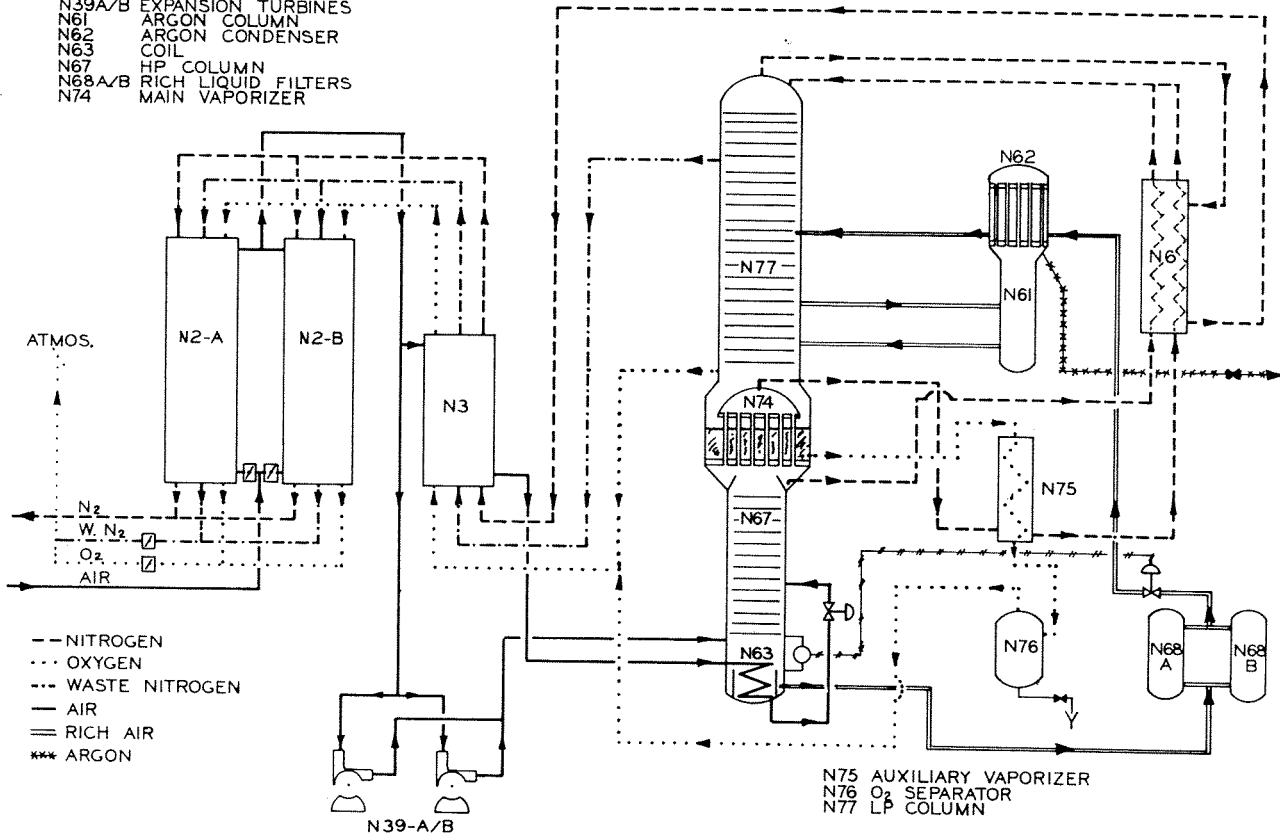N68A/B RICH LIQUID FILTERS
N74 MAIN VAPORIZER

ATMOS.

N2-A   N2-B   N3

N_2
W. N_2
O_2
AIR

N77

N62

N61

N6

N74

N75

N67

N63

N76

N68 A   N68 B

-- - NITROGEN
· · · OXYGEN
-·- WASTE NITROGEN
— AIR
= RICH AIR
*** ARGON

N39-A/B

N75 AUXILIARY VAPORIZER
N76 O_2 SEPARATOR
N77 LP COLUMN

Figure 2. Simplified flow diagram of the air separation unit.

2 AIR   1 AIR

AIR FILTER

3 AIR

AIR

2 N_2 3 N_2 C-301B

1 N_2

5 N_2 4 N_2

N_2 SUCTION
MP N_2
HP N_2

TO C-301A
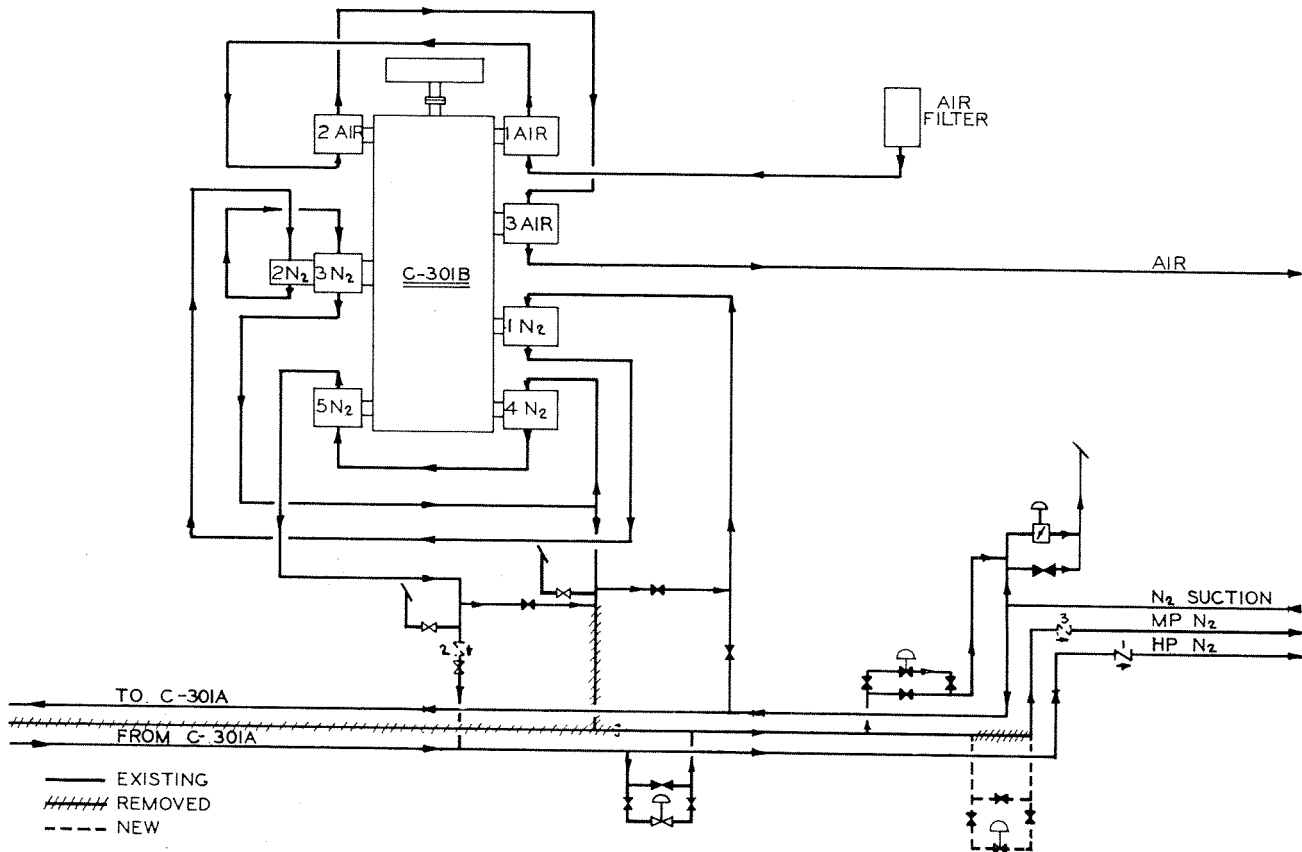
FROM C-301A

—— EXISTING
////// REMOVED
- - - NEW

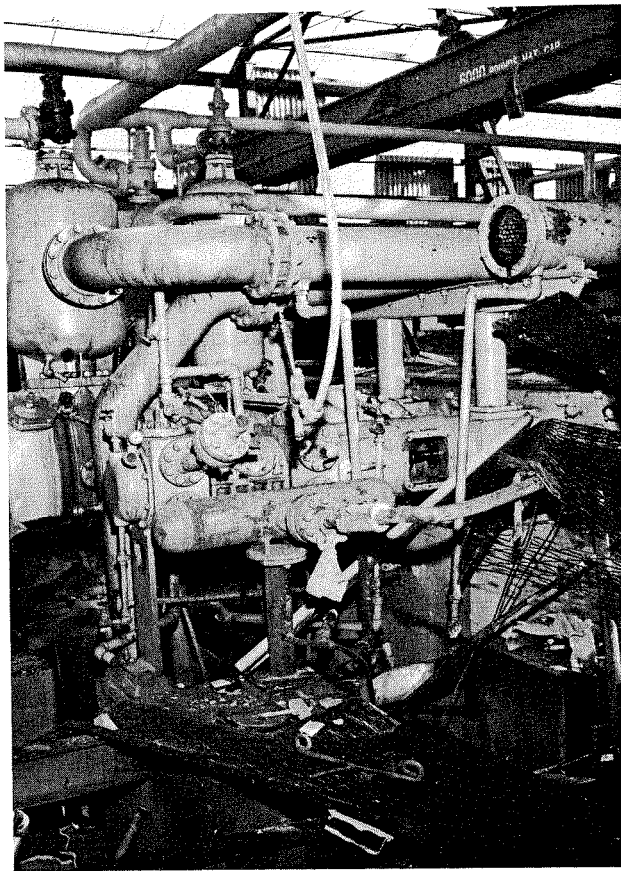Figure 3. Air-nitrogen compressor flow sheet.

Figure 4. View of north side of C-301A looking east. Fifth-stage 3,000 lb./sq.in. gauge nitrogen cylinder in foreground.

Source of ignition and fuel

The source of ignition could be from heat of compression plus possible rapid oxidation of activated particles on the walls of the pipes or separators.

The fuel for the explosion could be hydrogen or lubricating oil and lubricating oil vapor from the recycled gas. The plant was in start-up conditions with the crude hydrogen and synthesis gas compressor cylinders on by-pass. There was some residual hydrogen in the nitrogen wash and ammonia synthesis unit but, due to the time interval between isolation of the compressors and the explosion, it is believed that lubricating oil vapor, rather than hydrogen, was the most likely source of fuel.

Source of oxygen

The source of oxygen was a rapid and gross loss of purity of the product nitrogen from the air separation plant. This loss of purity was the end result of a chain of reactions set up by a malfunction of the main inlet exchangers, resulting in a loss of heat exchange which carried heat into the high pressure tower causing a vaporization of liquid in the tower, an increase in tower pressure, and a lowering of liquid level in the high pressure tower bottom. This lowering of liquid level caused the control valve on the rich air feed to the low pressure column to close allowing a substantial reduction of liquid on the trays of the low pressure column simultaneously with the increased heat input from the high pressure column through the reboiler. This increasing heat load caused a rapid

boiling of the liquid oxygen in the base of the low pressure column. The oxygen vapor rising up through the trays countercurrent to a sharply reduced liquid downflow is believed to have resulted in a breakthrough with a consequent rapid build-up of oxygen in the product nitrogen.

Prior exchanger damage

The main inlet exchangers were damaged on April 10, 1961, by a carryover of caustic solution from the wash tower. Two small leaks were found in the air section after washing and testing. One leak was to the oxygen product and was repaired by welding up one of the twenty parallel air passages. The other leak was to the waste nitrogen passage and due to the small size, no repair was made. The unit was placed back in operation on April 20, 1961.

A new replacement exchanger was ordered in April, 1961, due to the uncertainty of the performance of the repaired unit. The plant was running satisfactorily when the new exchanger arrived and it was felt that the over all performance did not warrant the down time to install a new unit.

The air separation plant continued to operate satisfactorily until the malfunction of November 7, 1963. The efficiency of the exchanger during this period was down somewhat as measured by the warm end temperature approach. The operators have at times experienced trouble in maintaining the optimum temperature balance which has necessitated several adjustments and readjustments of the butterfly valves on the air inlet.
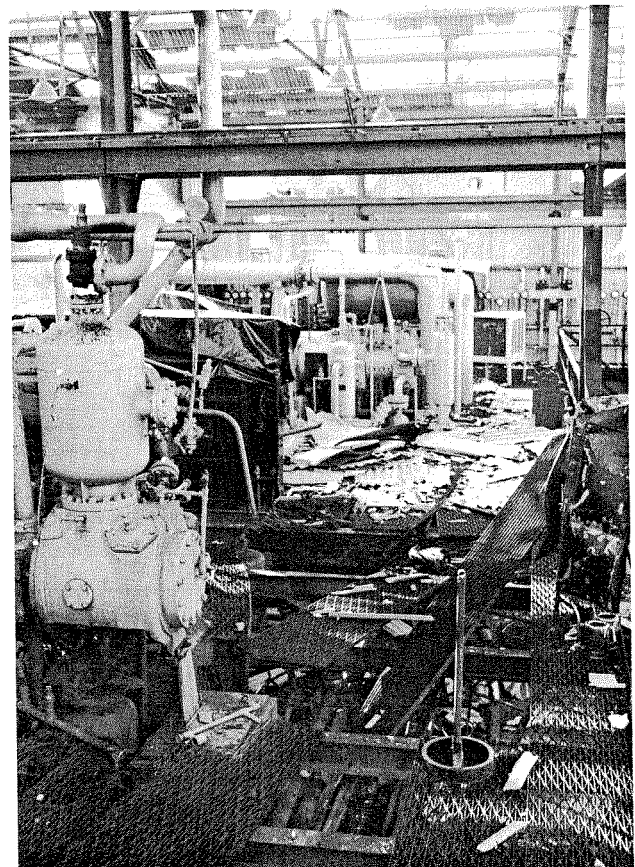

Figure 5. View of north side of C-301A looking east. Second-stage 160 lb./sq.in. gauge nitrogen cylinder in foreground.

Substantial flow shift

The malfunction of November 7, 1963, was apparently a sudden substantial flow shift of the inlet air. Subsequent flow testing has indicated a much greater pressure drop on the air passages of one side of the parallel unit versus the air passage of the other. This condition could be caused by collapsing or shifting of the internal extended surface, however, the unit has not yet been cut open to verify this point.

A new main inlet exchanger set and by-pass liquefier exchanger have been installed and the plant was back in full operation on January 17, 1964.

Safety improvements

It is assumed that a source of ignition always exists in an operating reciprocating compressor with a 3:1 or higher compression ratio. Therefore, efforts have been directed at eliminating or reducing possible fuels and preventing the oxygen concentration from rising above a predetermined level while the compressor is under pressure.

Hydrogen contamination

Possibility of hydrogen contamination is reduced by addition of second high pressure check valves shown as (2) in Figure 3. The original check valve is
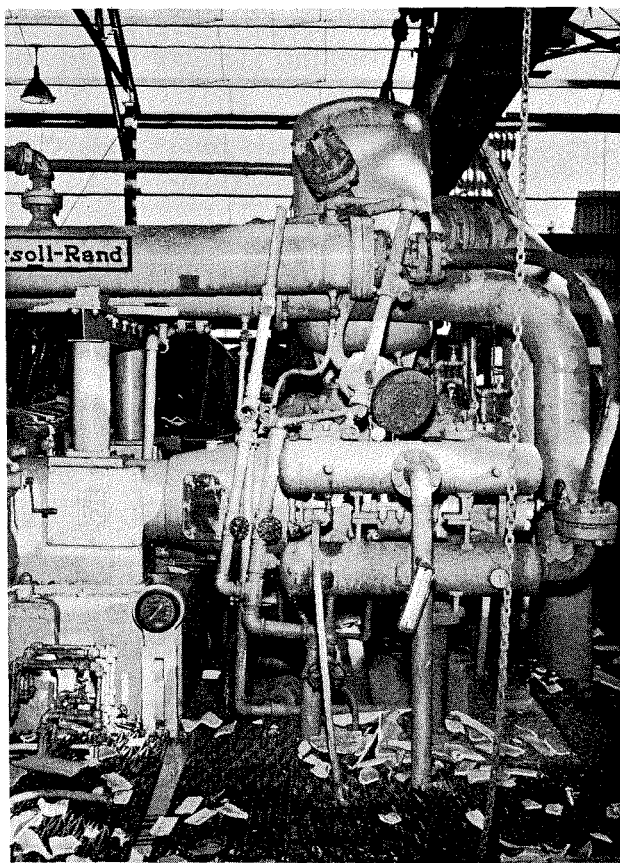

Figure 7. View of 250 lb./sq.in. gauge air separator. Damage to nozzle and outlet line from external force. No internal damage to air system.

shown at (1). Hydrogen contamination from the nitrogen wash unit is reduced by addition of check valve shown at (3), the elimination of the intermediate interstage compressor connection and the addition of a two stage letdown to the 300 lb./sq. in. nitrogen purge system. Also, the recycle line now enters on the branch line leading to the low pressure vent so that any recycled gas will be vented preferentially. This will provide a reduction of recycled oil vapors as well as minimizing possible hydrogen contamination. It is planned to switch to a minimum lubrication system using specially compounded Teflon piston rings and piston rod packing rings as a further step to reduce oil vapor contamination. Also, operating instructions are being changed to require maximum high pressure venting with minimum recycle. This will help to keep the system continuously purged of possible fuels.

Oxygen contamination

Oxygen contamination will be controlled by the addition of a second dual range oxygen analyzer. The normal range will cover 0 to 2,000 ppm and the high range will cover 0 to 1% oxygen. This instrument is set up to continuously monitor the product nitrogen header from the air separation plant. It will alarm at 75% of full scale (1,500 ppm of oxygen) and automatically switch over to the high scale. Then if the instrument again reaches 75% of full scale, (7,500 ppm of oxygen) it will open a normally-closed relay interlocked with the switch gear of the synchronous motors, to shut down the compressors. This will automatically
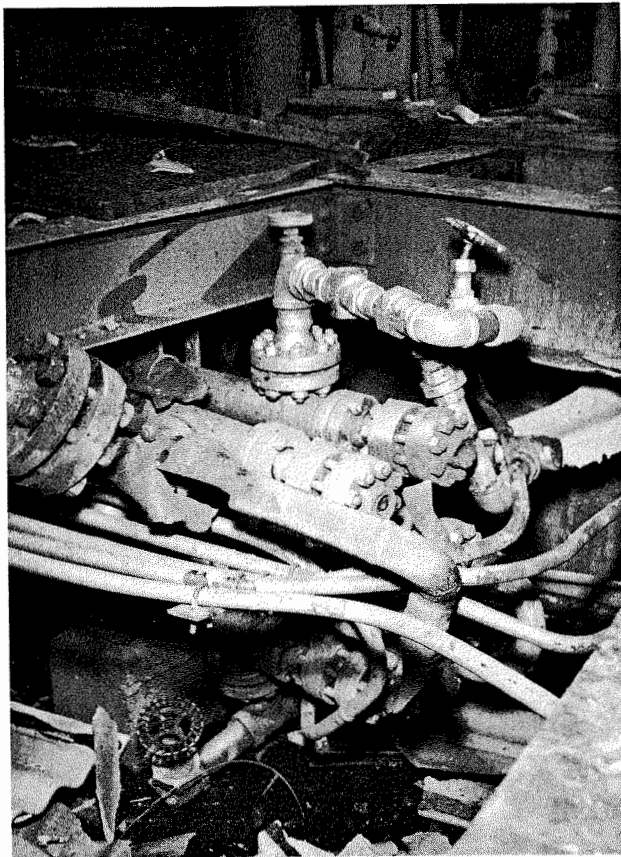

Figure 6. View of the south side of C-301A looking east. Fourth-stage 1,200 lb./sq.in. gauge nitrogen cylinder in foreground.

Figure 8. View of fifth-stage 3,000 lb./sq.in. gauge nitrogen aftercooler. Note rupture of 2-in. Schedule 160 line.
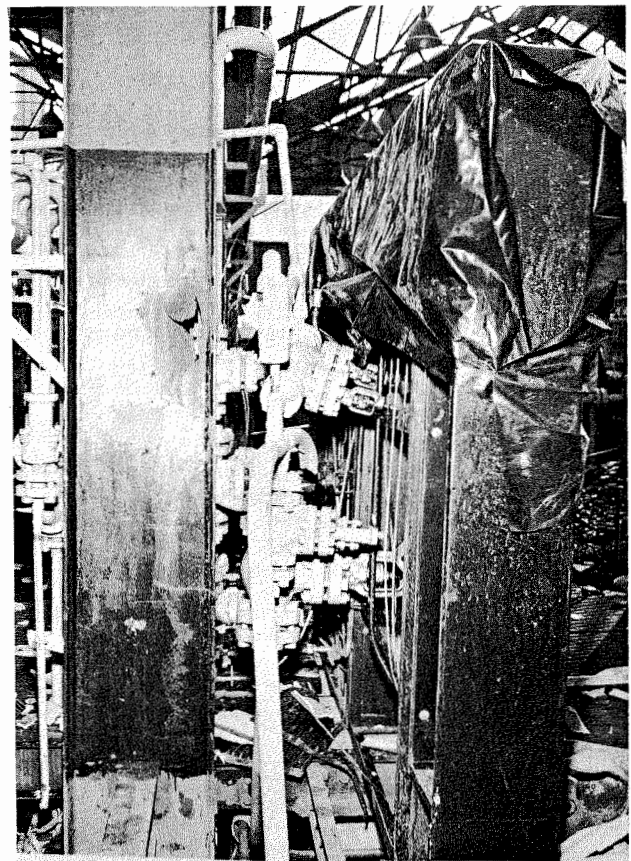

Figure 9. View of piping at control board. Note puncture of building column.

prevent the oxygen concentration from reaching 1% when the compressors are running under pressure. Note: This arrangement requires a by-pass for start-up conditions. This by-pass is provided by an automatic pressure switch relay, normally closed below 100 lb./sq. in. gauge. and open above 100 lb./sq. in. gauge, installed in parallel with the analyzer switch. In order for the power to the compressor motors to be interrupted, both of these relays must be open. Thus, on starting the analyzer relay will be open, but the pressure relay will be closed as long as the nitrogen cylinders are unloaded (below 100 lb./sq. in. gauge).

When the nitrogen product contains less than 0.75% oxygen (7,500 ppm) the analyzer relay will close. The nitrogen compressor can then be loaded above 100 lb./sq. in. gauge. If the oxygen content of the product nitrogen should now rise above 7,500 ppm, the analyzer relay will open. If the discharge pressure is still above 100 lb./sq. in. gauge, both relays will be open and the compressors will shut down.

Reference is made to the report published by the Compressed Gas Association "papers presented at the Air Separation Plant Safety Symposium," October 16-17, 1962, pages 60, 61, and 62 for information on the safe operating level of oxygen in nitrogen gas compressors.
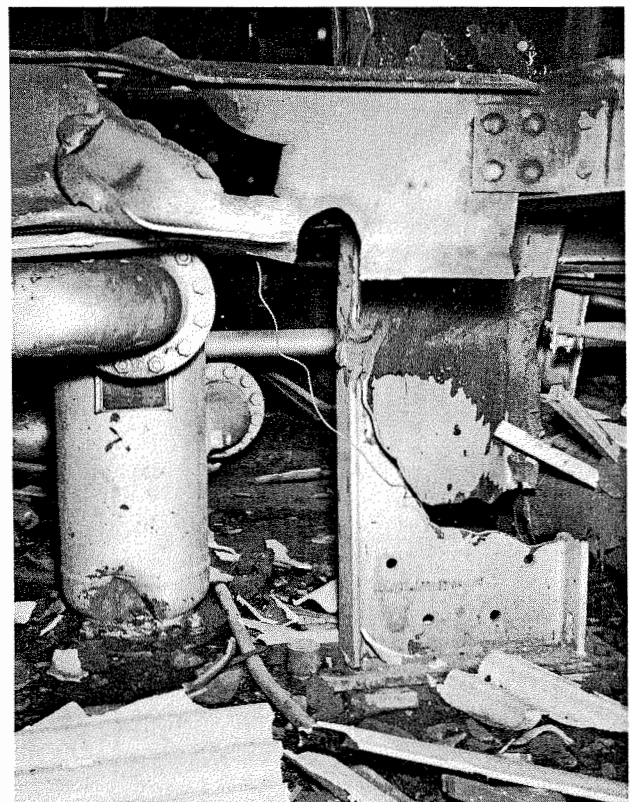
Acknowledgment

Figure 10. View of building damage.

DISCUSSION

BUTIKOFER—American Oil: I want to comment on a low temperature separation unit that exists in the Calumet Nitrogen Products Co. plant that American Oil operates. This happens to be one of the problems that has given us a lot of concern.

Now what we have done there is to establish a shutdown limit on it of about 750 ppm oxygen in the nitrogen going to the nitrogen compressors. If we reach that limit, all three nitrogen compressors and the nitrogen supplied to the synthesis gas for ratio adjustment are tripped in the main control room manually. We thought about using automatic trips for this, but felt that it might induce an instrumentation failure which would still get us into trouble, so we do this manually.

REYNOLDS—Standard Oil of California: I just wanted to comment that I did get a chance to see the Best plant approximately a month after the explosion. It was pretty well cleaned up but not all the damage had been repaired, and I was very impressed by the force of the explosion. There was one vertical 16-in. H-beam which was completely severed just below floor level. In the case of the steel separators or pulsation bottles, one of those was torn apart with such force that two pieces, about 6 or 8 in. in diameter, I would say, and about 1 in. thick, were thrown in opposite directions 200 or 300 ft., or possibly more. It was really a miracle that nobody was hurt any worse than they were. I think the most serious injury was from a piece of the transite roofing falling on the head of a man who was outside the building.

WALTON—SunOlin: One of the things mentioned in some of the previous talks was the importance of instrument reliability. Particularly one of them that was mentioned was thermocouples in secondary reformers. This is something that gives us considerable concern. In our particular secondary reformer we use oxygen instead of air, but otherwise its operation is the same.

Our thermocouples are platinum couples in the hot zone, and they only last about two months. In fact, in the last couple of weeks of those two months, they tend to be rather erratic. This is not only expensive but it's also worrisome. The wells are 304. We are changing them to Incoloy. I don't know whether this is going to help any or not. We're going to change these wells on the October 1st shutdown. I'd be interested in any comments that anybody has on reliability of thermocouples in secondary reformers.

ELLIS—DuPont: I'd like to ask more about Incoloy failure of the ell that Mr. Wilson mentioned, because there's a great tendency to go to this material to replace the 330 stainless steel that fail by sigma phase formation. Can you describe the failure any more?

WILSON: No, I can't describe it any more than to pass along what Mr. Rodgers told me in a very short conversation. He said that the original Incoloy 800 header was not annealed, and the second one wasn't solution annealed, therefore, he felt that this was an important point.

CROYSDALE—Farmers Chemical Assn. (Formerly with Best Fertilizer): The Incoloy failed basically on the tentative specs; the original stress data were incorrect.

Anonymous: This is right. That stress level had reduced I think in the past three years. It was down to 1500 lb./sq.in.

CROYSDALE: The header ballooned basically.

Anonymous: I want to mention a caution in regard to this. There is some tendency to use the Incoloy filler on this material, and with the packing you can get into a precipitation phenomenon and the welds will crack on you. It is better to use the Incoloy coated electrode, which has a lower titanium value, and will not crack on you.

WILSON: The header did not balloon. It apparently was not a stress condition in this case. I'm assuming this from what little I know about the accident.

SORRELL—M. W. Kellogg: With due respect to Incoloy, they have developed a new electrode, which is preferable to all these Incoloy aids and so on, and specifically, an Incoloy electrode, and I think that that should be noted.

ELLIS: How much experience do we have with the 182 rod or the 82 rod that has been suggested for the Incoloy welding. When you use this, they recommend that you stir in about 75% of the parent metal to get a good constituent there. Have you experience with the 182 or the 82?

We've been just a little bit cautious, we're going ahead with the rod without too much experience on the other materials and it's working for several years.

STAFFORD—Farmers Chemical Assn. I was going to comment on the thermowells in the secondary reformer. We had the same problem, and one of the solutions I feel is to shorten your thermocouples so that they only extend into the bed approximately 6 in. This does not affect either temperature sensing or reliability.

MCMAHON—Collier Carbon & Chemical: While we are discussing the subject of compressor failures, I would like to report an incident which occurred recently at our Brea plant. We suffered a detonation-type failure in the fourth-stage discharge system of a process air compressor.

Historically, numerous reports have been made at previous symposia concerning this subject. Representatives of our company have carried reports back and we have reviewed our operating practices very thoroughly—or so we thought.

We felt that our annual cleaning with steam and TSP were adequate to avoid this type failure in our equipment. However, after nearly ten years of operation, in January last year we experienced a detonation-type failure in our system. So we have again reviewed all of our practices, and after considerable study we have switched from the use of conventional hydrocarbon lubricant to the use of synthetic lubricant.

We considered converting our compressors for operation without lubrication. However, we didn't feel that there was enough practical experience to convince us to go in that direction. We hope to hear a good deal more about that.

We would also be interested in getting information from this group regarding the tendency of synthetic lubricants to decompose in the presence of caustic. I know there has been some discussion on this subject during previous meetings. I would like to hear whether there have been any new developments in the past year?

LARUE—Spencer Chemical: In reference to the discussion of synthetic lubricants, perhaps I can present a little background which may prove interesting. We

were one of the first plants to use a phosphate ester synthetic lubricant. In early 1956, two air compressors were converted to a synthetic lubricant. These compressors discharge air at 630 lb./sq. in. gauge into a 1,000 ton/day air plant. This was done in an effort to eliminate the fires and explosions which had been occurring in the air discharge headers and the aftercooler. From 1956 to August, 1964, no problems were experienced with the lubrication system on the air compressors. Several years ago the centrifugal compressor which provides the air to the suction of the two reciprocating air compressors tripped. The two reciprocating compressors were inadvertently left on the line, so there was a suction pressure of approximately 5 lb./sq. in. gauge to the compressor while a back pressure of 600 lb./sq. in. gauge was still being maintained into the air plant. One can vividly imagine the tremendously high compression ratios which were present for a short period. There is a multiple temperature recorder for various points on the air header, and during this period the temperatures approached 500°F. Under these extreme and severe conditions, no fires or explosions occurred. Thus, we were lulled into a false sense of security by the long trouble-free run and the experience just related.

In August, 1964, a fire occurred in the second-stage aftercooler. From the products of combustion and residue material found in this exchanger, we strongly suspect that a breakdown occurred on the synthetic oil. I would be very interested to hear any comments from others on whether anyone else has experienced anything of a like nature.