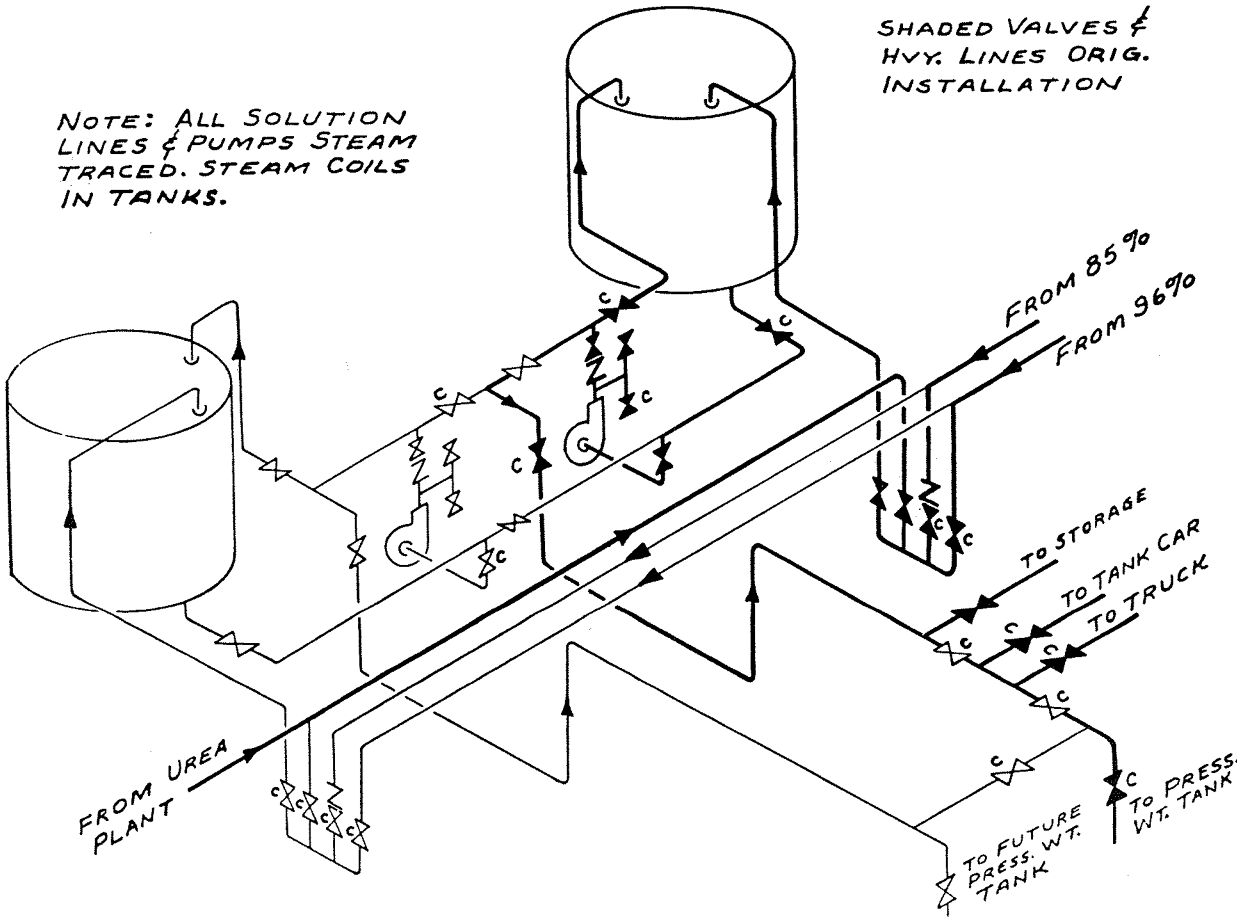

Figure 1. Schematic of solution blending installation.

Urea-ammonium nitrate solutions: Are they safe?

Explosion in the mixing installation of a fertilizer plant points out the potential hazards. Avoid contamination or conditions of temperature and concentration that result in explosive mixtures.

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Farmers Chemical Assoc., Inc.
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EXPLOSIONS INVOLVING ammonium nitrate or ammonium nitrate-oil mixtures have been reported in the literature, however, up till now, those involving urea-ammonium nitrate solutions have not been analyzed and reported on. More than one year ago, the Farmers Chemical Assoc., Inc., plant at Tyner, Tenn., was the scene of an incident attributable to the latter combination of materials.

Manufacturing facilities

FCAI manufactures ammonia by high pressure primary steam reforming (180 lb./sq. in. gauge) of natural gas, followed by secondary reforming, to produce synthesis gas which is then purified by utilizing two stages of CO conversion, CO_2 removal by MEA absorption, and methanation of remaining carbon oxides. The purified synthesis gas is compressed by two 5,000 hp Ingersoll-Rand electric-driven multiservice compressors and is delivered to a conventional 5,000 lb./sq. in. gauge synthesis loop. The ammonia formed in the ammonia converter is condensed and stored for sale or further processing.

Part of the ammonia is used to manufacture nitric acid. The acid is produced in standard Hercules designed 55-ton units employing electric-driven and power recovery In-

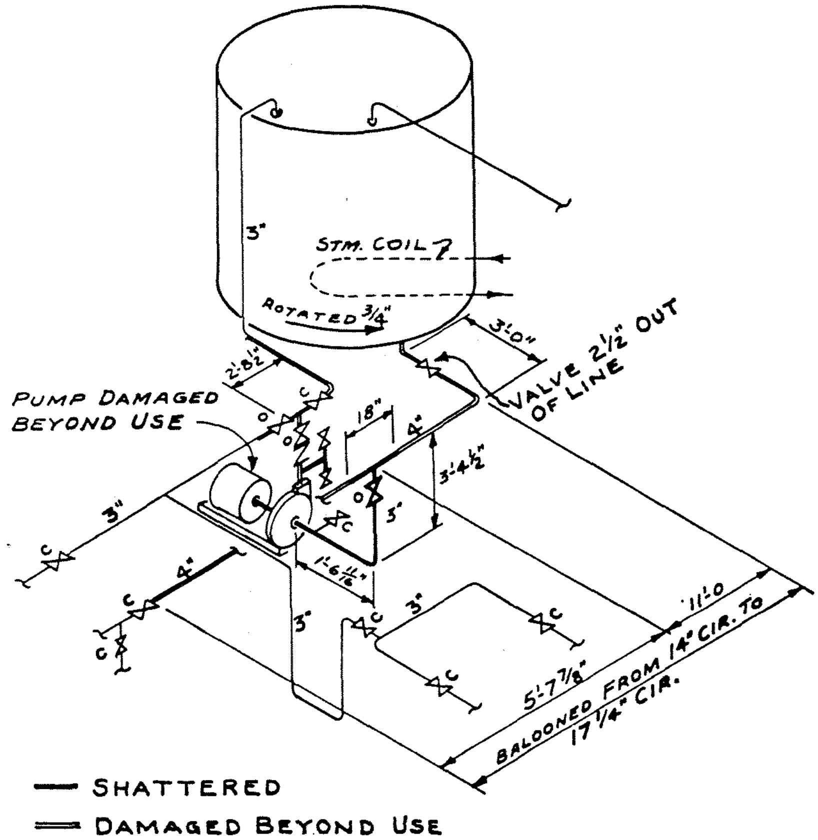

Figure 2. Details of area in which explosion occurred.

gersoll-Rand compressors, types PRE and XRD.

Ammonia and nitric acid are fed to a Girdler designed plant for the manufacture of ammonium nitrate. An 83% solution is produced in an atmospheric neutralizer which normally operates slightly on the acid side. The solution is made basic before further processing into prills or for storing by the addition of ammonia.

Urea is manufactured in a Chemico once-through plant with the off-gases being utilized in the ammonium nitrate neutralizer. A four-stage Ingersoll-Rand compressor is employed to compress the CO_2 gas to approximately 3,000 lb./sq. in. gauge. Ammonia is fed to the autoclave by an Aldrich triplex pump. Urea production is mixed with 83% ammonium nitrate by an in-line blending process to produce a finished solution according to predetermined specifications.

General supporting facilities include a complete potable water plant of 36 million gal./day capacity and a 150,000 lb./hr. coal fired boiler. These supporting facilities and the acid plant are part of a T.N.T. plant leased from the government.

Physical layout

The heavy lines and solid valves of Figure 1 show the original mixing solution installation (atmospheric pressure). The lighter lines and valves indicate the revised layout installed to increase the plant capacity. Basically, the unit was being mirrored; however, this was not the case from an operational viewpoint. Normal economical operation requires a minimum of switch operations; once a setup arrangement is made, an operator would open and close a minimum number of valves. Operators were well trained and thoroughly familiar with the original installation and did not entirely block in the system. With the increased isolation valves, it was quite easy to block in the system. At the time of the explosion, valves with a "C" beside them were closed and all the 85-lb. steam tracing systems and steam coils were in service. Specific revisions in operating procedures had not been considered necessary. In other words, safe procedures may have been violated as a result of the expansion and, as so often happens, not realized until after the incident. Unfortunately, this seems to be one of the contributing factors to numerous other similar industrial incidents.

Operating conditions

Checking back to 12:30 A.M. the morning of October 21, 1963, the plant log indicated that the following solutions were produced: Between 12:30 A.M. and 7:35 P.M., at which time the explosion occurred, three different batches were produced. The first batch was DA-333 stock solution which consisted of 80.6% of urea put in the scale tank and the addition of 85% ammonium nitrate blending by circulation, and then subsequent pumping to a 7,000-ton storage tank. The second batch consisted of a tank full of stock solution which was diluted with water to the required strength and then loaded into a tank truck. The third batch was the same as the first. Laboratory analysis of the final solution showed an analysis of 39.2% urea and 46.1% of ammonium nitrate. This solution was transferred into a storage tank. A fourth batch was being prepared at the time of the explosion. The third batch was completed at 6:30 P.M., the system blocked in, pump shut off, and 20,000 lb. of 83% urea put into the scale tank for pumping.

The operators had just completed their routine inspection and had left the vicinity of the solutions scale tanks only minutes prior to the explosion. Other operational and maintenance men on duty were on their dinner break.

The actual explosion

At 7:35 P.M., the explosion took place. Operators present reported it as a sharp shock. Maintenance personnel, approximately one mile away in the shop building, were startled but resumed their dinner break deciding a jet had broken the sound barrier. Plant personnel, living three to five miles away, confirmed hearing what they thought to be a jet breaking the sound barrier.

Figure 2 shows a schematic of the actual piping and associated equipment. The actual position of each valve is noted with a "C" for being closed and an "O" where the valve was open. The very heavy sections indicate the section of piping and valves which were actually shattered by the force of the explosion. Piping from the original tank to the isolation valve was severely ballooned and distorted from original circumference of 14

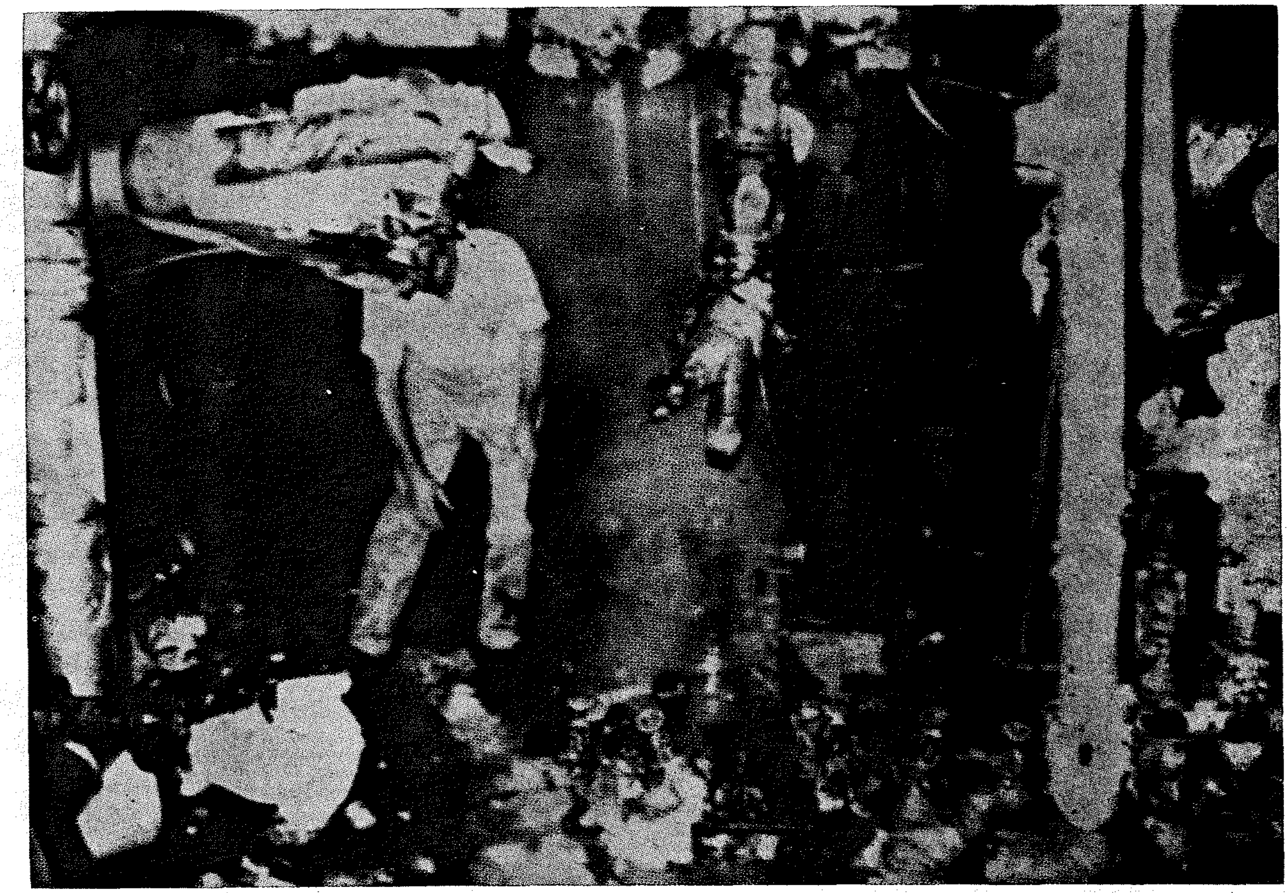

Figure 3. Scene of the explosion approximately one hour later.

in. to a circumference of 17¼ in., as was the discharge pipe to the tank isolation discharge valves. The pump, although destroyed beyond further use, did not disintegrate. All studs on the suction flange failed, the pump impeller was bent, the bracket supports and coupling housing cracked, the motor rotor pushed out the rear housing, and the entire unit sheared off the anchor bolts from the foundation. A small drain valve left its impression on the concrete foundation as the entire unit was forced away from the center of the explosion.

The weigh tank was rotated approximately three quarters of an inch and the bottom outlet connection was 2½-in. out of line. The focal point of the explosion is thought to have been in the 3-in. Aloyco pump suction valve.

Figures 3 and 4 show the scene approximately one hour after the explosion. Figure 5 is a plot plan showing the area involved and marked to show location of major recovered pieces of piping and valves as well as other damaged equipment. Pieces of the valve body and piping penetrated the insulation of all vessels and piping in the area. One hole was knocked in a 4-in. stainless steel line, and all vessels and considerable piping in the area had serious dents and gouges. Electrical conduit and instrument lines in the area sustained severe physical damage. One fragment of piping, approximately 2 by 3 in. was removed from the insulation on the 10,000-ton ammonium nitrate storage tank located 130 ft. away. A pipe flange knocked a hole in a boxcar over 100 ft. away. Numerous holes were knocked in the aluminum siding of the dryer room and several holes in the roof, over three stories high, indicated pieces of material had bounced off the dryer drums and gone out through the aluminum roofing. Undoubtedly, the insulation on numerous vessels and piping in the area greatly reduced the extent of physical damage. A hole was punched in an 8-in. H-beam almost 40-ft. north of the center of explosion.

Figure 6 shows two views of one of the 3-in. Aloyco valve body flanges. The large section in the lower right-hand corner is part of the valve bonnet flange. The miscellaneous small pieces are from the valve body, piping, and flanges. Discoloration showed that carbon was definitely present in some form. Figure 7 shows a photomicrograph of a section where the distortion was at a minimum. Figure 8 shows the pattern from a severely deformed section in which the delta ferrite structure and inclusions were elongated.

Scrapings of the flanges and samples of a standard solution were analyzed. The laboratory report stated that a considerable amount of difficulty was experienced in conducting the spectrographic analysis of the urea (solution). Several small explosions were encountered. It was further found that concentrations of the material, 250 ml. of liquid evaporated to a salt, were highly flammable just prior to completion of the evaporation process. The spectrum was scanned for 66 elements which included the trace elements. It is suspected these were not picked up from the piping. The report did not attempt to reduce the analysis to actual parts per million of the product analyzed; however, traces of Na, Mg, Al, Si, Cr, Mn, Cu, Pb, and numerous addi-

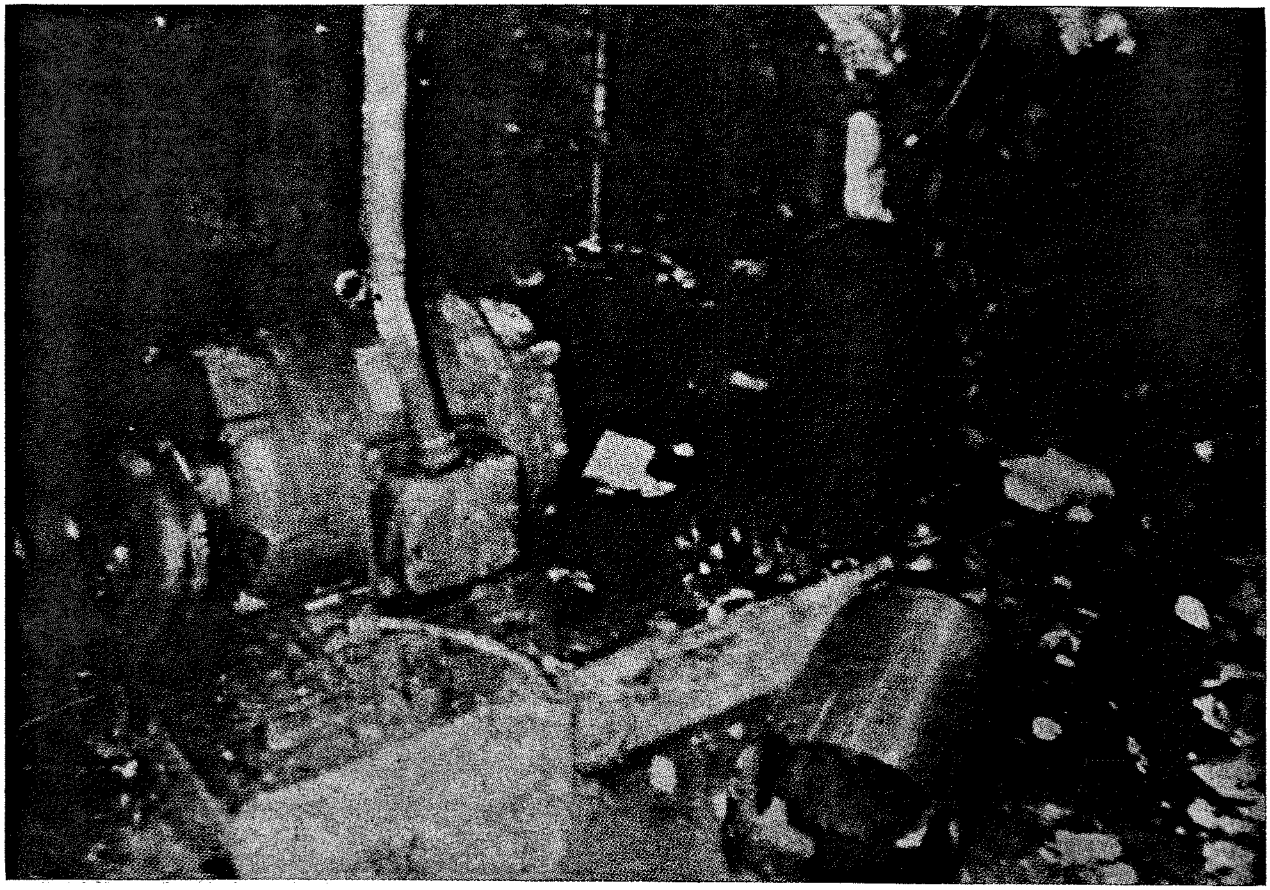

Figure 4. Scene of the explosion approximately one hour later.

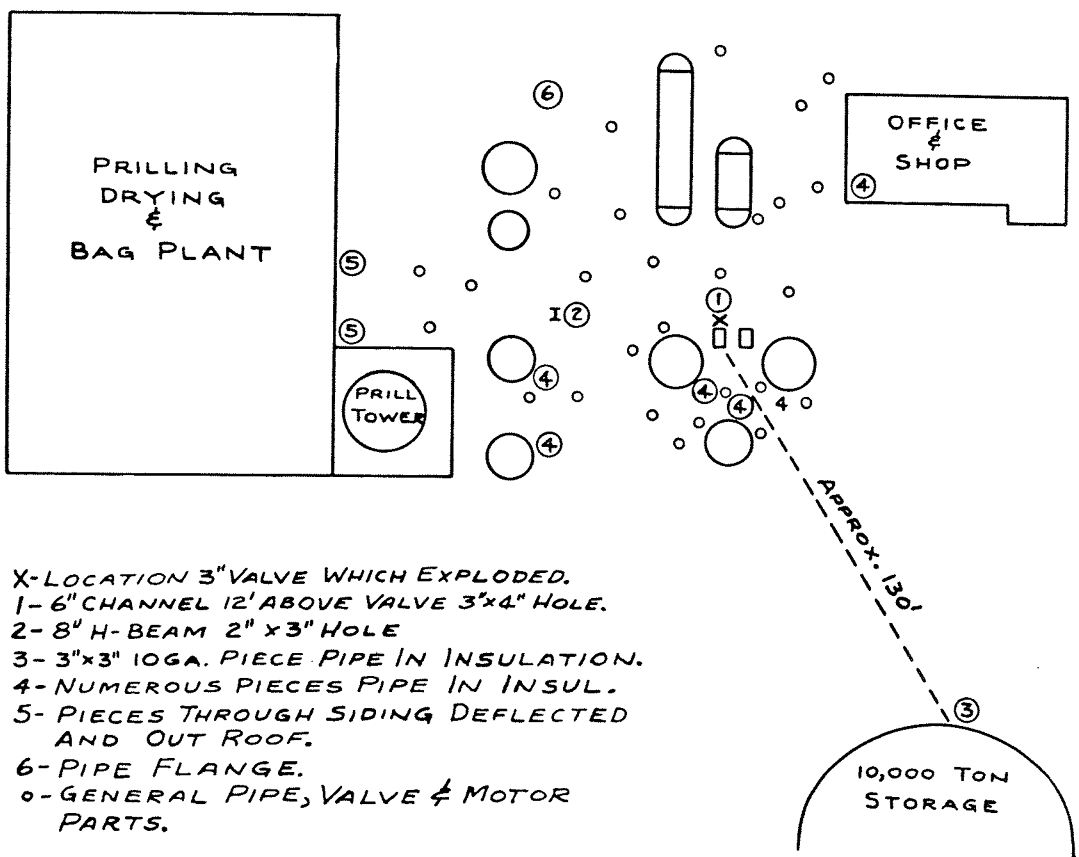

Figure 5. Plot plan of the area involved.

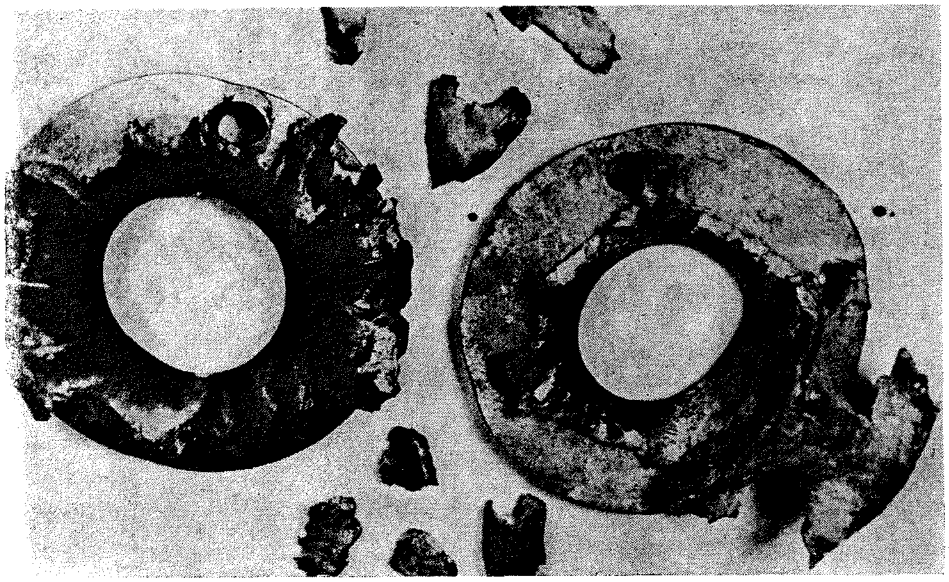

Figure 6. View of the 3-in Aloyco valve body flanges.

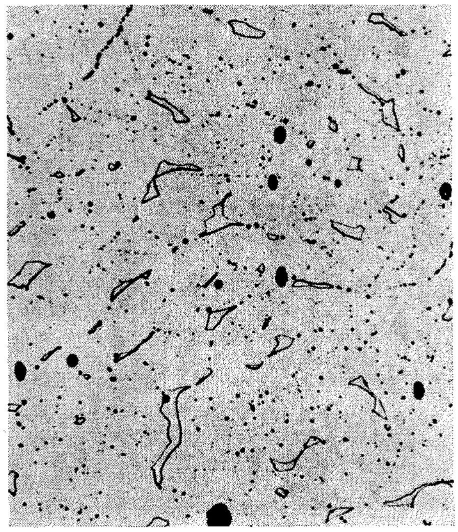

Figure 7. Photomicrograph of a section of the valve body flange where distortion was at a minimum.

tional elements were recorded. To date, no one has been able to determine the source of these elements, especially the high silicon content reported. Past experience shows that manufacturing techniques can possibly introduce these elements from the fabrication methods used on exchangers and vessels. No engineering data available has indicated such a source in the upstream facilities. Most fortunate is the fact that not one employee was scratched by any of the flying shrapnel. Even more fortunate is the fact that several men had completed a routine inspection and left the actual area only minutes before the explosion.

Operating action

The operators immediately surveyed the area and shut down all units as quickly as possible. Steam was also removed from tracing and tank coils. As the urea solution was leaking from the weigh tank, 83% ammonium nitrate was pumped into the tank in hopes of preventing the urea solution from freezing. The actual extent of the damage was misjudged due to the small amount of leakage. The urea had already frozen and with the introduction of the hot 83% ammonium nitrate solution, the plug dissolved and the entire contents of the tank was lost. Of interest, as a side result of the explosion, was the fact that a large number of fish were killed in the lake where the normal run-off water is dumped.

Cleanup was started as quickly as possible with a concentrated effort to avoid further damage to any parts and to recover all possible pieces scattered throughout the area. Every piece of equipment was inspected, cleaned with steam, and flushed with condensate. The laboratory technicians took samples throughout the plant. Small laboratory facilities limited these investigations. No report indicated contamination.

Reassembly of parts

All parts removed from the area were taken into the shop and laid out as closely as possible to the original pattern. Figure 9 shows an over-all view of the reassembled parts. The main header piping was fragmented and actually pulled back along the ballooned section. Stainless steel tubing was flattened into ribbons. The piping flanges were bent and dished. The pump housing and impeller were severely distorted. The 3-in. valve and the 1-in. drain valve, pipe flanges, and valve discs were all discolored. Of particular interest is the disc discoloration which was primarily restricted to the back side; only part of the actual faces were discolored. No discoloration was found on the actual valve stem which, incidentally, still turns freely.

Investigation

An immediate investigation was started in hopes of actually establishing the exact cause of the explosion. Like most explosions, there will never be proof as to actual cause as the necessary evidence was destroyed. Samples of solids found in the pump bowl were analyzed and showed 78.7% urea, 1.5% ammonium nitrate. Most remaining evidence was pure urea; no impurities were detected. All published known data indicate that the operating procedures were absolutely safe. The most confusing part of the investigation was the search for high pressures or temperature conditions to trigger a run-away reaction. With 85-lb. steam, the 550 to 650°F required for actual violent decomposition of the solution was impossible. Inquiries brought to light numerous other, unpublished, explosions around the country and in both South America and Europe. In none of these incidents was a similar urea-nitrate solution involved. In all cases, a known cause was determined. To date, the investigation reflects that all previous explosions involved only various concentrations of ammonium nitrate solutions. Transfer pumps have exploded when run dry, a head valve blew off when 800 ppm of oil contamination was found, a neutralizer heel tank exploded several days after being shut down, in which case steam coils were left energized and oil contamination existed. The only serious other recent explosion is the still unreported Finland explosion where 12 men reportedly lost their lives. It appears this latter explosion was prilled products with an organic coating and might well be classified similar to the Texas City explosion.

Literature on hazards

The investigation continued by reviewing all other sources of data including available papers on investigation of other explosions and published research. Some interesting highlights from these papers might be of interest.

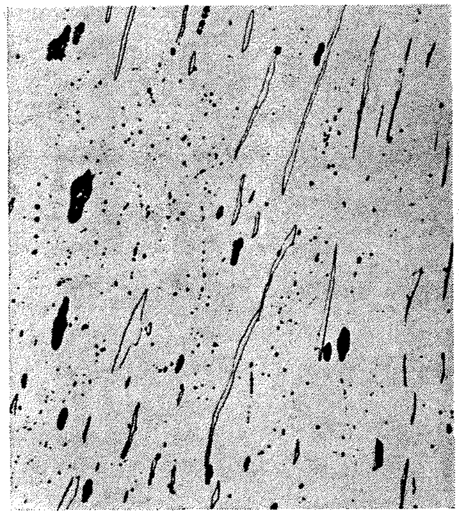

Figure 8. Pattern from a severely deformed section. Delta ferrite structure and inclusions are elongated.

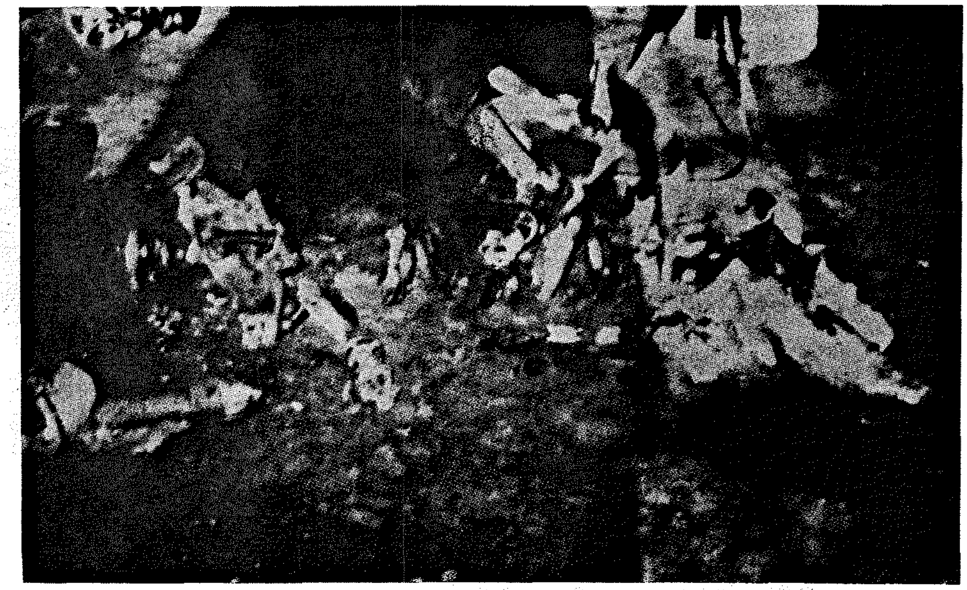

Figure 9. Over-all view of the reassembled parts.

1. A paper of Japanese origin showed that ammonium nitrate crystals, developed under certain conditions, are rather shock sensitive and far less stable than those formed in crystallizers or present prilling operations.

2. Several investigations show that pressure and contamination greatly reduce the decomposition temperature below the accepted run-away point.

3. Investigations show decomposition of both urea and ammonium nitrate takes place at relative operating temperatures which would lead to a pressure building up in a closed system.

4. Russian investigations of urea-ammonium nitrate solutions, the only published articles of this nature, introduce chemical reactions not normally believed to take place. These reactions could sensitize the solutions and lead to a similar explosion.

5. Investigations in this country show serious pressure being locally generated by the momentum required to accelerate gases away from a liquid; this results in surface shock with development of a possible thin heated layer of more sensitive material. This same investigation refers to confinement mechanism and points out that stoichiometric mixtures of urea and ammonium nitrate are very shock sensitive.

6. The Bureau of Mines reports that it has found ammonium nitrate-urea solutions can form an explosive mixture.

7. Industrial contractors, in their operating instructions, warn against contamination from utility water, especially those with considerable treatment being required.

8. One contractor cautions against allowing urea solution to enter the nitrate evaporator because of possible violent reaction.

9. Referring to the thin layer mentioned in point 5 above, the paper further states the self-accelerating runaway action might inevitably lead to explosion if a critical mass were attained.

Recommendations

As stated earlier, no definite pinpoint evidence has been developed as to the actual cause of this explosion. Unquestionably, a number of contributing factors were present including some of those referred to. One, therefore, can only offer the following suggestions:

1. Manufacturers of ammonium nitrate solutions should establish procedures to avoid confinement of the solutions, especially in the piping with steam tracing or jacketing in service.

2. Development of more accurate laboratory analytical control for the finding of oil or other known contaminants.

3. Considerable further investigation by industry appears necessary.

4. A greater exchange of experience is necessary on an operational and design level.

5. Careful and proper release of all such information is mandatory on a united level to prevent serious public reaction and governmental regulations and restrictions.

6. Closer coordination with all governmental bodies, especially legislative bodies, appears essential.

ACKNOWLEDGMENT

The authors wish to express special appreciation to many industrial associates, and especially, the following with whom considerable data were exchanged: W. L. Bulkey and R. E. Butikofer, American Oil Co.; R. K. Simms, Phillips Petroleum Co.; R. W. Van Dolah, Bureau of Mines; D. E. Carroll and H. M. Canavan, Mutual Boiler & Machinery Insurance Co.; and R. D. Hauck, TVA.



Croysdale Samuels Wagner

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J. A. Wagner received his B.S.Ch.E. from Iowa State University and is currently Ammonium Nitrate-Urea Production Supervisor. His background includes over twenty years of industrial experience, twelve of which have been in the nitrogen fertilizer industry.

DISCUSSION

BUCKLEY—American Oil: I don't have any explanation. We worked with Croysdale, as he indicated, and did attempt to set up in the laboratory the same conditions that we understood had existed at Farmer's Chemical Association, Inc.

We steam-heated UAN solutions in stainless steel bombs at roughly the same concentrations, the same temperatures that existed at the Farmer's Chemical plant. We tried various contaminants, including oils and the various metals that might sensitize a reaction. With some 30 odd tests of this sort we were able to get no indication of any runaway reaction. A blocked-in liquid-filled system, of course, will go up in pressure if the temperature increases, whether it's a UAN solution or ordinary water. We did split one bomb in this fashion, but it was a perfectly normal hydrostatic split.

However, in one of the last tests that we made, the nature of failure did suggest that possibly there had been more than just hydrostatic forces involved. The bomb opened up somewhat violently, but the conditions were more severe than existed at Farmer's Chemical. We were using oil-contaminated UAN solution heated to a temperature a little over 400°, which is higher than their steam tracing would have reached. After letting it sit at that temperature for a short time, we started to raise the temperature again when it let go.

Based on what measurements we had, the pressure at the time the temperature started up the second time was not high enough that liquid expansion alone would have caused failure; the failure was considerably more violent. I feel that it approached some of the failures induced in some of our gas detonation studies, but we don't have positive measurements so I can't say. That was the only indication of any violence in the reaction.

LAWRENCE—Central Nitrogen: I'm trying to recall Harold Maunie's report at Salt Lake City on the pump at Crystal City. I spent a lot of time looking at the record of that explosion. It sounded somewhat similar to this. Mr. Croysdale, did you talk to Maunie on this?

CROYSDALE: No, unfortunately I haven't. I've known Maunie too, from Festus, Missouri. I did get a report that he had had the pump explosion, that it was 83% ammonium nitrate solution that the pump contained and it did not distintegrate. But that was after I had contacted Phillips, American Oil, and the Bureau of Mines and I did not see that he had anything to contribute.

Particularly what we were looking for was the source of contaminant, and Maunie's was a purely ammonium nitrate solution, was it not?

LAWRENCE: It was ammonium nitrate. There was some thought that there could have been a little oil in the pump. I believe this is pretty well documented in Volume 2 of, "Safety in Air and Ammonia Plants."

CROYSDALE: That is one of the reports I missed.

LAWRENCE: There is still a big file on this at Crystal City. There was a tremendous amount of work done on it and a lot of pictures. They are in the same position you are, in all the years I was there the answer was never found, except that it was a very violent detonation. At Crystal City you can still see where a piece went up on top of the 225 ft. prilling tower, in addition to going through walls and other things. Actually this pump was not blocked-in, it was in service. Apparently suction was lost on the pump. I don't remember the details as well as the report does, but it may be of interest to look at.

CROYSDALE: It is, very much. In the paper we originally tabulated the reports that we could get our hands on. I think that there's 200 additional reports pertaining to the subject that are listed by these various papers.