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The investigation of a devastating accident — An accidental explosion of 40 tons of TNT

Guo-Shun Zhang[a] and Ming-Jun Tang[b,*]

[a]*China North Industries Group, Beijing (China)*
[b]*Chemical Engineering Department, East China Institute of Technology, Xiao Ling Wei No 200 Nanjing [210014] (China)*

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Abstract

A disastrous explosion accident with the force of 40 tons of TNT occurred on February 9, 1991. The explosion origin was defined by witness testimony, material evidence and field investigation. Two primary causes of the explosion were identified through "event tree analysis" by eliminating non-relevant factors and conducting a detailed study on relevant factors. It has been concluded that this was a "human element accident" which occurred due to poor safety in production. Lessons learned from this accident are summarized.

1. Background

TNT, a high explosive, is produced from toluene (methylbenzene) through a nitrating reaction by nitro-sulfuric acid [1]. The nitrating reaction comprises three stages: the first stage is to nitrate toluene into mononitrotoluene (MNT), which is accomplished by four nitrating reactors connected in parallel; the second stage is to nitrate mononitrotoluene to dinitrotoluene (DNT), which is accomplished by two nitrating reactors connected in parallel; the third stage is to nitrate dinitrotoluene into trinitrotoluene (TNT), which is accomplished by eleven nitrating reactors and their separators by series connection.

Equations of chemical reactions corresponding to the three stages are as follows:

*To whom correspondence should be addressed.

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$$CH_3C_6H_5 + HNO_3 \xrightarrow{H_2SO_4} CH_3C_6H_4(NO_2) + H_2O$$

$$CH_3C_6H_4(NO_2) + HNO_3 \xrightarrow{H_2SO_4} CH_3C_6H_3(NO_2)_2 + H_2O$$

$$CH_3C_6H_3(NO_2)_2 + HNO_3 \xrightarrow{H_2SO_4} CH_3C_6H_2(NO_2)_3 + H_2O$$

The third nitrating stage is much more difficult to accomplish than the other two stages. It requires longer reaction time and hence is performed in a series of many interconnected nitrating reactors. The process must be operated under higher temperature and by nitro-sulfuric acid of higher concentration. As a result, the third stage is the most dangerous in the process.

2. The accident

On February 9, 1991 at 7.30 p.m., a massive and devastating explosive accident occurred in the TNT production line of a factory in Liaoning province, China. Seventeen workers were killed and 107 injured, among them 13 in critical condition. Buildings of an area of 50,000 m^2 were totally demolished, 58,000 m^2 were seriously destroyed and 176,000 m^2 were damaged. 951 pieces of process equipment were completely destroyed. Direct property damage was 22.66 million RMB (ca. $5 million) and indirect property loss due to the interruption and rebuilding of this and neighboring production lines was enormous. The schematic of the production process is shown in Fig. 1.

By determining the quantity of explosives in each process equipment, the total amount of explosives exploded in this incident was estimated to be the equivalence of 40 tons of TNT. This figure is in agreement with damage analysis from buildings surrounding the explosion center and the size and shape of the crater.

The nitrating workshop, where the explosion occurred, consisted of three connected buildings. In the middle there was a three-layer, reinforced concrete building with the dimensions $9 \times 40 \times 15$ m^3 and an arched roof. The side buildings east and west of the central building were 8×40 m^2 and 12×40 m^2, respectively. Most nitrating reactors were placed in the west building and the laboratory for physical and chemical analysis was in the east building. The three buildings were surrounded by a soil barricade of 3 m in height. The entrance to the workshop was through culverts which penetrated the barricade. After the explosion, the workshop was completely eliminated leaving a huge crater of 40 m in diameter and 7 m in depth (Fig. 2).

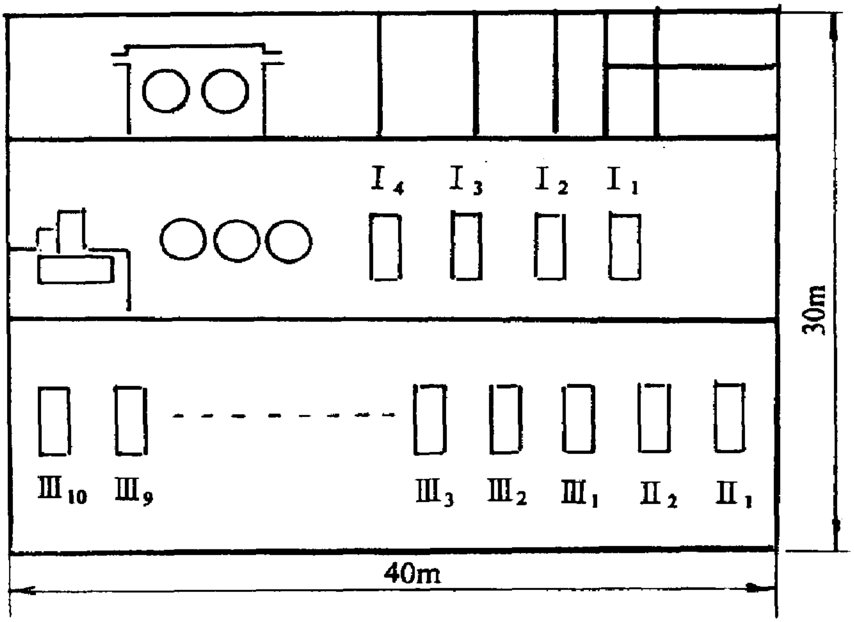

Fig. 1. Schematic of TNT production line.

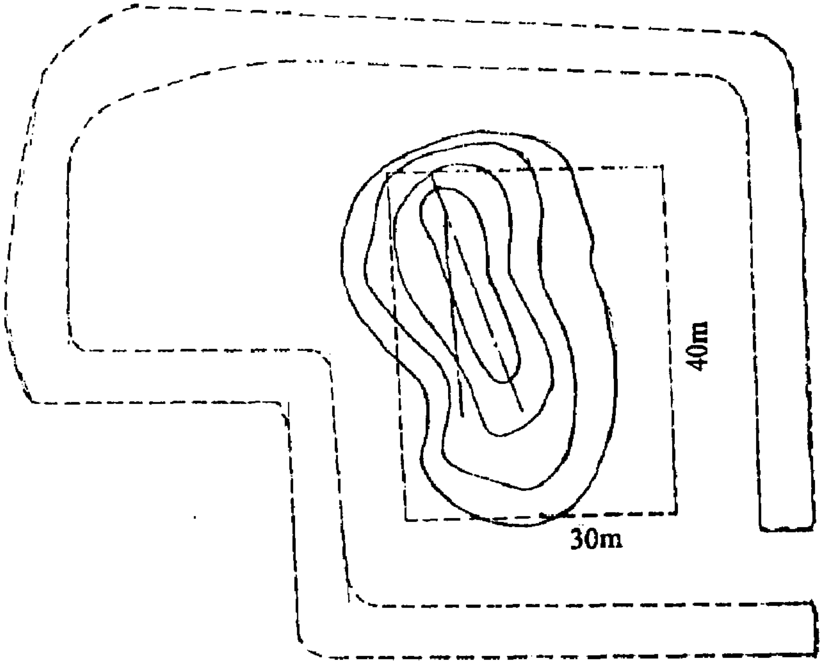

Fig. 2. Schematic of the crater. (—) Isohypers of the crater, (- - -) locations of the nitrating buildings and the barricades before the accident, and (· - ·) symmetry line of the crater or the reactors before the explosion.

The explosion not only demolished the nitrating workshop, but also seriously destroyed the refining and packaging buildings, the compressor station and the office building of the plant. Neighboring plants were also significantly damaged. All buildings within 600 m of the explosion center were destroyed, those within 1200 m were significantly damaged and those within 3000 m were partially damaged. Thousands of trees in this area were damaged by blast waves.

Most of the debris from the demolished buildings and equipment was deposited in an area of 300 m in radius around there. However, some debris was found very far from the center of the blast. For instance, a steel rod 0.8 m long and 8 cm in diameter was thrown 1685 m; a chunk of reinforced concrete, which was originally a part of the arched roof of the central building and weighing 50 tons, was found 487 m from the center. Pieces of debris weighing 50 kg, which had been a part of the concrete wall, penetrated the roof of a building 310 m from the center and seriously injured two workers inside the building. Water pipes 40 cm in diameter and 2 m depth under the ground were broken so that running water filled the crater to a depth of 2.7 m.

3. The investigation

The investigation, which was initiated immediately after the accident, was conducted by a team selected by the authorities, government labor department, workers' Union and regional administrators. The investigation into the origin and the causes of the explosion were very difficult because the production buildings and process equipment were completely demolished. Very few pieces of material evidence could be found since the scene was a large crater partially filled with water. Fortunately, there were 17 survivors among the 34 workers on the shift. During the extensive interview process they provided valuable information about conditions at the workshop immediately prior to the explosion.

In the course of the investigation, a large number of blueprints and documents were reviewed and simulating experiments were conducted by the investigation team. After detailed analysis on equipment conditions, work practices, raw material quality, process technology and production management, the origin of the explosion was determined to be the separator of No. 2 nitrating reactor in the third nitrating stage.

The determination of the origin was based on following facts.

(1) Witness statements. The operator of the No. 2 reactor said that at 7.00 p.m. he took samples from the reactor and sent the sample to the laboratory. Upon returning to his post at about 7.15 p.m. he found that the separator was smoking. He activated the shower cooler and provided cooling water to reduce the temperature. Meanwhile, he went to the control room to report his findings to the shift supervisor.

The shift supervisor agreed that at about 7.15 p.m., upon receiving the report, he took two other workers with him and went into the nitrating building. They observed that the separator of the No. 2 reactor was smoking heavily. He instructed the workers to open the valve to add concentrated sulphuric acid to the reactor in order to further reduce the temperature. Unfortunately, this measure was not successful. At this time, the building was full of nitride smoke. So, he and other workers withdrew to the door and observed fire bursting from the gap between the separator and its lid. They immediately ran towards the barricade, and upon reaching the culvert exit they heard a loud explosion.

The operator of reactor No. 10 said that he saw the separator of the No. 2 reactor smoking when returning to his post after sending samples to the laboratory at about 7.15 p.m. Then he observed the shift leader attempting to reduce the temperature and control smoke. Immediately, upon seeing the nitride smoke getting denser and fire bursting from the reactor, he ran through nearby culvert and managed to escape.

(2) Material evidence. Pieces of process records were found at the site of the collapsed control room. The records indicated that at 7.00 p.m. of February 9, the concentration of nitric acid in the reactors of the third nitrating stage was too high: 7.09% and 12.6% for No. 2 and No. 5 reactors respectively, while they should have been 1.0–3.5% and 2.0–4.0% according to standard operating procedures manuals [2]. Thus, the recorded concentrations were two to three times higher than the standard values. This would cause off-specification conditions and cause the lowest melting point to occur earlier than normal in the process. In other words, the most violent reaction occurred in the No. 2 reactor instead of in later reactors. The discovery of high concentrations of nitric acid again supported the witness testimony of the first appearence of smoke, fire and explosion in No. 2 reactor.

(3) Crater analysis. The ground mapping showed that there was an angle of 5° between the main axis of the crater and the axis of the original location of nitrating reactors. These data indicated that the explosion originated in the first few reactors, which is in agreement with witness testimony that smoke and fire were first observed in the No. 2 reactor. After the first explosion, displacement of other reactors resulted due to the shock waves produced by the explosion of No. 2 reactor. Then sympathetic detonations followed. Different displacements of each reactor before sympathetic detonation resulted in a tilt between the axes of the crater and the location of reactors before the incident.

4. Causes of the event

The method of "event tree analysis" was adopted and found effective by the investigation team. A flow chart was drawn by the experts to include all possible causes of combustion and explosion. Logical relationships among all factors which might result in the accident were also indicated in the analyses. Then, the status and effectiveness of each factor were examined.

After eliminating non-relevant factors and conducting a detailed study of relevant factors, causes of the accident were verified.

In the analysis non-relevant factors such as: leakage of cooling water, interruption or insufficient supply of cooling water, stirrer problems, breakdown of instrumentation and the presence of foreign matters in raw materials, etc. were eliminated. Then, two "cause-result chains" were formed from the few relevant factors, as shown in Fig. 3.

In the first "cause–result chain", the key is "incorrect reactant ratio and off-specification operating conditions", which were the result of "excessive concentration of nitric acid". Due to the violent reaction, the contents in the reactor flowed to the separator where they continued reacting violently. However, there were no cooling tubes or stirrer in the separator where local overheating might easily develop into dissociation and combustion. It was found during the investigation that the off-specification operating conditions were present prior to the accident. On the day shift of February 9, nitric acid valves of No. 6 and No. 7 reactors were found to be leaking. After the next shift took over at 4.30 p.m. maintenance workers repaired the valves at 5.00 p.m. Nevertheless, the leakage already resulted in an excessive concentration of nitric acid in the nitrating system. For instance, the nitric acid concentration in the No. 2 reactor reached 7.09%, which is two or three times above the concentration of No. 1 reactor – 3.5% according to the standard operating procedures manuals.

In the second "cause–result chain", the key is "contact of reactants with foreign combustibles", since combustibles such as cotton yarn, lubricant oil, rubber gloves or rubber spacer, etc. will react violently with nitric acid and the

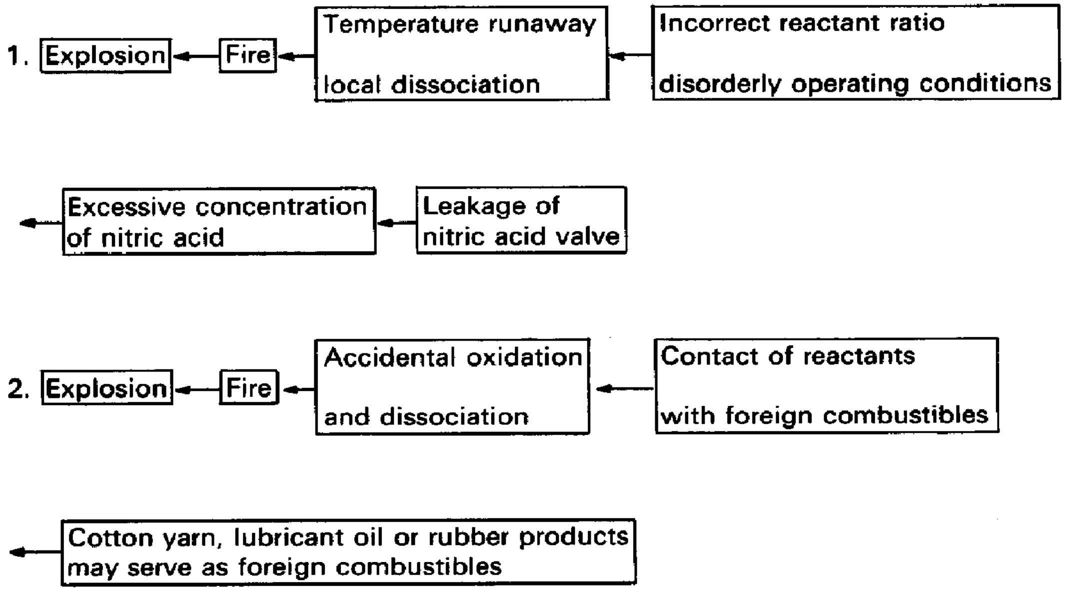

Fig. 3. Cause–result chains for a 40 tons TNT accidental explosion.

oxidation reaction may result in smoking or even fire. In the investigation, no foreign combustibles were determined to have entered the reactor before the explosion. However, it was discovered by further investigation that unapproved asbestos cord was used as the filler between the top of the separator and its upper lid. This asbestos cord might have served as the igniter of the fire when contacting nitro-sulfuric acid of high temperature and high concentration. Particularly, a large amount of concentrated sulphuric acid had been added into No. 2 reactor as a safety measure. In contrast with the original attempt, the addition of sulfuric acid would increase the chance for interaction between the asbestos cord and the concentrated nitro-sulfuric acid.

In general, asbestos cord is incombustible. However, the remainder of this asbestos cord found on the scene and that in storage could both be ignited by a match. The analysis report by the inspection center for labor safety and health in Liaoning province showed that this asbestos cord contained only 50% asbestos with combustible fiber and grease as the rest. In order to verify the interaction of this cord and nitro-sulfuric acid, simulation tests were conducted by the investigation team. It was proved in the experiments that this cord reacted violently with nitro-sulfuric acid of concentration specified by the standard operating manual. During the reaction, the production of large amount of yellow smoke and the sudden rise of temperature from 110 °C to 150 °C were observed. In contrast, process-acceptable asbestos cord hardly reacted in the same test. It was concluded, thus, that the application of the inappropriate asbestos cord as the filler in separators, which took place in June 1990 during the maintenance, might cause the ignition of nitro-compounds.

It was also found in the investigation that the fire starting in the No. 2 separator was propagated and transmitted through the venting system and the low wooden roof panels.

The transition from fire to explosion was due to the staff not taking the appropriate safety measure of emergency dumping. According to regulations, a nitrating reactor should be equipped with remote control, automatic and manual dumping devices in order to immediately open safety valves and let the contents of the reactor flow into the safety pool in case of emergency. Unfortunately, there was no automatic dumping device in the reactor because this was an old factory which was poorly equipped and did not have adequate automatic safety measures. In other words, this factory had poor safety conditions. In addition, the fact that the operator and the shift leader failed to manually dump the reactor, allowed the fire to develop and result in detonation.

The causes of the accident are summarized below.

The incident started as a result of the leakage of nitric acid valves on No. 6 and No. 7 reactors, which lead to excessive concentrations of nitric acid in the nitrating system and brought forward the lowest melting point in the reactor system. Then, a violent reaction and the generation of a large amount of smoke in the No. 2 reactor resulted. The interaction of unacceptable asbestos cord containing a large percentage of combustible fiber and grease with nitrating acid of high concentration and high temperature provided the ignition source. Another source of ignition might be dissociation and ignition of nitro-compounds due to local overheating resulted from violent reaction in No. 2 separator. Finally, the fire was able to transit to detonation because of the lack of automatic dumping device and the failure of the operators to manually dump the reactor.

Meanwhile, poor management is also responsible for this accident. Many problems occurred prior to the explosion but had not been properly addressed. For instance, the process equipment was not in good condition; workers had not been properly trained and the wrong asbestos cord was used, etc.

In conclusion, this is a human element accident which occurred due to poor safety conditions.

5. Lessons learned from the accident

The following lessons should be learned from the accident.

5.1 Regarding equipment and technology

(1) Buildings for producing explosives should meet the requirements for fire and explosion protection.

In this incident, the nitrating line was located in the west building which was constructed of wood and brickwork and the distance between the top of separator and the wooden roof was only 1.7 m. This construction allowed the wooden roof to become the medium for transmitting combustion. Moreover, the main building of the workshop was of reinforced concrete roof. In the explosion, the heavy roof yielded large pieces of debris which penetrated and destroyed surrounding buildings and injured people inside them.

(2) The process control and safety conditions of production equipment should be improved.

The production line should be equipped with protective devices such as an automatic alarm system and an automatic dumping devices. The number of process workers should also be reduced.

(3) The process flow should be well organized, not only for convenient operating but also for safe evacuating.

(4) Sufficient safe distance between explosive building and its surrounding buildings should be established.

The large number of casualties and significant property losses in this accident are directly related to improper factory layout which had insufficient distances between buildings and an insufficient blast resistant capacities of most buildings.

5.2 Regarding production and safety management

(1) Process equipment for producing explosives should be under strict control in order to reduce or even to eliminate leakage or other problems.

In the days preceding the explosion, according to the testimony of the workers, there had been many equipment problems, many cases of replacing and repairing valves and spacers, and frequent turning on and off the production. Unfortunately, the managers and engineers did not solve the problems in time and let them develop into a major event.

(2) A worker's training program should be conducted to increase their knowledge of safe production and increase their ability to prevent accidents, i.e. the correct safety measures to be taken in case of emergency.

In this accident burning was able to transit to detonation because the operator and the shift leader left the site without taking the safety measure of manual dumping.

(3) Material such as asbestos cord should be inspected for fire and acid resistance before use.

References

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2 Standard operating procedures manuals for TNT production, Internal Document, China Inc. of Explosives and Propellants, 1990.