

Lecture PA5

Explosion of Smokeless Powder Ingredients

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1. BRIEF DESCRIPTION OF THE ACCIDENT

- 1.1 Date & time: Wednesday, December 6th, 2000, around 9:45 a.m.
- 1.2 Accident location: Oita Propellant Plant, Oita, Japan
- 1.3 Short description: Fire and explosion of raw materials of smokeless powder while feeding into a mixer caused by static electricity.
- 1.4 Injuries/damages: one slight injury, a mixing room completely destroyed

2. COMPANY

- 2.1 Company name: Asahi Kasei Corporation (Asahi Chemical Industry Co., Ltd. when the accident occurred.)
- 2.2 Office address: 12F Arca East, 3-2-1 Kinshi, Sumidaku, Tokyo, Japan
- 2.3 Phone & Fax: 81-3-5610-6080 (phone), 81-3-5610-6088 (fax)
- 2.4 Contact: Takaaki Torikai, SHE Manager, Explosives Division
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3. WEATHER & TEMPERATURE OF THE DATE

- 3.1 Weather: Clear
- 3.2 Ambient Temp.: 13°C
- 3.3 Humidity: 47% RH (Oita Local Meteorological Observatory, 10:00 a.m.)
- 3.4 Site Temp: 14°C inside the mixing room at the accident
- 3.5 Site Humidity: 63% RH (before the start of the work, checked with a psychrometer in the room)
- 3.6 Remark: Doors of mixing room were kept open during operation

4. PLACE OF THE ACCIDENT

- 4.1 Address: 2620, Oaza-sato, Oita-shi, Oita-ken, Japan
- 4.2 Place: Smokeless powder mixing room No. 6
(Mixing rooms No.5, 6 and 7 are adjoined.)

5. THE MATERIAL INVOLVED

- 5.1 Type: Smokeless powder (Triple base gun propellant)
- 5.2 Quantities: The type, quantities and position of the raw materials involved are as follows.
 - (1) Inside the mixer:
 - Approx. 54 kg of Dehydrated Nitrocellulose (Nitrocellulose = approx. 41 kg, ethanol = approx. 13 kg)
 - Approx. 21 kg of Gelatinized Nitroglycerine (1 bag equivalent)
 - (2) On a transport cart of the raw materials in the mixing room:
 - Approx. 21 kg of Gelatinized Nitroglycerine (1 bag equivalent)
 - Approx. 76 kg of Material X (5 bags)
 - Approx. 2 kg of Material Y
 - Approx. 1 kg of Material Z

5.4 Description of the Materials:

1. The Dehydrated Nitrocellulose:

Nitrocellulose containing about 25% of ethanol. Pressed in a flat column shape of about 460 mm \varnothing in diameter and about 170 mm in thickness after going through the water removal process. (Approx. 25 kg/piece)

2. The Gelatinized Nitroglycerine:

A mixture of 18 kg of nitroglycerine, 2.86 kg of wet (moisture: 30%) nitrocellulose and 0.36 kg of ethanol. Gelatinoid muddy white substance. (Approx. 21 kg/piece. Packed in a polyethylene bag.)

(See Photos 1 and 2.)



Photo 1



Photo 2

5.5 The composition of a final product: See following table.

Name of raw material	Composition (Wt%)
Nitrocellulose	28.0
Nitroglycerine	22.5
Material X	47.7
Material Y	1.5
Material Z	0.3
Total	100.0

5.6 Sensitivity of Gelatinized Nitroglycerine:

Drop-Hammer Test = Grade 8 (JIS)

Friction sensitivity = Grade 6 (JIS)

6. SEQUENTIAL OUTLINE OF THE ACCIDENT

1. Mixing work of smokeless powder was performed using the mixing rooms No. 5 - No. 7. Manufacturing of the powder in question started on October 10th and was planned to conduct the mixing of 289 batches in total by December 7th, and the work was done without any trouble as scheduled.
2. In the morning on the day, Worker A took out the mixed powder from the mixer No. 7 and fed the 279th batch, and then took out the mixed powder from the mixer No. 5 and fed the 280th batch, followed by taking out the mixed powder in the mixing room No. 6, subsequently the 281st batch was to be fed by him.

3. The worker A checked the humidity of the mixing room No.6 with a psychrometer and found that it was 63% RH being more than the plant standard 55% RH. He fed the all of the Dehydrated Nitrocellulose into the mixer without blowing fresh steam for humidifying into the mixing room, put a lid on it and operated the mixer to start crushing the Dehydrated Nitrocellulose. (Time of operation = about 10 minutes. The temperature of the water jacket was controlled at 42.5°C)

(See Photo-3, 4 and 5 of the same type of the mixer)



Photo 3



Photo 4

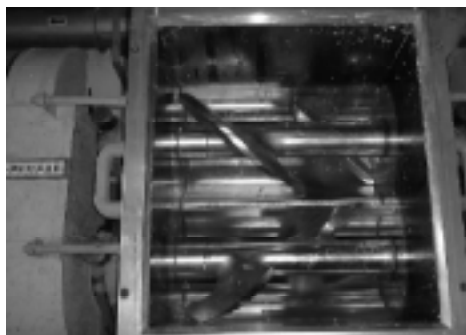


Photo 5



Photo 6

4. The Worker A put the raw material (2 bags of Gelatinized Nitroglycerine, 5 bags of material X, material Y and material Z) on the cart, came back to the mixing room No. 6 and stopped the mixer. At this time, Worker B entered the room.
5. As preparation work for the Gelatinized Nitroglycerine to be charged next, in order to take out the Gelatinized Nitroglycerine from a polyethylene bag completely, part of the Gelatinized Nitroglycerine that had been attached to inside the bag was stuck back to a big lump of the Gelatinized Nitroglycerine over the bag. Each person did this work on each bag. Afterwards the Worker B moved near to the entrance of the mixing room and stayed there.
6. The Worker A pressed the button for opening the lid of the mixer to raise and horizontally transfer the lid, stepped on the platform in front of the mixer and charged the first bag of Gelatinized Nitroglycerine into the mixer in such a way as to push the bottom of the bag with a hand to make it inside out. (See Photo-6 rendering of the work) At that instant, together with a sound 'puff', flame of orange color stuck out above the level of his eyes from the right side of the inside of the mixer.
7. The Worker B retreated at once, and the Worker A also got away from the mixer soon. When the Worker A was going out the mixing room, the upper part of the mixer was entirely covered with flame.

8. The Worker B went to inform workers in other manufacturing rooms of the danger. When the Worker A had gone out and retreated about 8 m away from the mixing room, he witnessed flame blowing out in front of the mixing room and there was a sound 'bang' (the first one).
9. After that, when the Worker A went over to the fireplug and tried to start spraying water, he saw flame blow up toward the ceiling and there was a sound 'bang' (the second one). (around 9:45)
10. An in-plant fire fighting activities were started instantly. Emergency notifications were made to the authorities concerned such as the fire fighting office, police, neighboring district autonomous committee members and so on.
11. At the time of the accident, the powder in the mixing room No. 5 was being mixed for about 50 minutes and the powder in the mixing room No. 7 was being mixed for about 80 minutes. The operation of the mixers in these two mixing rooms was stopped by disconnecting the power supply, while fire fighting activities to the mixing room No. 6.
12. As a result of the fire fighting activities, the fire was extinguished at 9:59.

7. INJURIES / DAMAGES

7.1 Injuries: one slight injury (at the left inner ear)
 (The Worker A; damage to the inner ear is suspected owing to acoustic injury.)

7.2 Damages:

(1) Neighboring district: None

(2) Mixing room No.6: Completely destroyed (See Fig.1, Photos 7–10)



Photo 7



Photo 8



Photo 9



Photo 10

(3) Mixing rooms No.5, 7: Mid to slight damages to windowpanes, slate of roofs, walls and so on.

(4) Remarks: In the evening of the same day, the powder was taken out from the mixers No. 5 and No.7. No abnormality was found in the powder inside the mixers. (both of the two mixers were covered with lids.)

8. ANALYSIS / REASON FOR THE ACCIDENT / LESSONS LEARNED

8.1 Result of analysis:

Analysis of the accident was performed by the Fault Tree Analysis. Furthermore, various kinds of data have been obtained and evaluated under the instructions of experts outside the company (Static electricity : Messrs. National Institute of Industrial Safety of the Ministry of Health, Labor and Welfare; Smokeless powder and raw materials : Professor S. Tamura, Tokyo University).

It has been presumed that the following phenomena (1) through (4) occurred simultaneously resulting in the ignition.

(1) Decrease of humidity owing to the weather conditions

As the humidity in the mixing room was checked to be 63% RH prior to the start of work, Worker A judged that humidification was not required, and started the operation. However, the humidity was in the trend of decreasing between 9 o'clock to 10 o'clock, and it is conjectured that it was less than 55% RH at the time of the accident. (Oita Local Meteorological Observatory: 9 o'clock 56% RH → 10 o'clock 47% RH)

(2) Electrification of the bag

In the preparation work for the charging of the Gelatinized Nitroglycerine, removing the Gelatinized Nitroglycerine that had been attached to the inside of the polyethylene bag was carried out, with the result that static electricity was accumulated on the bag.

(3) Increase in the amount of electrification and diffusion of the solvent

The charging work of the Gelatinized Nitroglycerine was done as if the bag was made upside down while pressing the bottom of the bag. During this work, the electrified charge increased because of the peeling-off of the Gelatinized Nitroglycerine from the bag and the rubbing (friction) of the bag against itself.

As a result of charging the Gelatinized Nitroglycerine, the vapor of solvent inside the mixer went up around the upper part of the mixer.

(4) Electrostatic induction to the human body/an electrostatic discharge

The electrostatic induction occurred to the human body that had been insulated from the floor by the non-conductive plastic of the platform legs. The static electricity of the human body was discharged onto the mixer main body, resulting in the ignition of the ethanol vapor. (Details are shown in attached 'Data'.)

(5) Fire and Explosion (Deflagration)

The flame of ethanol ignited Nitrocellulose and Gelatinized Nitroglycerine in the mixer. Burning of the Gelatinized Nitroglycerine was transferred to deflagration several minutes later. (the first 'bang')

Another lump of Gelatinized Nitroglycerine on the cart in the mixing room also started to burn and finally deflagrated. (the second 'bang')

8.2 Lessons learned:

When conductive materials are insulated (not grounded), they are easily electrostatic induced by the approach of the charged materials. The energy of static electricity of conductive materials is easily released to grounded materials at a time and the spark is generated.

One of the important actions to prevent the electrostatic induction and the discharge of static electricity is to ground conductive materials such as human body, metal, conductive rubber and so on.

Even a small piece of metal, like a spoon or scissors, could be the cause of the spark. The minimum energy of materials involved (ex. organic solvent) and the results of the static electricity measurement during operations should be considered.

9. ACTIONS TO PREVENT RECURRENCE

The actions are focused on static electricity as follows.

1. Improving how to remove static electricity

- 1) To install an grounding wire onto the platform and to remove the plastic cover at the bottom of the legs of the platform (to secure grounding of the platform)
- 2) To sprinkle water on the floor of the mixing room once per shift (to secure conductivity of the floor)
- 3) To check conductivity (resistance value) of antistatic shoes (to secure conductivity of the antistatic shoes)

2. Separation of generating source of static electricity from inflammable substances

“The work to take out the Gelatinized Nitroglycerine from the bag” is to be performed in the other manufacturing rooms, and then to be transported to the mixing room (to separate the generating source of static electricity)

3. Measures against the prevention of electrification

To change the type of polyethylene bag for packaging the Gelatinized Nitroglycerine into a polyethylene bag with its conductivity having been considered (to eliminate the generating source of static electricity)

In addition to the above, the following actions shall also be performed from viewpoints of safety education to operators.

4. To give explanations on the causes of the accident occurred this time and the actions to be taken

5. To hold meetings periodically in which lectures to be given by experts outside the company on the generation, electrification and induction of static electricity.

PA5 Data

Results of the test for presuming cause of the accident

1. PURPOSE OF THE TEST

Electrostatic discharge was presumed by the following two reasons.

1. In the result of analysis by FTA, possibility of electrostatic discharge could not be denied.
That is, possibility of electrostatic discharge in the ethanol atmosphere could not be denied, since the polyethylene bag packaging the Gelatinized Nitroglycerine is liable to be static-electrified.
2. The specialist on static electricity informed us that discharge was not directly caused from the polyethylene bag but electrostatic induction from the polyethylene bag to human body might have occurred, causing discharge from human body. Based on this view, the test for presuming cause of the accident was made, according to the instructions by the specialist.

2. TEST METHOD AND RESULTS

The test was performed in the laboratory. (temperature 26°C, humidity 45%RH)

Test methods are shown in Fig. 1.

1. Measurements of leakage resistance and electrostatic capacity of operators

- 1) In case the platform is conductive. Applied voltage = DC 250 V

	Leakage resistance	Electrostatic capacity
Operator A	3.5 MΩ	153 pF
Operator B	1.5 MΩ	149 pF
Operator C	4.0 MΩ	127 pF

- 2) In case the platform is insulated. Applied voltage = DC 1000 V

	Leakage resistance	Electrostatic capacity
Operator A	> 2000 MΩ	122 pF
Operator B	> 2000 MΩ	105 pF
Operator C	> 2000 MΩ	116 pF

The non-conductive plastic of the platform legs that was used in the mixing No.6 was still attached after the accident, and the platform was insulated from the ground.

In other mixing rooms, the plastic were worn and the aluminum frames were directly contacted to the floor. (The platforms were grounded.)

2. Measurement of resistivity of the Gelatinized Nitroglycerine

Volume resistivity	2.0 Ω 105 Ωim (Average of 3 measurements)
Surface resistivity	6.9 Ω 105 Ω (1 measurement)

Result showed that resistivity of the Gelatinized Nitroglycerine was low.

3. Human body electrification by peeling of the polyethylene bag

By peeling the polyethylene bag from the Gelatinized Nitroglycerine, electrified potential of human body and electrified charge of the polyethylene bag were measured.

Human body leakage resistance of operator = > 2000 M Ω ,

Electrostatic capacity of operator = 144 pF

Test No.	Human body electrified potential	Polyethylene bag electrified charge
1	1.1 kV	0.23 Ω C
2	1.1 kV (1.5 kV instantly)	0.24 Ω C
3	1.0 kV	0.14 Ω C
4	0.8 kV	0.21 Ω C

Note: Since the platform in the mixing room No.6 was insulated, test was made by insulating the platform from the ground.

3. UNDERSTANDING OBTAINED BY THE TEST

1. Electrostatic induction from the polyethylene bag to human body was proved.

It was shown that human body is electrified at about 1 kV, by electrostatic induction from the polyethylene bag.

2. It was proved that resistance of the Gelatinized Nitroglycerine was low.

Thus, it is presumed that electrification can be lowered by once replacing the Gelatinized Nitroglycerine into the conductive case grounded to the earth.

4. EVALUATION OF TEST RESULTS

4.1 Analysis of measurement results

1. Minimum ignition energy of ethanol

Ignition energy of ethanol is presumed to be around 0.2 mJ, since ignition energy of methanol is 0.14 mJ.

Since flame cannot be seen easily around the stoichiometric ratio being the density most easily taking ignition, ignited place cannot be determined.

2. Electrified potential of human body was low at approx. 1 KV in this test.

Following two reasons are presumable.

1) Generally, static electrified potential is affected by absolute humidity instead of relative humidity. The lower is absolute humidity, the higher is electrification amount. Humidity in the test room was 45%RH and temperature was high at 25 Ω C.

In the day of the accident, temperature was low at 15 Ω C, it is presumed that absolute humidity was lower than that in the test room.

2) Methods of peeling of the Gelatinized Nitroglycerine and polyethylene bag were different in the accident and in the test.

In the charging method in occurrence of the accident, adhesion strength of the Gelatinized Nitroglycerine and the polyethylene bag was different from that in the test and slippage was made at higher pressure; therefore, electrification amount is presumed to be higher.

3. Calculation of static electricity energy

Calculation is made by the formula of $0.5 Q \Omega V$.

In $Q = 0.24 \Omega C$, $V = 1.5 \text{ kV}$,

Static electricity energy can be calculated to be 0.18 mJ, which is similar to the (presumed) Min. ignition energy of ethanol.

Therefore, static electricity can be cause of the accident.

It is presumed that electrification amount was increased in the work site in the dry air in winter and electrostatic discharge occurred in the atmosphere that flammable condition of ethanol vapor was accidentally made.

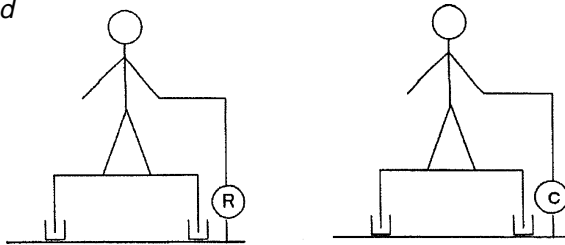
In considering these conditions and in judging from the test results, static electricity is presumed to be the cause of the accident. Resistivity of the Gelatinized Nitroglycerine is quite low, and special notice is unnecessary.

4.2 INSULATED PLATFORM

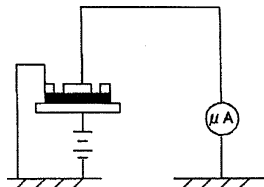
This is the key to this accident.

Wooden platforms were used until 8 years ago. Since wood has low electric resistance, electrification to human body might not have occurred.

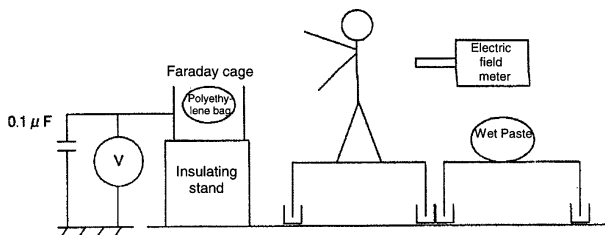
Fig. 1 Test method



1. Measurements of leakage resistance and electrostatic capacity of operator



2. Measurement of resistivity of Gelatinized Nitroglycerine



3. Measurements of electrified potential to human body and electrified charge of polyethylene bag