This Accident Investigation Committee Interim Report is a translation of the original; 'Jiko Chosa Iinkai Chukan Houkoku" written in Japanese, for convenience purpose only, and the original in Japanese shall prevail.

Accident Investigation Committee Interim Report

January 18, 2013
Accident Investigation Committee

1. Introduction

On September 29, 2012, an explosion occurred at the Nippon Shokubai Plant in Himeji, Hyogo Prefecture, Japan. The explosion and subsequent fire in an acrylic acid intermediate tank killed one person and injured 36. As a result, on October 5, 2012, an Accident Investigation Committee consisting of four external and three internal members was formed. The Accident Investigation Committee's purpose is to first of all clarify the situation that led into the accident, determine the causes and propose countermeasures to prevent the accident.

The committee has thus far convened four times and its investigation has thus far confirmed the circumstances that led to the explosion and fire as well as the direct causes. With these, this interim report has been prepared.

2. Overview of the Accident

At about 14:35 on September 29, 2012, an explosion and fire occurred in an intermediate tank (equipment item number: V-3138; nominal capacity: 70 m^3) that temporarily stored bottom liquid from the glacial acrylic acid rectifying column at Nippon Shokubai's Himeji Plant. The fire then spread to the nearby acrylic acid tanks, toluene tank and fire engines.

3. Location and Equipment Involved

(1) Location

Himeji Plant, Nippon Shokubai Co., Ltd.
992-1 Aza Nishioki, Okihama, Aboshi, Himeji, Hyogo, Japan

(2) Equipment involved

An intermediate tank in the acrylic acid production facility

4. Date and Time of Accident

Saturday, September 29, 2012 at about 14:35

5. Damages

(1) Casualties

- Fatality: 1 (firefighter)
- Severely injured: 5 (2 firefighters and 3 employees)
- Moderately injured: 13 (8 firefighters, 1 police officer, and 4 employees)
- Lightly injured: 18 (14 firefighters, 1 police officer, and 3 employees) Total: 37 persons

(2) Property damage

• The tank involved was destroyed and its surrounding equipment, racks, piping, cables, etc., were damaged.

6. Overview of the Acrylic Acid Production Facility

• The acrylic acid production facility has two production facilities: crude acrylic acid production facility and glacial acrylic acid production facility.

(1) Crude acrylic acid production facility

• The crude acrylic acid production facility consists of oxidation process and purification process. In the oxidation process, propylene is converted to acrylic acid vapor via vapor phase oxidation reaction. The acrylic acid vapor is subsequently absorbed with water and formed the acrylic acid aqueous solution. In the purification process, crude acrylic acid is obtained by separating out water and other impurities from the acrylic acid aqueous solution.

(2) Glacial acrylic acid production facility

• The glacial acrylic acid production facility consists of a rectifying column and a recovery column.

• The crude acrylic acid is fed into the rectifying column where the small quantities of impurities contained are separated and the glacial acrylic acid is obtained.

• The rectifying column bottom liquid which contains the removed impurities is fed into the recovery column. In the recovery column, the impurities are separated as waste oil and the recovered acrylic acid is recycled to crude acrylic acid production facility.

• Inhibitors contained in the crude acrylic acid and inhibitors fed into the rectifying column are concentrated in the rectifying column bottom liquid. This bottom liquid does not polymerize easily because it contains more inhibitors than glacial acrylic acid.

• Intermediate tank V-3138 was installed in the crude acrylic acid production facility area and was used for temporary storing the rectifying column bottom liquid.

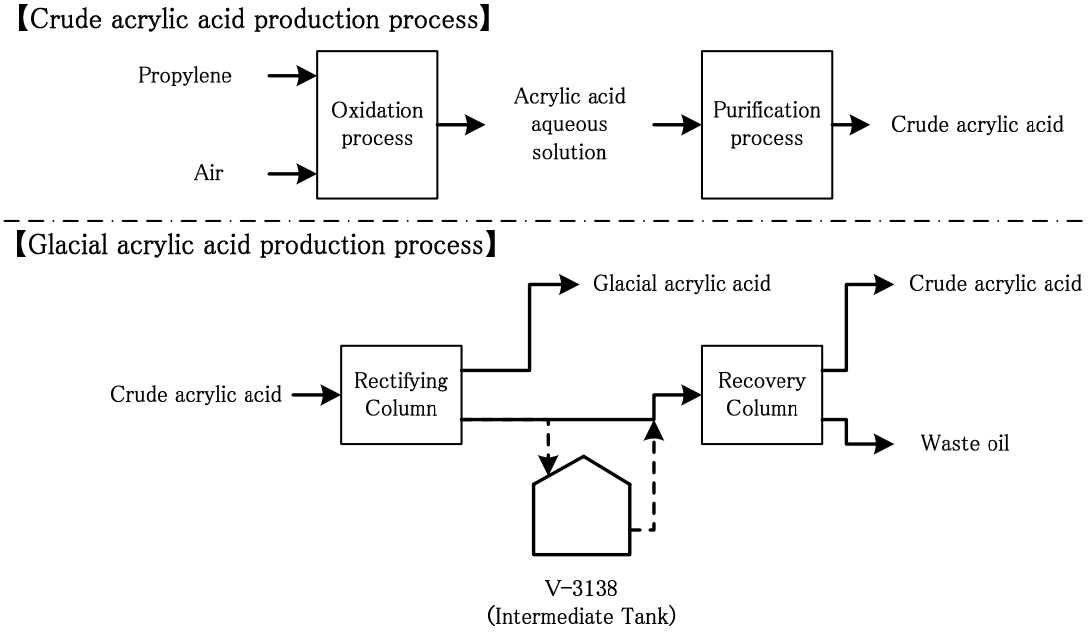


Figure 1. Schematic of the acrylic acid production facility

7. Overview of Intermediate Tank V-3138

- The intermediate tank V-3138 has a 70 m^3 nominal capacity with a cone roof. It was installed in November 1985.
- It is an intermediate tank used for temporarily storing bottom liquid from the rectifying column when for example the rectifying column stopped. During normal operation, the bottom liquid is fed directly into the recovery column without passing through V-3138 and therefore, the intermediate tank is kept stagnant.
- There was a cooling water coil inside V-3138 that serves to prevent freezing of acrylic acid and cool the liquid that was fed into V-3138. The amount of liquid necessary to fully cover the top of the coil is 25 m^3.
- Although acrylic acid is a flammable liquid, its vapor does not burn when it has an oxygen concentration of 8% by volume or less. Therefore, mixed gas (referred to as “M-Gas”) consisting of 7% oxygen and 93% nitrogen by volume is fed into the tank for sealing purpose.
- V-3138 liquid is circulated through pump P-3138C back into the same tank at two locations: liquid level gauge nozzle set near the lower side of tV-3138 wall (referred to as “Recycle to Level Gauge”) and nozzle set at V-3138 top (referred to as “Recycle to Top”).

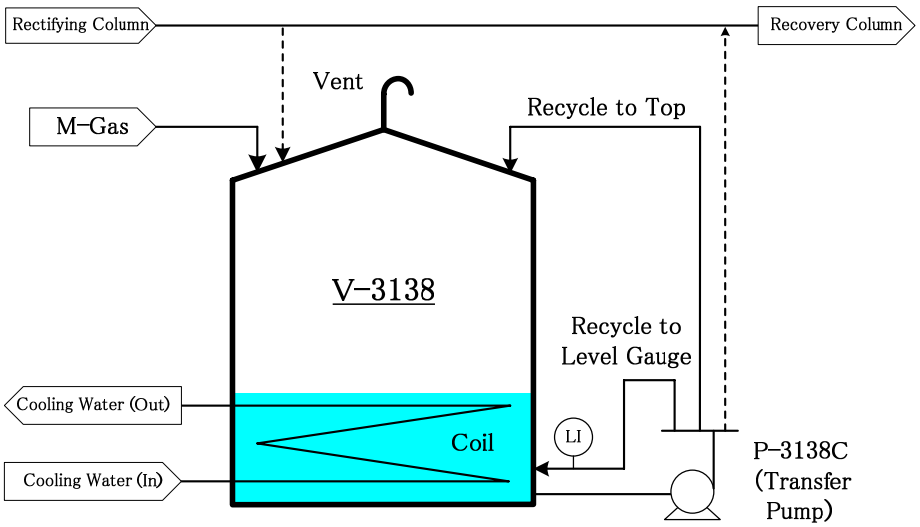


Figure 2. Schematic of tank V-3138

8. Sequences of Events

- Prior to the accident, there was a planned Total Power Shutdown in Himeji plant for electrical and instrumentation maintenance activities (refer to as “Total Power Shutdown Work”). The Total Power Shutdown Work was completed over a period of three days from September 18 to 20, 2012 as per plan. After which, each production facility was restarted in order.
- In light of this situation, the committee divided the sequence of events leading up to the accident into four stages and investigated the accident scenario and causes.

(1) From September 21 to about 9:30 on September 25, 2012 (after Total Power Shutdown Work to before start of the storing operation in V-3138)

- After the Total Power Shutdown Work was completed, cooling water was commissioned to pass through V-3138 coil and similarly M-Gas sealing was also commissioned. Circulation from Pump

P-3138C via Recycle to Level Gauge was commissioned too.

- There was no abnormality observed in the operations of crude acrylic acid production facility. The correct amount of inhibitors was also fed into the crude acrylic acid obtained from the purification process.
- Operations of the rectifying and recovery columns in the glacial acrylic acid production facility were started on September 21. At this point of time, the bottom liquid was fed directly into the recovery column without passing through V-3138.
- On September 24, the operation was switched to feed the rectifying column bottom liquid into V-3138, and from V-3138, the bottom liquid was fed from V-3138 into the recovery column. During this operation, the liquid volume in V-3138 was maintained constantly at about 10 m^3.
- The transfer piping of rectifying column bottom liquid was steam jacketed to prevent plugging due to precipitation. The temperature of the bottom liquid as it enters V-3138 was estimated at about 100°C, based on steam temperature and the length of the jacketed piping.
- Inhibitors were fed into the rectifying column in accordance with the operation standards.

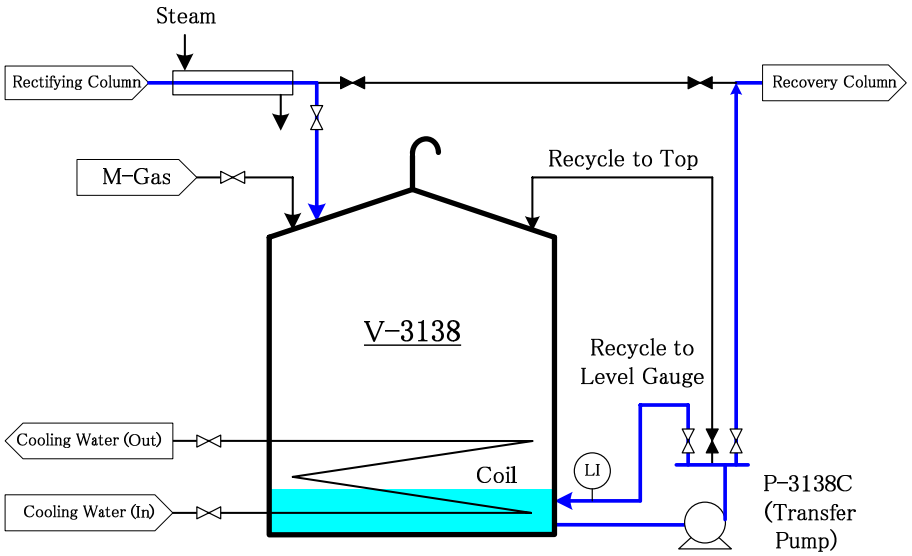


Figure 3. Status of tank V-3138 before liquid storing

(2) From about 9:30 on September 25 to about 14:00 on September 28, 2012 (during storing operation in V-3138)

- At about 9:30 on September 25, the feed of bottom liquid from V-3138 to the recovery column was stopped and commenced to build up the liquid volume in V-3138. This was to prepare a capacity load up test in the recovery column which was scheduled at a later date.
- There was no particular change in the crude acrylic acid fed to the rectifying column or in the inhibitors. Similarly, there was no abnormality observed in the operation conditions.
- The volume of liquid in V-3138 reached 60 m^3 at about 14:00 on September 28, approximately 77 hours after the commencement of storage. During this period, the circulation of Recycle to Top was not commissioned.
- The cooling water coil cooled the liquid in the bottom of V-3138 but was unable to cool the liquid above the top of the coil effectively. This had created an uneven temperature distribution in the

vertical direction of V-3138 liquid. It is presumed that this relatively high temperature section had gradually led to reaction forming acrylic acid dimer (diacrylic acid, referred to as “DAA”). With the heat of this reaction, V-3138 liquid temperature has increased steadily.

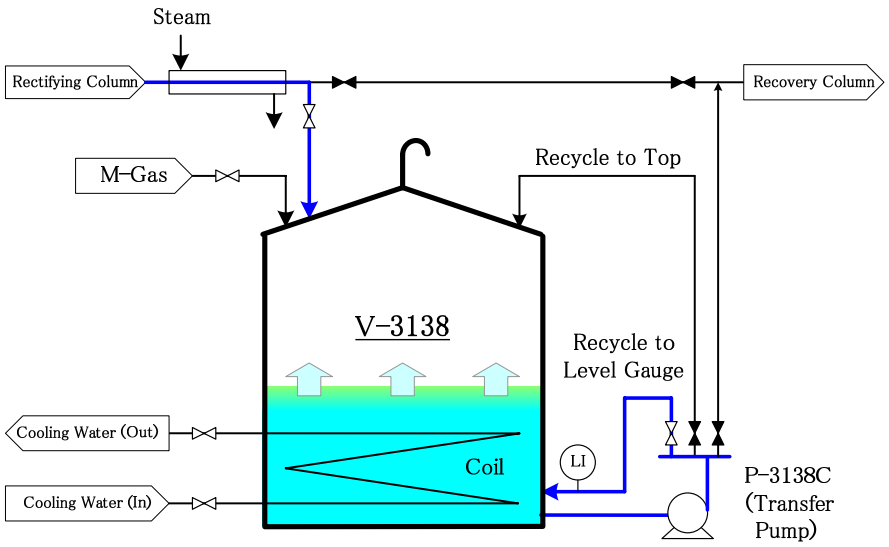


Figure 4. Status of tank V-3138 during liquid storing

(3) From about 14:00 to about 14:10 on September 28, 2012 (after storing operation in V-3138)

- At about 14:00 on September 28, the liquid volume in V-3138 reached 60 m^3. Hereafter, the rectifying column bottom liquid was switched back to feed the recovery column directly without passing through V-3138.
- Even then, the circulation of Recycle to Top was still not commissioned. Consequently, the liquid above the top of the coil was not cooled and remained at a relatively high temperature.

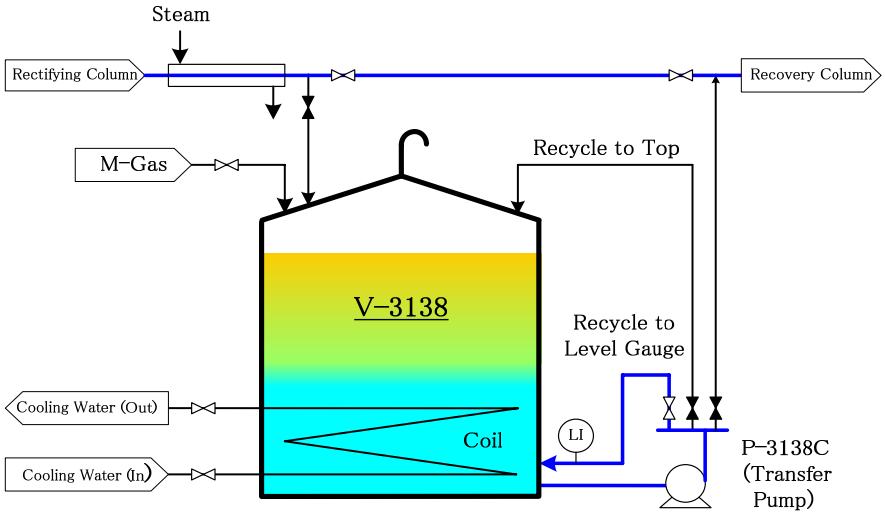


Figure 5. Status of tank V-3138 after liquid storing

(4) From about 14:10 on September 28 to about 14:35 on September 29, 2012 (from liquid holding in V-3138 to explosion and fire)

- It is presumed that the reaction of DAA formation continued in the liquid stored in V-3138 and the liquid temperature continued to increase from the heat of DAA formation.

- It is also presumed that this continued rise in temperature has started the polymerization of acrylic acid and the liquid temperature rose even more rapidly from the heat of polymerization.
- At about 13:20 on September 29, an operator discovered the acrylic acid vapor coming out from the vent of V-3138. It is estimated that the high temperature section of V-3138 liquid was about 160°C.
- Since then, the polymerization continued to progress further. This has caused the V-3138 liquid to boil and vaporized, which then exceeded the vent's discharge capacity. V-3138 pressure was thereafter started to build up.
- The V-3138 pressure continued to rise thereafter and cracks appeared in the tank. It is estimated that at the time the cracks appeared, the pressure was built up to 240～290 kPaG and the high temperature section of V-3138 liquid was about 230～240°C.
- The content of V-3138 started to leak from the cracks and caused the V-3138 pressure to drop drastically.
- At about 14:35 on September 29, V-3138 liquid started to boil violently due to the drastic drop of V-3138 pressure, while the liquid temperature still remained at high temperature. These resulted in Boiling Liquid Expanding Vapor Explosion (BLEVE) inside V-3138 and subsequently rupture the V-3138. Based on the distance of scattered debris, it is estimated that the explosion pressure was about 450 to 640 kPaG.
- Content scattered from the rupture of V-3138 ignited and caused the fire. The possible ignition sources were sparks generated from the impact of metals during the explosion or from the broken electrical wires. The explosion has also damaged the nearby tanks and the leaked acrylic acid and toluene from these tanks caused the fire to spread further.

(5) Scenario leading to the explosion and fire accident

- Based on the above four stages of sequence of events, the scenario leading to the explosion and fire accident are summarized as follows:

  The high temperature section which was not effectively cooled was formed in the upper section of the liquid stored in V-3138 and remained stagnant for a significant period of time. This has resulted in DAA formation and increased the liquid temperature further with the heat of dimerization.

  Since then, the liquid temperature reached the temperature which started the polymerization reaction. With the heat of polymerization reaction, the temperature increased even further. This caused V-3138 content to boil and built up V-3138 pressure until V-3138 started to crack.

  V-3138 content started to leak from the cracks, which caused the pressure to drop drastically and BLEVE occurred thereafter.

  As a result, V-3138 ruptured, scattered content ignited and caused the fire.

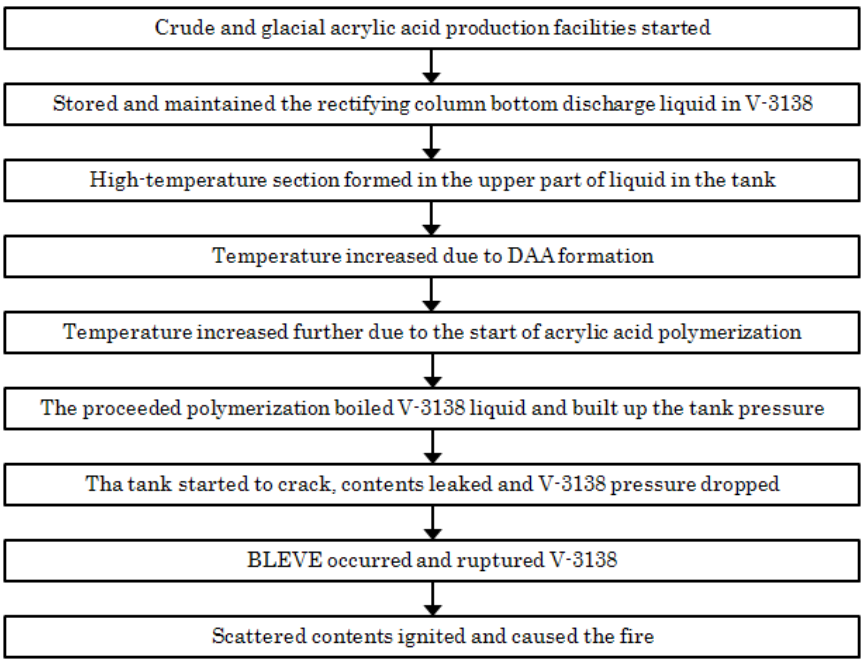


Figure 6. Accident scenario

9. Inference for the Causes of Accident

- The investigation has concluded the following direct causes, which led into the explosion and fire of intermediate tank V-3138:

(1) Even though high temperature of rectifying column bottom liquid was building up inside V-3138, the fact that the circulation of Recycle to Top was not commissioned caused insufficient cooling to the tank liquid. This resulted in acrylic acid remaining stagnant for a significant period of time at high temperature.

(2) Although it was known to the company that DAA would form at a faster rate at high temperature, there was still insufficient recognition of the potential risk of heat of DAA formation which could increase the liquid temperature, and lead to this accident.

(3) Due to lack of thermometers and inadequate temperature monitoring, it was not possible to detect the abnormal condition until the polymerization proceeded.

10. Countermeasures to Prevent Recurrence of the Accident

- The following countermeasures are proposed to prevent the recurrence of V-3138 accident

(1) Countermeasures related to equipment

i. Provide adequate thermometers and strengthen the means of temperature control (remote monitoring etc.)

ii. Revise the specifications for the transfer piping (steam jacket) of glacial acrylic acid rectifying column bottom liquid.

(2) Countermeasures related to management

i. Review the threshold of temperature control range and clearly define the responses to take if any deviations are detected.

ii. Ensure the circulation of Recycle to Top is always commissioned.

iii. Provide thorough education on the potential risks of DAA formation.

11. Future Initiatives

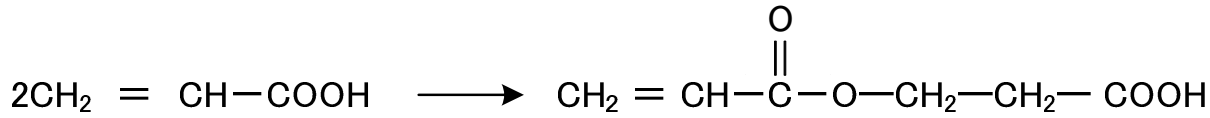
To restore the trust of society to Nippon Shokubai as a safe manufacturing company, the Accident Investigation Committee will propose countermeasures to prevent the recurrence of the accident by looking into issues such as equipment, operation and management that were behind the direct causes of this accident as well as the organization and culture of the company.

Dimerization and Polymerization of Acrylic Acid

※ Both dimerization and polymerization of acrylic acid involve reaction of double bonds in acrylic acid.

1 Dimerization of acrylic acid

Rate of dimerization of acrylic acid is increased with increasing of temperature.
The inhibitors used in acrylic acid is not able to prevent the dimerization of acrylic acid.
Heat of dimerization：145kJ/kg (ref: Plant Operation Progress Vol. 8, No.2 "The Anatomy of an Acrylic Acid Runaway Polymerization")



In this article, further reaction of DAA to form higher order trimers, tetramers, etc. has also been observed and they are represented by the above dimerization reaction.

2 Polymerization of acrylic acid

Acrylic acid will polymerize when exposed to heat, light, peroxide and others.
Normally inhibitors are added in acrylic acid for preventing polymerization reaction.
Heat of polymerization：1075kJ/kg (ref: Acrylic Acid and Acrylic Esters Safe Hadling Gudeline (7th edition), Japanese Acrylic Esters Manufacturers)