

Report on the Investigation of the Explosion and Fire Serious Incident at
Resorcinol Production Facility at Iwakuni-Ohtake Works (Summary)

1. Overview of the Accident

- At 23:20 on April 21, 2012, there was a problem with the steam supply system at Iwakuni-Ohtake Works. At 23:32, workers instituted an emergency shutdown of the resorcinol production plant. Air supply to the oxidation reactor of resorcinol plant was terminated and nitrogen replacement while cooling the oxidation reactor commenced.
- At 0:40 on April 22, the supply of nitrogen was terminated as was the agitator. Temperature of the oxidation reactor began to rise.
- At 2:15, the oxidation reactor burst causing an explosion and fire. The fire spread to the cymene plant and the utility piping rack.
- At 8:05, a second explosion occurred at the oxidation reactor.

2. Location

Resorcinol Production Facility, Iwakuni-Ohtake Works, Mitsui Chemicals Inc.
6-1-2 Waki, Waki-cho, Kuga-gun, Yamaguchi

3. Date and Time of Accident

April 22, 2012 at 2:15

4. Damages

(1) Casualties

1 dead, 25 injured

External areas

Residents of local communities: 14 injured

Employees of subcontractors at JX Nippon Oil & Energy Marifu Refinery: 2 injured

Within premises

Employees: 1 dead, 7 injured (2 seriously injured)

Employees of subcontractors: 2 injured

(2) Physical damage

External areas

Damage to buildings/homes: 999

Partial damage to facilities of neighboring companies

Within premises

Severe damage to resorcinol production plant around the oxidation reactor

The cymene plant and utilities piping rack were damaged by the force of the explosion and subsequent fire and flying debris.

15 nearby plants were also damaged from the force of the explosion and flying debris.

5. Overview of the Resorcinol Production Facility

- The plant started operations in 1980 and the oxidation reactor was installed in 1999.
- Production capability is 7,600 tons annually.
- The main processes of the facility are 1) oxidation, 2) reoxidation, 3) cleavage, and 4) refining processes.

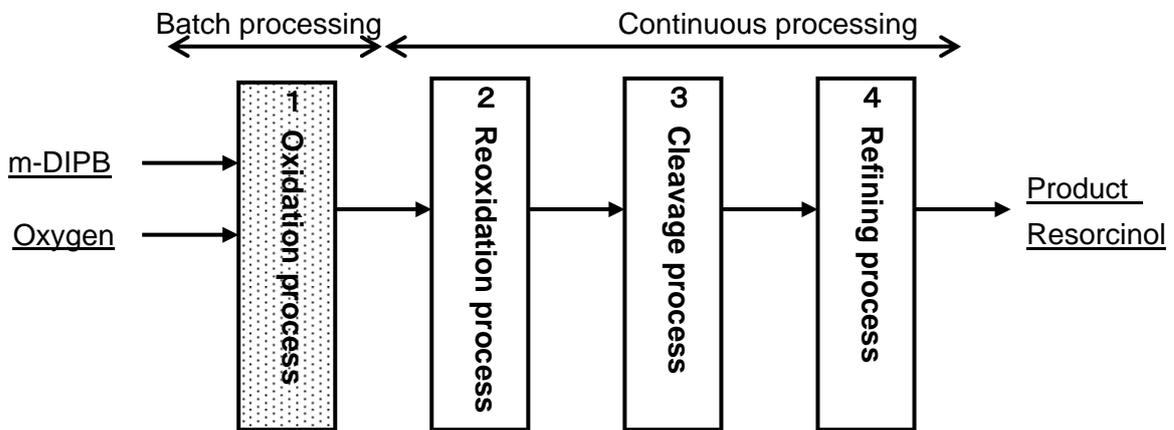


Figure 1. Block flow of the resorcinol production process

- 1) Oxidation process: The raw material meta-Diisopropylbenzene (hereinafter referred to as m-DIPB) is oxidized with oxygen in the air to create an intermediate.
$$\text{m-DIPB} + \text{oxygen} \rightarrow \text{Dihydroxy peroxide (hereinafter referred to as DHP)} + \text{Hydroxy hydroperoxide (hereinafter referred to as HHP)}$$
- 2) Reoxidation process: $\text{HHP} + \text{oxygen} \rightarrow \text{DHP}$
- 3) Cleavage process: $\text{DHP} \rightarrow \text{Resorcinol} + \text{Acetone}$
- 4) Refining process: After removing impurities through separation by distillation and crystallization, flaking is conducted to create products.

6. Accident investigation structure

- On April 24, 2012, Mitsui Chemicals, Inc. formed a “Accident Investigation Committee” to investigate the accident at the resorcinol production facility at Iwakuni-Ohtake Works (hereinafter referred to as the Committee)” which comprised of four members from the academia and external specialists from relevant organizations functioning as observers.

Committee members:

Dr. Terushige Ogawa Emeritus Professor, Yokohama National University
Executive Director, Research Institute for Safety Engineering

Dr. Kazuhiko Suzuki Professor, Okayama University Graduate School of Natural
Science and Technology

Mr. Jun Nakamura Director, Research Institute for Safety Engineering

Dr. Masayoshi Nakamura Professor, Tokyo University of Agriculture and Technology,
The Graduate School of Technology Management

Observers:

Nuclear Industrial Safety Agency, Ministry of Economy, Trade and Industry
Disaster Prevention & Crisis Management Division, General Affairs Department,
Yamaguchi Prefecture

District Fire Fighters, Iwakuni Fire Department

High Pressure Gas Safety Institute of Japan

- The committee met a total of 6 times (May 1, May 27, June 12, July 5, July 26 and Aug. 15, 2012) to determine the situation in which the accident occurred and the direct cause of the accident. Additionally, it approved measures to prevent recurrences.

7. Events leading up to the accident

- As for the events leading up to the accident, based on operation data (DCS data), testimonies from operators, thermal behavior measurements using adiabatic calorimeters (ARC test devices), and analysis of flow simulation, we have estimated the following.

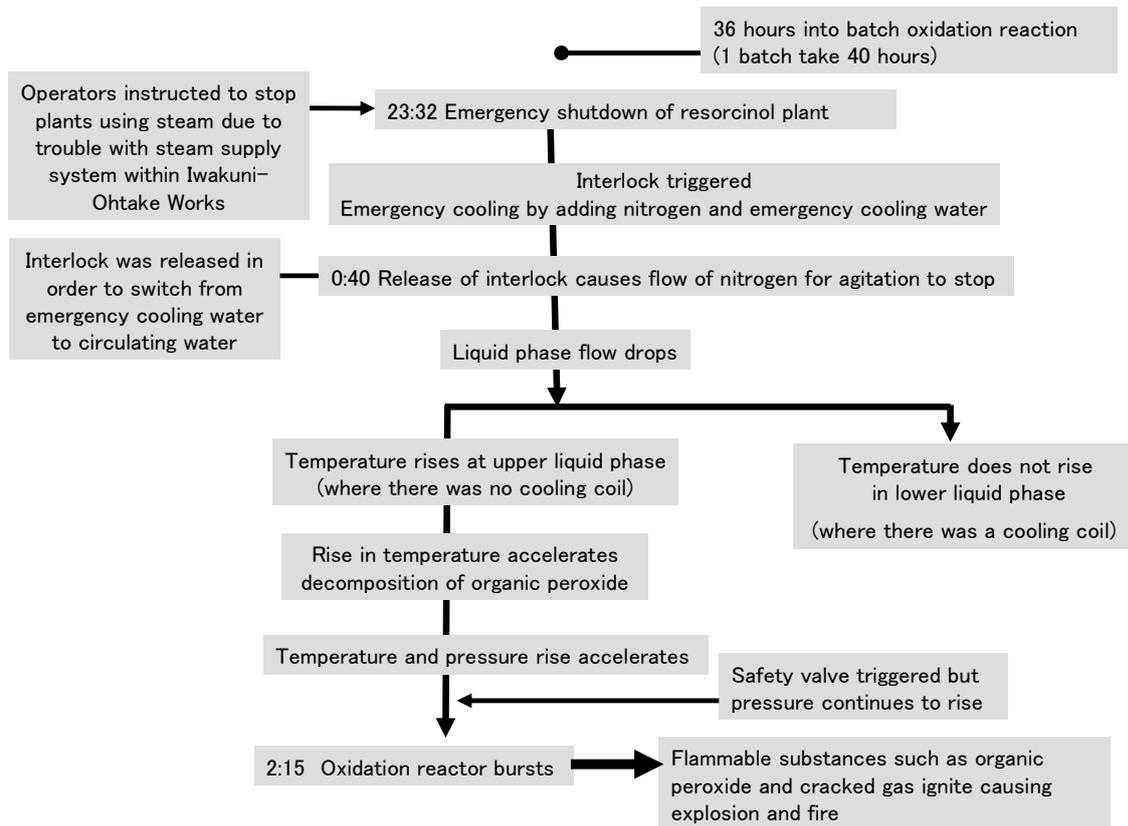


Figure 2. Events leading up to explosion and fire

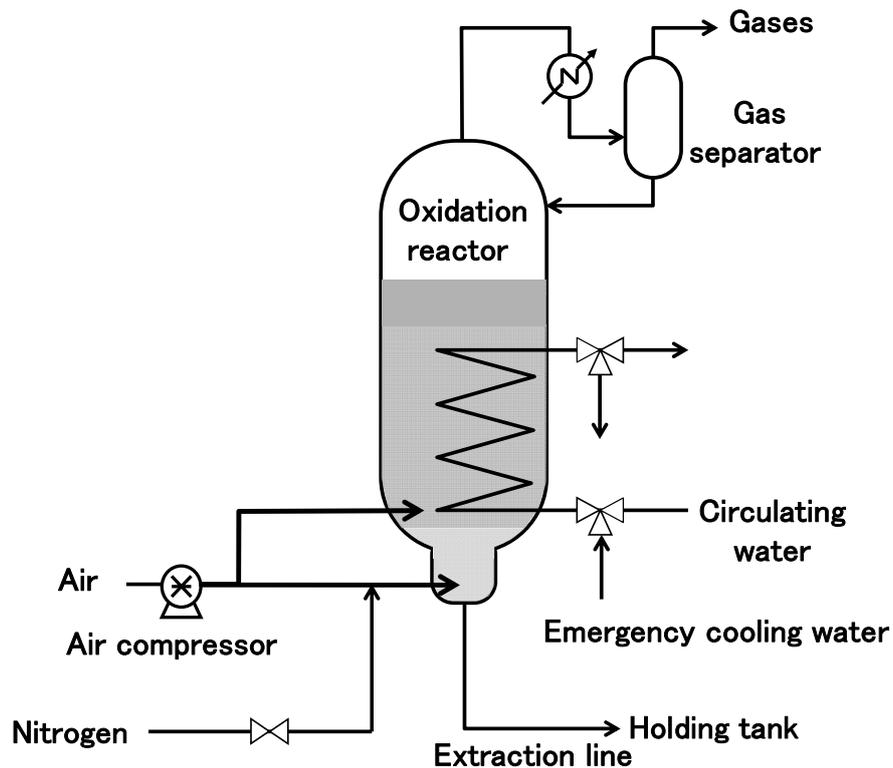


Figure 3. Flow sheet of resorcinol oxidation reactor

- The following events leading up to the accident have been summarized in two parts. The first starts with the emergency shutdown to release of the interlock. The second starts with the release of the interlock to the explosion and fire.

(1) Emergency shutdown to release of interlock

- At 23:20 on April 21, there was a problem with the steam supply system and were ordered to shut down all plants using steam.
- At 23:32, the emergency shutdown triggered the interlock and emergency shutdown was instituted for all processes at the resorcinol production plant.
- With triggering of the interlock, the valves were operated automatically and air supply to the oxidation reactor was replaced with nitrogen. Cooling water was switched from circulating water to emergency cooling water.
- Air in the oxidation reactor was replaced with nitrogen and agitation continued resulting in a gradual drop in temperature.
- At 0:40 on April 22, it was determined that temperature of the oxidation reactor had not dropped so the interlock was released to switch cooling water from emergency cooling water to circulating water.

(2) Release of interlock to explosion and fire

- With release of the interlock, the valve was automatically operated and nitrogen supply and agitation in the oxidation reactor was stopped. At the same time, cooling water was switched from emergency cooling water to circulating water.
- The upper liquid phase of the oxidation reactor did not have a cooling coil and decomposition heat from the organic peroxide could not be removed resulting in a gradual rise in temperature. (Temperature continued to drop for the lower liquid phase where there was a cooling coil.)
- Operators did not recognize the rise in temperature in the upper liquid phase. Organic peroxide continued to generate decomposition heat and temperatures continued to rise.
- At around 2:10, the decomposition reaction of the organic peroxide accelerated, temperatures rose and decomposition gas was also generated resulting in an increase in pressure.
- The safety valve was triggered but pressure continued to increase.
- At 2:15, the oxidation reactor burst, ignited, and exploded, causing a fire..

8. Determining the Cause of the Accident

- Using the cause analysis method, we determined the possible direct cause and reorganized factors into three primary causes and extracted secondary causes.

(1) Direct cause

- During the emergency shutdown of the oxidation reactor that produces organic peroxide, the interlock was released. This stopped nitrogen supplies to the oxidation reactor and stopped agitation of the liquid phases. As a result, decomposition heat of the organic peroxide could not be removed from the upper liquid phase where there was no cooling coil and temperatures rose. This rise in temperature accelerated the decomposition reaction of the organic peroxide, pressure increases in the oxidation reactor, and the reactor burst, causing an explosion and fire.

(2) Primary cause

- a. Operator decided that it would be better to release the interlock.
- b. The interlock is easily released.
- c. By releasing the interlock, nitrogen supply was terminated for an extended period of time and agitation was stopped causing temperatures to rise.

(3) Secondary cause

a. Operator decided that it would be better to release the interlock.

- In order to secure the flow rate of emergency cooling water necessary to cool the reactor, it is necessary to raise source pressure, however this is not automatic and is done on request by resorcinol plant operators.
- Even after pressure of emergency cooling water was increased and the flow rate of the emergency cooling water was secured, the temperature drop was very slow.
- The target temperature for maintaining stable conditions after an emergency shutdown and target speeds for temperature drops were not provided in the operating manual.
- Based on operator's experience with cooling after an oxidation reaction in normal operation, operator decided that it would be better to switch from emergency cooling water to circulating water.
- Conditions are confirmed by digital displays on the DCS main screen so it was difficult to determine trends in temperature drops.

b. The interlock is easily released.

- Conditions for determining "stable conditions" for releasing the interlock were not provided in the manual for emergency shutdown.
- Proper procedures were not taken when releasing the interlock.
- Operators lacked awareness of the significance of releasing the interlock.

c. By releasing the interlock, nitrogen supplies were terminated for an extended period of time and agitation stopped causing temperature to rise.

<Regarding stopping agitation>

- The system was such that if the interlock is released, nitrogen is stopped.

<Regarding rising temperature>

- Once agitation stopped, the upper liquid phase could not be cooled.
- The thermometer that triggers the interlock was only in the lower part of the oxidation reactor and not in the upper part.

<Regarding stopping agitation and delay in noticing temperature was rising>

- There was no alarm to detect that gas for agitation had stopped.
- The main screen of the DCS did not show nitrogen flow rate.
- If agitation is stopped, it was difficult to determine temperature distribution in the oxidation reactor by DCS screen.
- Operators did not recognize that the position of the thermometer failed to show temperature rises in all parts of the oxidation reactor and as a result they failed to recognize the abnormal rise in temperature.
- The operating manual and training materials did not state that nitrogen supply would be stopped when the interlock is released.

- Operators were not aware of the importance of agitation so though they knew nitrogen would stop when the interlock is released, they did not realize that it would affect agitation.
- Temperature at which organic peroxide would start to decompose was not clearly known to all workers resulting in a failure to notice rises in temperature.
- There was insufficient technical knowledge regarding heat decomposition behavior of organic peroxide.

9. Measures to prevent recurrence of similar accidents

- To prevent the recurrence of similar accidents, (1) fundamental measures to prevent accidents and (2) management of emergency operations and improvements in technology were established considering measures for hardware (equipment, devices, etc.) and software (procedures, rules, methods, etc.).

(1) Fundamental measures to prevent accidents

a. Secure necessary abilities for cooling oxidation reactor during emergency shutdown.

- 1) Cooling ability necessary for a pronounced drop in temperature (increase heat-transfer area of cooling coil and expand installation range)
- 2) System whereby pressure of emergency cooling water can be increased swiftly and strengthening of monitoring
- 3) Maintain agitation in oxidation reactor

b. Clarify conditions for releasing interlock

- 1) Set standards for “stable condition” at which the interlock can be released during emergency shutdown.
- 2) Compile and utilize a checklist for release of interlocks
 - Confirmation of stable conditions
 - Authorization from superiors

c. Review temperature management based on data on heat decomposition behavior of organic peroxide using latest methods (such as an adiabatic calorimeter) and educate all workers

- 1) Collect data on heat decomposition of organic peroxide
- 2) Reflect data on safety design philosophy
- 3) Educate workers regarding hazards of organic peroxide and hand down skills

(2) Management of emergency operations and improvements in technology

- a. Install multiple thermometers for triggering interlock in oxidation reactors
- b. Create a DCS screen that makes it easier to notice abnormalities during emergency shutdown and review alarms
 - Agitation condition (display nitrogen flow rate, alarm for stopped agitation gas)
 - Temperature distribution (improve display, alarm sound, etc.)
 - Temperature trends
- c. Compile training material regarding interlocks and conduct education and training
 - Importance of agitation in oxidation reactor
 - Rules within section and authorization for releasing interlocks
 - Details of process operation after interlock is released
- d. Review risks of operation procedures for emergency shutdown of oxidation reactor and equipment
 - Note that when resuming operations at the meta/para cresol (MPCR) and hydroquinone (HQ) production plants, which are similar to the resorcinol plant, measures will be securely implemented for the issues extracted in accordance with the characteristics of each production plant and approval will be obtained from supervisory agencies.

10. Consider underlying causes of the accident

- In the future, the Committee will continue to extract issues and consider measures regarding the underlying causes that led to the direct causes of this accident, such as work climate and corporate culture.

11. Our future

- Our company has implemented various safety activities under the management policy, "Safety is our top priority". However, unfortunately this tragic accident, which had a significant effect on society, occurred. We are strongly aware that we must thoroughly review the problems with safety at MCI through a companywide structure and consider and implement fundamental measures for safety. To this end, on June 19, 2012, we formed the Fundamental Safety Committee with the President of MCI as the chairperson.
- Through a team consisting of external advisors and members from various parts of the company, this committee will investigate the root causes in the people, organization, technology, and culture of the company and propose and implement strengthening measures for the fundamental aspects of safety at MCI.