Investigation Report

Chemical plant explosion caused by runaway reaction after stirring was suspended

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1. Overview

1.1. Disaster

An emergency shutdown of all processes in a high-purity terephthalic acid manufacturing plant was initiated because the steam supply stopped quickly. The cause of the trouble originated in the power plant. Approximately 2 hours and 45 minutes later, an explosion and fire occurred in the resorcin (adhesive material) plant, and the fire spread to the cymene plant, the power plant, and piping racks. After about 6 hours, a tank in the resorcin plant exploded. As a result, one worker died, seven were injured (two seriously) in the workplace. Two workers outside the workplace and 14 people in nearby neighborhoods were also injured.

1.2. Outline of resorcin manufacturing process

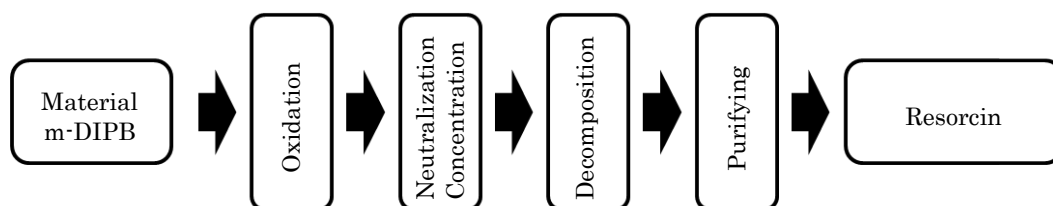An outline of the process for resorcin production is shown in Figure 1.

Figure 1. Outline of whole resorcin production process

1.3. Outline of the oxidation process

In resorcin production, two meta-position propyl groups of meta-di-isopropyl-benzene are peroxidized with oxygen, and the peroxide forms a hydroxyl group through acid decomposition (Figure 2). This reaction is called the (applied) cumene process and is widely used industrially. The decomposition reaction of peroxide is highly selective, depending on the acidity (Figure 3).[1,2]
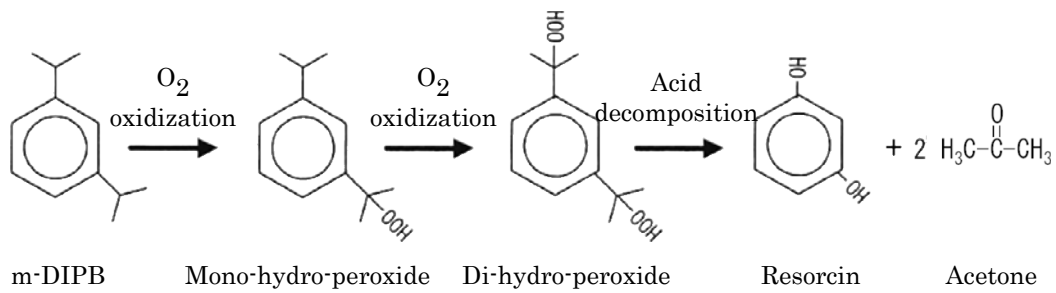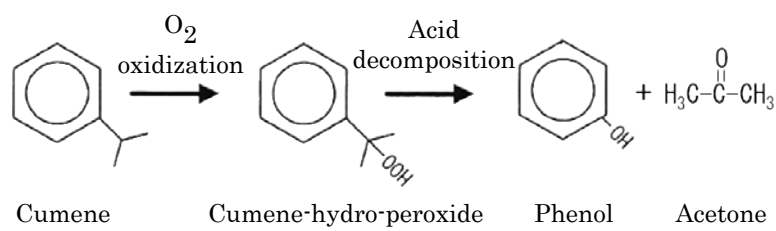
Figure 2. Oxidation of m-DIPB

**Figure 3. Reaction mechanism during cumene process
(phenol and acetone formation)**

The oxidation process was carried out in a column reactor, as shown in Figure 4.
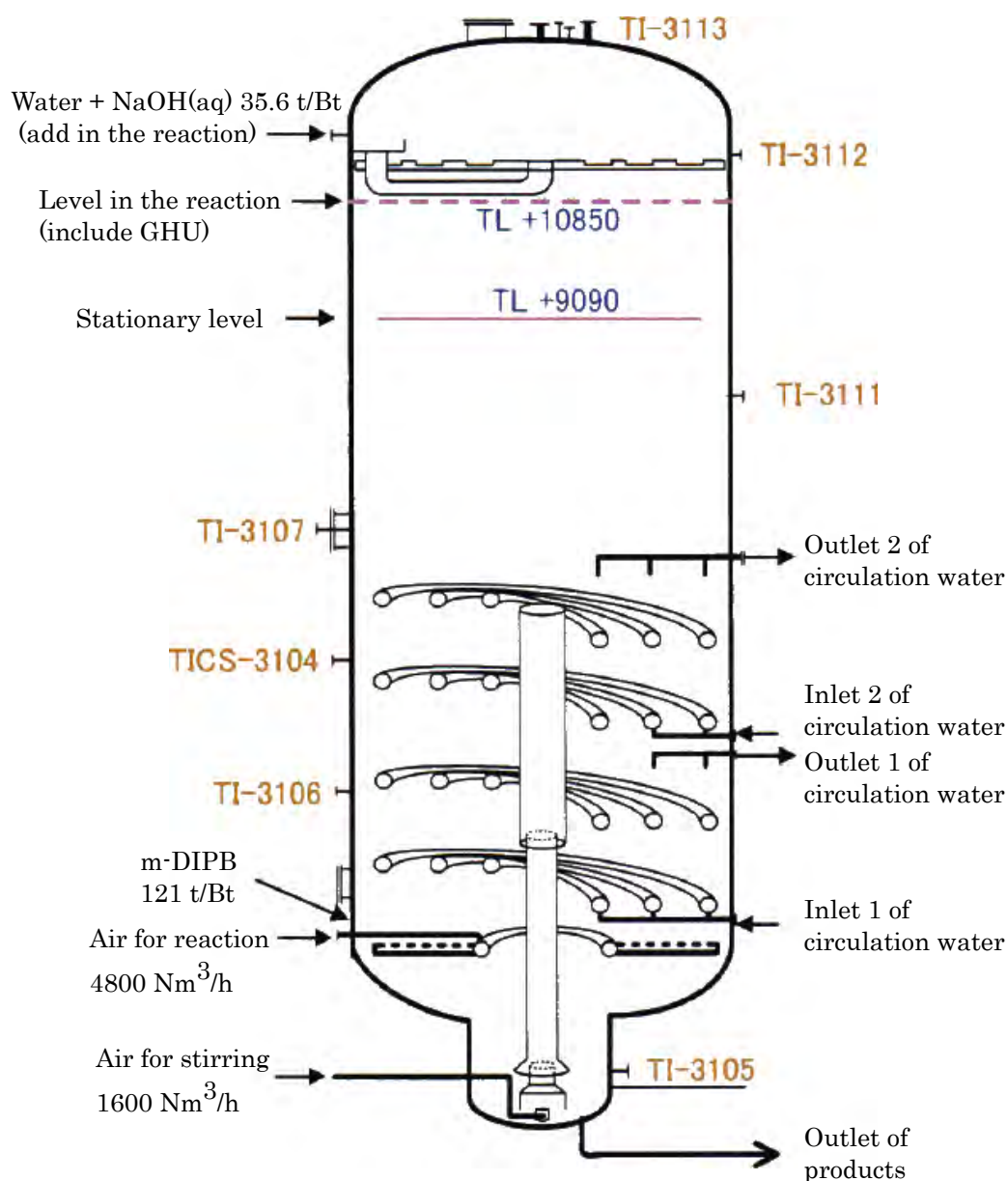
Figure 4. Outline of oxidation reactor

In operation, 121 t of m-DIPB (as the material), 10.2 t of sodium hydroxide aqueous solution, and 25.4 t of process water are introduced into an oxidation reactor. Then, 4,800 Nm3/h of air at a pressure of 0.52 MPa is oxidized in the mixture after raising the temperature to 96ºC. Mechanical stirring by a motor, etc. cannot be done in the reactor because the reaction is under high pressure. Therefore, air (1,600 Nm3/h) was supplied from the bottom of the oxidation reactor, which stirred the materials (airlift method).

The organic acid generated as the reaction progressed, but air oxidation

needs a weak alkalinity atmosphere. So adding a sodium hydroxide aqueous solution must neutralize the acid to make the oxidation reaction more efficient (Table 1).

Table 1. Materials sequentially added to the reactor

Sodium hydroxide aqueous solution		Process water	
T-HPO (%)*	Input (t/h)	T-HPO (%)*	Input (t/h)
45 ~ 65	0.78	122 ~ end of process	0.44
65 ~ 100	0.92		
100 ~ 115	0.65		
115 ~ 122	0.36		
122 ~ end of process	0.19		

*T-HPO is a peroxide concentration converted to hydro-peroxide concentration.

1.4. Timelines

A timeline leading up to the disaster is shown in Table 2. A timeline of the plant data is shown in Figure 5.

Table 2. Timeline up to the disaster

Time	Operation
23:20	70% of the plants sharing the same steam system experienced an emergency shutdown due to a problem in the power plant
23:32 ~	ESD (emergency shut down) (primary operation) began at the resorcin plant Automatic remote control operation by ESD switch Interlock of the oxidation reactor Reaction suspension Refrigerant entered the internal coil (circulating water -> emergency cooling water) Air compressor stopped supplying air to oxidation reactor Nitrogen supply started (stirring by

|	
	nitrogen)
23:32	Secondary ESD operation (onsite) Operations began for safe suspension of all equipment (heat source block, closing of receiving valve, etc.) *There was no secondary operation for the oxidation reactor.
0:40	Interlock was released and refrigerant in the cooling coil was switched (emergency cooling water -> circulating water) By releasing the interlock, nitrogen supply was stopped automatically (stop stirring by nitrogen)
	(Temperature rose in the oxidation reactor)
1:39	Cooling water was introduced from the top of the oxidation reactor
2:11	Air compressor was started, but flow rate was not directed
2:15	Explosion occurred
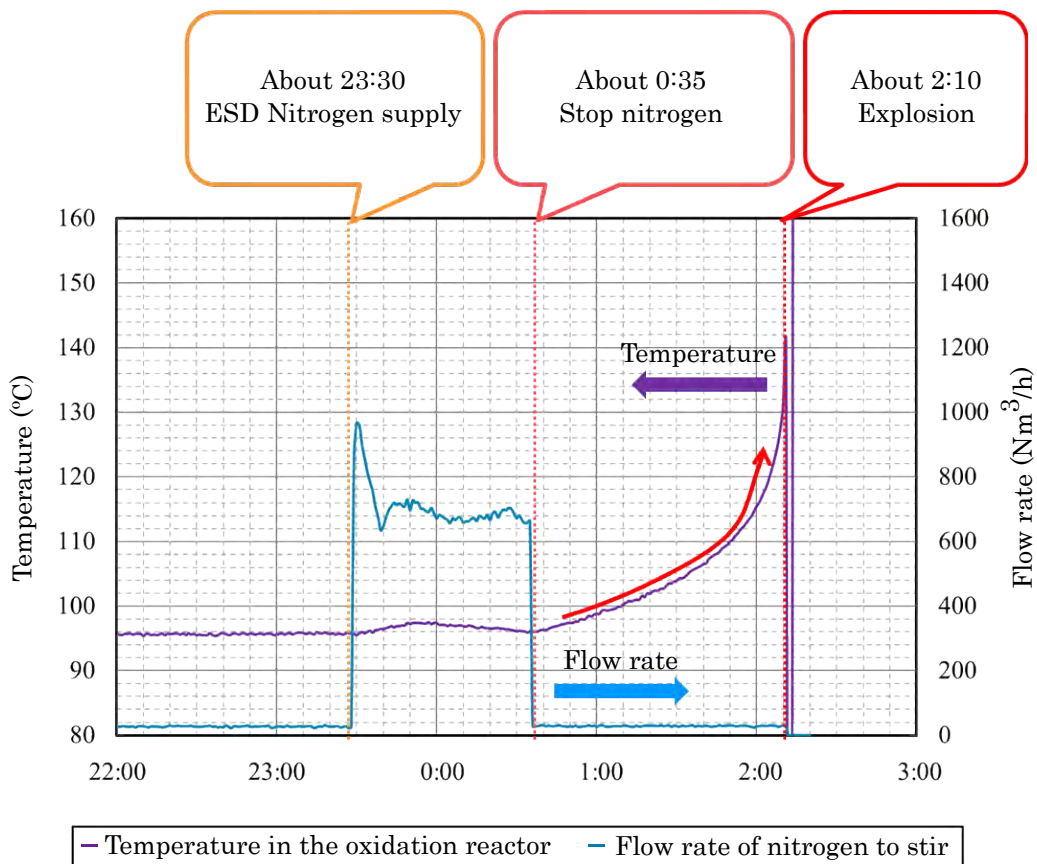
2. Investigation of Disaster Factors

It was determined that, in this disaster, stirring had stopped, the heat of the decomposition reaction rose in the system, then the overall temperature rose, the decomposition reaction accelerated, and there was a runaway reaction. Analysis results with the sources for drawing conclusions are shown as follows.

2.1. Identification of chemical reactions in the oxidation reactor

In Japan's Industrial Safety and Health Act, organic peroxides are categorized as "explosive." In the oxidation reactor, m-DIPB was oxidized with air to produce m-DIPB peroxide. Therefore, m-DIPB peroxide was determined to be the cause of the explosion. The risk associated with m-DIPB peroxide was defined using:

1) thermal analysis
2) measuring the thermal behavior under adiabatic conditions.

2.1.1. Thermal analysis of m-DIPB peroxide by differential scanning calorimeter

The appearance of the sample is shown in Figure 6.

Figure 6. Sample of m-DIPB peroxide

A thermal analysis test of m-DIPB peroxide was carried out using a

differential scanning calorimeter (DSC-1) manufactured by Mettler Toledo Inc. The sample was kept in a SUS 303 sealed container. About 1 mg of the sample was sealed in an air atmosphere. The temperature increase rate was 10 K/min, and the range of the measurement temperature was 25 ~ 500ºC.

The results of the exothermic behavior obtained are shown in Figure 7. Heat generation started around 110ºC. Near 150ºC, the exothermic rate sharply increased. The exotherm was about 1.46 kJ/g, measured up to about 200ºC.

The guidelines for estimating the explosion risk, calculated from heating value (Q_{DSC}), are shown as follows.[3]

i) Power: Detonation   Criteria: $2.1 \text{ kJ/g} \leq Q_{DSC}$
ii) Power: Deflagration or detonation   Criteria: $1.3 \text{ kJ/g} \leq Q_{DSC} < 2.1 \text{ kJ/g}$
iii) Power: Continuous decomposition or combustion

Criteria: $0.4 \text{ kJ/g} \leq Q_{DSC} < 1.3 \text{ kJ/g}$
iv) Power: Non-continuous decomposition Criteria: $Q_{DSC} < 0.4 \text{ kJ/g}$

Based on these guidelines, m-DIPB peroxide has a risk of deflagration or detonation.

Figure 7. Thermal analysis curve of m-DIPB peroxide

2.1.2. Runaway reaction test using adiabatic calorimeter

It was estimated that decomposition heat rose when stirring was suspended, the temperature increased, decomposition accelerated, and a runaway reaction occurred. To analyze these processes, it is necessary to measure exothermic behavior under adiabatic conditions. By simulating this situation, an adiabatic calorimeter can measure the behavior as the reaction accelerates and a runaway reaction occurs.

Therefore, the thermal behavior of m-DIPB peroxide under adiabatic conditions was measured by an adiabatic calorimeter (d-ARC) manufactured by OmniCal Inc. The amount of the sample was about 5 g.

Figure 8 shows the entire exothermic behavior and Figure 9 shows the part of the behavior at temperatures greater than the onset of heat generation (95℃ or higher). It was determined that m-DIPB peroxide started to generate heat at 95℃, the temperature rose at an accelerated pace with a rise in pressure, and the runaway reaction occurred. Also, the maximum pressure went above the safe limit of the reactor: about 12 MPa.

Figure 10 shows a comparison between the temperature data of the DCS (distributed control system) and the results of the adiabatic test. The sample was an m-DIPB peroxide of hydro-peroxide equivalent with a T-HPO concentration of 114%. There is about a 60-minute difference in the time to the runaway reaction. At the disaster, the time to reach runaway of the peroxide was estimated to be shorter than the time to runaway of the sample peroxide (experiment) because the higher T-HPO (134%) of the peroxide in the oxidation reactor has a faster rate of decomposition reaction than the T-HPO (114%) in the sample.

Based on these results, it was determined that the m-DIPB peroxide in the oxidation reactor caused the disaster.
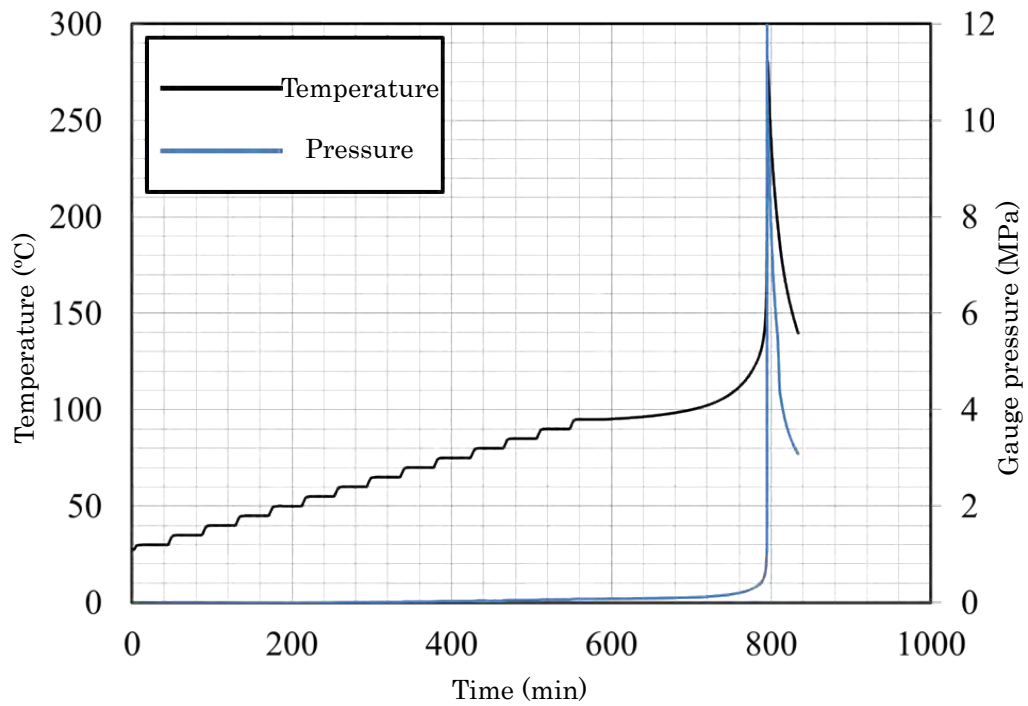
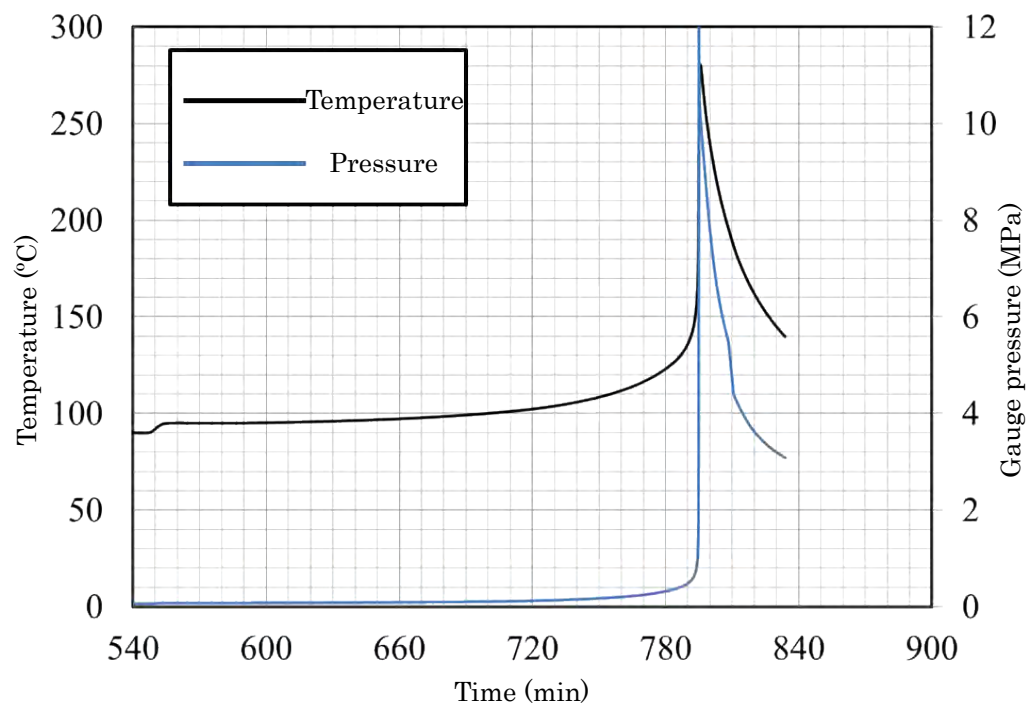**Figure 8. Temperature and pressure measured by adiabatic calorimeter (all results)**

Figure 9. Temperature and pressure measured by adiabatic calorimeter (more than about 95℃)
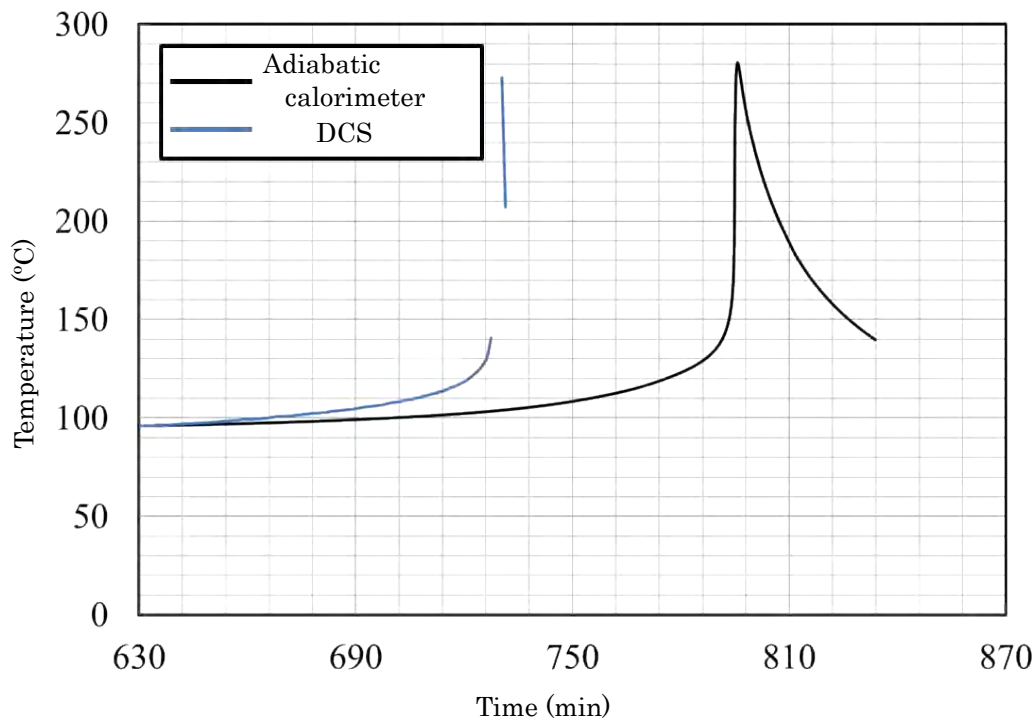
Figure 10. Comparison of measurement results of adiabatic calorimeter and DCS data

3. Prevention of a Reoccurrence of the Oxidation Reactor Disaster
3.1. Substances

m-DIPB peroxide can deflagrate and detonate from the energy (1.5 kJ/g) generated by thermal decomposition. Its self-accelerating decomposition temperature is 95ºC to runaway reaction. So, under the conditions in the reactor for oxidization (reaction temperature: 96ºC) the decomposition reaction occurred at the same time as the oxidation reaction. Therefore, this process is highly risky, because suspending cooling by stirring causes decomposition leading to a runaway reaction.

- It is important to reduce the temperature for safe handling of m-DIPB peroxide because the self-decomposition reaction of peroxide is suppressed at room temperature.
- By setting a lower temperature for oxidation than the current condition, self-decomposition of m-DIPB peroxide by suspension of stirring becomes

slower and enough time for taking measurements can be secured.

3.2. Equipment

From a past case (previous) accident report prepared by the company, after that emergency shutdown the temperature did not fall rapidly. This would not secure safety as soon as possible. Further, the concentration of T-HPO at this disaster was higher (134%) than the concentration during the previous emergency shutdown. The circumstances in this study resulted in high heat and difficulty with cooling.

In addition, the cooling coil at the bottom of the oxidation reactor cannot produce natural convection. This means that the bottom of the reactor was at a low temperature and the upper part was at a high temperature and these two parts were separated without forced flow by stirring. A cooling coil must be designed for safe operation taking into consideration this convection and the specific emergency shutdown as this disaster.

To prevent decomposition of m-DIPB peroxide and to secure safety, it is necessary to consider the following measures:

- The flow rate (700 Nm^3/h-N_2) for stirring gas during the emergency shutdown was lower than 1,600 Nm^3/h-Air, the rate during the oxidation reaction. The effectiveness of the stirring during the emergency shutdown was also lower. A larger amount of nitrogen gas is necessary for stirring and cooling because the viscosity of m-DIPB mixture increases by peroxidation.
- Nitrogen gas must not be stopped *automatically* when canceling an emergency shutdown based on a wrong decision or operation error. It is necessary to design a manual stop.
- In normal stop operations, an oxidation reactor is effectively cooled by air. However, for cooling with nitrogen gas during an emergency shutdown, a method to cool by air must also be designed (multiplexing).
- To prevent an explosion in the oxidation reactor caused by failure of these measures, additional equipment, such as an emergency buffer tank with a cooling system, must be installed.

3.3. Human factors

In this case, releasing the emergency stop by a worker onsite caused this disaster. Therefore, the following measures are necessary.

- Determine the *criteria*, such as a decreasing ratio of temperature, for failure an emergency shutdown, and workers must confirm it.
- Do not determine procedures onsite for emergencies. Follow the planned release procedure for an emergency shutdown.
- Determine a procedure for a *manual* stop when an emergency shutdown does not work.

References

1) Yoshio Kamiya, *Organic Oxidation Reaction: Theory and Application of Autoxidation*, Gihodo Shuppan, Tokyo, pp. 224–231, (1973)

2) Organic Peroxide Research Group, *Organic Peroxide: Its Chemistry and Industrial Application*, Kagaku Kogyo Sha, Tokyo, pp. 193–202, (1972)

3) Tadao Yoshida and Dayu Ding, *Safety Technology for Chemical Substances*, Tokyo Progress System, Tokyo, pp. 14–15, 94–96 (1996)