Fire during Ethylidenenorbornene Manufacturing

【October 18th, 1973　Kawasaki, Kanagawa, Japan】

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A series of explosion and fire accidents related to the petrochemical industry occurred in 1973. This accident was also one of them. When the course of the accident is carefully considered, a lesson will be learned regarding what to do for safety operation of plants developed inside the company.

On October 18th, 1973, a big fire occurred at an in-house developed manufacturing plant of Nippon Petrochemicals Co., Ltd., soon after the operation was shifted into a commercial run from performance run. Two operators died and two operators were injured severely. The construction of the plant was completed in July, the performance runs were carried out in August, and the runs were finished with the confirmation of obtaining the products manufactured to the specification. A total re-adjustment was carried out in September, and the accident occurred just after the start of the commercial production in October. Fortunately, the installation site was located in a littoral industrial area, and the plant developed first was not so big so the damage outside of the plant was not large.

The product ethylidenenorbornene (ENB) is formed from cyclopentadiene and butadiene through many reaction steps, and it is used as the third component for the manufacture of ethylene-propylene-diene-monomer (EPDM) rubber. The accident occurred in the reactor where vinylidenenorbornene (VNB), an ENB precursor, was being synthesized by a Diels-Alder reaction. Operators were working for a temporally shutdown of the reactor because of a failure of the purification section, which is down stream of the process. The reaction was a liquid phase exothermic reaction without a catalyst, and it was conducted in a liquid seal type vertical drum with an agitator and a cooling coil. On stopping the reaction, they stopped agitation without lowering the reactor temperature or changing the composition of the reaction liquid. The fire occurred in the upper part of the reactor two hours after the agitation was stopped. First, a little flame rose from the reactor, that became a comparatively big fire, and then the reactor and the periphery were wrapped in the fire with a big sound.

The direct cause of the accident is to have stopped the agitation thoughtlessly. Moreover, there were some basic factors leasing to the stopping of the agitation, such as insufficient operation manual, and transmission of information.

In the end, the plant was abandoned. Later, a manufacturing plant using the same process was constructed at another location with new design and new operation manuals based on the experience from the accident. At present, over 50% of the global production of ENB is manufactured at the plant.

1. Event

At around 15:19 on October 18th, 1973, there was a fire accident of a reactor in the Kawasaki littoral industrial area that was accompanied by a sound which seemed to indicate that an explosion occurred as well. The plant where the accident occurred manufactured ENB, a substance that is used as the third component of higher grade of EPDM rubber that shows good properties in heat resistance and oil resistance among many grades of EPDM rubber. The plant was constructed in July 1973, and after finishing a performance run in August and undergoing re-adjustment in September, the plant began the commercial production few days before the accident. A laboratory of the parent company Nippon Oil developed the technology of the process, and the basic design was carried out in-house. It was the second or third plant manufacturing ENB in the world and it was a small type plant with a manufacturing capacity of 3000 ton/year.

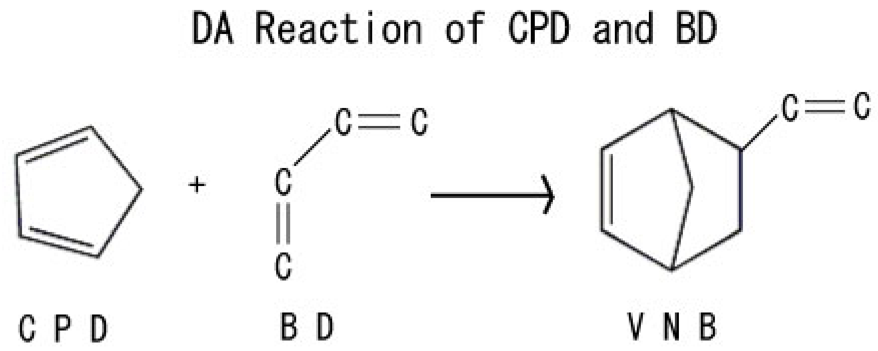

Fig. 1 Chemical Reaction Formula

ENB is formed by transferring the position of the double bond of VNB, which was synthesized first. The accident occurred in the reactor where VNB was synthesized. ENB is synthesized from two kinds of raw material: cyclopentadiene and butadiene. When the two raw materials are mixed in the liquid phase, one diene combines with the other diene, and various dimers and trimers are obtained, including VNB. For improving the VNB yield and decreasing the formation of substances that are difficult to separate, the operation conditions were set at 115°C and 2.1MPaG. The reactor was a liquid seal type for preventing the reagents from making contact with air, and it was equipped with an agitator and a cooling coil for mixing and cooling. This reaction, called the Diels-Alder (DA) reaction, is a non-catalytic reaction, and the only controlling elements are temperature and composition.

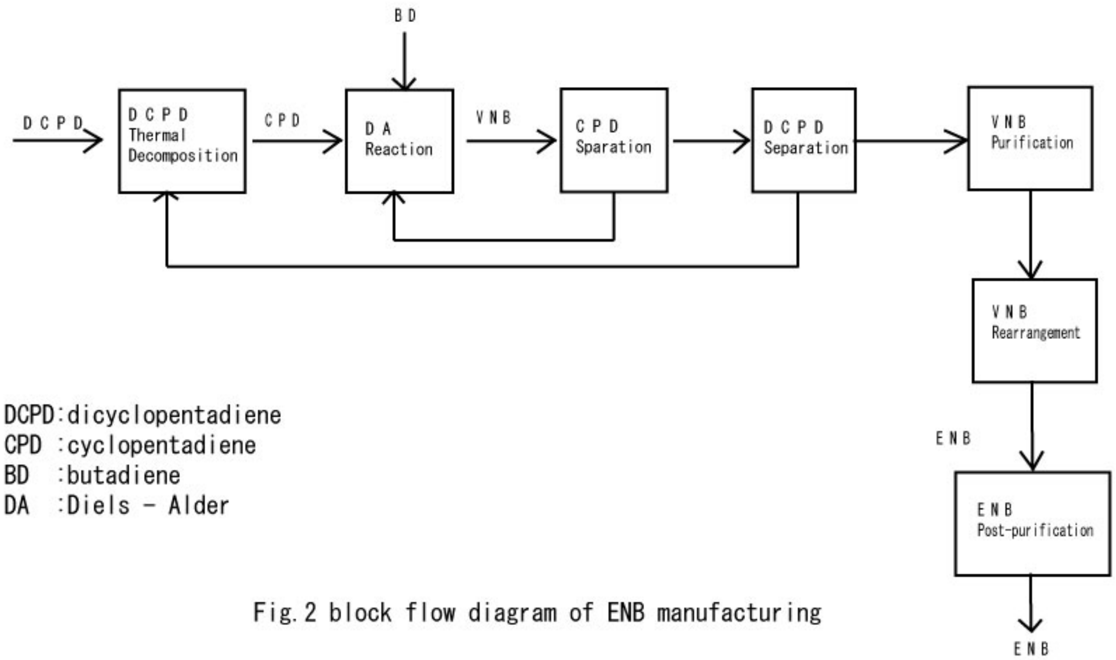

Fig. 2 block flow diagram of ENB manufacturing

On the day of the accident, the DA reactor for the VNB synthesis was stopped due to problems of the CPD separation section. The outline of the process is shown in Fig. 2. Agitation was stopped soon after the supply of raw materials was stopped. The pressure control valve at the reactor outlet was closed manually. The reactor pressure rose after temporally falling as a result of the supply stop, and then the pressure was released by opening the bypass valve of the control valve. The same operation was repeated. Soon after the operation, the reactor pressure rose suddenly, and the safety valve mounted in the upper part of the reactor operated. A fire was soon occurred in the upper part of the reactor. First a flame spouted out suddenly from the safety valve inlet flange. In addition, a slightly larger flame rose with a small sound in the upper part of the reactor. After few seconds, a large flame suddenly wrapped the reactor. At that moment a slightly larger sound was heard, but it was not recognized as an explosion, because there was no damage to the slate roof or window glass of the nearby building.

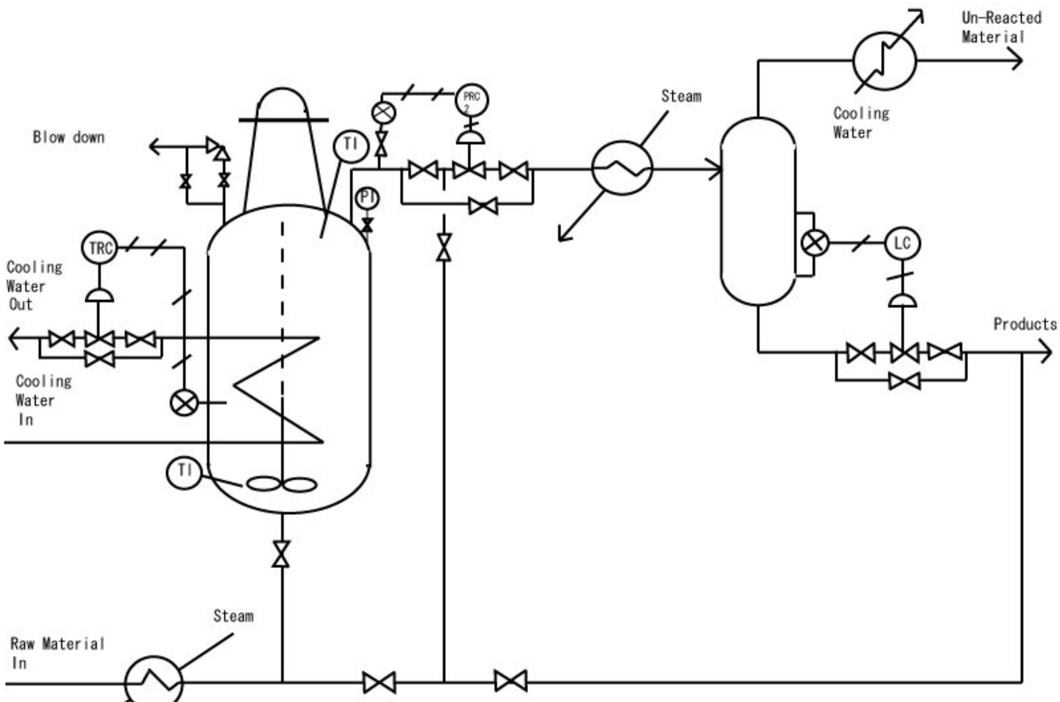

Fig. 3 Simplified flow sheet around the reactor

2. Course

At 11:30, the decision was made to stop the VNB reactor in the afternoon because of the failure in the CPD separation. The shutdown operation started at 13:05. The following steps were carried out during the shutdown operation: stopping of the feedstock supply to the reactor, stopping of the steam of the pre-heater, etc. The shutdown procedure of the reactor finished at 13:30. Soon after, the agitator was stopped and the pressure control valve outlet block valve of the reactor outlet was closed. The liquid in the reactor was perfectly enclosed as a result of this operation.

The reactor pressure dropped temporally after the feed was stopped, but after a while it increased gradually and soon exceeded the normal operation pressure of 2.1 MPaG. The pressure was released at 14:10 by opening the block valve of the control valve. The same operation was repeated at 14:15.

The pressure started to rise from 14:50, and reached to 2.1MPaG at around 14:55 and 2.2 MPaG at around 15:10. After that point, the pressure rose rapidly, and it reached 3.5MPaG in 10 minutes. The temperature chart went off the scale, indicating that the temperature in the reactor was higher than 150℃.

At around 15:20, a sound like the operation of the safety valve mounted on the reactor was heard, and the temperature of the outlet valve of the safety valve was observed to be extremely high. Soon after, a fire occurred. The public fire brigade arrived at around 15:25, and they sprayed water for cooling the site. Confirmation that the fire had been extinguished was made at 19:36.

3. Cause

The cause of the fire was concluded to be an increase of the temperature and pressure in the reactor as the result of a runaway reaction. High-temperature gas and liquid spouted out through the flange, which used a thermally weak Teflon gasket was used.

Agitation of the reactor had been stopped though the reactor still had the potential for an exothermic reaction. In other words, the contents of the reactor were still rich in monomer, the reactor temperature had not been lowered enough to the temperature at which the reaction would not occur, the reactor liquid had been enclosed in the reactor by closing the outlet block valve of the control valve, which is usually used for releasing the liquid from the reactor when the pressure roses. These factors are considered to have caused the fire.

The causes mentioned above are only outward factors, and not true causal factors. In a non-catalytic exothermic reaction controlled only by the temperature and composition in the reactor, the exothermic reaction continues if a monomer remains, and the temperature is sufficiently high. Furthermore, if agitation is stopped, removal of the reaction heat is not possible, so the temperature rises and eventually the reaction becomes a runaway reaction. This fact should be common knowledge for many chemists and chemical engineers in the chemical industry. However, this common knowledge was not described either in the operation manual or in the directions for the shutdown procedure on the day of the accident. The management staff of the manufacturing section or the staff of the technical section should have checked this important point. According to a chemist who was a member of the R&D team of this research the information on reaction hazards had been transferred from the researchers to the headquarters or the engineering department of the factory. There might be insufficient communication in the company or the persons who got the information might not take it seriously. If the researchers had prepared the basic part of the safety manual about the reaction, and had clearly explained the details to the factory staff and, the accident might not have occurred.

Besides, the pressure increased in spite of the operation of the safety valve. The initial bow-off quantity is determined according to a safety valve capacity, and this capacity should be large enough to prevent a runaway reaction. If the setting of the blow-off pressure of the safety valve is below the critical pressure, cooling of the reaction liquid may be possible through the release of the heat of evaporation of the butadiene in the reactor. The setting of the blow-off quantity and blow-off pressure of the safety might be one of the causes of the accident.

4. Process of cause elucidation

The danger of a runaway reaction should have been known in the research phase. A rise in temperature and pressure could have been confirmed by simulations on the premise of the homogenous condition in perfect hear insulation. From the records that have remained in the control room and the investigation of the accident site, evidence of the temperature actually rose in the reactor was found, providing that a runaway reaction occurred. The Teflon gasket at the spot where the safety valve was mounted disappeared almost completely. Furthermore, the gasket of the manhole where the agitator was mounted was also damaged. According to the estimation of the remaining gasket by the gasket manufacturer, it appears that the gasket at the manhole had been heated to 360-370℃ and that the gasket at the mounting sheet of the agitator was exposed to a high temperature of over 450℃.

5. Countermeasure

In the accident investigation report, it was indicated that the plant where the accident occurred was the newly developed and that there were problems related to technology development. The problems included those related to the safety management system, education, and technical details. The problems of the way of technology development are shown below.

"It is necessary to establish a technique for safety assessment in a developing new technology. It is also necessary to have sufficient consideration for ensuring the process safety through all stages such as research and development stage in a laboratory, process design stage, plant detailed design stage, construction stage, performance run stage, and commercial run stage. Moreover, it is also important to establish the rule of the information exchange from one stage to the following stage and to establish the follow-up system for the following stage. Finally, it is necessary to prepare the operation manual based on the consideration of all possible cases."

When we apply the items indicated in the report in general expression to this accident as well as to other similar accidents from the aspect of operation and facilities, the countermeasures can be expressed as follows.

a. In the operation aspect, the work procedure should be decided based on full considerations of the possibility of a runaway reaction. For example, stopping of the agitation of a reactor should be absolutely forbidden, until the temperature in the reactor is lowered to the point at which the reaction cannot occur.

b. Facilities for controlling a runaway reaction in the initial stage or before that should be installed. The cooling capacity of the coil or jacket should be increased about 150% or 200% to meet the potential demand in the case of emergency. Another cooling function without using cooling water should be given. If the cooling using the latent heat of vaporization of the reaction liquid in the reactor is possible, it is desirable to use it. Moreover, a total blowdown system should be installed as a last resort.

c. Duplication of the power supply should be considered.

6. Knowledge

a. Even if the side having information sends the information, it is not sure whether information is transmitted. Whether the information is transmitted or not completely depends on the receiver side. For transmission of critical information, the side having the information must send the information many times and check both the receiver's action and the results of the action. For example, effective transmission of critical information can be confirmed by checking the content of the operation manual.

b. For newly developed equipment, sufficient time should be taken to ensure the complete safety of the equipment. A performance run of about one or two months is not enough for all of the weak points of the plant and possible omissions during R&D and process design to be found. The follow-up system including all the related person must be necessary.

7. Influence of failure

As for the human damage, two persons died and two persons were injured severely. As for the physical damage, the reactor and nearby objects were completely destroyed, and the monetary damage was estimated to be about 300 million yen. The plant was closed down and re-constructed in the different location after several years. The total damage was enormous considering the loss of business and new plant investment.

8. On the side

Later, the operation manual was greatly revised, and the plant with strengthened safety equipment was constructed. Recently, the same plant with the same design was also constructed in the U.S.A., and over 50% of the world share of ENB production is occupied by the plants. Therefore, this is an example in which the facilities and a mode of operation were successfully changed by utilizing experience from the failure.

A "runaway reaction" is an uncontrolled exothermic reaction, and it finally results in an explosion and fire. In short, a runaway reaction should be prevented by the suppression of the reaction. Conceivable methods are cooling down the reaction liquid to decrease the reaction rate, removal of a catalyst, and removal of a reactant. It is reported that when the reactant temperature rises by 10℃, the reaction rate is doubled. The effective measures for suppressing the reaction are determined by the material and other features of the reaction. For example, a runaway reaction can be stopped by using a larger heat exchanger. Alternatively, the latent heat of vaporization can be used for cooling, all of the liquid can be drawn off by blowdown or high-pressure nitrogen can be used for the fixed bed catalytic reaction.

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