Explosion of Organic Peroxide caused due to Warehouse Fire [July 14th, 1964 Shinagawa, Tokyo, Japan]

Terushige Ogawa. (Faculty of Engineering, Yokohama National University) Mitsuo Kobayashi (Graduate School of New Frontier Sciences, University of Tokyo) Masamitsu Tamura (Graduate School of New Frontier Sciences, University of Tokyo)

At around 21:56 on July 14th, 1964, from the warehouse zo ne in the coastal reclaimed land that adjoins the Tokyo Metropolitan Expressway No.1, suddenly a pillar of flames rose like firework s with an explosion sound up into the night sky. The explosion occurred at the Katsushima warehouse of Takaragumi Co., Ltd. There were many dangerous substances as well as non-dangerous materials in the warehouses and open freight storage. The dangerous substance s consisted of self reactive materials such as nitrocellulose, organic peroxides like methyl-ethyl-ketone-peroxide (MEKPO), and inflammable fluids such as acetone.

The fire station still conducted fire t ower observation at this time, and this fire was discovered by at least two fire s tations almost simultaneously . Op en freighting materials, such as nitrocellu lose, and organic so lvents, such as acetone, caused small explosions incessantly and continued to burn. A large number of professional and voluntary firemen fought a fire. M any reporters gathered to collect information about the fire, since it occurred just near the Metropolitan Expressway Haneda, which is a major expressway between Tokyo and Yokohama. At 22:56, when it appeared that the fire would be extinguished at last, a larg e explosion happened inside the warehouse. Fragments of the roofs of thr ee warehous es were scattered by the explosion, which produced a 100m high pillar of flames. As a result of this explosion, a total of 19 persons were killed including 18 professional firemen and one voluntary fireman, and a total of 1 17 persons w ere injured includ ing 80 professional firemen, 12 voluntary firemen, and 25 policemen and journalists.

The first ex plosion and fire se emed to be caused by the sp ontaneous ignition of nitrocellulose in d rum cans that had been sto red in the op en freight st orage. Acetone and alcohol that were also stored there ignited, causing repeated explosions. MEKPO stored inside the warehouse was ignited by the fire and exploded. In addition, the fire spread to another warehouse which stored sundries, and thus the fire spread.

The reason why the fire became so large was the illegal storage of many substances that were designated as dangerous materials and controlled by the fire protection law everywhere in the yard. Moreover, it was indicated that the management system h ad been very loose. Furthermore, the data that was given to the fire fighting team was old, and it showed different stored materials from the practice. In addition, the request that was made by the emp loyees to the fire fighters was only to p rotect the aceton e and nitrocellulose in the open freight storage. The fire fighters were only informed that the contents of the warehouse were canned food. Since most of the fire men did not know the actual c onditions of the war ehouse in which dangerous substances were stored, it became a large disaster.

In short, careless management and control of the warehouse operation by managers and supervisors caused the disaster.

Although the first ignition was caused by spontaneous ignition of nitro cellulose in the open freight storage, in the appealed court decision in the Tokyo High Court, the judge did not affirm clearly that the cause of the explosion was spontaneous ignition of the nitrocellulose based on the r esult of a certain exp eriment. However, nitrocellulose should be h andled under the premise that sp ontaneous ignition may occur, be cause nitrocellulose is definitely unstable, and there have been many accidents related to spontaneous ignition of nitrocellulose before this accident.

1. Event

On the night of July 14th, 1964, an explosion and fire occurred at warehouse for dangerous materials and the op en freight st orage located along the Metrop olitan Expressway No.1 near Shibaura. The fire fighters noticed the fire by fire tow er observation and mobilized the second grade f ire fighting team immediately, which consisted of 13 to 15 pump cars and one ambulance. At the site where the fire occurred, the employees who lived in the company houses at the site and voluntary firemen tried initial firefighting using a small pump, but th ey could not do anything at all, and the fire spread to engulf the whole open freight st orage. The fire brigad e judged that the fire was involved in dangerous materials from the observation of the flames on the way to the site, and they requested the mobilizat ion of the chemical fire brigade, which consisted of six fire engines for chemical fire.

The initial target of the fire brigade was to put out the fire of nitrocellulose, oils and fats in the open freight storage. However, the force of the fire was strong and the fire spread from a warehouse to another warehouse one after another. Given this situation, the fire fighting crew w as strengthened by the third grade and then the fourth g rade mobilization. Finally 26 pump cars, 14 chemi cal fire fighting engines, 12 material transportation vehicles and seven fire boats tur ned out. The No.3 area where the fire occurred and the No.5 area that was adjacent to the No.3 area on the north side were surrounded with firefighters, and the fire in oth er areas seemed to be extinguished at last. Until that moment, the firefighters knew only that the contents of buildings 6, 7, and 8 in the No.3 area were paper and ciga rettes, the building of 5 in the same area contained miscellaneous articles and canned food, and the building 1 in the same area and the op en freight storage contained nitrocellulose. In addition, the persons related to the warehouse requested the firefighters to protect area No.5 because there was a large amount of acetone, alcohol, and nitrocellulose in the open freight storage.



Fig.1 warehouse location

Under this situation, at 22:56, about an hour after the fire started, a large explosion occurred at the warehouse No.12 for gen eral materials, which had been reported to contain canned food. The roofs of the warehouse No.12 and the other two warehouses adjoined the No.12 warehouse were scattered instantly, and an enormous pillar of flames with a large mushroom cloud rose from the site. The external walls were blown away, and many firemen were buried under the wall. A crater over one meter in depth was made at the center of the explosion.



There were 2,000 nitrocellulose at the open freighting area The front was estimated as the fire occuring point

Fig.2 photo after the fire

The trigg er of this large exp losion and fire seems to have been the spontaneous ignition of nitrocellulose at the open freight storage in the third area. Excessive storage of un-licens ed d angerous materials was the ereason of increase in damage. Many victims wer e sacrificed because t he employees d id not know that the wareh ouse contained organic peroxide MEKPO. However, the problem was not that the employees did not know what the warehouse contained. More serious cause of t he disaster was that the managers and sup erintendents had stor ed a large am ount of d angerous materials illegally, that they had not informed the employees about the stored material nor had they introduced countermeasures ag ainst the accident, and furthermore t hat they did not give sufficient information to the firefighting team.

The p resident of this wareh ouse c ompany had started business with the e management of a h otel, and he also carried on businesses such as a contractor of civil engineering and construction and sales and processing of seafood, w arehousing and shipping. It was not known whether or n ot he had managed the wareh ouse business with sufficient kn owledge of the danger cau sed by a l arge am ount of d angerous materials stored in the warehous es and th e d angers of n itrocellulose and ME KPO. However, at lease the president should assign a qualified person for the manager of the warehouse, a required number of qualified persons for supervisors and operators for the actual operations, and make sure that laws are observed.



Fig.3 fired area

2. Course

At around 21:56 on July 14th, a fi re occurred. At 22:00, t he public fire brigade turned out. Although this was the second grade order, soon after it was changed to the third grade, and then the fourth grade order were issued at 22:13.

At 20:56, a large explosion happened.

At 00:27 on July 15th, the spreading of fire was successfully prevented. At 01:38, the fire was extinguished, but the complete treatment of the embers was not completed until 14:00.

3. Cause

The t rue c ause of t his accid ent was the ca reless man agement. D angerous materials that far exceeded the permitted qu antity limits were stored without care. In addition, the sup erintendents who d id not train and educate the operators on the contents of the stored materials, the methods of treating the materials a nd countermeasures against the fire should be blamed. Refusing the storage of materials over the permitted quantity is originally the responsibility of the manager. It is the duty of the managers and superintendents to grasp clearly the stored materials at that time, to establish correct methods to treat the material, and to give correct information to the authorities including the fire fighting team. The first spontaneous ignition might have been prevented, and a large number of victims sacrificed to the disaster could

have been avoided, if the correct information had been provided.

Nitrocellulose is well known as a substance that ignites spontaneousl y. There are many p ersons who estimate that t he caus e of this fire is spontaneous ignition of nitrocellulose.

Furthermore, considering the size of the explosion, it must be the explosion of 2500 kg of MEKPO that was stored.

4. Process of cause elucidation

At first the ignition point was determined. On the basis of twenty testimonies by observers who saw the first pillar of flames near the accident site, straight lines were obtained by connecting each observer's standing point and the reported direction of the flame, and the lines intersected at the open freight storage in front of the warehouse No.103. There were four layers of drum cans of nitrocellu lose at this position. The conditions for spontaneous ignition of nitr ocellulose are a s follows (quoted from the (1) Stor age in a dry state. (2) Storage for a literature of Professor Kitagawa) comparatively long period at a high temperature. (3) Storage of a comparatively large amount of material such that the heat of decomposition will be accumulated as the diffusion of the heat o f d ecomposition is p revented. The weather was fine and the maximum temperature was also high for a few days before the day of the accident, and the temperature at the drum surface appeared to reach a maximum of 60-70 , so the condition (2) was satisfi ed. In addit ion, one drum contained 60 kg nitrocellulose in a dry state. This quantity is enoug h to sati sfy the condition (3). The satisfaction of condition (1) is considered as follow s. Although the nitrocellulose was in a wet state that contained 25% et hanol, it can be hy pothesized that the inn er bag mad e o f polyethylene had split. This hypot hesis is substantiated by the observation by other users that the polyethylene bags of all of the e d rum can s had almost split at the shoulder. If the polyethylene bag had split, the alcohol would have evaporated from the upper part, because it was heated to about 70 in the dr um can upper surfac e upon which the sun shone. A part of the evaporated ethanol would have be en pushed out from the opening of the lid of the drum can with hot exp anded air. Fresh air would have been drawn into the can, when the drum can was cooled at the ni ght. The upper part would dry as a result of the r epetition of this process. An employee testified that he had observed this condition when he conducted sampling from the drum cans on June 10th. From the facts above, it was su pposed that the following events occurred. Nitrocellulose decomposed spontaneously, the heat of decomposition was accumulated, the temperature reached ignition temperature at around 22:00, and the nitroc ellulose

explosively decomposed. The lids of the drum cans came off from the piled up drum cans, and the drum cans scattered like rockets with jetting flames from the lid side. The nitrocellulose and alcohol were included in the material that spouted from the lid side, and these materials helped to spread fire.

However, as described in the "Outline" above, in the criminal trial, a different judgment was also given. In the hearing of intermediate appeal in the Tokyo High Court, the "spontaneous ignition theory" was not adopted as the fire accident cause, because the evidence supporting the "spontaneous ignition the ory" was insufficient compared to than that of the theory "the spontaneous ignition was not being generated" based on the different estimation results. It is considered that they did not regard the facts as denying the spontaneous ignition theory, but they chose to apply the principle of "giving a p erson the ben efit of the doubt". Nitrocellulose should be regarded as a substance that ignites spontaneously if storage conditions are bad. In the warehouse where the large exp losion o ccurred, a label for MEKPO was found during the investigation after the explosion, and after the firefighting authorities investigated the actual receiving and sh ipping records of the warehouse, they were certain that the warehouse had contained MEKPO. Therefore, they determined that the warehouse was the center of the explosion.

5. Immediate action

The employees who lived in the company house at the site tried to extinguish the initial fire with some voluntary fi remen using a small pump right after the first explosion, but it was of no avail.

6. Countermeasure

There is a rule of handl ing dangerous materials. The amount, the distance, and methods of treating those materials etc. ar e prescribed in the fire protection law and other laws. The first countermeasure is at least to follow these laws.

More concretely, the following measures may be required: the quantity of storage must be kept under the permitted limit, the correct storage method must be taken with sufficient knowledge of the danger of nitrocellulose, the quantity and properties of the stored materials must be correctly underst ood, suitable countermeasures against emergencies should be prepared at any time, and suitable information must be provided to the fire fighting authorities and police at need.

7. Knowledge

The laws that control d angerous materials, such as the fire p rotection law, show the minimum regulations. It is reasonable that the minimum regulations given by the laws must be kept.

Often chemical substances can unexpected changes when storage and other handling methods are incorrectly applied, and the substances may be transformed into a d angerous state. N of only so-c alled d angerous materials are d angerous. It is important to remember that we are always su rrounded with danger and that safety should be maintained by attention and action in our normal activities.

8. Influence of failure

As for the human damage, 19 persons died and 117 persons were injured. All of the fatalities and 92 of the injured w ere from the fire fighting brigades. Policemen and members of the p ress were also i ncluded among the inj ured. A ccording to anothe r report, 158 persons were injured.

As for the physical da mage, fifteen bu ildings including t he warehouse burned down, two buildings were half destroyed by fire, and eight buildings bur ned partially. The monetary damage was estimated to be 55 hundred million yen in the current price of 1964. In addition, regulation of traffic and other effects caused social damage.

9. On the side

The fire t riggered a re vision of the effire p rotection law. The r evised contents included the following: extension of the authority of the firefighting, such as giving an authority to do on-the-s pot inspection, to order the measures to b e taken, to approve the t emporary storage of d angerous materials, and to r equire the n ecessary information at the accident site.

An article of the special edition of "Modern Fire Fighting, July, 2000" which dealt with this explosion, says that "although it may seem that the most dangerous materials are explosives, the explosives that are used industrially are safe and mass production is possible, as long as the handling process is not mistaken. What are really dangerous are materials such as M EKPO and other organic peroxide that are used as catalysts. Therefore, these materials cannot be used as explosives."

References

· Tetsuzo Kitagawa, "Explosion of nitrocellulose and organic peroxide warehouse",

Analysis of Explosion Accidents, 195-210, Nikkan Kogyo (1980)

- Second la boratory of Fire Fighti ng Scie nce Laboratory, Tokyo Fire Dep. "Burning characteristics of Methyl-ethyl-ketone peroxide", Gekkan Shobo, 40, 57-64(1981)
- Kippei Takeuchi, "Reminiscence of the Kats ushima warehouse fire", Kindai Sh obo, extra ed., July, 2000, 61-68 (2000)