Case Study

Tetramethylammonium Hydroxide Poisoning during a Pallet Cleaning Demonstration

Seung-Hyun PARK¹, Jungsun PARK¹, Ki-Ho YOU¹, Hae-Chul SHIN² and Hyun-Ock KIM³

¹Occupational Safety and Health Research Institute, Korea Occupational Safety and Health Agency, Republic of Korea, ²Gyeonggi Nambu Area office, Korea Occupational Safety and Health Agency, Republic of Korea and

³Department of Occupational Health, Korea Occupational Safety and Health Agency, Republic of Korea

Abstract: Tetramethylammonium Hydroxide Poisoning during a Pallet Cleaning Demonstration: Seung-Hyun PARK, et al. Occupational Safety and Health Research Institute, Korea Occupational Safety and Health Agency, Republic of Korea—Objectives: The purpose of this study was to examine the cause of an accidental death from acute poisoning resulting from exposure to a cleaner containing tetramethylammonium hydroxide (TMAH) and to consider measures to prevent future cases. **Methods:** The authors examined the details and the reason for the accidental death from acute poisoning based on the autopsy report. **Results:** The victim was a 39-year-old male researcher with 7 years of work experience employed by a surfactant production company. The accident occurred when he was conducting a field test of a newly developed cleaner, containing 8.75% TMAH solution. The researcher spilled the cleaner on his work clothes in the area of both the hands/arms and legs. He was unconscious when discovered. An autopsy found no damage or injury that could have resulted in death other than burns to 12% of his body, and the cause of death was found to be acute poisoning by TMAH. **Discussion:** TMAH is widely used in the electronics industry as a developer or cleaner. It is a dangerous material, causing neurotoxicity leading to respiratory failure by ganglion block that occurs through skin absorption, and no antidote has been developed yet. For this reason, it is best to completely prevent exposure by wearing proper personal protective equipment. Despite this fatal toxicity of TMAH, it is not classified in Korea as a “chemical requiring legal control”. For this reason, it is urgent to raise awareness of the toxic properties of TMAH to prevent additional cases of TMAH poisoning. (J Occup Health 2013; 55: 120–124)

Key words: Dermal exposure, Pallet cleaner,

Poisoning, Tetramethylammonium hydroxide (TMAH)

Tetramethylammonium (TMA) is a well-known ganglion blocker and was first extracted from the sea anemone in 1923¹⁾. Today, TMA's hydroxide, tetramethylammonium hydroxide (TMAH), is used as a developer, etchant and polishing agent in the semiconductor manufacturing process, as well as a surfactant to prevent agglomeration^{2–6)}. One national survey found that about 20,000 tons of TMAH are being used in Korea each year.

TMAH is a strong base, like sodium hydroxide. According to its Material Safety Data Sheet (MSDS), if TMAH solution contacts the skin, it can be fatal or cause serious burning or eye damage^{7–9)}. Cases of poisoning and death by skin exposure to TMAH have previously been reported in Taiwan^{1, 10, 11)}. Recently, there was an accident in Korea in which the hands, arms and legs of a worker were exposed to a newly developed TMAH-containing cleaner, and the worker died within a few hours. This study examines the details and the reason for this accidental death due to acute poisoning resulting from exposure to TMAH based on the autopsy report.

Case Presentation

The accident occurred when an employee of a surfactant production company (W) was conducting a field test of a pallet cleaner sample at a pallet rental company (L) (L company was renting a previously rented pallet that it had sorted and cleansed). The victim was a 39-year-old male researcher with 7 years work experience in the same industry.

At 10:00 a.m. on the day of the accident, Dec. 15, 2011, the victim went to company L with coworkers from company W (one fellow researcher and one driver) to deliver a pallet cleaner. He was to make a cleaning bath at the factory of company L and conduct a sample test by pouring the cleaner and

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Correspondence to: J. Park, 478 Munemi-ro, Bupyeong-gu, Incheon, 403-711, Republic of Korea (e-mail: jsunpark@chol.com)

Table 1. Components and contents of the pallet cleaner

Components	CAS No.	Contents (%)
Water	7732-18-5	49.5 (75.75)
Tetramethylammonium hydroxide (TMAH, 25% solution)	75-59-2	35 (8.75)
Monoethanolamine	141-43-5	5
Sodium nitrilotriacetate (NTA powder)	18662-53-8	0.5
Ethoxylated alcohol	84133-50-6	10.0

The actual contents of water and TMAH in the pallet cleaner are indicated in parentheses.

water (1:5) into the cleaning bath, soaking a pallet in the bath for 5 minutes and then taking it out. The composition of the cleaner developed by company W is shown in Table 1. The pallet cleaner contained a 35% content of 25% TMAH solution. The actual TMAH content in the pallet cleaner was 8.75%, and 75.75% of the cleaner was water.

At 10:50 a.m., after finishing preparatory work (Fig. 1), the victim loosened the stopper in the drum container slightly using a screwdriver to pour the cleaner from the drum container (180 l) into the temporary cleansing bath (set up by placing pallets on the floor to form a frame, with a “well” in the center for the bath), leaned the drum container to the side and removed the stopper completely near the bottom of the bath (Fig. 2). The cleaner quickly poured out of the drum and wet his work clothes in the area of both his hands/arms and legs. A witness stated that the victim was wearing safety shoes, cotton gloves and ordinary work clothes.

The victim continued with the work of filling the cleaning bath with cleaner and water for about 10 minutes while wearing the wet clothes and went to a washroom to rinse his clothes at 11:08 a.m. (about 30 m away from the work location). However, he returned to the work location after 2–3 minutes because he could not rinse the chemical substance off his clothes. An employee of company L told the victim the location of a shower room (2nd floor, 50 m away from the temporary cleaning area), and the victim went to the shower room at 11:15 a.m., asking the other researcher (female) to bring him some clothes. At 12:20 p.m., the other researcher (female) asked an employee of company L (male) to go into the shower room, and they went to the shower room together. They found the victim had fallen to the floor in front of the shower room (the door to the shower room was closed). They moved him to the next office, and the researcher performed cardiopulmonary resuscitation (CPR). He was sent to a hospital in an ambulance but was declared dead on arrival.

Fig. 1. Temporary bath set up for cleaning demonstration. **Fig. 2.** Reenactment of pallet cleaning demonstration.

The victim was unconscious when discovered. He had tidied up his work clothes and was wearing underwear and socks (there was no moisture on his body). A witness stated that it seemed that the victim had fallen down before taking a shower. A paramedic used an automatic external defibrillator, but the victim did not respond, indicating that he was already dead.

Autopsy Findings

The major findings and opinions in the autopsy report are as follows.

The victim was 179 cm in height, and had a normal physique. His jacket and pants were found to contain both TMAH and polyoxyethylene alkyl ether (ethoxylated alcohol), of which only TMAH can cause a skin burn in a short period of time. Some parts of the right upper arm and forearm, and the inside of the left forearm and hand had second-degree burns, and second-degree burns were also found on the left knee, the front calf and the front and inside of the

right thigh and knee. In total, the victim had burns on 12% of his skin. The back of the left forearm had two spots 0.8×0.3 cm in size where the skin was peeling. The right elbow had multiple areas of skin peeling with a maximum size of 2×1 cm. The right flank had skin peeling over an area of 7×1.5 cm, and the right thigh region had skin peeling over an area of 12×3 cm. The rear of the left knee had skin peeling over an area of 1.5×1 cm. A blister had formed in the epithelium of the burnt skin. The larynx and bronchus contained liquid foam, but it seems to have been caused by intubation. Edema, congestion and alveolar bleeding were found in the lungs, which weighed 668 and 610 g. However, this was not apparently related to the cause of death. The heart weighed 452 g and was heavy with fat and light arteriosclerosis, but this was not apparently related to the cause of death. It seems improbable that a heart attack was the cause of death, as the victim died immediately after being burned by TMAH. No specific points of damage were found in the brain, cranial cavity or stomach. The liver weight is 2,530 g with moderate hepatomegaly, but this was not related to the cause of death. No damage was found that was related to his death other than congestion in the spleen, intestine and kidney. There was no damage or disease that could have been related to his death other than that described above.

Generally, burns on 12% of the skin without any complications rarely cause death. However, TMAH blocks neurotransmission and depolarization at the neuromuscular joint, which can cause loss of respiratory and cardiac function in a short period of time. Thus, it was determined that the cause of death was TMAH poisoning.

Discussion

This poisoning case occurred when an employee of a cleaner manufacturer was carrying out a palette cleaning demonstration using a newly developed cleaner. The victim finished the work while wearing contaminated clothing, with liquid on his hands, feet and legs. TMAH is one of the main ingredients of the cleaner, but the employee did not utilize proper personal protective equipment for a strong base.

According to the autopsy report, there were second-degree burns on both arms and legs, and TMAH was detected in his work clothes. The report also states that although normally burns on 12% of the skin without any complications do not cause death, the material may have blocked nerve conduction from the nerve cells and blocked depolarization, which can cause respiratory and cardiac arrest in a short period of time. Other ingredients in the cleaner do not cause acute poisoning. Monoethanolamine may cause

skin irritation but does not cause acute poisoning¹²⁾. Ethoxylated alcohol is a material that irritates the skin and respiratory system, and sodium nitrilotriacetate is a corrosive alkali material^{13, 14)}. Therefore, it seems that these materials caused skin irritation and damage in addition to TMAH. However, these materials have not previously been reported as being involved with acute poisoning such as ganglion blockage and respiratory failure. Accordingly, the autopsy report concluded that the cause of death was acute TMAH poisoning.

Though there had been no cases of TMAH poisoning previously reported in Korea, there had been some cases of poisoning and death by skin exposure reported in the electronics industry in Taiwan^{1, 10, 11)}. In TMAH skin exposure cases reported to the Taiwan Poison Control Center (PCC-Taiwan), it was noted that the strong alkali TMAH caused chemical burning and respiratory failure by skin absorption¹⁾. Four out of 13 reported cases of TMAH skin exposure were exposed to 25% TMAH solution, and the remaining 9 were exposed to 2.38% TMAH solution. Three out of 4 exposed to the 25% TMAH solution died. The three victims had chemical burns on over 7% of the skin, and one survivor had chemical burns on 3% of the skin. When one is exposed to 2.38% TMAH solution, it does not lead to death. However, one of the reported cases had 1–2 level chemical burns on 28% of the body and experienced similar symptoms to those of cases that died from TMAH poisoning. Lin *et al.* reported that the ganglion toxicity effect of the skin-absorbed TMA ion plays an important role after chemical burning with strong alkali TMAH¹⁾.

Another study by Taiwanese researchers described a case of death from TMAH skin exposure in detail. Wu *et al.* reported a case in which a 22-year-old male engineer was doused with concentrated TMAH solution (25%, pH 13.5) while conducting a routine inspection of the pipe system in a plant manufacturing thin film transistor liquid crystal displays (TFT-LCDs)¹⁰⁾. He was wearing a clean room suit with plastic goggles, but no mask. He closed the shutoff valve while TMAH was spraying onto his head and took a shower at a nearby emergency shower facility immediately for decontamination. He subsequently lost consciousness 30 minutes after the accident and died shortly after arrival at a hospital. Leukocytosis, hyperglycemia and metabolic acidosis were checked, and 2nd degree burns on 24% of his body and 3rd degree burns on 5% of his body were found. The researchers considered TMAH skin absorption to be the most likely cause of death and reported that skin damage by TMAH facilitated skin absorption.

Another report by Lee *et al.* from Taiwan describes a case of two persons evacuated to an emergency unit

following TMAH exposure¹¹). Two males, 28 years old and 35 years old, were evacuated to an emergency unit after TMAH was spilled on their skin. When they arrived, no breathing or pulse was detected, and there were 2nd–3rd degree burns on 7% of their bodies. Both died during treatment despite emergency measures. Examinations showed respiratory acidosis, leukocytosis, hyperglycemia and abnormal liver enzymes. The researchers reported the cause of death as respiratory failure resulting from TMA.

The case of death by acute TMAH poisoning that occurred in Korea involved TMAH solution of a lower concentration than in Taiwan, 8.75% TMAH compared with 25% TMAH. There was a critical case with 2.38% TMAH exposure in Taiwan, but this involved burns on 28% of the skin, covering a wide area of the body. While cases in Taiwan occurred during checks of pipes supplying TMAH in the electronics industries such as semiconductor and LCD manufacturers, the case in Korea involved exposure during demonstration of a cleaner containing TMAH. The TMAH-containing cleaner was developed as a substitute for strong alkali materials with widely known harmful effects, such as sodium hydroxide, as TMAH is a strong alkali material used for developing liquids, etching liquids and cleaners in the electronics industry like the semiconductor industry^{2–6}) and has proven solubility to other materials but no occupational exposure criteria or legal obligations with regard to control.

This is the first report of a TMAH poisoning accident during pallet cleaning work with detailed autopsy findings. The autopsy opinions support the presumption of Taiwanese researchers that TMAH blocks ganglions, leading to respiratory failure. It seems that the employee finished the work without taking proper exposure countermeasures, as there was no immediate pain or apparent life-threatening symptom. However, the TMA ion in the TMAH-containing solution is a neurotoxin, causing respiratory failure in a very short time by ganglion blockage through skin absorption¹¹). Thus, first aid must be carried out immediately. As there is no antidote for TMAH yet, it is very helpful to wash with a sufficient amount of water in cases of skin contact, as TMAH is water-soluble.

The most frequent cause of an acute poisoning accident is careless handling of a chemical material. Though TMAH is not classified as a “Chemical requiring legal control” by the Occupational Safety and Health Regulations in Korea, the accident could have been prevented if the worker bore in mind the hazard of TMAH documented in the MSDS. In particular, every company that manufactures TMAH-containing cleaners must notify employees and users regarding the hazards of TMAH and provide instruc-

tions on its use. In the present case, the victim did not wear personal protective gear when handling the cleaner. In addition, he should have washed with a large volume of water immediately after skin exposure but was left unattended for 17 minutes. According to studies of Wu *et al.*, the chemical burn caused by hydroxide ion plays an essential role in the toxicity, and acute respiratory failure is involved in cases of death caused by TMA^{15, 16}). Therefore, TMAH should be neutralized rapidly in the event of exposure, and prompt respiratory support is required to prevent respiratory failure.

Accordingly, the authors advise employers to educate employees regarding the harmfulness of this material, to ensure that employees wear suitable personal protective equipment for a strong base material, to meticulously follow the standard working procedure and to cleanse exposure areas immediately a sufficient amount of water and provide prompt respiratory support in the event of an emergency.

In the present report, the authors described a case of poisoning by respiratory failure due to exposure of the skin to TMAH during work and examined the detailed autopsy findings. TMAH is a dangerous material causing neurotoxicity leading to respiratory failure by ganglion blockage through skin absorption, and no antidote has been developed yet. For this reason, it is best to completely prevent exposure by wearing proper personal protective equipment.

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