Review

Fire and explosion of dinitrosopentamethylenetetramine - a review

Takeshi Suzuki*†

*National Research Institute of Fire and Disaster

4-35-3, Jindaiji-Higashi-machi, Chofu-shi, Tokyo 182-8508, JAPAN

Phone: +81-422-44-8331

[†]Corresponding author: tsuzuki@fri.go.jp

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Abstract

Dinitrosopentamethylenetetramine, which was introduced in 1947, is a widely used chemical blowing agent in the rubber industry. One of important characteristics of dinitrosopentamethylenetetramine is that the decomposition proceeds by an exothermic reaction at relatively low temperature especially in contact with acidic materials. Dinitrosopentamethylenetetramine has been reported as being responsible for fire or explosion accidents. For example, a local newspaper in Dhaka in Bangladesh reported that a fire had occurred in a building in downtown and spread to neighboring buildings causing more than one hundred fatalities on 3 June dinitrosopentamethylenetetramine stored in the building had been one of the major causes of the spread of the fire. The thermal decomposition of dinitrosopentamethylenetetramine has been investigated for nearly half a century by a lot of researchers with many methods such as thermal analytical methods or sensitivity testing methods. The results of those investigations on decomposition, ignition, case histories of fire and explosion accidents, and safety measures are reviewed.

Keywords: dinitrosopentamethylenetetramine, blowing agent, explosion, fire, case history

1. Introduction

Blowing agents (or foaming agents) are materials which are used to create a foamed or cellular structure within a given polymer system. They do this by causing a gas to be generated at the appropriate time during polymer processing. Blowing agents may be divided into two principal categories according to their mode of gas generation: physical blowing agent and chemical blowing agent. Physical blowing agents generate gas by a physical change of state. They change from a liquid to a gas without changing their chemical identity during the foaming process. Chemical blowing agents generate gas by a chemical reaction. This chemical reaction is a thermal decomposition of chemical blowing agent in which one or more of the major products of decomposition is a noncondensable gas. Within the chemical blowing agent category, there are two main sub-types: organic and inorganic. The organic blowing agents are mainly based on hydrazine derivative, azo compound, and nitroso compound chemistry and decompose exothermically to produce nitrogen gas. The inorganic blowing agents are

mainly based on carbonate and bicarbonate chemistry and decompose endothermically to produce primarily carbon dioxide gas. Lasman¹⁾, Yamashita and Waki²⁾, Geelan³⁾, Mayama⁴⁾, and Kondo⁵⁾ have published excellent review articles describing the properties and the use of various blowing agents

Dinitrosopentamethylenetetramine has a long history of usage as organic chemical blowing agent since it was introduced in 1947¹⁾. It is a widely used blowing agent in the rubber industry. However it has been reported as being responsible for fire or explosion accidents. Figure 1 shows its chemical structure. It is a nitroso compound. And its chemical structure suggests that it is an energetic material. In order to prevent accidents, knowledge of its hazard is needed. Information on case histories of fire and explosion accidents, safety data, and safety measures was collected from open literatures and summarized in this review article. Information shown in this article will be helpful to manufacturers in the rubber industry as well as fire departments handling fire and explosion accidents related with dinitrosopentamethylenetetramine.

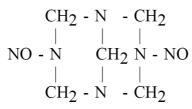


Figure 1 Chemical structure.

2. Case histories

Fire or explosion accidents are highly undesirable in any situation. Learning from case histories, i.e., accounts of fire or explosion accidents that have actually occurred, is very important for preventing accidents. Records of fire or explosion accidents were collected from open literatures. Dinitrosopentamethylenetetramine is obtained nitrosation involving the addition of an acid to hexamethylenetetramine and sodium nitrate in a reaction chamber in a manufacturing plant. After recrystallization, dinitrosopentamethylenetetramine is dried and milled into powder. The powder is stored in a container and transported. It may be blended with diluents to lessen fire hazard. After being transported to another plant, the container is opened. The powder is mixed with plastics or rubbers and heated for foaming. Cases 1 to 7 happened in drying process. Cases 8 to 10 happened in storing. Case 11 happened during transport. Cases 12 to 14 happened in handling. These fourteen cases show that fire or explosion accidents occurred at every process from manufacturing to handling.

Case 1

An accident occurred in rubber industry on 10 June 1954 in Aichi prefecture in Japan. Dinitrosopentamethylenetetramine was ignited in a drying room. The drying room was heated by steam pipes⁶.

Case 2

An accident occurred on 19 July 1954 in Osaka city in Japan. Baskets were stacked and heated from below using an electric heater for drying. Dinitrosopentamethylenetetramine in the basket was ignited⁶.

Case 3

An explosion occurred on 8 December 1954 in Kobe city in Japan. Dinitrosopentamethylenetetramine was ignited and exploded when it was heated for drying on heavy-oil-fired boiler⁶⁾.

Case 4

An accident occurred on 15 March 1955 in Kyoto prefecture in Japan. Dinitrosopentamethylenetetramine was ignited when it was heated for drying by hot gas⁶⁾.

Case 5

An accident occurred on 3 June 1955 in Osaka prefecture in Japan. Dinitrosopentamethylenetetramine was ignited by hot particles emitted from a smokestack when it was dried using sunlight⁶⁾.

Case 6

Dinitrosopentamethylenetetramine was heated for drying in the range of 50 to 70 °C. Spontaneous ignition occurred⁷⁾.

Case 7

A worker was taking shoes whose bottoms were contaminated with hydrochloric acid. The worker entered a room where dinitrosopentamethylenetetramine was heated for drying. Hydrochloric acid on the bottoms of the shoes reacted with dinitrosopentamethylenetetramine spilled on the floor. Ignition occurred⁷⁾.

Case 8

An accident occurred in a manufacturing plant on 21 November 1955 in Saitama prefecture in Japan. When the lid of a container was removed, dinitrosopentamethylenetetramine inside the container was ignited⁶⁾.

Case 9

A fork lift truck operating in a storage warehouse punctured a fibre drum containing a blowing agent. The blowing agent involved was a mixture of 40 % dinitrosopentamethylenetetramine and 60 % inert (fine silica). The stock in the storage warehouse consisted of a wide variety of raw materials used in rubber and plastic products manufacturing plant. The operator reported that a flame was seen when the drum was punctured. Sprinklers were activated and extinguished fire. Probable cause of ignition was friction heat when the fibre drum was penetrated by the fork of the truck⁸⁾.

Case 10

A fire occurred in a building in congested area of downtown in Dhaka in Bangladesh on 3 June 2010. It spread to neighboring buildings causing more than one hundred fatalities and more than two hundred people who received severe burn injuries. Dinitrosopentamethylenetetramine stored in the basement of the building was one of the major causes of the spread of the fire⁹⁾.

Case 11

At about 6 a.m. on 28 July 1979 at the fourth pier of Maya Wharf of the Kobe Harbour in Japan, a security guard heard big sound, saw a big flame (20 m in height), and called to the local fire department. Two containers at the fire origin were burnt. Several others were damaged. The burnt container stored 250 steel drums. The drums exploded and were blown into the surrounding area. Each drum contained 50 kg of Unicell-G (main component is dinitrosopentamethylenetetramine). The cause explosion was thought to be spontaneous ignition of dinitrosopentamethylenetetramine. Impurities lowered the decomposition temperature. Sunny and hot days continued and temperature inside the container was increased10).

Case 12

A fire occurred on 24 November 1955 in Osaka city in Japan. When dinitrosopentamethylenetetramine and raw rubber were mixed in a roll machine, the mixture was ignited. Probable cause of ignition was static electricity⁶.

Case 13

Dinitrosopentamethylenetetramine and rubber were mixed and kneaded in a roll machine. Friction heat generated on the roller ignited the mixture⁷⁾.

Case 14

Polyvinyl chloride was on a mixing roll which was heated by steam. Dinitrosopentamethylenetetramine was sprayed on polyvinyl chloride and kneaded.

Table 1 Properties.							
Molecular weight	Appearance		composition nperature	Gas evolved	Specific gravity	Heat of decomposition	Heat of combustion
186.2	Yellowish whit	e powder 210)℃	$240~\mathrm{ml}~\mathrm{g}^{-1}$	1.54	$2.86~{\rm kJ~g^{-1}}$	$19.6 \; {\rm kJ} \; {\rm g}^{-1}$
at $20 ^{\circ}\mathbb{C} [\mathrm{g}(100\mathrm{ml})^{-1}]$							
SADT	Solubility, g (1	00 ml) ⁻¹ at 20	$^{\circ}\mathbb{C}$				
(estimated)	Water	DMF	MEK	Acetone	Ethanol	Hydrochloric ac	cid (7%)
76 ℃	0.48	14.7	1.6	1.7	0.3	decompose	

DMF: N, N-dimethylformamide, MEK: methyl ethyl ketone.

Dinitrosopentamethylenetetramine which was not mixed with polyvinyl chloride was ignited¹¹⁾.

3. Safety data

Before conducting any work with energetic materials, all the safety data must be known. These data make it possible to evaluate both the various risks of fire or explosion accidents associated with handling and processing the material, and expected consequences of such fire or explosion accidents.

Basic properties are collected from reference 5 and are shown in Table 1. Dinitrosopentamethylenetetramine melts with decomposition at 200–210 °C. In decomposition essentially nitrogen and solid white residue are produced. Among the gaseous decomposition products, minor quantities of nitrous oxide, carbon dioxide, oxygen, water, formaldehyde have been identified. The decomposition reaction is highly exothermic. Dinitrosopentamethylenetetramine is readily soluble in N, N-dimethylformamide. It is virtually insoluble in water and alcohol. In dilute hydrochloric acid, hydrolysis occurs.

Dinitrosopentamethylenetetramine is sensitive to mineral acids or salt of these acids, which may cause a violent decomposition at low temperature. Organic acids, e.g., salicyclic or phthalic acids, substantially decrease the decomposition temperature. Organic bases such as urea also lower decomposition temperature. Ikuta and Nishimoto¹²⁾ heated substance in an oil-heated test tube and measured decomposition temperature as shown in Table 2. Wakazono and Ando⁷⁾ measured ignition temperature using open cup furnace. Ignition temperature of dinitrosopentamethylenetetramine was 152°C. Ignition temperatures of mixture with organic acids were measured as shown in Table 3. Also ignition temperatures of mixture with sodium nitrate were measured as shown in Table 4. Ignition temperature lowered when mixed with organic acids or salt. The effects of acids on the decomposition temperature of dinitrosopentamethylenetetramine are proportional to their dissociation constants¹²⁾. The higher the dissociation constant is, the lower the decomposition temperature is as shown in Table 5. As shown in Table 1

dinitrosopentamethylenetetramine decomposes near 200°C. However it decomposes at lower temperature in contact with acids, salts, or urea as shown in Tables 2 to 5.

A pressure differential scanning calorimeter (DSC) was used for the measurement of decomposition heats.

 Table 2
 Decomposition in air.

Dinitrosopenta- methylenetetramine		Salicylic acid	Phthalic acid	urea	Decomposition temperature	Note
1					206 [℃]	
1	0.1				157	***
1	0.5				156	***
1	1				72	***
1		0.1			72	*
1		0.5			69	*
1		1			68	*
1			0.1		68	*
1			0.5		68	*
1			1		58	*
1	0.1	0.1			76	*
1	0.5	0.1			79	*
1	1	0.1			134	***
1	0.1	0.5			71	*
1	0.5	0.5			79	*
1	1	0.5			80	***
1	0.1	1			69	*
1	0.5	1			72	*
1	1	1			75	***
1				1	120	**

^{***} decompose spontaneously

Table 3 Ignition temperature when mixed with organic acid.

Organic acid	Concentration [%]						
	1.0	2.0	4.0	6.0	8.0	10.0	
Salicylic acid	145	143	75	73	71	71	
Stearic acid	152	151	150	141	139	135	
Oxalic acid	63	63	57	56	55	51	
Phthalic anhydride	93.5	90	87	67	65	64	

Unit of temperature: °C.

Table 4 Ignition temperature when mixed with sodium nitrate.

Salt	Concentration [%]				
	0.1	0.25	0.5	1.0	5.0
Sodium nitrate	140	125	116	108	85

Unit of temperature: °C.

^{**} decompose semi-spontaneously

^{*} melt and decompose slowly

Table 5 Variation of decomposition temperature with dissociation constant.

Acid	Dissociation constant	Decomposition temperature [°C]
Oxalic acid	5.90×10 ⁻² 6.40×10 ⁻⁵	60-70
Salicylic acid	1.07×10^{-3} 4.0×10^{-14}	95-100
Phthalic acid	1.0×10 ⁻³ 5.4×10 ⁻⁶	100-115
Benzoic acid Boric acid	6.31×10^{-5} 6.53×10^{-10}	125-135 100-135

Nitrogen or air was introduced in the DSC cell at pressure up to 5.3 MPa^{13,14}. Dinitrosopentamethylenetetramine decomposed at relatively high temperature of about 200°C and reacted violently, releasing a large amount of heat. The decomposition heat and exothermic onset temperature are shown in Table 6. Once decomposition reaction starts, large amount of heat is released. Decomposition heat increased with pressure both in nitrogen and air. Exothermic onset temperature decreased with the increase in pressure. These results suggest that risks of fire or explosion vary with pressure. In using decomposition heat for risk analysis, pressure and temperature should be specified.

Electrically-heated vessel was used to decompose dinitrosopentamethylenetetramine in helium at pressures ranging from 0.1 to 10.1 MPa^{15),16)}. Evolved gas was analysed using GC-MS as shown in Table 7. Chemical composition of evolved gas varied with pressure. Variation of decomposition heat with pressure affected composition of evolved gas. It should be taken into consideration that combustible gases (methane, ethane, and ethylene) are formed in high pressure.

Adiabatic calorimeters maintain a sample in an adiabatic condition once an exothermic reaction is detected. Accelerating rate calorimeter (ARC)¹⁷⁾ and automatic pressure tracking adiabatic calorimeter (APTAC)^{18),19)} were used as shown in Table 8. Samples for APTAC were not pure dinitrosopentamethylenetetramine.

Table 7 Variation of composition of evolved gas with He gas

Pressure [MPa]					
0.1		5.1		10.1	
N ₂ +NO	95.4	N_2	67.3	N_2	57.9
CO_2	1.2	CH_4	10.8	CH_4	12.9
N_2O	1.8	CO_2	0.6	CO_2	1.2
H_2O	1.6	N_2O	3.8	N_2O	1.9
		C_2H_4	0.7	C_2H_4	0.6
		C_2H_6	0.9	C_2H_6	1.3
		H_2O	8.4	H_2O	21.0
		others	7.5	others	3.2

Unit: mol%.

Dinitrosopentamethylenetetramine with 85-90% aluminum oxide were selected since rate of heat release of pure one was too high to control. As shown in Table 6 decomposition heat is large and moreover as shown in Table 8 rate of heat release is also large. This should be taken into consideration when it is handled in a confined chamber or stored in a confined area.

Testing methods for explosives have been used to evaluate explosibility and stability of dinitrosopentamethylenetetramine by Wakazono and Ando⁷⁾. Table 9 shows results of fall hammer test. Table 10 shows results of Yamada's friction sensitivity test. Table 11 shows results of ballistic mortar test. For comparison results of trinitrotoluene (TNT) or gelignite (Sakura dynamite) were attached. Velocity of detonation of dinitrosopentamethylenetetramine measured by Dautriche methods was 1410 m s⁻¹. That of TNT was 6700 m s⁻¹. That of gelignite (Sakura dynamite) was 4000 m s⁻¹. As shown in Tables 9 and 10, sensitivity of dinitrosopentamethylenetetramine was low compared with TNT or Sakura dynamite. As shown in Table 11, dinitrosopentamethylenetetramine is weak compared with TNT. Also velocity of detonation of dinitrosopentamethylenetetramine is small compared with TNT or Sakura dynamite. However dinitrosopentamethylenetetramine can be detonated and its power is not Wakazono Ando⁷⁾ negligible. and wrote dinitrosopentamethylenetetramine should be handled in a manner similar to low explosives. This should be kept in

Table 6 Decomposition heat and exothermic onset temperature.

Decomposition heat [kJ g ⁻¹]			Exothermic onset temperature [°C]				
in N ₂		in air		in N_2		in air	
5.3 MPa	0.1 MPa	5.3 MPa	0.1 MPa	5.3 MPa	0.1 MPa	5.3 MPa	0.1 MPa
3.27	2.23	4.34	2.06	163	171	144	166

 Table 8
 Results of adiabatic calorimetry.

Calorimeter	Onset temperature [°C]	Heat of reaction [kJ g ⁻¹]	Maximum rate of heat release [K min ⁻¹]	Maximum rate of pressure rise	Maximum pressure
ARC			379	62 MPa min ⁻¹	17.3 MPa
APTAC	145	3.20	17	44 kPa min ⁻¹	657 kPa

Table 9 Fall hammer test.

Sample	Height [cm]	Reaction/Tests	Note
Dinitrosopenta-	10	0/10	
methylenetetramine	12	0/10	
	15	2/10	decomposed
	20	4/10	decomposed
	30	7/10	decomposed
	40	9/10	decomposed
	50	10/10	decomposed
TNT	110	10/10	detonated
Gelignite	55	10/10	detonated
(Sakura dynamite)			

Table10 Yamada's friction sensitivity test.

Sample	Load [kg cm ⁻²]	Explosion
Dinitrosopenta- methylenetetramine	296 591 739	no explosion no explosion no explosion
TNT	100	complete explosion
Gelignite (Sakura dynamite)	80	complete explosion

Table11 Ballistic mortar test.

Sample	Detonator	Pendulum deflection θ	Energy [kg m]	Relative value
Dinitrosopenta -methylenetetramine	No.8	4° 30' 4° 50' 9° 00'	112 129 449	18 18 46
TNT	No.8 No.6 No.8 No.8	8° 35' 12° 35' 13° 15' 13° 15' 13° 10'	408 876 971 971 959	100 100 104 104

mind.

Yoshida²⁰⁾ and Yoshida et al.²¹⁾ compiled data of reactive chemicals. Results obtained by test methods for explosives are collected from references 20 and 21 and tabulated in Tables 12 to 15. Compositions of samples shown in Tables 12 to 15 are as follows;

- A: Dinitrosopentamethylenetetramine (pure)
- B: Dinitrosopentamethylenetetramine with 10 %MgO
- C: Dinitrosopentamethylenetetramine with 15 %CaCO₃ and 10 % aliphatic hydrocarbon
- D: Dinitrosopentamethylenetetramine with 15 %CaCO₃ and 10 % oil
- E : Dinitrosopentamethylenetetramine with 15 $\% CaCO_3$ and 10 % mineral oil
- F: Dinitrosopentamethylenetetramine with 25 %CaCO $_3$ and 10 % oil
- G: Dinitrosopentamethylenetetramine with 17-20 %

Table12 Results of BAM 50/60 tube test.

Sample	Results
A	Detonation (velocity= $3700 \mathrm{m\ s^{-1}}$)
	tube fragmented (stripes)
В	Detonation (velocity= $3040 \mathrm{m\ s^{-1}}$)
	tube fragmented (stripes)
С	Partial explosion
	24 cm of 50 cm-tube and some substance
	remained.
G	Detonation
	tube fragmented (strips and splinters)
M	Deflagration
	substance completely reacted
	tube tore up 17 cm from upper end and 3 cm from
	the bottom

Table13 Results of Trauzl test.

Sample	Results	
A	147 ml/10 g	
В	$26\mathrm{ml}/10\mathrm{g}$	
G	$7\mathrm{ml}/10\mathrm{g}$	
K	$9\mathrm{ml}/10\mathrm{g}$	
	$78\mathrm{ml}/10\mathrm{g}$ (3caps)	
M	29ml/10g	

Table14 Results of red glowing steel dish test.

Sample	Results	
A	Burns off within 18 s with high flame	
В	Immediate ignition; burns off within 5 s with	
	high flames	
F	Ignition after 5 s; burns quietly for further 23 s	
I	Ignition after 1 s; burns out within further 8 s;	
	height of flame 60 cm	
J	Burns off within 15 s	
L	Immediate ignition; burns fiercely within 6 s	

inert inorganic solid and 3-5 % mineral oil

- H: Dinitrosopentamethylenetetramine with 20 % inert solid and 5 % mineral oil
- I: Dinitrosopentamethylenetetramine with 20 % inert solid and 5 % oil
- J: Dinitrosopentamethylenetetramine with 10 % oil
- K: Dinitrosopentamethylenetetramine with 10 % mineral oil
- L: Dinitrosopentamethylenetetramine with 30 % oil
- M: Dinitrosopentamethylenetetramine with 30 % mineral oil
- N: Dinitrosopentamethylenetetramine with 20 % urea.

Table 12 shows results of BAM 50/60 tube test. Samples of high concentration can be detonated. Also velocities of detonation are not low. Table 13 shows results of Trauzl test. Sample A (pure dinitrosopentamethylenetetramine) which detonated gave high value. However samples B (dinitrosopentamethylenetetramine with 10 %MgO) and G (Dinitrosopentamethylenetetramine with 17–20 % inert inorganic solid and 3–5 % mineral oil) which detonated

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Lable 15	Overview	of safety	measures.

	Prevention	Mitigation
Manufacturing	Avoid formation of unstable by-products. Avoid impurities which lower thermal stability. Control temperature in drying. Control dust in milling. Cool before storing.	
Storing	Keep away from sparks, humidity, heat or acids. Clean.	Store in sprinklered area. Isolate from other storage. Do not store too much.
Transporting	Keep away from sparks, heat or acids.	
By sea	Keep away from acids or alkalis.	Prepare detector tubes.
Handling	Have knowledge. Control temperature in mixing. Avoid impurities.	

gave low value. It should be taken into consideration that samples which give low value in Trauzl test can be detonated.

Table 14 shows results of red glowing steel dish test. All samples began burning. Samples A (pure dinitrosopentamethylenetetramine) and B (dinitrosopentamethylenetetramine with 10 %MgO) which detonated showed burning with high flames. It is suggested that dinitrosopentamethylenetetramine do not undergo detonation when it is burning in an open environment.

TNO deflagration test was carried out for dinitrosopentamethylenetetramine with 40 % urea and 10 % oil^{20), 21)}. Rate of spread for vertical tube was 1.25 mm s⁻¹. That for horizontal tube was 2.2 mm s⁻¹. Decomposition occurred being accompanied by the release of combustible gases. These results show that deflagration can proceed even if the concentration of dinitrosopentamethylenetetramine is as low as 50 %. One or two mm s⁻¹ is not low as rate of spread. If detection of ignition is delayed, large volume may burn before detection. And it may make fire-fighting activities difficult.

BAM heat accumulation storage test was carried out^{20), 21)}. Sample (dinitrosopentamethylenetetramine with 30 % mineral oil) exploded at 60 °C and oven was destroyed. At 50 °C decomposition did not occur for 9 days. Results of BAM heat accumulation tests show that spontaneous ignition may occur when a large amount of dinitrosopentamethylenetetramine is stored in a warm environment. It decomposes at lower temperature in contact with acids, salts, or urea as shown in Tables 2 to 5. Thus, being mixed with them may accelerate spontaneous ignition.

As depicted in this section, combustion behaviour varies with compositions. It is shown that combustion behaviour can be controlled by changing compositions. Also it is suggested mistakes in mixing dinitrosopentamethylenetetramine with additives may lead to fire or explosion accidents.

4. Safety measures

Safety measures in manufacturing, storing, transporting, or handling dinitrosopentamethylenetetramine were collected from articles.

Lasman¹⁾ described safety measures in manufacturing.

1) Dinitrosopentamethylenetetramine can be obtained by nitrosation involving the addition of an acid to hexamethylenetetramine and sodium nitrate. Either organic acids or mineral acids may be used. An excess of nitrous acids leads to the formation of trimethylene trinitrosoamine as by-product. Because of the instability of dinitrosopentamethylenetetramine in acidic medium, the nitrosation should be carried out with theoretical quantity of acid. A more stable product may be obtained by neutralizing any excess of acid with alkaline materials.

Wakazono and Ando⁷⁾described following measures to prevent dinitrosopentamethylenetetramine from fire or explosion accidents.

- 1) Handle in a manner similar to low explosives. Impurities lower its thermal stability. Low thermal stability may lead to spontaneous ignition. Spontaneous ignition causes deflagration. Its power is similar to low explosives.
- 2) Workers who are familiar with its properties should bandle
- 3) Keep away from heat, open flame, or contact with acids in transport or storing.
- 4) Control environmental humidity and temperature in storing. Avoid exposing to sunlight in storing.
- 5) In mixing by a roll mill machine in rubber industry, be cautious in heat transmitted from the roll.
- 6) Wash the product fully.
- 7) In drying process, keep the dryer temperature below 50 °C.

Safety measures for storing in warehouses were described by Manufacturing Chemists Association⁸⁾.

- 1) Store in sprinklered area cutting off from other storage.
- 2) Store in rows not over two pallets high and three pallets long.
- 3) Keep away from steam pipes or other heat sources.

- 4) Leave four feet aisles between pallet rows.
- 5) A high degree of cleanliness is needed in warehouse and operating area.
- 6) Never open drums in the storage area.
- 7) Limit amount on hand in operating area to one day's supply.

Safety measures for manufacturing, storing transporting, and handling are described in reference 22.

- 1) Workers who are familiar with the properties should handle
- 2) In manufacturing process following cautions should be taken.
 - 2-1) Always keep the reaction chamber clean.
 - 2-2) Wash the product fully after nitrosation process.
 - 2-3) Acidic grease should be avoided for bearings of the mixer.
 - 2-4) Temperature in the dryer should be less than 50°C. Take the risk of impurities (such as acids) into consideration.
 - 2-5) Avoid contaminants (such as metals) in powdering process.
 - 2-6) Prevent fine particles from dispersing in powdering process.
 - 2-7) Explosion-proof electrical apparatus should be used.
 - 2-8) Dinitrosopentamethylenetetramine should be cooled before pouring into a bag for storing.
- 3) Avoid strictly sparks or acidic substances in storing or transporting.
- 4) Control humidity and temperature in transporting.
- 5) Control the surface temperature of the roll in mixing process.

Safety measures for transport by sea are described in reference 23.

- 1) In storing on deck, keep more than 6 m away from acids or alkalis.
- 2) In storing under deck, keep in different hold from that storing acids or alkalis.
- 3) In decomposing by heating, formaldehyde, ammonia, nitrogen gas are formed. One can find the start of decomposition by using detector tubes for formaldehyde.

An overview of safety measures is given in Table 15. They can be divided into two groups, namely measures for preventing fire and explosion accidents and measures for their mitigation. Safety measures shown may be common to those in explosive industries. One should keep in mind that it should be handled in a manner similar to low explosives as shown in reference 7. Most of safety measures are drawn from articles published in 1960's to 1970's. Some of readers may find them outdated. However the author believes that they are worth noting.

5. Conclusions

Dinitrosopentamethylenetetramine has been reported

as being responsible for fire or explosion accidents. In order to prevent accidents knowledge of its hazard is needed. Information on case histories of fire and explosion accidents, safety data, and safety measures was surveyed from open literatures. The author hopes that this information will prove helpful.

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ジニトロソペンタメチレンテトラミンの 火災および爆発について

鈴木健**

ジニトロソペンタメチレンテトラミンは広く使われている化学発泡剤である。その特徴の一つは、比較的低い温度で発熱分解反応を起こすことである。ジニトロソペンタメチレンテトラミンはこれまで何回も火災の原因となってきた。例えば、ダッカ市(バングラデシュの首都)の地元新聞によると、2010年6月にダッカ市内の建物で火災が発生した。延焼した結果、100人以上が死亡した。被害が拡大した原因の一つとして、建物に保管されていたジニトロソペンタメチレンテトラミンがあげられている。ジニトロソペンタメチレンテトラミンの反応性については、半世紀近くの間、様々な方法で調べられてきた。ジニトロソペンタメチレンテトラミンの分解、着火、事故事例、安全対策について、過去の公開文献から調査し、まとめた。ジニトロソペンタメチレンテトラミンに関わる災害の防止に役立つことを期待するものである。

*消防研究センター 〒182-8508 東京都調布市深大寺東町4-35-3

Phone: 0422-44-8331

†Corresponding author: tsuzuki@fri.go.jp