BLOWING AGENTS

Table of Contents

Page

List of Tables

1.0 SCOPE

This document provides guidance on the storage and handling of physical and chemical blowing agents. Blowing agents are used to create foam plastic products.

Properties and hazards of several commercial chemical blowing agents are provided.

Processes which mix chemical blowing agents with oxidizers present severe explosion potentials and are excluded from this data sheet.

1.1 Changes

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Introduction

2.1.1 Appropriate FM standards should be followed for the storage and handling of ignitable physical blowing agents.

2.2 Construction and Location

2.2.1 All buildings containing Group A or B chemical blowing agents and ignitable physical blowing agents should be of damage limiting construction.

2.2.2 Storage quantities of chemical blowing agents should be limited in accordance with Table 1. Group A and B blowing agents should be stored in cut-off rooms or detached buildings. Group C agents may be stored with other materials of low combustibility.

Table 1. Maximum Recommended Quantities of Chemical Blowing Agents.

Group	*Process Areas*	*Storage in Cut-off or Attached Areas*	*Storage in Detached Areas*	*Recommended Storage Arrangement*	
				Drums	*Cartons*
A	Shift supply	2000 lb (900 kg)	100,000 lb (45,000 kg)	Piles one high and two pallets* wide with 6 ft (2m) between piles; 9-ft (3m) cross aisles every 30 ft (10m).	Piles one high and two pallets* wide with 6 ft (2m) between piles; 12-ft (4m) cross aisles every 30 ft (10 m).
B	One day supply	50,000 lb (22,500 kg)	1,000,000 lb (450,000 kg)	Piles two high and two pallets* wide with 3 ft (l m) between piles; 9-ft (3m) cross aisles every 30 ft (10 m).	Piles two high and two pallets* wide with 3 ft (l m) between piles; 12-ft (4m) cross aisles every 30 ft (10 m)
C	One day supply	Unlimited. Taking into consideration values and exposure from and to adjoining storages and occupancies.			

*Pallets assumed to be 4 ft × 4 ft(1.2 m × 1.2 m)

2.2.3 Provide explosion vents on closed equipment containing Group A or B blowing agents. Of particular concern is equipment where the agent is either heated (ovens or dryers) or agitated thereby producing static electricity (e.g., blenders). A minimum vent ratio of 1 square foot venting per 15 cubic foot of volume is recommended.

2.3 Protection

2.3.1 Where ignitable physical blowing agents are used. Exhaust ventilation for equipment and buildings should be designed to prevent explosive vapor-air mixtures from forming. Where it is not possible to prevent equipment from operating within the explosive range, such equipment should be of damage-limiting construction or be protected by an approved explosion protection system.

2.3.2 Where chemical blowing agents are used, automatic sprinkler protection and hose stream requirements should be provided in accordance with Table 2 for the following areas:

1. Blowing agent manufacturing and storage areas.

2. Plastic process areas where the storage of blowing agents exceeds the recommended quantities for process areas in Table 1.

Table 2. Sprinkler and Hose Stream Requirements for Blowing Agents

	STORAGE AREAS AND MANUFACTURING AREAS WITH ADJACENT STORAGE[1]			*MANUFACTURING AREAS WITHOUT ADJACENT STORAGE*		
Group	*Type of System*	*Density*	*Temp. Rating of Sprinkler*	*Area*	*Density*	*Temp. Rating of Sprinkler*
A	Deluge	0.40 gpm/sq ft (16 mm/min)		Wet 3000 sq ft (280 sq m)	0.30 gpm/sq ft (12 mm/min)	155-165°F (71-75°C)
	Wet	0.40 gpm/sq ft (16 mm/min)	155-165°F (71-75°C)	Dry 5000 sq ft (465 sq m)	0.30 gpm/sq ft (12 mm/min)	155-165°F (71-75°C)
B	Deluge	0.30 gpm/sq ft (12 mm/min)		Wet 2000 sq ft (185 sq m)	0.20 gpm/sq ft (8 mm/min)	155-165°F (71-75°C)
	Wet	0.30 gpm/sq ft (12 mm/min)	165°F (75°C)	Dry 3000 sq ft (280 sq m)	0.20 gpm/sq ft (8 mm/min)	155-165°F (71-75°C)
C	Wet 2000 sq ft (185 sq m)	0.20 gpm/sq ft (8 mm/min)	165°F (75°C)	Wet 1500 sq ft (140 sq m)	0.15 gpm/sq ft (6 mm/min)	155-165°F (71-75°C)
	Dry 3000 sq ft (280 sq m)	0.20 gpm/sq ft (8 mm/min)	165°F (75°C)	Dry 2000 sq ft (185 sq m)	0.15 gpm/sq ft (6 mm/min)	155-165°F (71-75°C)
Hose Stream Demand	Group	Demand	Duration (min)	Group	Demand	Duration (min)
	Groups A & B	750 gpm (2840 dm^3)	120	Groups A & B	500 gpm (1900 dm^3)	60
	Group C	250 gpm (950 dm^3)	60	Group C	250 gpm (950 dm^3)	60

[1] All of the sprinklers over storage areas and manufacturing areas having adjacent storage of Group A and B blowing agents are expected to operate. Water supplies should be capable of providing the recommended densities over the entire area.

2.3.3 For plastics processing areas where the storage of chemical blowing agents is in accordance with Table 1, Automatic sprinkler protection and hose stream requirements should be provided in accordance with Data Sheet 3-26, *Fire Protection Water Demand for Nonstorage Sprinklered Properties*.

2.3.4 Sprinkler protection should be provided in ovens, dryers, ducts, and dust handling equipment where Group A or B chemical blowing agents are used or manufactured.

2.4 Contingency Planning

2.4.1 Manual firefighting of a chemical blowing agent fire can be extremely difficult and dangerous. Firefighting in storage buildings should be left to automatic sprinkler protection. An efficient plant emergency organization is necessary to assure that valves are left open until the fire and subsequent decomposition reactions have subsided. Preplanning with the local fire department is particularly important.

2.5 Ignition Source Control

2.5.1 Electrical equipment in manufacturing areas handling chemical blowing agents should be suitable for Class II locations. Where ignitable physical blowing agents are used, the equipment should be suitable for Class I location. (See Data Sheet 5-1, *Electrical Equipment in Hazardous Locations*).

2.5.2 All equipment used to handle, mix or transport Group A or B chemical blowing agents or ignitable physical blowing agents should be electrostatically bonded and grounded.

2.5.3 Storage and process areas containing blowing agents should be free of ignition sources such as open flames, smoking, spark producing tools, etc.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Hazards of Blowing Agents

3.1.1 Physical Blowing Agents

Physical blowing agents include:

1. Ignitable liquids and gases such as pentanes, benzene, alcohols, ketones, etc.

2. Nonignitable liquids and gases such as carbon dioxide, nitrogen and halogenated hydrocarbons (trichlorofluoromethane [R-11] and 1, 1, 2-trichlorotrifluoroethane [R-113]).

3. Mixtures of halogenated hydrocarbons and ignitable liquids or gases.

The most important polymers manufactured with physical blowing agents are polystyrene foam which is manufactured using a pentane or a pentane/halogenated hydrocarbon mixture; and polyurethane foam, which is often manufactured using a halogenated hydrocarbon to increase the expansion.

3.1.2 Hazards pf Physical Blowing Agents

The hazards of physical blowing agents are those of ignitable liquids or gases. Without adequate ventilation, ignitable agents may produce explosive vapor-air mixtures in equipment and buildings during plastic manufacturing and subsequent curing operations. If special mixtures of ignitable and nonignitable materials are used (such as isopentane and trichlorofluoromethane), the hazard will be determined by the flammability of the mixture. Because of the potentially large number of such mixtures, it is not possible to indicate the relative hazards of these materials. Where doubt exists as to the flammability of the mixture, tests should be conducted to determine the hazard.

3.1.3 Chemical Blowing Agents

Chemical blowing agents are generally fine powders which are easily dispersed or are readily soluble in a polymer. These agents decompose exothermically when heated, liberating noncondensable gaseous products, usually leaving a solid noncombustible residue which is compatible with the polymer. Generally, nitrogen is the principal gaseous product of decomposition, but additional gases, such as carbon monoxide, carbon dioxide, and hydrogen are usually present in various percentages. The high percentage of nitrogen relative to the ignitable components will generally inhibit flame propagation in the gaseous products.

Chemical blowing agents include a variety of chemicals such as carbonates and bicarbonates, nitrites, hydrides, peroxides (hydrogen peroxide is used for foaming latex rubber; see Data Sheet 7-91, *Hydrogen*), and oxalic acid derivatives. The most common are derivatives of nitrogen-containing materials such as aliphatic azo compounds, hydrazides, N-nitroso compounds, etc. In particular, five blowing agents are widely used by industry. Their properties are described below and summarized in Table 4.:

1.*2,2'-Azobis (isobutyronitrile).* This compound was the first commercially important chemical blowing agent. It is a fine crystalline powder which is soluble in various elastomers, vinyl monomers, and conventional solvents; it is insoluble in water.

Storage stability tests indicate that at 75°F (24°C), it decomposes at a rate of 0.6 percent by weight per month. With each 10°F (5°C) rise in temperature, the decomposition rate approximately doubles. At 195°F (90°C) it decomposes at a rate of 33 percent per hour. The principal decomposition reaction is: $(CH_3)_2C(CN)N = NC(CN)(CH_3)_2 \rightarrow N_2 + (CH_3)_2C(CN) + (CH_3)_2CN - CN - (CH_3)_2$. The primary products of decomposition are 0.136 cu m of nitrogen per kg of compound and an extremely toxic residue, tetramethylsuccinonitrile.

Because of the toxicity of the residue, this compound has largely been replaced by other materials as a blowing agent. It is still used as a polymerization initiator for common vinyl monomers.

2. *Dinitrosopentamethylenetetramine (DNPT).* This compound is a fine powder with a decomposition temperature of 355°F (180°C). Storage stability of DNPT is excellent. It is not as toxic as 2, 2' - azobis (isobutyronitrile). It is commercially available in 40-42, 80 and 100 percent concentrations. The remaining materials generally consist of inorganic diluents (ground silica or clay), processing aids, and stabilizers. Its greatest usage is in the rubber industry. It is occasionally used in plastics manufacture.

The decomposition reaction is highly exothermic. The 42 percent material releases approximately 0.105 cu m/kg of noncondensable gases. The gases primarily consist of nitrogen (90-96 percent) along with minor quantities of nitrous oxide, ammonia, carbon dioxide, oxygen, water, and formaldehyde. Because of the high decomposition temperature and the highly exothermic decomposition reaction, DNPT is generally used with activators to lower the reaction temperature. Table 3 lists some of these activators and their effect on lowering decomposition temperature.

Table 3. Decomposition Temperatures of DNPT With Various Additives.

Activator	*Decomposition Temp.*	
None	355 - 375°F	(180-190°C)
Glycols	280 - 290°F	(138-143°C)
Urea	250 - 270°F	(121-132°C)
Water	220 - 250°F	(105-121°C)
Organic Acids	160 - 180°F	(71 - 82°C)

3. *N, N'-dimethyl-N, N' - dinitrosoterephthalamide (NTA)*. NTA is most widely used in manufacture of poly (vinylchloride) plastics, with additional applications in the manufacture of polyurethane elastomers and silicone rubbers. The pure compound is a crystalline solid which decomposes at 345°F (118°C), releasing 0.180 cu m/kg of nitrogen with traces of water vapor and carbon dioxide. The residue is a crystalline solid primarily composed of dimethyl terephthalate. Both NTA and its decomposition products exhibit low toxicity.

The most widely used commercial product is a blend with 70 percent active agent and a mineral oil diluent. The presence of mineral oil lowers the decomposition temperature to 220°F (105°C) and reduces the gas yield to 0.126 cu m/kg. Prolonged heating at temperatures between 175-190°F (80-90°C) results in a rapid sustained decomposition. At ambient temperatures, storage stability is excellent, and the agent has an indefinite shelf life.

4. *p,p'-Oxybis (benzenesulfonylhydrazide) (OBSH)* OBSH is one of the most widely used chemical blowing agents. It is used with all types of elastomers and plastics including polyethylene, poly (vinylchloride) plastisols and phenolic and epoxy resins. Its primary usage is in the manufacture of thermal insulation materials made from synthetic rubbers and thermoplastics (e.g., nitrile-butadiene rubbers, poly (vinylchloride)) in which OBSH acts as both a blowing agent and a cross linking agent.

OBSH is a crystalline oil-treated powder. Decomposition begins at 235°F (118°C) and progresses rapidly at 300-320°F (150-160°C). When OBSH decomposes, it releases 0.125 cu m/kg of noncondensable gases, of which 98 percent is nitrogen. Other decomposition products include water, disulfoxides, thiosulfoxides, and

a solid dark grey polymeric residue. Both OBSH and its decomposition products exhibit low toxicity.

5. *1, 1' -Azobisformamide (also Azodicarbonamide) (ABFA).* This compound is widely used for expanding synthetic and natural rubbers, poly (vinylchloride), highimpact polystyrene and polyolefin resins. It is a crystalline powder having a decomposition temperature of 383° F (195°C). It yields 0.220 cu m/kg of noncondensable gas, the highest of the five most common blowing agents. The gaseous products of decomposition comprise 32 weight percent of the agent and contain 65 percent nitrogen, 32 percent carbon monoxide, and 3 percent carbon dioxide. The residue is primarily hydrazobisformamide (biurea), cyanuric acid, urazole, and oxamide. The decomposition of ABFA is exothermic. Because of the high decomposition temperature, activators are often used in the expansion process. Typical activators are urea, certain organic acids, basic metal salts (lead, cadmium or zinc), polyols, etc. Storage stability is excellent.

Because of its low toxicity, ABFA mixed with starch and potassium bromate has been used as an accelerator for flour bleaching and maturing. The mixing of such a powerful oxidizer with combustibles presents a serious explosion hazard in manufacturing processes and in storage and at least one serious explosion has occurred.

3.1.4 Hazards of Chemical Blowing Agents

Chemical blowing agents vary in their fire and explosion characteristics. Most are highly combustible solids. All are capable of exothermic decomposition reactions which could result in containers or drums filled with an agent violently rupturing, propelling large quantities of fumes and particles into the air. With ignitable blowing agents, such an incident would result in the formation of a large fireball. With the exception of azobisformamide, these compounds are capable of dust explosion pressure development comparable to most agricultural dusts. The dense fumes produced during the decomposition would obscure a fire and make manual fire fighting extremely difficult. In addition, the decomposition gases contain nearly 100 percent inert or toxic gases (nitrogen, carbon dioxide, carbon monoxide, etc.) which could induce unconsciousness if inhaled in high enough concentrations.

Chemical blowing agents are grouped into the following three categories:

GROUP A: Highly combustible solids which decompose exothermically accompanied by spontaneous ignition in air. They present a serious dust explosion hazard. The products of decomposition may include flammable gases.

GROUP B: Highly combustible solids which decompose exothermically without spontaneous ignition. They present a serious dust explosion hazard. The products of decomposition may include flammable gases.

GROUP C: Noncombustible solids which may undergo an exothermic decomposition reaction. They do not present a dust explosion hazard. The products of decomposition may include flammable gases.

Table 4 lists the known hazardous properties of the five most common chemical blowing agents with the respective grouping. In addition to these agents, there are other chemical blowing agents available (see Table 5) on which test data is limited. In many cases, however, these compounds have chemical properties similar to one of the five most common agents. The indicated hazard group has not been substantiated by test data and should be used with judgment.

Table 4. Hazardous Properties of Major Commercial Chemical Blowing Agents.

Property	*2,2' Azobis (isobutyronitrile)*	*Dinitrosopentamethylene tetramine*	*N,N' — Dimethyl—N,N' dinitrosoterephthalamide*	*p,p' — Oxybis (benzenesulfonylhydrazide)*	*1.1'— Azobisformamide*
Combustibility *— of Agent* *— of Gaseous Decomposition Products* *—of Residue*	Highly combustible No No	Highly combustible. Barely ignitable No	Highly combustible No No	Highly combustible No No	Noncombustible Supports flame No
Decomposition Temp	120°F (49°C)	326°F (210°C)	195°F (commercial prod.) (90°C)	245°F (118°C)	383°F (195°C)
Dust Explosion Hazard **— Sealed** **— Vented 1:180** **— " 1:100** **— " 1:65** **— " 1:35**	Severe. See other properties. — — — —	Severe 89 psi (6.2 kg/sq cm) 54 " (3.9 kg/sq cm) 37 " (2.6 kg/sq cm) 29 " (2.0 kg/sq cm) 13 " (0.9 kg/sq cm)	Severe — — — — —	Severe 90 psi (6.3 kg/sq cm) 65 psi (4.5 kg/sq cm) — 48 psi (3.3 kg/sq cm) 40 psi (2.8 kg/sq cm)	None 0 psi (0 kg/sq cm) — — — —
Ignition Energy (Spark)	50 mj	—	—	66 mj	None
Shock Sensitivity (Drop Weight Test)	No. Decomposes	No. Decomposes and Ignites	No. Decomposes and ignites	No. May decompose	No
Toxicity information **— of Agent** **— of Gaseous Decomposition Products** **— of Residue**	— Low Tetramethyl-succinonitrile	— Oxides of Nitrogen —	— Low—	— Low —	Low Carbon monoxide present Low
Other Properties	Lower explosive limit: 0.02 oz/ft 3(.02 g/1) Rate of pressure rise: 10,280 psi/sec (720 kg/cm^2/sec)	Oxidizing material easily ignited by sparks, friction and static. Spontaneously ignites at temperatures in excess of 390°F (200°C)	Decomposes violently in air above 200°F (93°C).	Heat of combustion: 9000 Btu/lb (5000 cal/g) Heat of decomposition: 1800 Btu/lb) (1000 cal/g)	Mixed with starth and potassium bromate for bleaching flour;presents severe explosion hazard.
Group	B	A	A	B	C

Table 5. Probable Hazard Ratings of Various Chemical Blowing Agents.

Compound	*Group*
Urea Oxalate	C
Urea - Biuret Mixture	C
N - Nitrourea	See Note
Diazoaminobenzene	B
1, 1' - Azobiscyclohexanecarbonitrile	B
Barium Azodicarboxylate	C
Benzenesulfonyl Hydrazide	B
1,3-Benzenedisulfonyl dihydrazide	B
3, 3'-Sulfonylbis (benzenesulfonylhydrazide)	B
p, p' -Diphenyldisulfonyl hydrazide	B
p-Toluene sulfonyl semi-carbazide	B

Note: N-Nitrourea has been described as being highly sensitive to shock and capable of detonating when heated. This material should be stored and handled as a Class I organic peroxide.

4.0 REFERENCES

There are no NFPA standards covering the storage and handling of blowing agents.

Data Sheet 3-26, *Fire Protection Water Demand for Nonstorage Sprinklered Properties*.

Data Sheet 5-1, *Electrical Equipment in Hazardous Locations*.

Data Sheet 7-91, *Hydrogen*.

APPENDIX A — GLOSSARY OF TERMS

Blowing agents: Substances used to produce pores or cells in polymeric compounds.

Chemical blowing agents: Decompose when they are mixed with the polymer and heated to liberate noncondensable gases, thus expanding the polymer.

Ignitable Liquid: Any liquid or liquid mixture that is capable of fueling a fire, including flammable liquids, combustible liquids, inflammable liquids, or any other reference to a liquid that will burn. An ignitable liquid must have a fire point.

Physical blowing agents: Expand the polymer by expansion of a compressed gas, evaporation of a liquid, or dissolution of solids.

APPENDIX B — DOCUMENT REVISION HISTORY

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

June 1999. This document has been reorganized to provide a consistent format.

May 1973 Document created.