

November 2000

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Polyurethane Amine Catalysts: Guidelines for Safe Handling and Disposal

Foreword

This Technical Bulletin provides general information to workers, supervisory personnel, and others about health and safety issues associated with the use of polyurethane amine catalysts. Although the bulletin reflects the current scientific knowledge and experience of experts, it is not intended to be a comprehensive discussion of the subject, but rather a brief overview of major concerns and considerations. Users of polyurethane amine catalysts should keep themselves informed of new developments in this field and should consult the current scientific literature, as well as manufacturers' and suppliers' Material Safety Data Sheets (MSDSs).

The safety and health information provided in this bulletin is for the pure amine catalysts only.

Chemical Composition of Polyurethanes

Polyurethanes are generally made by reacting a diisocyanate, for example, toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI), and a blended polyol. Amine and/or metallic salt catalysts, auxiliary blowing agents, and silicone surfactants also are used to produce a foam with the desired properties. The principal ingredients are typically supplied in bulk to large volume users with storage tanks. Other ingredients may be supplied in pails, drums, portable tanks, or returnable totes. The ingredients are metered in the proper ratio through proportioning pumps to a mixing head or spray gun, where they are mixed and dispensed to produce a finished foam.

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technical bulletin

Polyurethane Amine Catalysts

Various chemical agents or compounds are used as catalysts in the manufacture of both polyurethanes and polyisocyanurates. These catalysts are used to control and/or balance both the gelling reaction and, in foams, the gas-forming or foaming reaction responsible for foam formation. Although a number of organometallic compounds or salts may be used as catalysts in the production of polyurethanes, most manufacturers use tertiary aliphatic amines as well as organometallic compounds. Amine catalysts are typically 0.1 to 5.0 percent of a polyurethane formulation.

Amine catalysts are a class of organic compounds derived from ammonia (NH₃) by replacing one or more of the hydrogen atoms with alkyl groups or nonacidic radicals containing hydrogen and carbon atoms—e.g., dimethylcyclohexylamine [(CH₃)₂NC₆H₁₁]. The amine is primary, secondary, or tertiary depending on whether one, two, or three of the hydrogen atoms of ammonia are replaced. All amines are basic and usually combine readily with acids to form salts. Some amine salts are useful as delayed-action catalysts. The catalytic activity of a tertiary amine depends on its structure and basicity.

Amines possess a characteristic fishlike odor. Some liquid amine catalysts exhibit flash points in the range of 20°F to 115°F (-7°C to 46°C). Many catalysts have flash points above the flammable range. Flash points of mixtures or blended components may be altered in the presence of water or other components. The appropriate MSDS should be consulted for details. Specific Department of Transportation (DOT) and Occupational Safety and Health Administration (OSHA) regulations have been established for flammable and combustible liquids having closed cup flash points below 200°F.

Industrial Hygiene

During handling and processing of polyurethane chemicals, potential exposure to catalysts poses distinct health and safety concerns. While it is difficult to summarize the full range of health effects resulting from excessive exposure to sixty or more amine compounds used to manufacture polyurethane and polyisocyanurate foams, excessive exposure may result in a variety of health effects. Refer to the "Health Effects," p. 5, for further information.

Exposure Guidelines

To minimize the risk of irritation, sensitization, and/or other injury, professional organizations such as the American Conference of Governmental Industrial Hygienists (ACGIH) recommend exposure limits. Only a few of the polyurethane amine catalysts have been reviewed and assigned such limits (See Table 1). These recommended exposure limits, called Threshold Limit Values (TLVs), are airborne concentrations of substances to which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. These recommendations are intended for use in the practice of industrial hygiene and are based on the best available information. The exposure guidelines are reviewed periodically by occupational health professionals and are updated as new information becomes available. Individuals who work with amine catalysts should keep themselves informed of the most current standards governing exposure, understand the hazards associated with their use, and take precautions to avoid excessive exposure.

An exposure assessment should be conducted by an industrial hygiene professional to assess potential worker exposure risks. As part of the exposure assessment, industrial hygiene monitoring may be necessary to determine airborne concentrations of amine catalysts in the work environment. Specific industrial hygiene monitoring methods can be found in Table 2 (p. 4) of this technical document.

Methods of Compliance/Engineering Controls and Work Practices

Inhalation of amine catalyst vapor or aerosol presents potential health risks to exposed workers. In those instances where the results of the industrial hygiene evaluation indicates excessive catalyst exposure, concentrations should be reduced by the use of engineering controls, such as local exhaust ventilation where feasible. Local exhaust ventilation work practices. No food or beverage should be stored or consumed in the work area. Use of tobacco products or application of cosmetics in the area should be prohibited to prevent inadvertent contact with amine catalysts.

Respiratory Protection

Where engineering controls are not feasible and work practices do not reduce airborne amine concentrations below recommended exposure limits, appropriate respiratory protection should be used. In

> such cases, air-purifying respirators equipped with cartridges designed to protect against amines are recommended. The manufacturers' MSDS should be consulted for specific information regarding respirator use and selection.

> For firefighting, cleaning up large spills, and other emergency operations, workers must wear a selfcontained breathing apparatus with full face-piece, operated in a pressure-demand mode. Airline and air

purifying respirators should not be worn for firefighting or other emergency or upset conditions. Respirators should be used in conjunction with a respiratory protection program, which would include suitable fit testing and medical evaluation of the user.

Other Personal Protective Equipment Routine Operations

As previously discussed, airborne amine catalyst exposures should be controlled by appropriate engineering controls (such as adequate ventilation and equipment design), by adhering to safe work practice procedures and by using personal protective equipment where engineering controls are not adequate.

Table 1—Permissible Exposure Levels and Threshold Limit Valuesof Some Polyurethane Amine Catalysts

Permissible Exposure Levels ^a US				Threshold Limit Values Adopted by ACGIH ^b		
NAME	PEL (ppm)	STEL (ppm)	TWA (ppm)	(mg/m³)	STEL (ppm)	(mg/m³)
Ethanolamine	3	_	3	7.5	6	15
N-ethylmorpholine	20	_	5(skin)	24(skin)	_	_
bis (2-Dimethylaminoethyl) ether			0.05		0.15	

Key

TWA = Time-weighted average for an 8-hour day

STEL = Short-term exposure limit (15 minute TWA)

(Skin) = Hazardous by skin absorption

a Occupational Safety and Health Administration, CFR 1910.1000, January 1, 1977 (Amended 1989)

b Threshold Limit Values for 2000, American Conference of Governmental Industrial Hygienists

should be designed to draw vapors or aerosols away from the operator's breathing zone and designed to reduce airborne amine catalyst vapor concentrations to acceptable concentrations at all work stations. This would include processing, fabricating, pouring, or frothing operations—or wherever amine catalyst vapors or mists may be released to the atmosphere. In addition, workers handling amine catalysts should follow proper handling procedures and utilize good

Table 2—Physical Properties and Industrial Hygiene Sampling/Analytical Procedures for Common Polyurethane Amine Catalysts

Chemical Name	Trade Names, Common Names	Vapor Pressure, mm Hg, 20°C	Industrial Hygiene Sampling/ Analytical Procedures
bis(2-Dimethylaminoethyl)ether	NIAX A-99; DABCO BL-19; TOYOCAT ETS; JEFFCAT ZF-20	0.28	Crompton Method XAD-2 Resin (100 mg/50 mg) Bayer Method 2.10.1 XAD-2Resin (400 mg/200 mg)
N,N-Dimethylcyclohexylamine	POLYCAT 8; JEFFCAT DMCHA	2.2	Huntsman Method – Chromosorb-102 Resin Air Products Method - XAD-2 Resin BTR Method – Porasil B Resin +5% KOH NIOSH XAD-2 Resin
N,N,N',N',N"-Pentamethyldiethylenetriamine	DESMORAPID PV; POLYCAT 5; TOYOCAT DT; JEFFCAT PMDETA	0.42	Bayer Method 2.10.1 XAD-2 Resin (400 mg/200 mg) Air Products Method - XAD-2 Resin
Triethylenediamine	TEDA; DABCO Crystal; RC Catalyst 105; JEFFCAT TD-100	0.45	Bayer Method 2.10.1 XAD-2 Resin (400 mg/200 mg) Huntsman Method – Chromosorb-102 Resin
Diethanolamine	DABCO DEOA; DEOA LFG	0.01	Crompton Method 38c-17g2-R2 NIOSH Method 3509 Impinger (hexanesulfonic acid) Swenden Publication Naphthylisothiocyanate-impregnated glass fiber filters
2(2-Dimethylaminoethoxy)ethanol	DABCO DMAEE; PAK-LOC V; JEFFCAT ZR-70	0.05	Crompton Method 38C-6L15-R2 XAD-2 Resin (400 mg/200 mg)
N-[2-(dimethylamino)ethyl]-N-methylethanolamine	DABCO T	0.5	
N,N-Dimethylaminopropylamine	DMAPA	5	
Dimethylethanolamine	DABCO DMEA; JEFFCAT DMEA	4	Crompton Method 38C-17G1-R2 XAD-8 Resin (250 mg/110 mg) Huntsman Method – Chromosorb-102 Resin
3-Dimethylamino-N,N-Dimethylpropionamide	DDPA; NIAX A4; NIAX C-191	<1	
N-Ethylmorpholine	DABCO NEM; JEFFCAT NEM	6.1	BTR Method – Porasil B Resin +5% KOH NIOSH Method #S146 – Silica Gel Tube

The maximum achievable vapor concentration at room ("saturated atmosphere") in parts per million corresponds to [vapor pressure (mm Hg)]/760 mm Hg x 10⁶

For example, a saturated atmosphere of triethylenediamine, which has a vapor pressure of 0.45 mm Hg, would be 592 ppm.

Where there is a possibility of exposure to liquid amines skin and eye protection should include:

- Chemical goggles and face shield
- Neoprene, Nitrile, or Butyl gloves (DO NOT USE latex)
- Rubber apron
- Long-sleeve coveralls
- · Safety shoes or rubber boots

Emergency Situations

Protective equipment should be used during emergency situations whenever there is a likelihood of exposure to liquid amines or to excessive concentrations of amine vapor. "Emergency" may be defined as any occurrence, such as, but not limited to, equipment failure, rupture of containers, or failure of control equipment that results in an uncontrolled release of amine liquid or vapor.

Emergency protective equipment should include:

- Self-contained breathing apparatus, with full facepiece, operated in positive pressure or pressure-demand mode.
- Neoprene, Nitrile, or Butyl gloves
- · Long-sleeve coveralls or impervious full body suit
- Head protection, such as a hood, made of material(s) providing protection against amine catalysts

Medical Surveillance

Laboratory animal studies have shown that a few amines are suspected of causing depletion of certain white blood cells and their precursors in lymphoid tissue. These effects may be due to an immunosuppressive mechanism.

Some persons with hyperreactive airways (e.g., asthmatic persons) may experience wheezing attacks (bronchospasm) when exposed to airway irritants. Lung injury may result following a single massive overexposure to high vapor concentrations or multiple exposures to lower concentrations of any pulmonary irritant material. Health effects of amines, such as skin irritation and transient corneal edema ("blue haze," "halo effect," "glaucopsia"), can be prevented by means of formal worker education, industrial hygiene monitoring, and exposure control methods. Persons who are highly sensitive to the triggering effect of non-specific irritants should not be assigned to jobs in which such agents are used, handled, or manufactured.

Medical surveillance programs should consist of a pre-placement evaluation to determine if workers or applicants have any impairments (e.g., hyperreactive airways or bronchial asthma) that would limit their fitness for work in jobs with potential for exposure to amines. A clinical baseline can be established at the time of this evaluation.

Periodic medical evaluations can have significant value in the early detection of disease and in providing an opportunity for health counseling.

Medical personnel conducting medical surveillance of individuals potentially exposed to polyurethane amine catalysts should consider the following:

- Health history, with emphasis on the respiratory system and history of infections
- Physical examination, with emphasis on the respiratory system and the lymphoreticular organs (lymph nodes, spleen, etc.)
- Lung function tests, pre- and post-bronchodilator if indicated
- Total and differential white blood cell count
- Serum protein electrophoresis

Persons who are concurrently exposed to isocyanates also should be kept under medical surveillance.

Health Effects

While it is difficult to generalize about the full range of potential health effects posed by exposure to the many different amine compounds used in the

manufacture of polyurethane and polyisocyanurate foams, overexposure to the majority of these materials may cause adverse health effects. Some known acute toxicological effects of a number of polyurethane amine catalysts are listed in Table 3. Consult the appropriate MSDS for specific details about both the acute and chronic effects of the particular amine catalyst used. For example:

- Many amine-based compounds can induce histamine liberation, which, in turn, can trigger allergic and other physiological effects, including bronchoconstriction or bronchial asthma and rhinitis.
- Systemic symptoms include headache, nausea, faintness, anxiety, a decrease in blood pressure, tachycardia (rapid heartbeat), itching, erythema (reddening of the skin), urticaria (hives), and facial edema (swelling). Systemic effects (those affecting the body) that are related to the pharmacological action of amines are usually transient.

Typically, there are four routes of possible or potential exposure: inhalation, skin contact, eye contact, and ingestion.

Inhalation

Inhalation of vapors may—depending upon the physical and chemical properties of the specific product and the degree and length of exposure result in moderate to severe irritation of the tissues of the nose and throat and can irritate the lungs. Products with higher vapor pressures have a greater potential for higher airborne concentrations. This increases the probability of worker exposure.

Higher concentrations of certain amines can produce severe respiratory irritation, characterized by nasal discharge, coughing, difficulty in breathing, and chest pains. Chronic exposure via inhalation may cause headache, nausea, vomiting, drowsiness, sore throat, bronchopneumonia, and possible lung damage. Also, repeated and/or prolonged exposure to some amines may result in liver disorders, jaundice, and liver enlargement. Some amines have been shown to cause kidney, blood, and central nervous system disorders in laboratory animal studies.

While most polyurethane amine catalysts are not sensitizers, certain individuals may become sensitized to some amines and may experience respiratory distress—including asthma-like attacks—whenever they are subsequently exposed to even very small amounts of vapor. Once sensitized, these individuals must avoid any further exposure to amines. Although chronic or repeated inhalation of vapor concentrations below hazardous or recommended exposure limits should not ordinarily affect healthy individuals, chronic overexposure may lead to permanent pulmonary injury, including a reduction in lung function, breathlessness, chronic bronchitis, and immunologic lung disease.

Inhalation hazards are increased when exposure to amine catalysts occurs in situations that produce aerosols, mists, or heated vapors. Such situations include leaks in fitting or transfer lines. Medical conditions generally aggravated by inhalation exposure include asthma, bronchitis, and emphysema.

Skin Contact

Skin contact with amine catalysts poses a number of concerns. Direct skin contact can cause moderate to severe irritation and injury—i.e., from simple redness and swelling to painful blistering, ulceration, and chemical burns. Repeated or prolonged exposure may also result in severe cumulative dermatitis. Skin contact with some amines may result in allergic sensitization. Many of the laboratory animal skin sensitization studies reflect repeated exposures to minimally irritating concentrations of the amine. This is an appropriate procedure, but may not reflect gross overexposure. Sensitized persons should avoid all contact with amine catalysts. Systemic effects resulting from the absorption of the amines through skin exposure may include headaches, nausea, faintness, anxiety, decrease in blood pressure, reddening of the skin, hives, and facial swelling. These symptoms may be related to the pharmacological action of the amines, and they are usually transient.

Eye Contact

Amine catalysts are alkaline in nature and their vapors are irritating to the eyes, even at low concentrations. Exposed persons may experience excessive tearing, burning, conjunctivitis, and corneal swelling. The corneal swelling may manifest itself in visual disinstalled, and kept in good working order, wherever amine catalysts are used. *CAUTION: Ordinary safety glasses or faceshields will not prevent eye irritation from high concentrations of vapor.* In operations where positive-pressure, air-supplied breathing apparatus is not required, all persons handling liquid amine catalysts or other polyurethane components in open containers should wear chemical workers safety goggles.

Ingestion

The oral toxicity of amine catalysts varies from moderately to very toxic. For the 11 materials listed in Table 3, the acute oral LD_{50} (a calculated dose that

would kill 50% of rats given that amount of the test material) varies from 272 to 2337 mg/kg. Some amines can cause severe irritation, ulceration, or burns of the mouth, throat, esophagus, and gastrointestinal tract. Material aspirated (due to vomiting) can damage the bronchial tubes and the lungs.

Affected persons also may experience pain in the chest or

abdomen, nausea, bleeding of the throat and the gastrointestinal tract, diarrhea, dizziness, drowsiness, thirst, circulatory collapse, coma, and even death.

Medical Information

Pre-existing medical conditions generally aggravated by exposure include skin disorders and allergies, chronic respiratory disease (e.g. bronchitis, asthma, emphysema), liver disorders, kidney disease, and eye disease.

Broadly speaking, exposure to amine catalysts may cause effects similar to those caused by exposure to ammonia. As such, amine catalysts should be considered potentially injurious to any tissue that is directly contacted. Inhalation of aerosol mists or vapors especially of heated product—can result in chemical

Acute Oral and Dermal Toxicity Classification*

Classification	Acute Oral LD₅₀ (rat mg/kg)	Acute Dermal LD₅₀ (rabbit, mg/kg)			
Practically Nontoxic Slightly Toxic Moderately Toxic Toxic Vizbly Toxic	>5000 2000-5000 500-2000 50-500	>3000 1000-3000 500-1000 200-500			
Highly Toxic <50					

Regulatory requirements vary around the world, but this Table gives a general idea of toxicit

turbances such as blurred or "foggy" vision with a blue tint ("blue haze") and sometimes a halo phenomenon around lights. These symptoms are transient and usually disappear when exposure ceases. Some individuals may experience this effect even when exposed to concentrations below doses that ordinarily cause respiratory irritation.

Direct contact with the liquid amine may cause severe irritation and tissue injury, and the "burning" may lead to blindness. (Contact with solid products may result in mechanical irritation, pain, and corneal injury.)

Appropriate eye protection should be worn whenever amine catalysts are handled or whenever there is any possibility of direct contact with liquid products, vapors, or aerosol mists. Eyewash fountains should be

Table 3—Summary of Acute Toxicity Studies of Amines Commonly Used in Polyurethanes

Chemical Name	Trade Names Common Names	Skin Effects	Eye Effects	Skin Sensitization ^o
Alkyl Amines				
bis(2-Dimethylaminoethyl)ether	NIAX A-99; DABCO BL-19; TOYOCAT ETS; JEFFCAT ZF-20	corrosive	corrosive halovision ^a	No
N,N-Dimethylaminopropylamine	DMAPA	corrosive	corrosive halovision ^a	Yes
N,N-Dimethylcyclohexylamine	POLYCAT 8; JEFFCAT DMCHA	corrosive	corrosive	No
N,N,N',N',N"-Pentamethyldiethylenetriamine	DESMORAPID PV; POLYCAT 5; TOYOCAT DT; JEFFCAT PMDETA	corrosive	corrosive	No
Triethylenediamine	TEDA; DABCO Crystal; RC Catalyst 105; JEFFCAT TD-100	mild/moderate irritant	moderate to severe irritant halovision [,]	No
Ethanol Amines				
Diethanolamine	DABCO DEOA; DEOA LFG	moderate/ severe irritant	severe irritant halovision ^a	No
2(2-Dimethylaminoethoxy)ethanol	DABCO DMAEE; PAK-LOC V; JEFFCAT ZR-70	severe irritant/ corrosive	severe irritant halovision ^a	No
N-methyl, N-(N',N'-Dimethylaminoethyl)ethanolamine	DABCO T	severe irritant	severe irritant	No
Dimethylethanolamine	DABCO DMEA; JEFFCAT DMEA	corrosive	corrosive	No
Other				
3-Dimethylamino-N,N-Dimethylpropionamide	DDPA; NIAX A4; NIAX C-191	corrosive	corrosive	No
N-Ethylmorpholine	DABCO NEM; JEFFCAT NEM	corrosive	corrosive halovision ^a	No

a Halovision is a phenomenon associated with many amines (See "Eye Contact," p. 7). The compounds listed as causing halovision are ones for which the effect has been documented.

b ND = not determined

c Skin sensitization studies are typically conducted at minimally irritating concentrations.

Inhalation LC₅₀ (rat) ppm	Oral LD₅₀ (rat) mg/kg	Dermal LD ₅₀ (rabbit) mg/kg
117 ppm (6 hr)	570-1230	238-750
>1031 ppm (4 hr)	500-1870	490
476 ppm (females) 375 ppm (males) (6 hr)	272-650	210-400
290 ppm (6 hr) male & female rats	1630	280
>4402 ppm (1 hr)	700-2366	>2000
ND ⁶	680-3460	3000-13000
ND ⁶	2337	1340
1670 ppm (1 hr)	1580-2520	>1800
1461-1641 (4 hr)	1420-2340	1215
>41.7 ppm	1474-2400	1162-1767
>2000 ppm (4 hr)	1780	1980

pneumonitis, pulmonary edema, laryngeal edema, and delayed scarring of the airway or other affected organs. There is no specific treatment. Clinical management is based upon supportive treatment, similar to that for thermal burns. Persons with major skin contact should be maintained under medical observation for at least 24 hours due to the possibility of delayed reactions.

First Aid

Employees working in areas where contact with amine catalysts is possible should be thoroughly trained in the administration of appropriate first aid procedures.

Experience has demonstrated that prompt administration of such aid can minimize the effects of accidental exposure. For detailed information, consult the MSDS for the specific amine being used.

Inhalation

Promptly move the affected person away from the contaminated area to an area of fresh air. Keep the affected person calm and warm, but not hot. If breathing is difficult, oxygen may be administered by a qualified person. If breathing stops, give artificial respiration. Call a physician at once.

Skin Contact

In case of major exposure to liquid amine, promptly remove any contaminated clothing—including rings, watches, and shoes—preferably under a safety shower. Wash skin for 15 to 30 minutes with plenty of flowing water. Call a physician immediately. Remove and dry-clean or launder clothing soaked or soiled with this material before reuse. Dry cleaning of contaminated clothing may be more effective than normal laundering. Inform individuals responsible for cleaning to avoid direct skin contact with those areas of clothing contaminated. Discard contaminated leather articles such as shoes, belts, and watchbands. Note to Physician: Treat any skin burns as thermal burns. After decontamination, consider the use of cold packs and topical antibiotics.

Eye Contact

If liquid amines come in contact with the eyes, irrigate immediately and continuously with low pressure flowing water, preferably from an eye wash fountain, for 15 to 30 minutes. For more effective flushing of the eyes, use the fingers to spread apart and hold open the eyelids. The eyes should then be "rolled" or moved in all directions. Seek immediate medical attention, preferably from an ophthalmologist.

Ingestion

If amine catalysts are ingested, have the affected person drink several glasses of water or milk. Do not induce vomiting. Immediately transport to a medical facility and inform medical personnel about the nature of the exposure. The decision of whether to induce vomiting should be made by an attending physician. Certain amines are corrosive and may cause injury to the respiratory tract and lungs if aspirated. Also, such products may cause tissue destruction leading to stricture. If lavage is performed, endotracheal and/or esophagoscopic control is suggested. No specific antidote is known. Care should be supportive and treatment based on the judgement of the physician in response to the reaction of the patient.

Combustibility

Like many organic materials, amine-containing compounds will burn when exposed to sufficient heat, a source of ignition, and oxygen. This is especially true of vapors and mists, which are susceptible to sudden spontaneous combustion when mixed with air. Ignition temperatures will decrease with increasing vapor volume and vapor/air contact time. Smoking during amine-handling or processing operations should be strictly prohibited. Also, amine-containing compounds should not be processed or prepared near heating elements, open flames, welding operations, or other ignition sources.

Products of Combustion

The combustion of tertiary amine catalysts may yield a variety of toxic gases, including carbon monoxide, hydrogen cyanide, as well as other gases including carbon dioxide and oxides of nitrogen.

In the event of a large fire, apply alcohol foam or all-purpose foams; for small fires, use CO₂ or dry chemical media. Also, water fog or water spray may be used to protect firefighters from the heat, to cool fireexposed containers, or to disperse vapors; however, water will likely have little or no effect on extinguishing the fire itself. Spent liquids used to fight or extinguish fires should be contained for proper waste disposal.

Firefighters should be well-trained in techniques proven effective against chemical fires. They also should be properly equipped for protection against both the fire itself and to the products of combustion. They should be equipped with appropriate protective clothing and a self-contained positive-pressure breathing apparatus. Finally, appropriate fire suppression devices and fire-fighting equipment should be readily available and in good working order.

Chemical Incompatibilities

Violent reaction and fire may result when amine catalysts are exposed to, or mixed with, oxidizing agents such as perchlorates, nitrates, permanganates, chromates, nitric acid, halogens, peroxides, and some cleaning solutions containing acids. The large amount of heat generated by the reaction of the catalyst with the oxidizing agent may be sufficient to cause vigorous boiling, which can cause the hot material to splash or splatter.

Handling of Spills and Leaks

First remove all ignition sources from the spill area. Have firefighting equipment nearby, and have firefighting personnel fully trained in the proper use of the equipment and in the procedures used in fighting a chemical fire. Spills and leaks of polyurethane amine catalysts should be contained by diking, if necessary, and cleaned up only by properly trained and equipped personnel. All others should promptly leave the contaminated area and stay upwind. Protective equipment for cleanup crews should include appropriate respiratory protective devices and impervious clothing, footwear, and gloves. Work areas should be equipped with safety showers and eyewash fountains in good working order. Any amine catalyst material spilled or splashed onto the skin should be quickly washed off.

Spills or releases of some polyurethane amine catalysts may need to be reported to federal, state, and local authorities. This reporting contingency should be a part of a site's emergency response plan. Consult the MSDS for product-specific regulatory information.

Minor Spills and Leaks

If possible (i.e., without risk of contact or exposure), stop the leak. Contain the spilled material by diking, then neutralize it with solution/material recommended in the manufacturer's MSDS. Next, absorb the neutralized product with clay, sawdust, vermiculite, or other inert absorbent and shovel into containers. Store the containers appropriately outdoors. Dispose of the material in full accordance with all federal, state, and local laws and regulations governing the disposal of chemical wastes. (See "Disposal," p. 11.) Waste materials from an amine catalyst spill or leak may be "hazardous wastes" that are regulated by the Resource Conservation and Recovery Act (RCRA).

Major Spills

In addition to impervious clothing, footwear, and gloves, cleanup crews handling a major spill must wear a positive-pressure, self-contained breathing apparatus, equipped with a full facepiece, hood, or helmet. If necessary, and feasible, dike the spill to prevent entry into municipal water systems, waterways, etc. Call the supplier's emergency response center for advice and/or assistance. If the spill involves a tank car or tank truck, call CHEMTREC (1-800-424-9300). Large quantities of the spilled material may be pumped into drums. These may be closed and transported to an appropriate facility for disposal—again in strict compliance with all federal, state, and local laws and regulations governing the disposal of chemical wastes. (See "Disposal," p. 11.)

Cleanup and Decontamination

Brooms and mops should be disposed of—along with any remaining absorbent—in accordance with all applicable federal, state, and local regulations and requirements. Decontamination of floors and other hard surfaces after the spilled material has been removed may be accomplished by using a 5% solution of acetic acid, followed by very hot water.

CHEMTREC

CHEMTREC, or the Chemical Transportation Emergency Center, is a public service of the American Chemistry Council. It is intended to collaborate with, and enhance the effectiveness of, the organized response capabilities of individual companies. Thus, the correct action in a transportation emergency is to call 1-800-424-9300 and provide the required information. After giving immediate advice to those on the scene of the emergency, CHEMTREC will contact the shipper of the product involved to acquire more detailed information and assistance.

Disposal

Most polyurethane amine catalysts and their byproducts can be chemically or biologically degraded. Incineration is the preferred method of disposal; however, nitrogen oxide emission control may be required to meet current environmental regulations. Landfill disposal of amine-containing wastes is acceptable only where landfill sites are governmentally approved

to receive this type of waste. A suitable industrial or municipal waste treatment system also can be used, depending upon the quality and quantity of waste to be treated, the treatment plant capability, and discharge water quality standards.

Finally, all relevant local, state, and federal regulations and requirements governing the disposal of amine-containing wastes must be adhered to strictly. Among the various federal enactments that may govern the disposal of these materials are The Resource Conservation and Recovery Act (RCRA); The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (also known as "Superfund") and The Hazardous Materials Transportation Act (HMTA), as well as its 1990 Amendment, The Hazardous Materials Transportation Uniform Safety Act (HMTUSA).

Drum Disposal

While the many laws, regulations, and ordinances governing the disposal of empty containers are varied and complex, one principle is common to all: the responsibility for the proper disposal of empty containers lies with the generator. Moreover, the generator is also responsible for any injury to health or environment caused by improper disposal. It is imperative, therefore, that all persons responsible for the disposal of chemical wastes (including "empty" drums) be familiar with the requirements of the legislation governing such disposal. Again this would include RCRA, CERCLA, HMTA, and HMTUSA.

Although many federal regulations have been adopted by the states, certain states may have requirements that are even more stringent. Thus, drum generators should also be familiar with state regulatory agencies and their requirements, as well as with all local ordinances that may affect disposal operations. For a detailed list of State Hazardous Waste Management Agencies, see *Understanding* the Hazardous Waste Rules: A Handbook for Small Business—1999 Update (EPA530-K-95-001), which can be ordered by calling the RCRA Hotline at 1-800-424-9346.

Summary Issues for Operating Procedures

The following issues should be addressed to minimize the hazards associated with the handling, use, storage, and disposal of amine catalysts:

- Isolation, enclosure, and local exhaust ventilation will reduce concentrations of airborne amine catalysts.
- Avoid exposure to amine catalyst vapors. Work areas should be adequately ventilated to reduce the concentrations of airborne amines. When necessary, wear proper respiratory protection.
- Avoid skin and eye contact with amine catalysts. If there is a possibility of direct contact, wear appropriate protective clothing and eye protection.
- Persons with a history of skin or respiratory sensitivity to amine catalysts should avoid any contact with these products, including waste materials and "empty" containers.
- Have an adequate supply of absorbent and neutralizing materials on hand for prompt cleanup of a spill or leak.
- Do not expose polyurethane amine catalysts to elevated temperatures or open flames.
- Dispose of any waste product and empty containers in strict accordance with all applicable federal, state, and local regulations and requirements.
- Trained and knowledgeable workers should handle amine catalysts, or dispose of waste material and/or empty containers.

 Finally, current Material Safety Data Sheets (MSDSs) and similar documents should be read and understood before amine catalysts are handled. Also, all federal, state, and local regulations and requirements governing the use, shipment, and disposal of amine catalysts should be fully understood and adhered to strictly.

For further information on handling other polyurethane chemicals, consult these Alliance for the Polyurethanes Industry publications:

MDI-Based Polyurethane Foam Systems: Guidelines for Safe Handling and Disposal, AX119

TDI-Based Polyurethane Foam Systems: Guidelines for Safe Handling and Disposal, AX142

Hyperreactivity and Other Health Effects of Diisocyanates: Guidelines for Medical Personnel, AX150

Guidelines for the Responsible Disposal of Containers and Wastes from Polyurethane Raw Materials Processing AX151

These publications may be obtained by calling The American Plastics Council (APC) at 1-800-243-5790, or visiting the APC website at www.plastics.org. When ordering, reference the "AX" document numbers (e.g., AX119).

Additional Information

For additional information on toxicological properties, health effects, protective clothing, and safe handling, consult the following sources:

Akesson, Beng, et al. 1986. Visual Disturbances After Industrial Triethylamine Exposure. *Int. Arch. Occup. Environ. Health*, 57:297-302.

Albrecht, William N., and Richard L. Stephenson. 1988. Health Hazards of Tertiary Amine Catalysts. *Scand. J. Work Environ. Health*, 14:209-219. American Conference of Governmental Industrial Hygienists. 1987. *Guidelines for the Selection of Chemical Protective Clothing*, 3rd Edition. Cincinnati, OH.

American Conference of Industrial Hygienists. Annual Publication. *TVLs, Threshold Limit Values for Chemical Substances and Physical Agents*. Cincinnati, OH.

Belin, L., et al. 1983. Amines: Possible Causative Agents in the Development of Bronchial Hyperreactivity in Workers Manufacturing Polyurethanes from Isocyanates. *British Journal of Industrial Medicine*, 40:251-257.

Clayton, George D., and Florence E. Clayton (eds.). 1994. Aliphatic and Alicyclic Amines. *Patty's Industrial Hygiene and Toxicology*, Vol. IIB, Fourth Revised Edition. New York: John Wiley & Sons.

Holsapple, Michael P., et al. 2000. Characterization of the Irritation and Sensitization Potential of Amine Catalysts Used in Polyurethanes. (Unpublished API Report)

Hurd, R. 1991. Some Actions Taken by Flexible Foam Producers in Europe to Meet the Requirements of Legislation on Health and the Environment. *Polyurethanes World Congress 1991*.

Oertel, Günter (ed.). 1994. *Polyurethane Handbook,* 2nd Edition. Munich: Hanser Publishers.

Potts, Albert M., et al. 1986. An Unusual type of Keratopathy Observed in Polyurethane Workers and its Reproduction in Experimental Animals. *American Journal of Medicine*, 9:203-213.

Technical Data Sheets (TDS), Material Safety Data Sheets (MSDS), and OSHA Form 20 or equivalent for each amine catalyst used. (Copies of these documents are available from the chemical suppliers.)

Appendix A: Amine Catalysts Used in the Manufacture of Polyurethanes

Chemical Name	CAS Number	Trade Names, Common Names
bis(2-Dimethylaminoethyl)ether	3033-62-3	NIAX A-99; DABCO BL-19; TOYOCAT ETS; JEFFCAT ZF-20; RC Catalyst 6433
N,N-Dimethylcyclohexylamine	98-94-2	POLYCAT 8; JEFFCAT DMCHA; Desmorapid 762/b
N,N,N',N',N''-Pentamethyldiethylenetriamine	3030-47-5	DESMORAPID PV; POLYCAT 5; TOYOCAT DT; JEFFCAT PMDETA
Triethylenediamine	280-57-9	TEDA; DABCO Crystal; RC Catalyst 105; JEFFCAT TD-100; TOYOCAT TEDA; RC Catalyst 104
Diethanolamine	111-42-2	DABCO DEOA; DEOA LFG
2(2-Dimethylaminoethoxy)ethanol	1704-62-7	DABCO DMAEE; PAK-LOC V; JEFFCAT ZR-70
N-[2-(dimethylamino)ethyl]-N-methylethanolamine	2212-32-0	DABCO T; TOYOCAT RX5
N,N-Dimethylaminopropylamine	109-55-7	DMAPA; TOYOCAT RH2
Dimethylethanolamine	108-01-0	DABCO DMEA; JEFFCAT DMEA; Desmorapid DMEA
3-Dimethylamino-N,N-Dimethylpropionamide	17268-47-2	DDPA; NIAX A4; NIAX C-191
N-Ethylmorpholine	100-74-3	DABCO NEM; JEFFCAT NEM; TOYOCAT NEM; RC Catalyst 6072
4-butyl-morpholine	1005-67-0	NBM
N-Cocomorpholine	72906-09-3	DABCO NCM; JEFFCAT NCM
1,8-diazabicyclo[5.4.0]undec-7-ene	6674-22-2	POLYCAT DBU; RC Catalyst 6180
Tris(3-Dimethylamino)propylamine	33329-35-0	POLYCAT 9; JEFFCAT Z80
N,N-dimethyl-(4-methyl-1-piperazinyl)-ethanamine	29589-40-0	JEFFCAT TAP; RC Catalyst 6076
4-[2-(dimethylamino)ethyl]-morpholine	4385-05-1	DABCO XDM
2,4,6-Tris(Dimethylaminomethyl)phenol	90-72-2	DABCO TMR-30; JEFFCAT TR30; RC Catalyst 6330
N-Methyl,N-(N',N'-2-Dimethylaminopropyl)ethanolamine	82136-26-3	POLYCAT 17
2-propanol,1,1'-[[2-[(2-hydroxypropyl)amino]ethyl]imino]bis-	10507-78-5	JEFFCAT DPA
1-[bis(3-dimethylaminopropyl)amino]-2-propanol	67151-63-7	JEFFCAT ZR-50
1,3,5-tris[3-(dimethylamino)propyl]hexahydro-s-triazine	15875-13-5	POLYCAT 41; JEFFCAT TR41; TOYOCAT TRC; RC Catalyst 6099
N,N'-Dimethylpiperazine	106-58-1	JEFFCAT DMP; RC Catalyst 6117
4-Hexadecylmorpholine	25727-91-7	ДАВСО СЕМ
N-Methyldicyclohexylamine	7560-83-0	POLYCAT 12
N-Methylmorpholine	109-02-4	JEFFCAT NNM; DABCO NMM; RC Catalyst 101
1,4-diazabicyclo[2.2.2]octane, 2-methyl-	1193-66-4	DABCO M
N,N,N',N'-Tetramethyl-1,3-butanediamine	97-84-7	тмвда

DABCO, POLYCAT and PAK-LOC V are trade names of Air Products and Chemicals, Inc. NIAX is a trade name of Crompton Corporation. JEFFCAT is a tradename of Huntsman Corporation. TOYOCAT is a trade name of TOSOH Corporation. RC Catalyst is a tradename for Bayer Corporation.

Chemical Name	CAS Number	Trade Names, Common Names
N-[3-(dimethylamino)propyl]-N,N',N'-trimethyl-1,3-propanediamine	3855-32-1	POLYCAT 77; JEFFCAT ZR40; TOYOCAT PMA; RC Catalyst 6177
N,N,N',N'-Tetramethyl-hexamethylenediamine	111-18-2	TMHDA; POLYCAT 6; TOYOCAT MR; RC Catalyst 115
N,N,N',N'-Tetramethylethylenediamine	110-18-9	TMEDA; TOYOCAT TE; DABCO TMEDA; JEFFCAT TMEDA; RC Catalyst 6090
Tetramethylimino-bis(propylamine)	6711-48-4	POLYCAT 15; JEFFCAT ZR-50B; RC Additive KE9528
Triethanolamine	102-71-6	TEA
Triethylamine	121-44-8	ACCURE C (Allied); DABCO TETN; RC Catalyst 6140
2-(2-(2-dimethylamino ethoxy)-ethylmethylamino)-amino	83016-70-0	JEFFCAT ZF-10
N-(3-Dimethylaminopropyl)formamide	5922-69-0	PS-220 (Bayer)
N,N-dimethylhexadecylamine	112-69-6	DM-16D; DABCO B-16
1,2-Dimethylimidazole	1739-84-0	DIME 12
2,2'-dimorpholinodiethylether	6425-39-4	JEFFCAT DMDEE; RC Catalyst 6135
N-Hydroxyethyl-N'-methylpiperazine	5464-12-0	тоуосат нр
4-(2-methoxyethyl)-morpholine	10220-23-2	JEFFCAT MM
N,N,4-Trimethyl-1-piperazineethanamine	104-19-8	TOYOCAT NP
N,N,N',N'-2-pentamethyl-1,2-propanediamine	68367-53-3	РМТ
N-cyclohexyldiethanolamine	4500-29-2	DECA
N,N-Diethylethanolamine	100-37-8	DEEA
N,N-Diisopropylethanolamine	121-93-7	DIEA
Dimethyldodecylamine	112-18-5	DM-12D
N,N'-bis(1,4-dimethylpentyl)1,4-benzenediamine	3081-14-9	TENAMENE 4
Ethanolamine	141-43-5	EA
1-azabicyclo[2.2.2]octane	100-76-5	QUINICLIDINE
4-(3-Methoxypropyl)-morpholine	P86-491	POLYCAT 50
1-Methyl-4-(3-methoxypropyl)-piperazine	P86-492	POLYCAT 51
4-(2-aminopropyl)morpholine	50998-05-5	маем
1,3-bis(Dimethylamino)-2-propanol	5966-51-8	UC-2 (Sipene)
1,3-bis(Dimethylamino)propane	110-95-2	
ethanamine, 2,2'-[methylene bis(oxy)]bis[N,N-dimethyl-	36996-87-9	Cl-710

Tyl, Rochelle W., et al. 1986. Evaluation of the Teratogenicity of Bis(2-Dimethylaminoethyl) Ether After Dermal Application in New Zealand White Rabbits. *J. Toxicol. Cutaneous Ocul. Toxicol.*, 5(4):2634-284.

Warren, Donald W., Jr., and Dale F. Selchan. 1988. An Industrial Hygiene Appraisal of Triethylamine and Dimethyethylamine Exposure Limits in the Foundry Industry. *American Industrial Hygiene Association Journal*, 49(12):630-634.

Woods, George. 1990. *The ICI Polyurethanes Book*, 2nd Edition. New York: ICI Polyurethanes and John Wiley & Sons. **Note:** The principal purpose of this bulletin is to provide information about the health and safety hazards or potential hazards, associated with the handling and disposal of amine catalysts. The information herein is offered in good faith and is believed to be accurate and reliable as of the date of publication; however, it is offered WITHOUT WARRANTY, EXPRESS OR IMPLIED, AS TO MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR ANY OTHER MATTER.

This guide was developed by the Alliance for the Polyurethanes Industry (API), a business unit of the American Plastics Council. It is intended to briefly summarize the current state of health hazard and safety information associated with handling and disposal of amine catalysts as provided in good faith by API members. It is not intended to provide specific legal or technical advice, nor to endorse specific polyurethane proprietary products or processes, and is made WITHOUT WARRANTY, EXPRESSED OR IMPLIED AS TO MER-CHANT-ABILITY, FITNESS FOR PARTICULAR PURPOSE, OR ANY OTHER MATTER. Persons setting up polyurethane operations should consult with their own technical and legal advisors and other appropriate sources of safety and handling information, including information from product suppliers, product labels, technical bulletins, MSDSs, and other sales literature.

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1300 WILSON BOULEVARD, SUITE 800 ARLINGTON, VA 22209 703.253.0656 FAX 703.253.0658 www.polyurethane.org www.plastics.org