OCCUPATIONAL HEALTH GROUP
CHAMBERS WORKS

cc: WJVogler/WENeeld
Medical (F)

7 4I-0791-000946

84940000046

(A)

May 15, 1986

To: A. B. Palmer
B-16373

From: K. A. Chen
Bldg. 588 (X)
Chambers Works

FYI-94-000946
INIT 07/26/94

METHYLAMINES ON CHAMBERS WORKS

Monomethylamine is no longer used on Chambers Works. However, in September of 1985, a truck containing drums of monomethylamine was diverted to Chambers Works as a result of a TERP incident. During the dedrumming of the material to a tank trailer, air monitoring was conducted. The results showed less than 0.01 ppm for all but one sample, which was 0.4 ppm, of fourteen.

Dimethylamine is listed as an ingredient in Fuel Oil Additive No. 3. No air monitoring has been done for this material and no more than eight (8) employees would be affected by any imposed exposure limit.

Trimethylamine is used in the Specialty Chemicals Area, White Products A. No air monitoring has been done for this material and any imposed exposure limit would impact no more than eight (8) employees.

KAC/dld
0929T

MAY 19 1986

KENNEDY
LOMBARDO
GENTILUCCI
LARSON
LOJEWSKI
MATTSON
HARTSTEIN
DONALD
PALMER
HARDT
FILE
SHRED

94 JUL 26 AM 8:45
RECEIVED

RECEIVED
04/05/96

ISSUE DATE: 7/20/83

REVIEW DATE: 6/12/85 REVIEWER: G. C. ANDERSON/W. J. HOBBS

JOB ASSIGNMENT DESCRIPTION

AREA: C&P-East

JOB ASSIGNMENT TITLE: Amines Operator

LOCATOR CODE: AM1 NUMBER OF OPERATORS: 2 per shift

DUTIES:

Operates the amines control panel and does some field work (valving). Most of the time spent in the control room.

CHEMICALS PRESENT:

- Methanol**
- Ammonia
- Sodium Hydroxide
- Monomethylamine (MMA)*,**
- Dimethylamine (DMA)*,**
- Trimethylamine (TMA)*,**
- Carbon Monoxide (CO)**
- Sulfur Dioxide (SO_2)
- Harshaw Catalyst (AL1602)
- Dimethylacetamide (DMAC)*,**
- Dimethylformamide (DMF)*,**
- Amine Solutions
- Monomethylformamide (MMF)*,**
- Zimmite

PROTECTIVE EQUIPMENT (INDICATE WHERE IMPERVIOUS GLOVES, RESPIRATOR, ETC., ARE USED AND WHAT TYPE:

- Coverall goggles
- Neoprene and butyl gloves/boots
- Hard hat
- Ear plugs

CHEMICALS MONITORED:

*Air Samples
**Detector Tubes

PREPARER: D. S. FONG

PAP/amr
0326A-13

ISSUE DATE: 7/20/83

REVIEW DATE: 6/12/85 REVIEWER: G. C. ANDERSON/W. J. HOBBS

JOB ASSIGNMENT DESCRIPTION

AREA: C&P-East

JOB ASSIGNMENT TITLE: Amines Environmental Operator

LOCATOR CODE: AM3 NUMBER OF OPERATORS: 1 per shift

DUTIES:

Operates waste stripper control panel and field; assists field work (primarily sampling). Performs most leak tests.

CHEMICALS PRESENT:

- Methanol**
- Ammonia
- Sodium Hydroxide
- Carbon Monoxide (CO)**
- Monomethylamine (MMA)*,**
- Dimethylamine (DMA)*,**
- Trimethylamine (TMA)*,**
- Dimethyl Sulfate (DMS)*,**
- Dimethyl Ether (DME)
- Sulfur Dioxide (SO_2)
- Dimethylacetamide (DMAC)*,**
- Dimethylformamide (DMF)*,**
- Sodium Methylate
- Monomethylformamide***,**,*
- Monomethylacetamide**,*
- Harshaw Catalyst AL1602
- Activated Alumina

PROTECTIVE EQUIPMENT (INDICATE WHERE IMPERVIOUS GLOVES, RESPIRATOR, ETC., ARE USED AND WHAT TYPE:

- Goggles
- Neoprene/butyl gloves
- Hard hat
- Ear plugs

CHEMICALS MONITORED:

* Air Samples
** Detector Tubes
*** Haskell Lab bi-annual survey

PREPARER: D. S. FONG

PAP/amr
0326A-15

ISSUE DATE: 7/20/83

REVIEW DATE: 6/12/85 REVIEWER: G. C. ANDERSON/W. J. HOBBS

JOB ASSIGNMENT DESCRIPTION

AREA: C&P-East

JOB ASSIGNMENT TITLE: Amines/DMS/DME Field Operator

LOCATOR CODE: AM4 NUMBER OF OPERATORS: 4 per shift

DUTIES:

Loads products (Amines, solutions, DMF, DMAC, methanol, DME, DMS) and samples them. Loads waste T/W's. Unloads off-grade and raw materials (acetic acid, sodium methylate, caustic). Make up solutions. Does DME/DMS field work. Unloads SO_3 trucks.

CHEMICALS PRESENT:

Methanol**
Ammonia
Sodium Hydroxide
Monomethylamine (MMA)*,**
Dimethylamine (DMA)*,**
Trimethylamine (TMA)*,**
Sulfur Dioxide (SO_2)
Sulfur Trioxide (SO_3)
Dimethyl Ether (DME)
Sodium Carbonate (Soda Ash)
Dimethylsulfate (DMS)*,**
Dimethylacetamide (DMAC)*,**
Acetic Acid*,**
Monomethylacetamide (MMAC)***
Dimethylformamide (DMF)*
Sodium Methylate
Sodium Formate
Monomethylformamide (MMF)***,**,*
Zimmite Solutions

PROTECTIVE EQUIPMENT (INDICATE WHERE IMPERVIOUS GLOVES, RESPIRATOR, ETC., ARE USED AND WHAT TYPE:

Goggles
Neoprene/butyl gloves/boots
Hard hats
Ear plugs
Butyl acid suits
Face shield (acetic acid sampling)
Positive pressure fresh air respirator - DMS Loader

CHEMICALS MONITORED:

* Personal air samples
** Detector tubes
*** Haskell bi-annual survey

PREPARER: D. S. FONG

PAP/amr
0326A-16

ISSUE DATE: 7/20/83

REVIEW DATE: 6/12/85 REVIEWER: G. C. ANDERSON/W. J. HOBBS

JOB ASSIGNMENT DESCRIPTION

AREA: C&P-East

JOB ASSIGNMENT TITLE: Maintenance Coordinator Operator

LOCATOR CODE: AM5 NUMBER OF OPERATORS: 1 per day shift

DUTIES:

Prepares equipment for maintenance work.

CHEMICALS PRESENT:

Monomethylamine (MMA)*,**
Dimethylamine (DMA)*,**
Trimethylamine (TMA)*,**
Methanol**
Ammonia
Dimethylformamide (DMF)*,**
Dimethylacetamide (DMAC)*,**
Dimethyl Sulfate (DMS)*,**
Dimethyl Ether (DME
Carbon Monoxide (CO)**
Acetic Acid*,**
Sodium Methylate
Sodium Hydroxide
Monomethylformamide (MMF)***,**,*
Monomethylacetamide (MMAC)***
Sodium Formate
Harshaw Catalyst AL1602
Activated Alumina

PROTECTIVE EQUIPMENT (INDICATE WHERE IMPERVIOUS GLOVES, RESPIRATOR, ETC., ARE USED AND WHAT TYPE:

Goggles
Neoprene/butyl gloves
Hard hats
Ear plugs

CHEMICALS MONITORED:

* Personnel air samples
** Detector tubes
*** Haskell Lab bi-annual survey

PREPARER: D. S. FONG

PAP/amr
0326A-17

ISSUE DATE: 7/20/83

REVIEW DATE: 6/12/85 REVIEWER: G. C. ANDERSON/W. J. HOBBS

JOB ASSIGNMENT DESCRIPTION

AREA: C&P-East

JOB ASSIGNMENT TITLE: Amines Utility Operator

LOCATOR CODE: AMU NUMBER OF OPERATORS: 1 per day shift

DUTIES:

Checks outgoing tank cars for leaks and placards, assists field operators when needed. Checks safety equipment (90%) in area. Performs weekly detector tube tests.

CHEMICALS PRESENT:

Methanol**
Ammonia
Monomethylamine (MMA)*,**
Dimethylamine (DMA)*,**
Trimethylamine (TMA)*,**
Sulfur Dioxide (SO_2)
Dimethyl Ether (DME)
Dimethylsulfate (DMS)*,**
Dimethylacetamide (DMAC)*,**
Dimethylformamide (DMF)*,**
Solutions
Monomethylformamide (MMF)*,**
Monomethylacetamide (MMAC)***

PROTECTIVE EQUIPMENT (INDICATE WHERE IMPERVIOUS GLOVES, RESPIRATOR, ETC., ARE USED AND WHAT TYPE:

Goggles
Neoprene/butyl gloves
Hard hat
Ear plugs

CHEMICALS MONITORED:

* Personnel air samples
** Detector tube test
***Haskell Lab bi-annual survey

PREPARER: D. S. FONG

PAP/amr
0326A-19

ISSUE DATE: 12/19/83
REVIEW DATE: 10/1/85 REVIEWER: E. C. RICHARDSON

MECHANICAL DEPARTMENT JOB ASSIGNMENT DESCRIPTION

JOB ASSIGNMENT TITLE: AMINES, DMF/DMAC, MMF, DRUM PLANT MECHANIC

LOCATOR CODE: A2C NUMBER OF EMPLOYEES:

Mechanics in this job assignment spend about 45% of their time in Amines, 25% in DMF/DMAC, 5% in MMF, and about 5% at the Drum Plant. About 20% of their total time is spent in the shop.

Mechanics working at Amines perform the following activities:

1. Equipment repairs.
2. Piping repairs
3. New equipment and piping installation
4. Maint. work other than a) insulating, b) elect./instrument, c) welding, d) carpentry

While in Amines, the mechanic has about the same exposure as AM1.

Mechanics working at DMF/DMAC perform the following activities:

1. Equipment repairs
2. Piping repairs
3. New equipment and piping installation
4. Maint. work other than a) insulating, b) elect./instrument, c) welding, d) carpentry

While in DMF/DMAC, the mechanic has about the same exposure as AM2.

Mechanics working at MMF perform the following activities:

1. Equipment repairs.
2. Piping repairs
3. New equipment and piping installation
4. Maint. work other than a) insulating, b) elect. instruments, c) welding, d) carpentry.

While in MMF, the mechanic has about the same exposure as AM2.

Mechanics working at Drum Plant perform the following activities:

1. Equipment repairs
2. Piping repairs
3. New equipment and piping installation
4. Maint. work other than a) insulating, b) elect./instrument, c) welding, d) carpentry

While in Drum Plant, the mechanic has about the same exposure as DP2.

PREPARER: J. A. STEBBINS

PAP/amr
0719A-24

ISSUE DATE: 1/4/84

REVIEW DATE: 10/1/85 REVIEWER: E. C. RICHARDSON

MECHANICAL DEPARTMENT JOB ASSIGNMENT DESCRIPTION

JOB ASSIGNMENT TITLE: AMINES, DMF, MMF, DMAC, DME/DMS, DRUM PLANT E&I MECHANIC

LOCATOR CODE: A2G NUMBER OF EMPLOYEES:

Mechanics in this job assignment spend about 95% of their time in all areas listed under this job assignment and about 5% of their time in the shop.

Mechanics working in Drum Plant, Amines, DMAC, DMF, MMF, and DME/DMS areas perform the following activities:

1. Instrument repair.
2. Electrical equipment repair.
3. Routine maintanence work such as changing light bulbs, recalibration of instruments, etc.
4. Install new instrument/electrical equipment.

While in Amines, the mechanic has about the same exposure as AM1. While in DMF/DMAC, the mechanic has about the same exposure as AM2. While in MMF the mechanic has about the same exposure as AM2. While in DME/DMS, the mechanic has about the same exposure as DS1. While in Drum Plant, the mechanic has about the same exposure as DP3.

PREPARER: E. C. RICHARDSON

PAP/amr
0719A-27

CC: R. D. Porter
D. L. Furry
H. J. Alferink
P. A. Pokrzywa
G. C. Anderson
G. M. Volker
T. E. Palenchar
J. E. Kahre
R. W. Arthur
J. B. Whittington
G. J. Chen
K. K. Hsieh
J. R. Hoffman/Skiles/Jennings/Fields
R. A. Kuhn
T. F. Triplett/E&I Mechanics
R. D. Wolfe/Mechs. & Insulators
D. D. Goins/A shift Operators
R. L. Siders/B shift Operators
J. E. Sharp/C shift Operators
R. S. Hess/Drum Plant
L. S. Jack/D shift Operators

April 18, 1986

TO: E. C. RICHARDSON

FROM: W. J. HOBBS W.J.H.

1986 C&P-EAST OCCUPATIONAL HEALTH

PROGRAM OBJECTIVES

FIRST QUARTER REPORT

Attached is the C&P-East and Drum Plant occupational health first quarter report. Included are the first quarter air monitoring results of which 22% are complete.

Some first quarter highlights are listed below:

o All personnel air monitoring results were within AEL requirements.

- o All hazardous intermediate MSDS's were reviewed, revised and completed by Bill Dobbs. They are now being entered into the MSDS computer system.

- o All containers and vessels have been labeled. The following area personnel contributed to the effort: Bob Cavender, Gary Scragg, Bob Stutler, Scott Birch, Bill Goodwin and Ken Skiles.

- o Nutsche blowdown to the atmosphere has been eliminated. This reduced potential for personnel exposure to MMF and reduced process emissions to the atmosphere.

WJH/bjb

Attachments

I. Required Air Monitoring for Airborne Hazardous Material

A. Schedule for sampling:

Chemical	Job Assignment	Pers	Total Samples To Be Taken	Number Implemented	Quarterly Schedule 1st	2nd	3rd	4th
Acetic Acid	DMAC Operator	AM2	2			1	1	
Acetic Acid	Unloading Operator	AM4	2	1	1	1		
Acetic Acid	Mech. During Lewa Pump Maint.	A2C	2			1	1	
MMA	Amines Operator	AM1	1	2	1			
MMA	Loading Operator	AM4	2			1	1	
MMA Solutions	Loading Operator	AM4	2	1	1	1		
MMA	Amines Oper.-1st Day of S/D	AM1	2			1	1	
MMA	Mech. During Routine Maint.	A2C	2	1	1	1		
MMA	Mech. During Shutdown	A2C	2			1	1	
DMA	Amines Operator	AM1	1	2	1			
DMA	Loading Operator	AM4	2	1	1	1		
DMA Solutions	Loading Operator	AM4	2			1	1	
DMA	Amines Oper.-1st Day of S/D	AM1	2			1	1	
DMA	Mech. During Routine Maint.	A2C	2	1	1	1		
DMA	Mech. During Shutdown	A2C	2			1	1	
TMA	Amines Operator	AM1	1	2	1			
TMA	Loading Operator	AM4	2	1	1	1		
TMA Solutions	Loading Operator	AM4	2			1	1	
TMA	Amines Oper.-1st Day of S/D	AM1	2			1	1	

I. Required Air Monitoring for Airborne Hazardous Material (Cont'd)

A. Schedule for sampling: (Cont'd)

Chemical	Job Assignment	Pers	Total Samples To Be Taken	Number Implemented	Quarterly Schedule 1st	2nd	3rd	4th
TMA	Mech. During Routine Maint.	A2C	2	1	1	1		
TMA	Mech. During Shutdown	A2C	2			1	1	
Asbestos	Insulators	A2IN	2			1	1	
DMF	DMF Operator	AM2	2			1	1	
DMF	Loading Operator	AM4	3	1	1	1	1	
DMF	Mech. During Shutdown	A2C	2	1	1	1		
DMF/DMAC	Mech. During Routine Maint.	A2C	2			1	1	
DMAC	DMAC Operator	AM2	2	2	2			
DMAC	Loading Operator	AM4	3	1	1	1	1	
DMAC	Mech. During Shutdown	AC2	2			1	1	
MMF	MMF Operator	AM2	6			3	3	
MMF	Mech. During Routine Maint.	A2C	3			2	1	
MMF	MMF Loading Oper.	AM4	6			3	3	
DMS	DMS Operator	DS1	6			3	3	
DMS	DMS Loader	AM4	2			1	1	
DMS	DMS Mech. During Routine Maint.	A2D	2			1	1	
DMS	DMS Mech. During Shutdown	A2D	2			1	1	
Formaldehyde	DME/DMS Operator	DS1	3	1	1	1	1	
DMF	Drum Plant Utility Worker	DPU	2	1	1	1		

I. Required Air Monitoring for Airborne Hazardous Material (Cont'd)

A. Schedule for sampling: (Cont'd)

Chemical	Job Assignment	Pers	Total Samples To Be Taken	Number Implemented	Quarterly Schedule 1st	2nd	3rd	4th
DMAC	Drum Plant Utility Worker	DPU	2	2	2			
Methacrylic Acid	Drum Plant Utility Worker	DPU	2			1	1	
Methyl Methacrylate	Drum Plant Utility Worker	DPU	2			1	1	
Ethyl Methacrylate	Drum Plant Utility Worker	DPU	2			1	1	
Butyl Methacrylate	Drum Plant Utility Worker	DPU	2			1	1	
Isobutyl Methacrylate	Drum Plant Utility Worker	DPU	2			1	1	
2-Ethyl Hexyl Methacrylate	Drum Plant Utility Worker	DPU	3			1	2	
TOTAL SAMPLES			104	22	19	47	38	

	Percent Implemented	Responsibility	Goal
B. Conduct required monitoring per the established quarterly schedule.	On-going	W. J. Hobbs	12/86
C. Investigate, analyze, and document the reason for any single sample that characterizes employee exposure being greater than 1/2 the AEL by making appropriate comments on the Industrial Hygiene Data Sheet.	On-going	W. J. Hobbs	As occurring
D. Forward completed Industrial Hygiene Data Forms (Form ER-8559) to P. A. Pokrzywa for entry into PERS.	On-going	W. J. Hobbs	As data is available
E. Analyze sampling data using LOGAN and recommend resample frequencies.	On-going	P. A. Pokrzywa	As data is available
F. Communicate chemical monitoring results per Safety Manual Procedure O-1.	On-going	W. J. Hobbs	Per O-1
G. Monitor DMF area for CO leaks.	On-going	R. W. Arthur	Every shift
1. Personal CO monitoring device to be worn by area personnel.	Evaluating	G. J. Chen	06/86

II. Respiratory Protection

	Percent Implemented	Responsibility	Goal
A. Attend annual respirator training classes and retraining classes.			
1. For all employees who wear or are potential users of respiratory equipment as required by law.	27%	1st line supervisors	12/86
B. Arrange to have persons who may use a SCBA under emergency situations to don SCBA every 6 months.			
1. Required by S&F Guideline 9.13.			
a. First 6-month donning.	27%	1st line supervisors	06/86
2. One donning of SCBA will be done during the annual training class conducted by the Safety Department.			
a. Second 6-month donning.	0%	1st line supervisors	12/86
C. Issue compliance plan for respirator use (E-5).	0%	W. J. Hobbs	06/30/86

III. Noise

A. Conduct annual noise surveys per Safety Manual Procedure H-3.	On schedule	W. J. Hobbs	05/86
B. Prepare noise contour maps for each area showing the 90 dBA contour, 87 dBA contour, and 85 dBA contour.	On schedule	W. J. Hobbs	06/86
C. Update noise compliance plan and forward a copy to P. A. Pokrzywa (do this within 6 weeks of annual survey).	On schedule	W. J. Hobbs	06/86
D. Annual personnel noise monitoring with audio dosimeter (this should be done during the same month that the annual noise survey is done).	On schedule	W. J. Hobbs	05/86
E. Annual hearing test of employees.	On-going	1st line supervisors	12/86

IV. Ventilation

	Percent Implemented	Responsibility	Goal
A. Annual check of hoods and ventilation systems per H4T.	On schedule	W. J. Hobbs	12/86

V. Heat Stress

A. Take annual botzball temperature readings at Drum Plant.	0%	W. J. Hobbs	08/86

VI. Annual Communications

A. Communicate occupational health hazard information to all employees per Safety Procedure O-1.	On schedule	W. J. Hobbs	12/86
B. Inform all employees of the effects of high noise levels per H-3.	On schedule	W. J. Hobbs	12/86

VII. New MSDS Program

A. Develop/obtain Material Safety Data Sheets that meet OSHA's 1910.1200 Hazard Communication Standard:			
1. Obtain vendor MSDS for all raw materials by May, 1986.	100%	P. A. Pokrzywa W. J. Hobbs	05/86
2. Develop MSDS for all non-RCRA wastes disposed on plant.	100%	Area Supv.	05/86
3. Develop MSDS for all hazardous intermediates generated/remaining on plant.	100%	G. J. Chen K. K. Hsieh W. J. Hobbs	05/86
B. Train area employees on the plant's hazard communication program as specified in OSHA's 1910.1200 hazard communication standard.	33%	E. C. Richardson D. L. Tong	05/86

VIII. Labeling of Containers

A. Label all containers of hazardous materials to meet OSHA's 1910.1200 Hazard Communication Standard.			
1. Label all in plant containers of materials by May, 1986.	100%	W. J. Hobbs	05/86

IX. Additional On-Going Programs

		Percent Implemented	Responsibility	Goal
A.	Re-evaluate C&P-East policy on female assignment in area.	0%	E. C. Richardson P. A. Pokrzywa W. J. Hobbs	12/86
B.	Implement closed dome loading on solutions tank wagons.	Evaluation complete; should be implemented by 3Q86.	G. C. Anderson J. E. Kahre	09/86
C.	Install breathing air bottle station at DMS.	MCN circulating (4B).	R. W. Arthur	12/86
D.	Improve conditions for maintenance in old DMS CCR.	Evaluating	E. C. Richardson R. D. Wolfe R. W. Arthur	12/86
E.	Train all supervisors and minimum of one operator per shift on air monitoring sampling techniques.	On-going	W. J. Hobbs	12/86
F.	Comply with recommendations of all items on Occupational Health Audits.	On-going	E. C. Richardson/ D. L. Tong	Continuing
G.	Include review of area hazards as part of new employee orientation.	On-going/ as occurs.	W. J. Hobbs	As occurs
H.	Complete the plant and area Occupational Health Programs (plant and area occupational health subcommittee) items to achieve 100% of goal/recommendations.	Continuing	Supervisors	Per program schedule
I.	Eliminate Nusche blowdown to the atmosphere.	100%	T. E. Palenchar R. W. Arthur	03/86
J.	Eliminate steam out point to the Nusche feed line from blowing into the atmosphere (located on ground level at bottom of filter feed pump).	100%	T. E. Palenchar R. W. Arthur	03/86
K.	Eliminate block and bleed at separator (on 35' level) from bleeding to the atmosphere.	100%	T. E. Palenchar R. W. Arthur	03/86

IX. Additional On-Going Programs (Cont'd)

		Percent Implemented	Responsibility	Goal
L.	Continue to administer the plant program to replace/contain asbestos insulation where the potential exists for asbestos exposure.	On-going	J. R. Hoffman R. D. Wolfe	Continuing
M.	Communicate all new information on toxicities and carcinogens to all employees.	Continuing	W. J. Hobbs	As occurs

WJH/bjb

1986 FIRST QUARTER AIR MONITORING RESULTS

DRUM PLANT, METHYLAMINES, DMS, DME, DMF, MMF, DMAC

Chemical	Date	Source	Job or Location	Analysis	AEL
Acetic Acid	03/04/86	J. H. Burkes	Acetic Acid Unloader	HOAC 0.2 ppm	10.0 PPM
Methylamines	03/05/86	Tom Smith	Amines Board Operator	TMA 0.1 ppm	5.0 ppm
				DMA 0.1 ppm	10.0 ppm
				MMA 0.1 ppm	10.0 ppm
Methylamines	03/10/86	Charlie Mays	Amines Board Operator	TMA <0.1 ppm	5.0 ppm
				DMA 0.1 ppm	10.0 ppm
				MMA <0.1 ppm	10.0 ppm
Methylamines	03/10/86	Brett Legg	Amines Loading Operator	TMA 0.5 ppm	5.0 ppm
			(Loaded TMA Blimp and DMA T/C)	DMA 0.5 ppm	10.0 ppm
				MMA <0.1 ppm	10.0 ppm
Monomethylamines	03/27/86	Brett Legg	40% MMA Solutions Loader	MMA 2.8 ppm	10.0 ppm
Methylamines	03/18/86	Greg Carney	Mechanic/Routine Maintenance	TMA 0.2 ppm	5.0 ppm
				DMA 0.3 ppm	10.0 ppm
				MMA 1.4 ppm	10.0 ppm
Dimethylformamide	03/18/86	Bill Linville	DMF Loading Operator	DMF 3.0 ppm	10.0 ppm
Dimethylformamide	03/25/86	Dean Stewart	DMF Mechanic/Shutdown	DMF 0.2 ppm	10.0 ppm
Dimethylacetamide	02/03/86	Bill Linville	DMAC Board Operator	DMAC 0.15 ppm	10.0 ppm
Dimethylacetamide	02/04/86	Ken Skiles	DMAC Board Operator	DMAC 0.1 ppm	10.0 ppm
Dimethylacetamide	03/27/86	Brett Legg	DMAC Loading Operator	DMAC 0.3 ppm	10.0 ppm
Formaldehyde	03/10/86	Dave Brasseur	DME/DMS Board Operator	HCHO 0.11 ppm	1.0 ppm
Dimethylformamide	03/17/86	Ed Holt	Drum Plant	DMF 2.4 ppm	10.0 ppm
Dimethylacetamide	02/26/86	Dave Murphy	Drum Plant	DMAC 0.24 ppm	10.0 ppm
Dimethylacetamide	03/25/86	Ed Holt	Drum Plant	DMAC 1.2 ppm	10.0 ppm

WJH/bjb
4/18/86

BELLE WORKS
SAFETY DUPONT RULES

REG. U.S. PAT. OFF.

C&P-EAST AREA

CHEMICAL SPILL SITUATIONS

The table below specifies the protective equipment to be worn when investigating or cleaning up small and large spills. A small spill is defined as less than 10 pounds of spilled material and a large spill is defined as greater than 10 pounds of spilled material. The table also lists the atmospheric monitoring that should be performed.

	SMALL SPILL (<10 LBS.)		LARGE SPILL (>10 LBS.)	
CHEMICAL SPILLED	PPE* REQ'D	MONITORING REQ'D	PPE* REQ'D	MONITORING REQ'D
DMF, DMAC	2A+Boots	None	5E	Detector tube
MMA, DMA, TMA	2B+Boots	None	5E	Detector tube
Acetic Acid	2B+Boots	None	5E	Detector tubes
Caustic	2B+Boots	None	5C	None
MMA, DMA, TMA Solutions	2B+Boots	None	5E	Detector tube
DME	2B+Boots	None	5E	None
Methanol	2A+Boots	None	4E	Detector tube
Sodium Methylate	2A+Boots	None	5C	None
Stripper Waste	2B+Boots	None	5E	Detector tube
DMF/DMAC Wash Water	2A+Boots	None	4E	Detector tube
SO_3	5E	None	5E	None
DMS	5E	Detector tube	5E	Detector tube
Sulfuric Acid	2B+Boots	None	5E	None
MMF	2A+Boots	Detector tube	2D or G**+Boots	Detector tube

*Refers to Personal Protective Equipment Codes in Safety Manual E-3.

**G-Full face respirator.

Revised by W. J. Hobbs 1/31/86

Personal Equipmemt for Protection Against Chemicals

DUPONT

FOR HANDS AND BODY

1.

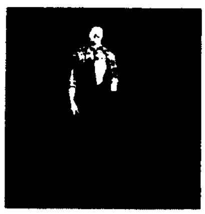
DUST RESISTANT GLOVES

2.

CHEMICAL GLOVES

3.

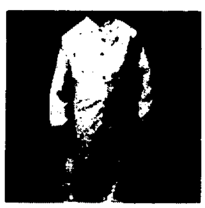
CHEMICAL GLOVES +



CHEMICAL APRON

4.

CHEMICAL GLOVES +

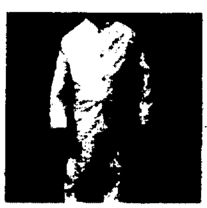


CHEMICAL SUIT +

CHEMICAL BOOTS

5.

CHEMICAL GLOVES +



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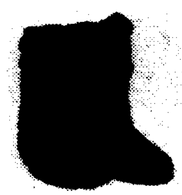
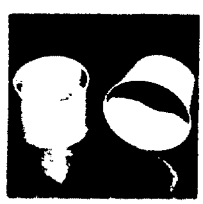


CHEMICAL BOOTS

+



SEALANT CONES

6.

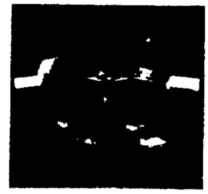
SPACE SUIT (AIR-SUPPLIED)

FOR EYES, HEAD, AND RESPIRATORY SYSTE

A.

GOGGLES

B.



GOGGLES +

FACE SHIELD

C.

CHEMICAL HOOD

(MAY BE SUPPLIED WITH COOLING AIR)

D.

SUPPLIED AIR RESPIRATOR (MASK)

SCOTT AIR PAK OR MASK WITH HOSE SUPPLY

E.

CHEMICAL HOOD +

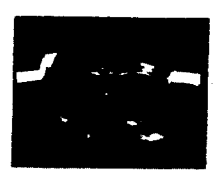
SUPPLIED AIR RESPIRATOR (MASK)

F.

DUST RESPIRATOR

G.

FULL FACE DUST RESPIRATOR



OR GOGGLES +

DUST RESPIRATOR

BELLE WORKS

SAFETY DUPONT RULES

REG. U.S. PAT. OFF.

C&P-EAST

GENERAL SAFETY RULES

1. All Belle Plant standard safety rules and regulations are to be followed.

2. No smoking is allowed in outside plant areas or in laboratory except where smoking stands are set up.

3. All persons not regularly assigned to work in the C&P-East area must notify production before entering the operating areas.

4. Coverall goggles must be worn by all persons within all curbed areas and in other marked operating areas. Safety shoes and hardhat must be worn in all operating areas.

5. Safety glasses must be worn by all persons except when in central control rooms, offices, lunchrooms, restrooms, or while wearing goggles.

6. Access to all safety equipment must be clear.

7. Refer to DME/DMS plant house rules for additional safety rules for working at DME/DMS plant.

8. Refer to Drum Plant safety rules for additional safety rules for working at Drum Plant.

9. Rubber gloves must be worn when opening and closing valves on process and loading equipment such as tanks, pumps, lines, etc.

10. All mechanical work must be performed in compliance with the standard locking and tagging procedure.

11. No burning or welding will be permitted without a signed work permit approved by the production superintendent if the plans are working.

12. Tote boxes and drop cloths must be used to avoid dropping bolts, gaskets, fittings, and other objects through the grating.

13. The CO content of the DMF synthesis area atmosphere must be checked with the MSA tester or continuous analyzer twice each shift.

14. CO leaks will be repaired at once or the DMF synthesis unit must be shut down until the leak is repaired.

(Continued on Next Page)

15. At any indication of CO exposure (i. e. headache, dizziness, or nausea), all personnel are to leave the DMF area until the cause for the illness is determined. Breathing air must then be worn to go back into area to find leak or shut down equipment.

16. Protective equipment required - refer to chart.

Product	Sampling	Connecting/Disconnecting Or Breaking Into Lines
DMF	2-A	2-B[1]
MMF	2-A	2-D or G[1] and 2
DMAC	2-A	2-B[1]
MMA, DMA, TMA	2-B	2-B
Acetic Acid	2-B	5-C
Caustic	2-B	5-C
MMA, DMA, TMA Solutions	2D or G[3]	5D or G[3]
DME	2-A	2-A
Methanol	2-A	2-A
Sodium Methylate	2-B	4-C
Stripper Waste	2-B	4-C
DMF/DMAC Heel	2-A	2-B
DMF/DMAC Wash Water	2-A	2-B[1]
SO_3	4-E	S-E
Carbon Monoxide	1-A	1-D
DMS	4-E	5-E
Ammonia	2-D	5-E
Sulfuric Acid	2-B	5-C

[1] Only if hose is connected at both ends. Use 2-A for open dome loading thru dip pipe.
[2] MSA ultra twin respirator with GMA cartridges.
[3] Wear an MSA ultra twin respirator with GMD cartridges.

17. Ear plugs are to be worn inside the amines/DMF process areas.

18. Ear plugs are to be worn inside the amines/DMF process areas.

GMV/bjb
Revised: W. J. Hobbs 1/31/86

Personal Equipmemt for Protection Against Chemicals

DUPONT

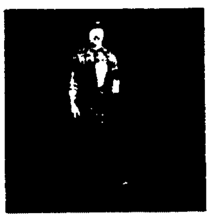
FOR HANDS AND BODY

1. 

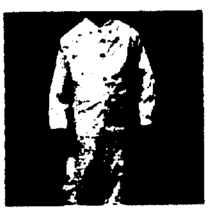
DUST RESISTANT GLOVES

2. 

CHEMICAL GLOVES

3.  

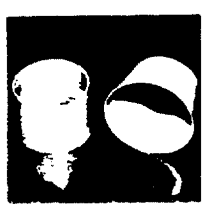
CHEMICAL GLOVES + CHEMICAL APRON

4.   

CHEMICAL GLOVES + CHEMICAL SUIT + CHEMICAL BOOTS

5.   

CHEMICAL GLOVES + CHEMICAL SUIT + CHEMICAL BOOTS



+ SEALANT CONES

6. 

SPACE SUIT (AIR-SUPPLIED)

PB 209

FOR EYES, HEAD, AND RESPIRATORY SYSTE

A. 

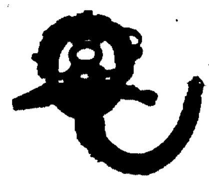
GOGGLES

B.  

GOGGLES + FACE SHIELD

C. 

CHEMICAL HOOD (MAY BE SUPPLIED WITH COOLING AIR)

D. 

SUPPLIED AIR RESPIRATOR (MASK) SCOTT AIR PAK OR MASK WITH HOSE SUPPLY

E.  

CHEMICAL HOOD + SUPPLIED AIR RESPIRATOR (MASK)

F. 

DUST RESPIRATOR

G.   

FULL FACE DUST RESPIRATOR OR GOGGLES - DUST RESPIRATO

BELLE WORKS

SAFETY DUPONT RULES

REG. U.S. PAT. OFF.

C&P-EAST

SAFETY RULES FOR TANK CAR SPOTS #1, 2, 3, 5, 6, 7, 8, 14, 25, 28

1. All C&P-East general safety rules are to be followed.

2. Coverall goggles must be worn when on any tank car or tank car loading platform.

3. Before starting work on a tank car be sure that:

   - The car is properly spotted.
   - The car is red-flagged at both ends.
   - The car is chocked.
   - The car is grounded.
   - The derails are all locked in place and a red flag placed at the derail.
   - The car spot signal lights operate properly.
   - The safety guardrail is installed on the safety platform handrail.
   - The car has been inspected for defects including valves, relief valves, rupture discs, etc.

4. No one is allowed outside the handrail of a tank car unless they are properly tied off to prevent falling.

5. Connections on amines tank cars must be checked for leaks by using SO_2.

6. Persons working on tank cars should stay upwind from any open dome on the tank car.

7. Always test nearest safety shower and inspect safety equipment before loading any tank car.

8. Protective equipment required - refer to chart.

(Continued on Next Page)

Product	Sampling	Connecting or Disconnecting Hoses
DMF	2-A	2-B[1]
MMF	2-A	2D[1] or G[1] and 2
DMAC	2-A	2-B[1]
MMA, DMA, TMA	2-B	2-B
Acetic Acid	2-B	5-C
Caustic	2-B	5-C
MMA, DMA, or TMA Solutions	2-B	5-B
DME	2-A	2-A
Methanol	2-A	2-A

[1] Only if hose is connected at both ends. Use 2-A for open dome loading thru dip pipe.

[2] MSA ultra twin respirator with GMA cartridges.

Leaks or spills call amines foreman - 1449

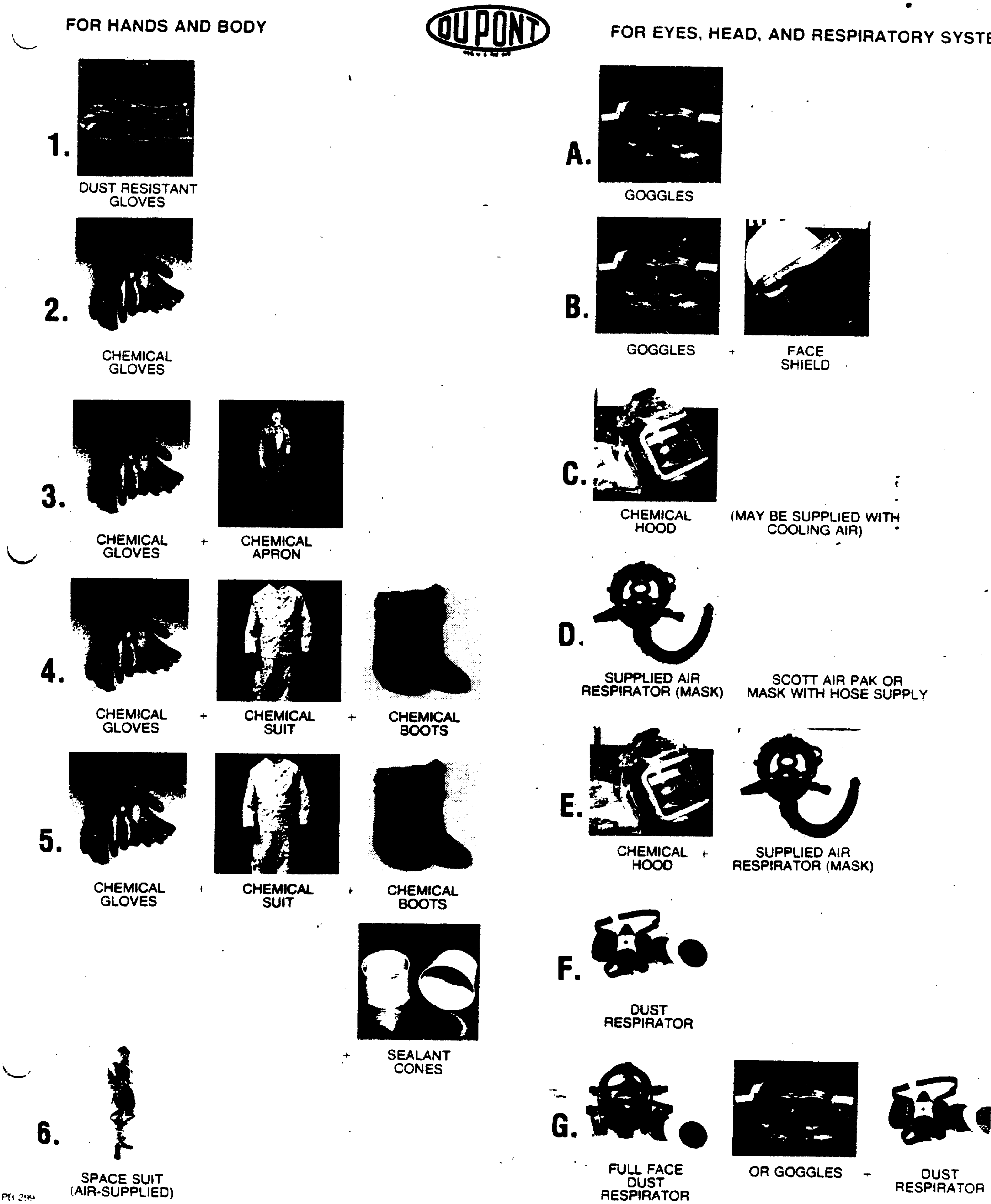
GM Volker

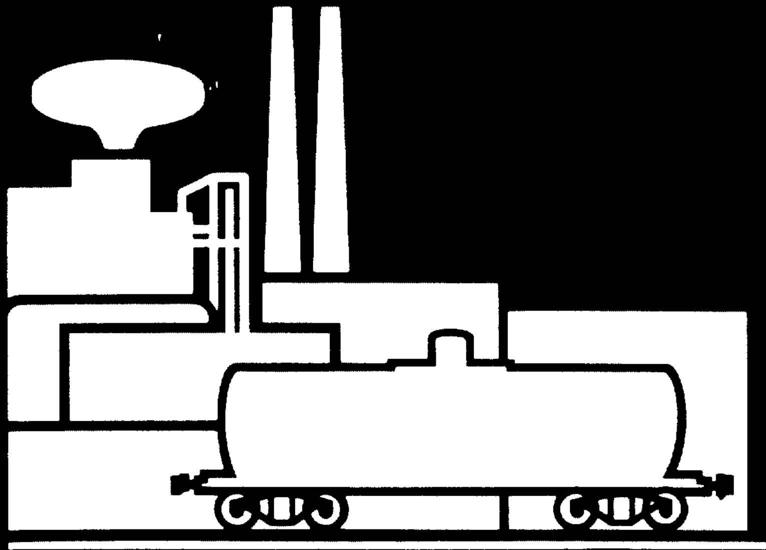
G. M. VOLKER

GMV/bjb

Revised 1/31/86 W. J. Hobbs

Personal Equipmemt for Protection Against Chemicals





METHYLAMINES

Storage & Handling

DU PONT
REG U.S. PAT & TM OFF

TABLE OF CONTENTS

PRODUCT INFORMATION

The three methylamines, monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) are the simplest members of the alkylamine series. Because of their low cost, methylamines are economical sources of basic organic nitrogen and methylamino radicals. Thus, these highly reactive compounds are widely used in the preparation of such diverse products as insecticides, fungicides, pharmaceuticals, vulcanization accelerators and surface active agents.

High-purity methylamines are available from Du Pont both as anhydrous liquefied gases and as aqueous solutions. Methylamines can be ordered in the following concentrations:

- MMA—Anhydrous and 40% aqueous solution.
- DMA—Anhydrous, 40% and 60% aqueous solutions.
- TMA—Anhydrous and 25% aqueous solution.

The Chemical Abstracts Service name for MMA is methanamine (CAS Registry Number 74-89-5); DMA is methanamine, N-methyl- (CAS Registry Number 124-40-3) and TMA is methanamine, N,N-dimethyl- (CAS Registry Number 75-50-3).

PROPERTIES

Methylamine gases are colorless and can be compressed into clear, water-white liquids. The aqueous solutions range from water-white to pale straw in color.

The methylamines are somewhat stronger bases than ammonia. Like ammonia, they readily form salts with mineral acids. MMA and DMA react with acyl halides, acid anhydrides, and esters to give N-methyl- and N,N-dimethylamides, respectively. DMA and TMA condense with ethylene oxide to yield, respectively, dimethylaminoethanol and choline [(β-hydroxyethyl) trimethylammonium hydroxide].

A summary of methylamine physical properties [1,2,3,4]* is contained in the tables on page 2. Additional physical property data and figures appear in the Appendices, pages 22 to 29.

*Superscript numbers in parentheses refer to References and Notes on page 21

PERSONAL SAFETY AND FIRST AID

HEALTH HAZARDS

Methylamines are highly alkaline materials. Both the anhydrous materials and the water solutions cause burns to the eyes and skin. Occasional dermatitis and conjunctivitis have been observed after prolonged exposure to vapors, but no systemic effects have been noted. Sensitization has not been observed. Methylamine vapors are irritating when inhaled.

See Hazardous Chemical Reactions section for possible generation of nitrosamines which are suspected carcinogens.

The U.S. Department of Labor (OSHA)† has ruled that an employee's exposure to monomethylamine or dimethylamine vapor in any 8-hour work shift of a 40-hour work week shall not exceed a time-weighted average (TWA) of 10 ppm in air by volume (29 CFR 1910.1000 Air Contaminants). While no limit has been established by OSHA for trimethylamine, the American Conference of Governmental Industrial Hygienists (ACGIH) recommends a TLV® of 10 ppm. Du Pont observes a trimethylamine airborne exposure limit of 5 ppm, 8-hour TWA.

Methylamines have good warning properties due to their fishy odor which is detectable at less than 1 ppm. The "MSA"-Universal Tester[6] with Detector Tube 92115 (amines) can be used to measure air concentration in these ranges:

- MMA—10 to 500 ppm
- DMA— 5 to 150 ppm
- TMA— 5 to 150 ppm

†Due to changing governmental regulations, such as those of the Department of Transportation, Department of Labor, U.S. Environmental Protection Agency, and the Food and Drug Administration, references herein to governmental requirements may be superseded. Each user should consult and follow the current governmental regulations, such as Hazard Classification, Labeling, Food Use Clearances, Worker Exposure Limitations, and Waste Disposal Procedures for the up-to-date requirements for the products described in this literature.

NOTICE: Methylamines are extremely flammable and cause chemical burns to the eyes and skin. See sections on PERSONAL SAFETY AND FIRST AID and STORAGE AND HANDLING.

METHYLAMINES—PHYSICAL PROPERTIES

ANHYDROUS METHYLAMINES

Property	MMA	DMA	TMA
Chemical formula	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
Molecular weight	31.06	45.08	59.11
Boiling point, C	−6.3	6.9	2.9
F	20.6	44.4	37.2
Freezing point, C	−93.5	−92.2	−117.3
F	−136.2	−133.9	−179.1
Density (liquid), at 25 C (77 F)			
g/mL (Mg/m³)	0.6562	0.6496	0.6270
lb/gal	5.48	5.42	5.23
Vapor pressure, at 25 C (77 F)			
psia	50.7	29.0	31.9
mm Hg	2622	1500	1650
kPa	350	200	220
Flammable limits, vol. %			
—lower	4.9	2.8	2.0
—upper	20.7	14.4	11.6

AQUEOUS METHYLAMINES

Property	40% MMA	40% DMA	60% DMA	25% TMA
Boiling point, C	48	54	36	43
F	118	129	97	109
Freezing point, C	−38	−37	−74.5	6
F	−36	−35	−103	43
Density (liquid), at 25 C (77 F)				
g/mL (Mg/m³)	0.897	0.892	0.829	0.930
lb/gal	7.49	7.44	6.92	7.76
Vapor pressure, at 25 C (77 F)				
psia	5.8	4.2	9.7	6.6
mm Hg	300	215	500	340
kPa	40	29	67	45
Flash point, Closed cup, (ASTM D-92), C	−12	−18	−52	6
F	10	−1	−61	42

SPECIFICATIONS AND TYPICAL ANALYSES*
DU PONT METHYLAMINES TECHNICAL

Anhydrous Compressed Gases	MMA		DMA		TMA	
	Specifications	Typical Analyses	Specifications	Typical Analyses	Specifications	Typical Analyses
Monomethylamine, wt %	99.3 min	99.7	0.1 max	0.02	0.06 max	0.01
Dimethylamine, wt %	0.5 max	0.10	99.3 min	99.8	0.12 max	0.08
Trimethylamine, wt %	0.2 max	0.02	0.3 max	0.02	99.0 min	99.3
Ammonia, wt %	0.05 max	0.01	0.05 max	0.01	0.05 max	0.02
Water, wt %	0.3 max	0.13	0.3 max	0.10	0.82 max	0.60
Formaldehyde, wt %	—	—	0.0 max	0.00	—	—
Density, 25 C (77 F), approx.						
g/mL (Mg/m³)	—	0.655	—	0.650	—	0.627
lb/gal	—	5.5	—	5.4	—	5.2

Aqueous Solutions	40% MMA		40% DMA		60% DMA		25% TMA	
	Specs.	Typ. Anal.	Specs.	Typ. Anal.	Specs.	Typ. Anal.	Specs.	Typ. Anal.
Monomethylamine, wt %	40.0 min	40.3	0.04 max	0.01	0.06 max	0.02	0.02 max	0.01
Dimethylamine, wt %	0.40 max	0.16	40.0 min	40.68	60.0 min	60.5	0.04 max	0.01
Trimethylamine, wt %	0.08 max	0.06	0.16 max	0.03	0.24 max	0.04	25.0 min	25.3
Ammonia, wt %	0.05 max	0.0	0.05 max	0.01	0.05 max	0.00	0.05 max	0.0
Formaldehyde, wt %	—	—	0.0 max	0.01	0.0 max	0.00	—	—
Density, 25 C (77 F), approx.								
g/mL (Mg/m³)	—	0.912	—	0.900	—	0.840	—	0.936
lb/gal	—	7.6	—	7.5	—	7.0	—	7.8

**Typical analyses are based on historical production performance. Du Pont does not make any express or implied warranty that all future production will demonstrate or continue to possess these typical analyses.*

SAFETY PRECAUTIONS

Avoid contact with methylamine solutions or vapors. Do not get in eyes, on skin or on clothing. Do not breathe gases or vapors. Use only with adequate ventilation. Observe OSHA standards. Self-contained breathing equipment or full-face air-line respirators and full-body protective clothing should be available for use in emergencies. Wash thoroughly after handling. Wash contaminated clothing before re-use.

FIRST AID

In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before re-use.

If vapors are inhaled, remove to fresh air. If breathing has stopped, give artificial respiration, preferably mouth to mouth. If breathing is difficult, give oxygen. Call a physician.

PERSONAL PROTECTIVE EQUIPMENT

The following personal protective equipment should be available and worn as appropriate:

- Hard hat with brim
- Chemical splash goggles
- Full length face shield
- Rubber gauntlet gloves
- Rubber apron
- Rubber safety shoes or rubber boots over leather shoes
- Complete rubber suit
- Self contained breathing apparatus or full-face air-line respirator.[7]

When making or breaking methylamines connections, or when performing any work in the vicinity of methylamine hoses under pressure, wear a face shield in addition to hard hat, chemical splash goggles and gloves.

In emergencies or in performing work where there is a possibility of direct or repeated contact, a complete rubber suit with hood and breathing air supply should be worn.

SPECIAL SAFETY FACILITIES

The following safety facilities should be readily accessible in all areas where methylamines are handled or stored:

- Fire extinguishers—carbon dioxide or dry chemical for small fires; alcohol-resistant foam plus water spray or fog for large fires.
- Safety showers—or water hoses connected to spigots with quick opening valves which stay open.
- Eye wash fountains—or other means for washing the eyes with a gentle flow of tap water.
- Water hydrant and hose—or other means of flushing spills with large volumes of low pressure water to a waste methylamine collection system.

SHIPPING CONTAINERS

Anhydrous methylamines are shipped in pressure-type tank cars and tank trucks. Tank cars used are Department of Transportation (DOT) specification 105A300-W, 105A400-W, 112T340-W and 112T400-W and are available in 10M, 20M, 25M and 30M gallon nominal sizes. Tank trucks are DOT specification MC-330/331 and are filled to a 32,000 lb to 38,000 lb maximum load depending upon gross vehicle weight restrictions.

DOT regulations limit the maximum net weight of liquefied gases carried by tank cars to a certain percentage of the weight of water that can be carried. Also each size and type of car has a maximum gross weight rating which may limit the net weight shipped. The nominal weights shipped in the four sizes of anhydrous methylamine tank cars are 50M, 110M, 130M, and 150M lbs, but the actual weight shipped may vary a small percentage from this amount.

Aqueous methylamines are shipped in tank cars (10, 20, 25 and 30M gallon nominal sizes), tank trucks and 55-gallon steel drums. Drum loading is as follows:

55-GALLON DRUM LOADING			
Aqueous Methylamine	**Drum Class**	**Gross Wt (lbs)**	**Net Wt (lbs)**
40% MMA	DOT 17E	423.5	375
40% DMA	DOT 17E	423.5	375
60% DMA	DOT 17C	421	360
25% TMA	DOT 17E	423.5	375

The DOT Hazard Class for anhydrous methylamines is FLAMMABLE GAS and for aqueous methylamines, FLAMMABLE LIQUID (49 CFR 172.101, Hazardous Materials Table).[5] UN numbers are listed below:

	UN Numbers Anhydrous	Aqueous
MMA	1061	1235
DMA	1032	1160
TMA	1083	1297

STORAGE AND HANDLING

PRECAUTIONS IN USE

Fire and Explosion Hazards

The Department of Transportation (DOT) has classified anhydrous methylamines as flammable gases and aqueous methylamines as flammable liquids (49 CFR 172.101, Hazardous Materials Table).[5] In addition to DOT requirements, federal, state and local ordinances as well as insurance company regulations may apply to the shipping, handling and storage of methylamines. The recommendations of the National Electrical Code for Class I Hazardous Locations[8] should be followed. The aqueous methylamines are Class IB flammable liquids except 60% DMA which is Class IA. OSHA Regulations for "Flammable and Combustible Liquids" are contained in Title 29 of the Code of Federal Regulations (CFR) Section 1910.106 and must be followed when handling methylamine solutions.

Even dilute methylamine-water solutions will burn and should be treated as flammable liquids. Consequently, water may not be effective on large fires (see Fire Fighting). Methylamine spills, even if not ignited, should be thoroughly diluted with a water spray to minimize the fire hazard by raising the boiling and flash points.

All equipment such as moving machinery, vehicles, methylamine storage tanks and containers must be properly grounded to prevent generation sparks. Tank cars, tank trucks and drums must be grounded prior to unloading. Storage and handling areas should be well ventilated to keep vapor concentrations below the lower explosive limit. (See limits of flammability listed under PHYSICAL PROPERTIES on page 2.)

Air must be excluded from lines, tanks and equipment used for the storage and handling of anhydrous methylamines to avoid a fire and explosion hazard. Before initial service and after shutdowns for inspection and maintenance, work systems should be purged with nitrogen.

Before inspection or maintenance, lines, tanks and equipment should always be evacuated and purged free of methylamines with water, steam or nitrogen. Equipment to be worked on should be disconnected and tested for explosive atmosphere. The equipment and the entire work area should be well ventilated and tested before doing any welding.

An evacuation plan should be prepared since anhydrous methylamines are capable of generating hazardous vapor clouds if released.

Fire Fighting

In case of fire, immediately stop the flow of methylamine gas or liquid provided this can be done with little risk of personal injury. In case of line or equipment ruptures without fire, immediately shut off the anhydrous amine flow to avoid accumulation of large volumes of flammable vapor and the risk of a vapor cloud explosion.

Carbon dioxide or dry chemical extinguishers are effective on small fires. Water spray (to dilute and cool) and a polar-solvent, aqueous film forming foam (AFFF), such as National "Universal" foam[13] should be used to extinguish large fires. Use water to protect personnel effecting the shut-off and to cool cylinders, tanks and lines not yet involved in the fire. Depending on circumstances, it may be safer to permit the fire to burn until the flow of anhydrous amine can be stopped.

Hazardous Chemical Reactions

Direct contact of the methylamines with mercury may produce an explosive reaction if ammonia also happens to be present in the methylamines. Avoid using instruments containing mercury for measurements and tests on methylamines.

Both dimethylamine and trimethylamine[9] will react with a nitrosating agent (e.g., nitrous acid, sodium nitrite, oxides of nitrogen) to form N,N-dimethyl-nitrosamine (DMN), $(CH_3)_2N\text{-}NO$. DMN will form under acid or alkaline conditions, although acid media favor the reaction. DMN is not especially stable in the environment. It is rapidly metabolized by animals and is decomposed in sunlight with a half-life of about 30 minutes[10]. While there is no direct evidence that DMN is carcinogenic in man, it has been shown to be carcinogenic to several animal species. Thus, care should be taken that dimethylamine or trimethylamine not be inadvertently stored, contacted or mixed with a nitrosating agent such as sodium nitrite. DMN is regulated as a cancer-suspect agent by the Occupational Safety and Health Administration (OSHA) under 29 CFR 1910.1016 (N-Nitrosodimethylamine).[5]

Corrosion Hazards

The methylamines are corrosive to aluminum, copper, copper alloys, galvanized metal, magnesium and zinc alloys. Iron and steel are satisfactory materials of construction for handling both the anhydrous methylamines and their aqueous solutions.

Engineering Control of Hazards

The design of methylamines storage and handling facilities should recognize the following key points:

- Store and handle methylamines in totally enclosed equipment where possible, or in systems designed to avoid human contact. If contact cannot be avoided, personnel must wear proper personal protective equipment to prevent serious irritation or burns of the skin, eyes or respiratory system. Special design features should be included to minimize the possibility of leaks.
- Methylamines are extremely flammable and should be stored and used in areas protected from flames, sparks and excessive heat.
- Lines, tanks and equipment which have been opened to the air must be purged with nitrogen before use in anhydrous methylamines service.
- Storage tanks and equipment must be electrically grounded.
- Solution storage tank vents must be equipped with suitable flame arrestors. Fill pipes must extend to within six inches of tank bottom.
- Electrical equipment, wiring and fixtures must meet the requirements of National Electrical Code, Article 500.[8]
- OSHA Regulations pertaining to storage and handling of methylamines solutions are given in 29 CFR 1910.106.
- Vents and pressure relief devices must be designed to handle pressure limitations and volumes of vapor that could be expected in emergency fire conditions.
- The process and storage tank vents should be located so that hazardous vapors given off during fires or emergency conditions will not harm personnel or increase the fire hazard.
- Dikes, waste drains and collection facilities must be provided to contain possible spills or leaks during unloading and other transfers. Spills, leaks and rinsings containing methylamines must be safely collected for later disposal or recovery.
- The storage and process layout must include provisions for more than one escape route in the event of fire, explosion or release of hazardous vapors or liquid.

Transportation Emergencies

In the event of an accident or emergency involving Du Pont methylamines in transit anywhere in the continental United States, make a toll free telephone call (day or night) to the Chemical Manufacturers Association's Chemical Transportation Emergency Center ("CHEMTREC") in Washington, DC 800-424-9300. In District of Columbia only, use 800-483-7616.

The information specialist on duty will ask the name and location of the caller, the name of the shipper, the product, the shipping point and destination, what happened, nature of any injuries, weather conditions, proximity to populated areas and such other questions as may be necessary to define the extent of the emergency. He will then give the caller recommendations for controlling the emergency situation until the shipper's specialist can relay help. "CHEMTREC" will immediately advise Du Pont of the emergency and one of our specialists will get in touch with the caller promptly.

In CANADA, call Canadian Chemical Producers Association TEAP (Transportation Emergency Assistance Plan).

UNLOADING AND TRANSFER OF ANHYDROUS METHYLAMINES

Du Pont ships anhydrous methylamines in tank cars and tank trucks. The U.S. Department of Transportation (DOT) classifies anhydrous methylamines as flammable gases. See PERSONAL SAFETY AND FIRST AID on page 1.

Tank cars and tank trucks of anhydrous methylamines may be unloaded by pump, compressor or nitrogen pressure. Du Pont tank truck shipments are manually unloaded by tractor mounted compressor.

OSHA requirements (29 CFR 1910.101b, Compressed Gases) state that the in-plant handling, storage and utilization of all compressed gases in cylinders, portable tanks, rail tank cars or motor vehicle cargo tanks shall be in accordance with the Compressed Gas Association Pamphlet P-1-1974[11].

For personal protective equipment, refer to page 3.

Tank Cars

Before unloading any methylamine tank car, the user should be familiar with the contents of this bulletin. The following actions should be taken before making any connections to the car:

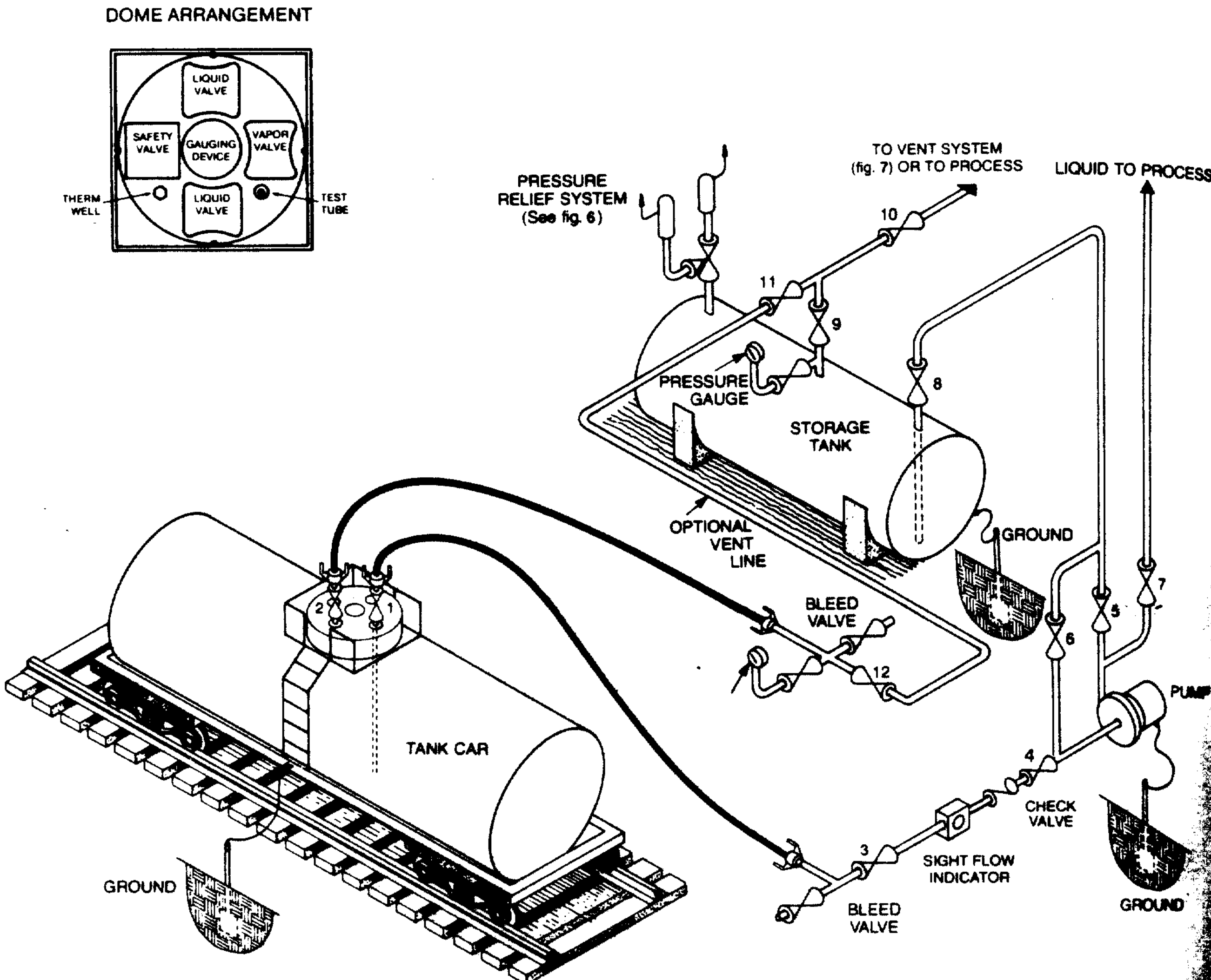
1. Set the brakes and block the wheels.
2. Place blue* caution signs at open end(s) of the car.
3. Place derails on track at open end(s) of siding unless car is protected by a closed and locked switch.
4. Properly ground car by attaching a ground wire.

Unloading Tank Cars by Pump

Unloading by pump is shown in Figure 1. Connections are made at the top of the car. If a high unloading rate is desired, the two liquid standpipes on the tank car can be connected together. As the liquid is pumped out of the

*Federal Regulation 49 CFR 174.67

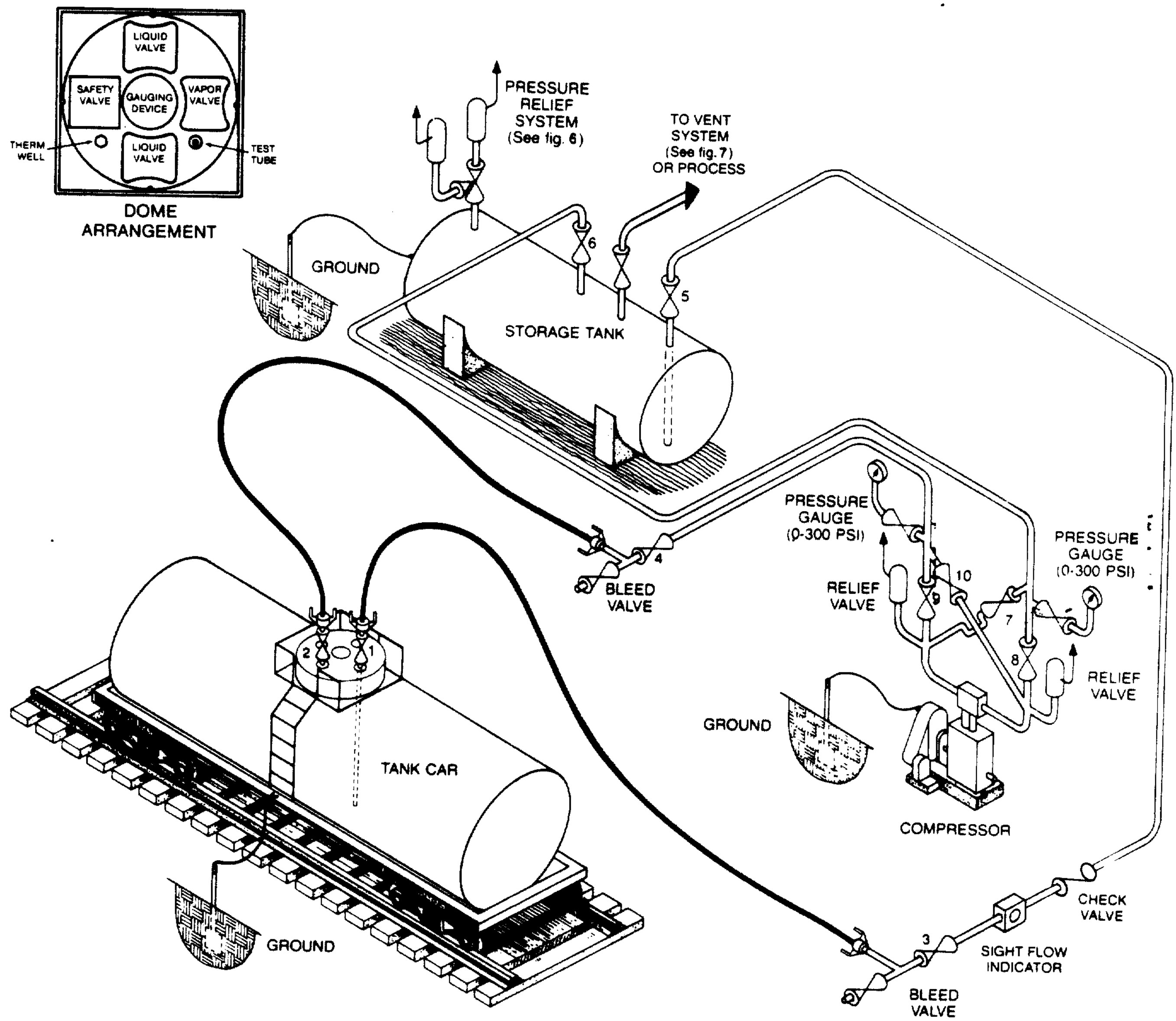
Figure 1
UNLOADING ANHYDROUS METHYLAMINES TANK CAR BY PUMP



UNLOADING NOTES

1. Connect tank car as shown (including ground).
2. Open valves 2, 3, 4, 5, 8 (close 6 and 7) and start pump.
3. To initiate flow, the liquid manual valve on the tank car (valve 1) should be opened slowly. The tank car liquid piping contains an internal excess flow check valve. A surge of flow when opening the liquid valve too quickly may cause the excess flow valve to snap shut prematurely, usually with an audible sound. If the excess flow valve closes, close the manual valve which will reopen the excess flow valve. Then open the manual valve (valve 1) more slowly.
4. Vent line, if used, should be opened (valves 12, 11 and when pressure (as shown by gauges) in tank is gre than in tank car.
5. When tank car is empty, turn off pump, close valves 3, 4 and 5. Open valves 6 and 7 so pump will be pump to process when desired.
6. If desired, open valves 2, 12, 11 and 10 and pu pressure in car to process. Valve 9 should be clo
7. To avoid atmospheric pollution and possible expo of operating personnel, all connections should evacuated before being broken.
8. Disconnect tank car.

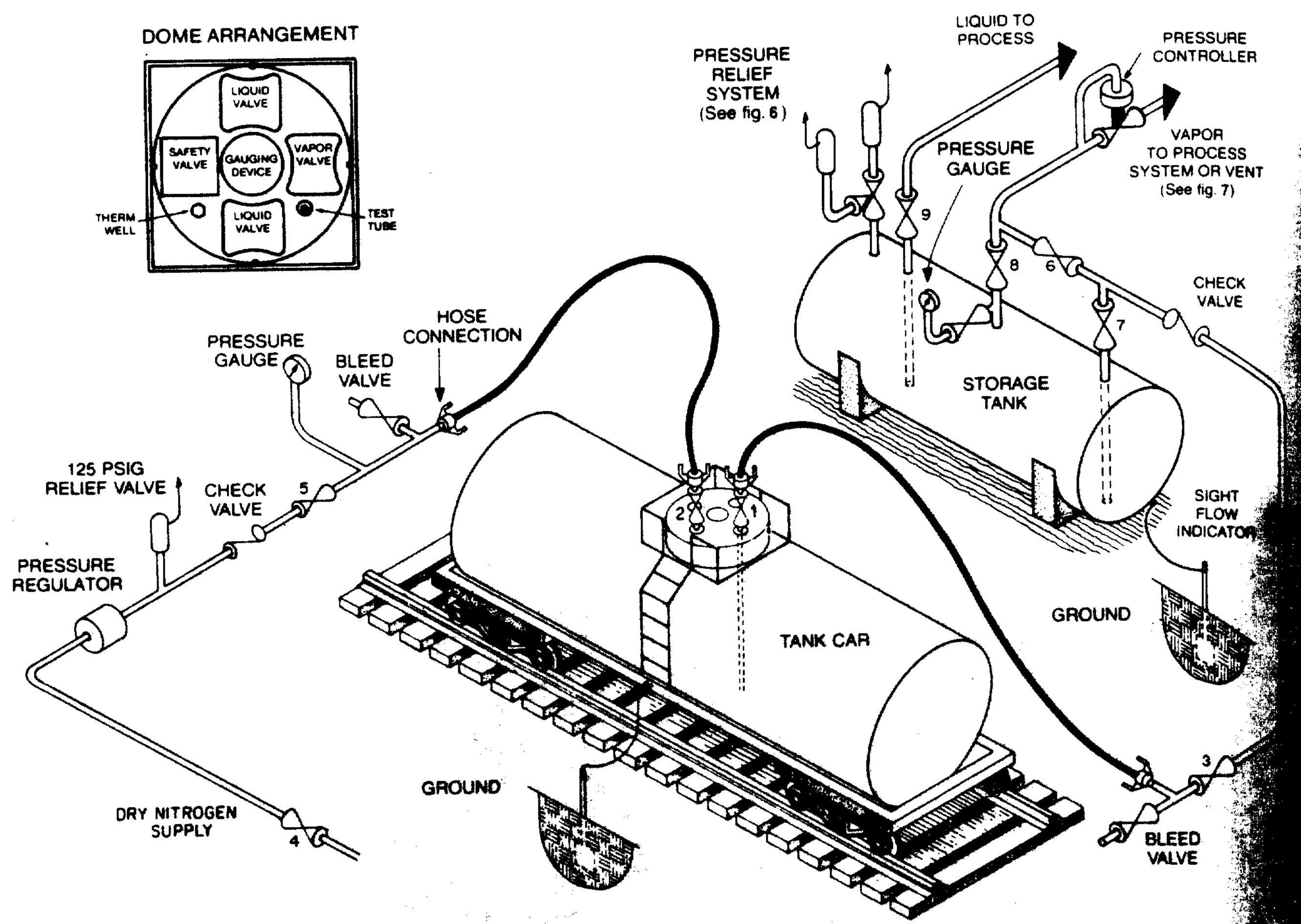
Figure 2
UNLOADING ANHYDROUS METHYLAMINES TANK CAR BY COMPRESSOR



UNLOADING NOTES

1. Connect tank car as shown (including ground).
2. Open valves 2, 3, 4, 5, 6, 8 and 9, and turn on the compressor. To initiate flow, slowly open valve 1. See step 3, Figure 1.
3. Vapor pumped out of storage into the tank car will cause transfer to take place.
4. When transfer is complete, close valves 1, 2, 5, 8 and 9. Open valves 7 and 10 and the compressor will pump gas from the car to storage. *CAUTION:* Do not reduce pressure in the tank car below zero gauge pressure or air may be sucked into the system forming an explosive mixture.
5. Close all valves when the car pressure is approximately atmospheric.
6. To avoid atmospheric pollution and possible exposure of operating personnel, all connections should be evacuated before being broken.
7. Disconnect tank car.

Figure 3
UNLOADING ANHYDROUS METHYLAMINES TANK CAR WITH NITROGEN PRESSURE



UNLOADING NOTES

1. Connect tank car and nitrogen supply as shown (including ground).
2. Open valve 4 and set pressure regulator for desired pressure.
3. Open valves 2, 3, 5 and 7. To initiate flow, the liquid manual valve on the tank car (valve 1) should be opened slowly. The tank car liquid piping contains an internal excess flow check valve. A surge of flow when opening the liquid valve too quickly may cause the excess flow valve to snap shut prematurely, usually with an audible sound. If the excess flow valve closes, close the manual valve which will reopen the excess flow valve, open the manual valve (valve 1) more slowly.
4. When unloading is complete, nitrogen will blow th the unloading line. Close valves 2, 4 and 5 imme and 1, 3 and 7 when nitrogen flow out of tank c stopped. (It may be desirable to throttle valve 1 n end of unloading to prevent the sudden "blow th of nitrogen.)
5. To avoid atmospheric pollution and possible e of operating personnel, all connections sh evacuated before being broken.
6. Disconnect tank car.

tank car, vaporization of the methylamines will cool the contents of the car and the pressure will drop. A pump with adequate suction characteristics is required to empty a tank car satisfactorily. A vent connection between the vapor space in the tank car and the storage tank is recommended to permit closed loop unloading. After unloading has been completed, excess pressure in the tank car may be vented to the process.

The type of pump is important because methylamines are volatile and are usually handled at or near their boiling points. A tight shaft seal on the pump is essential. Sealless pumps are preferred. Steel canned-rotor centrifugal pumps are satisfactory for unloading anhydrous methylamines. **A low level or low-flow cut-off is required for sealless or canned centrifugal pumps because these pumps are easily damaged if run dry.**

Unloading Tank Cars by Compressor

Another method of unloading methylamines is to utilize a gas compressor as illustrated in Figure 2. This procedure is commonly used in ammonia service and can be applied to methylamines. Vapors from the methylamine storage tank are compressed and then injected into the vapor space of the methylamine tank car. The pressure differential thus created causes liquid methylamines to flow from the tank car or tank truck directly into the storage tank. While basically simple, this system is slower than the pumping method and requires the purchase and maintenance of a compressor. However, unloading by compressor allows a closed loop vent system and minimizes venting and odors. Compressors must be rated for "ammonia service" and cannot contain any copper or copper alloys. Storage tank vapor must be free of air since this could cause an explosion in the compressor.

Unloading Tank Cars With Nitrogen Pressure

A third method to transfer anhydrous methylamines from tank car to storage tank is by use of nitrogen pressure on the delivery tank. Figure 3 shows a typical nitrogen unloading system. If it is more convenient use nitrogen cylinders, it is better to manifold all the required cylinders before unloading rather than change cylinders as the unloading progresses. The pressure reducing valve and the flexible connections from the cylinder to the manifold are available from the nitrogen supplier. See section on Tank Accessories for further discussion and a list of suggested equipment.

Nitrogen pressure also can be supplied by a liquid nitrogen system equipped with a properly sized evaporator and controls.

Do NOT use compressed air to unload under any circumstances.

Nitrogen pressure unloading should employ a storage tank vent absorber or a process scrubber to minimize venting methylamine vapors to the atmosphere.

Anhydrous methylamine tank cars are equipped with pressure relief valves. However, it is recommended that the unloading pressure be kept below 60 psig. Nitrogen will be conserved and venting minimized if the unloading pressure is kept just high enough to effect the transfer. Maximum conservation of nitrogen will occur in cases where it is possible to vent the storage tank to the process.

Too much pressure drop between the tank car and the storage tank may cause excess flow. An undesired closing of the excess flow valve on the tank car dip pipe will occur.

Unloading Tank Trucks

The standard method for unloading tank trucks containing Du Pont anhydrous methylamines is by use of the tractor mounted compressor. Alternatives to this method are use of a plant-side compressor, pump or nitrogen pressure. Figure 4 shows a typical tank truck unloading arrangement. If one of the other methods is used to unload, please refer to the tank car figures.

Hoses required for connecting truck vapor and liquid lines to storage tank piping are supplied on the truck. Hose connections are 2000 psi Huber-Yale screw unions. A 2 inch male union is required on the receiver's liquid piping and a 1 inch male union is required on the vapor line. These Huber-Yale screw unions are *not* compatible with other unions; do *NOT* mix half unions from different manufacturers.

In order to assure the safe unloading of tank trucks, plant personnel should:

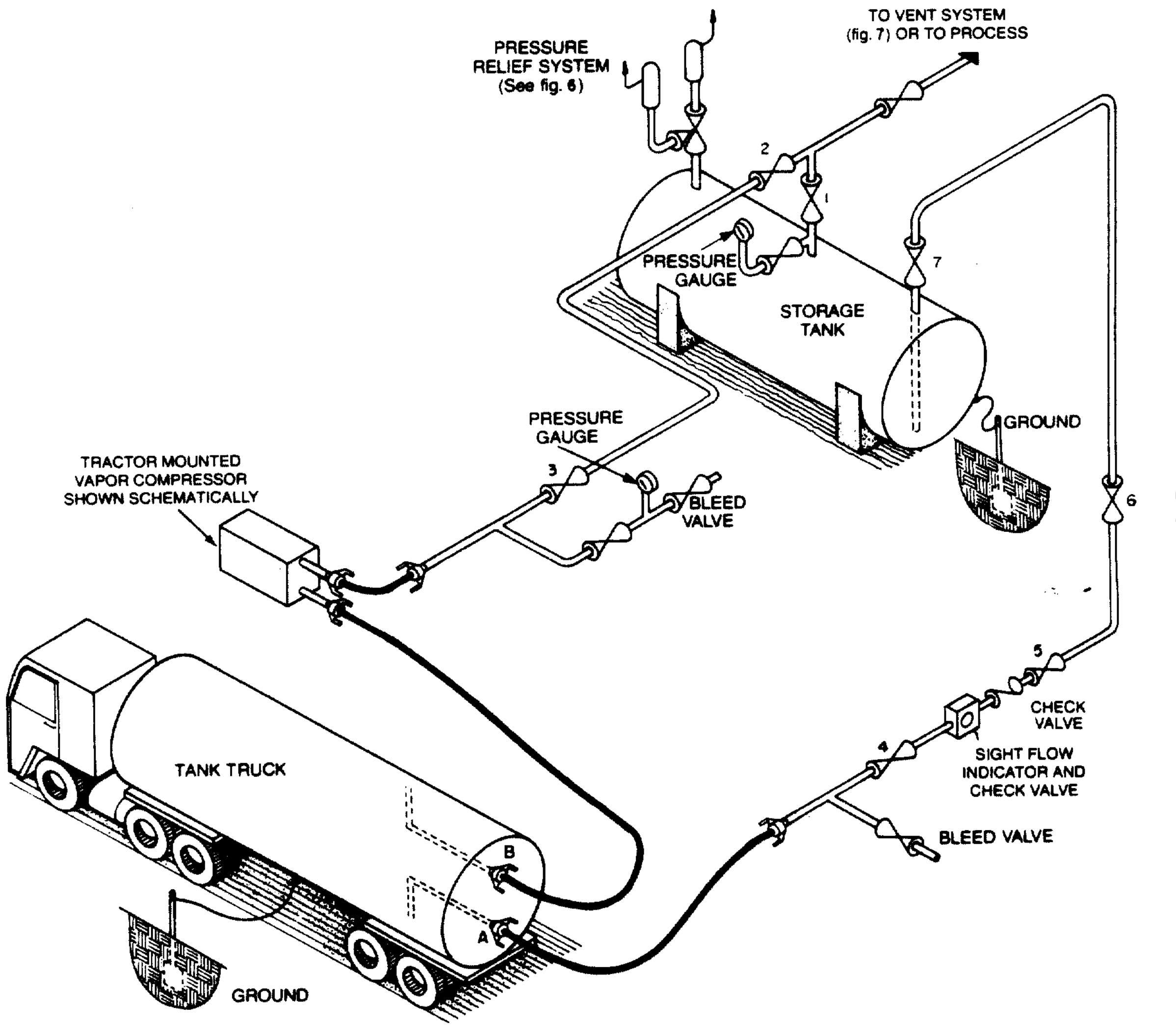
- be certain to wear personal protective equipment;
- be sure the storage tank can take the entire delivery;
- make certain the truck liquid and vapor hoses are securely attached to the proper plant lines;
- check safety shower or provide water hose;
- be sure that all valves in the line to the storage tank are open;
- be sure the tank truck is securely grounded;
- operate or supervise the operation of all the plant equipment involved in the unloading.

Driver will:

- observe DOT Regulations spelled out for common carrier shipments in 49 CFR 177.834, General Requirements, or in Tariff No. BOE-6000;
- spot the trailer properly and prepare it for unloading;
- ground the tank truck to customer's grounding station;
- connect the truck hoses to the plant lines;
- operate all truck equipment.

At locations A and B, methylamine tank trucks are equipped with both internal excess flow and external manual valves. Excess flow valves are required by DOT regula-

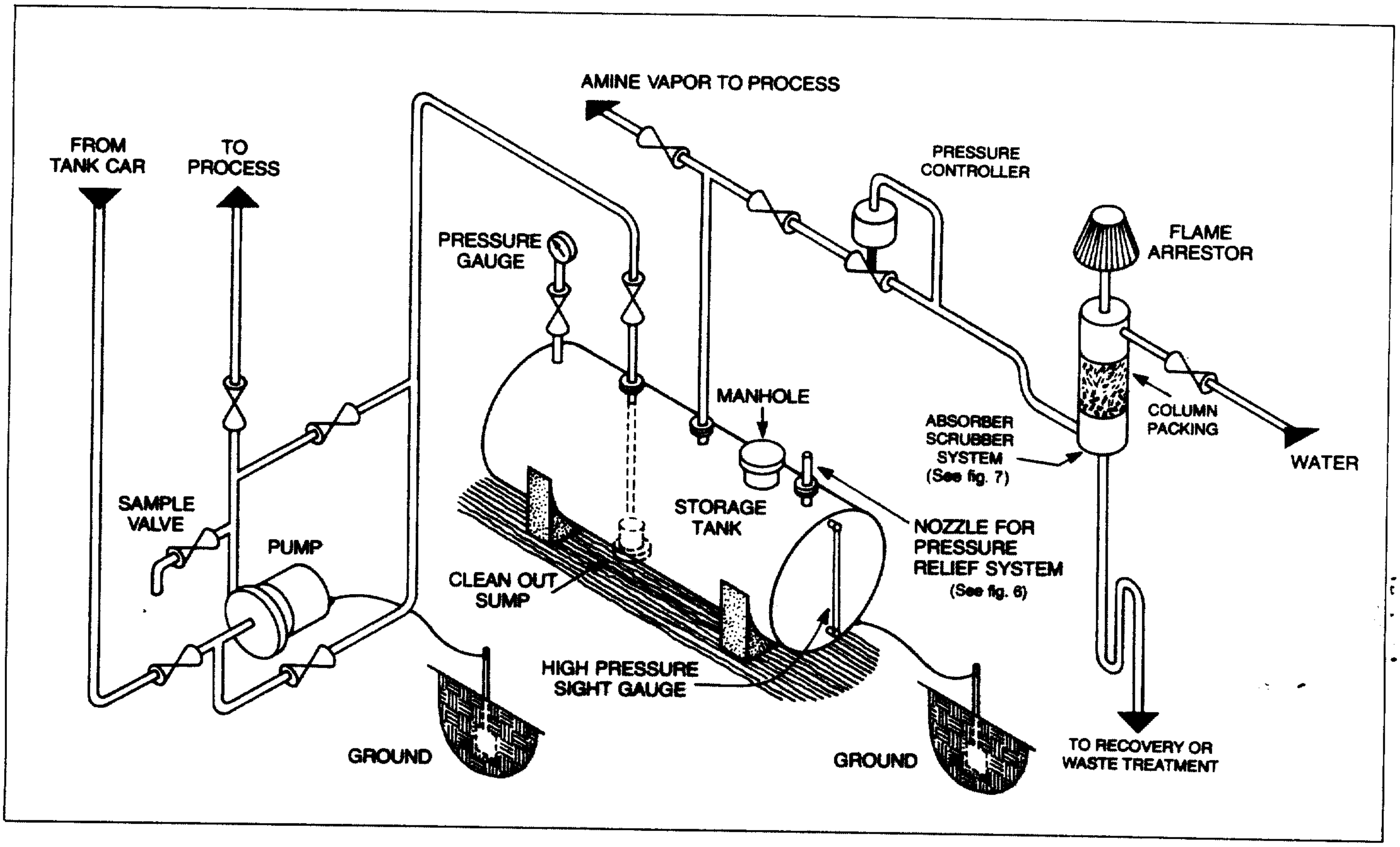
Figure 4
UNLOADING ANHYDROUS METHYLAMINES TANK TRUCK BY COMPRESSOR



UNLOADING NOTES

1. Driver will make hose connections. See Unloading Tank Truck section for important information on hose fittings.
2. Driver will open tank truck product and vent valves A and B.
3. Open vent line valves 1, 2, and 3 between storage tank and tractor mounted compressor.
4. Driver will start tractor mounted compressor.
5. Open product valves 5, 6 and 7, then slowly open valve 4 to commence flow. Storage tank vapor will be drawn by the tractor mounted compressor into the tank truck to pressure product into storage.
6. When unloading is complete, driver will shut off compressor and close truck valves. Close valves 1 through 7.
7. Bleed pressure from product and vapor hoses to vacuum system, then disconnect.

Figure 5
ANHYDROUS METHYLAMINE STORAGE TANK ARRANGEMENT



tions for truck cargo tanks used for anhydrous methylamines. Excess flow valves must be leak-free before shipment. These excess flow valves are designed to automatically close at a flow of 125 gpm or more, and therefore, are intended to close if a major leak occurs. Sometimes as flow is initiated, a surge of flow will cause the excess flow valve to close prematurely.

The truck valves are to be operated only by the drivers. Valves at 3 and 4 are opened first. Then the lever-operated excess flow valves are opened. Next the vapor manual valve is opened. Finally, the liquid manual valve is slowly opened. A surge of flow from opening the liquid valve too fast may cause the excess flow valve to snap shut prematurely. If the liquid excess flow valve closes prematurely, the driver must then close the liquid manual valve and repeat the procedure, opening the liquid manual valve more slowly.

The truck compressor must not be operated with the valves at A, B, 3 or 4 closed.

STORAGE OF ANHYDROUS METHYLAMINES

Anhydrous methylamines are stored in totally enclosed systems which exclude air.

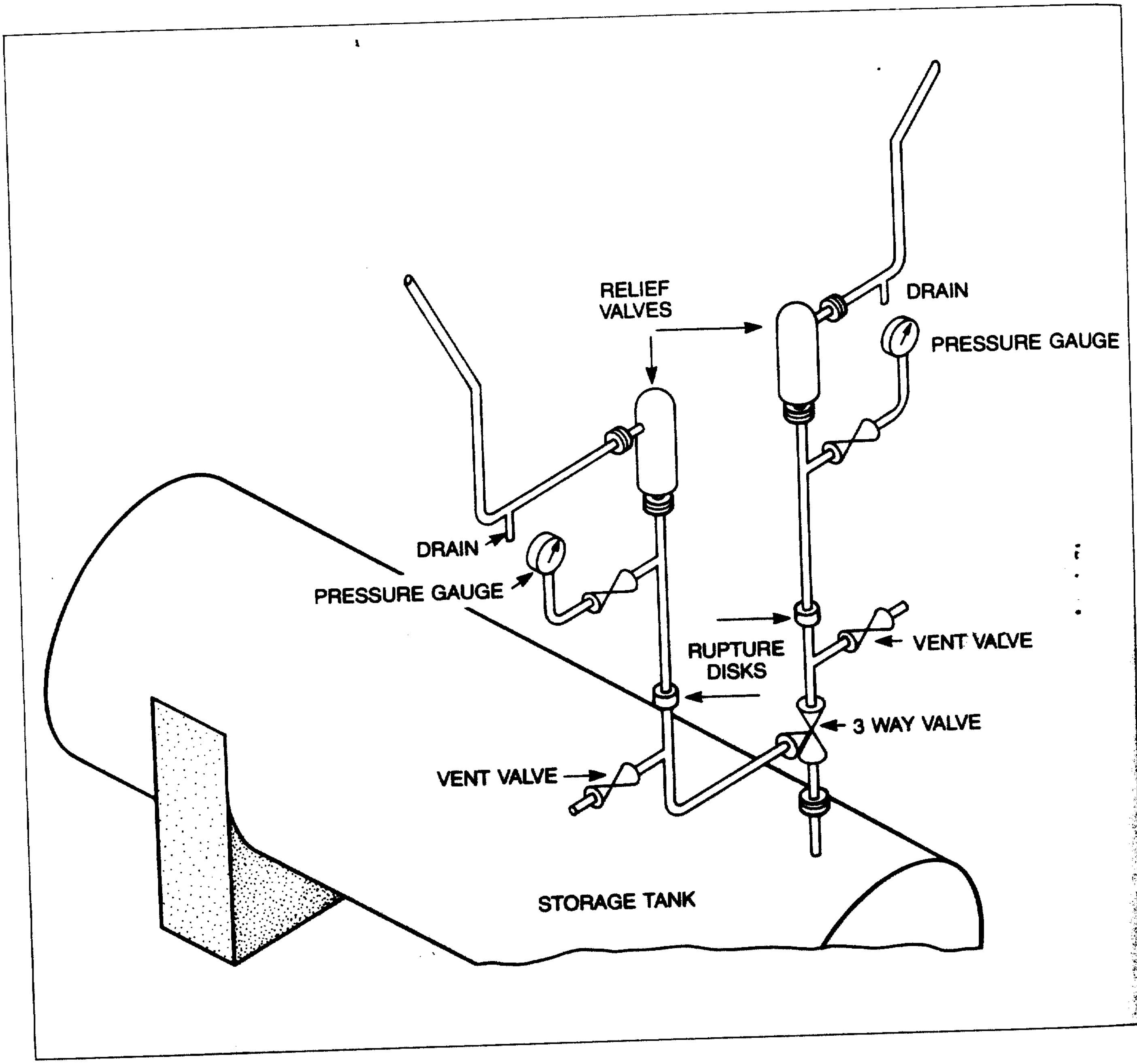
Storage Tank

Storage tank capacity of at least 1½ times the normal shipment is recommended to provide adequate inventory protection. Tank car shipments usually range from 10,000 to 30,000 gallons. Tanks should never be filled shell-full because of the high coefficient of expansion of methylamines. Leave at least 15 percent of the volume of the tank as vapor space for adequate protection.

Tanks containing anhydrous methylamines should conform to the latest ASME-API code for Unfired Pressure Vessels, as well as other local standards for pressure tank construction. A working pressure of 110 psig is suggested for design purposes. However, if the tank is heated, higher pressures may be encountered and must be specified in the design. Tanks should be hydrostatically tested at one and one-half times the design pressure before being placed in service.

Tanks are usually located out-of-doors. No insulation is required on anhydrous storage tanks unless pressure buildup from an outside source of heat is a problem. Dikes, drains and collection facilities for anhydrous methylamines must conform to Federal, state and local

Figure 6
PRESSURE RELIEF SYSTEM



regulations. Consult NFPA Standard No. 30, "Flammable and Combustible Liquids Code". A closed dike sufficient to hold the tank contents may be built. A three-sided dike about 18-inches high can be used to divert the tank contents into a safe drainage area or a waste pond.

Since methylamines are highly flammable, the entire storage system must be electrically grounded. This includes grounding tank cars and tank trucks by means of portable ground connectors. Piping flanges should be electrically bonded.

Grounding efficiency should be tested periodically by qualified electricians.

Tank Pressure Relief System

The recommended pressure relief system for an anhydrous methylamines storage tank is shown in Figure 6.

The exhaust stack should extend upwards, terminating with a 45 degree, long radius elbow directing the discharge away from operating areas. The bottom of each stack should have a drain hole for rainwater, pointed or piped away from areas of personnel exposure. The stack should be supported to handle potential reactive forces. Note the rupture disks which protect the relief valves from direct chemical attack or leakage. These disks should have stainless steel vacuum supports and a pressure rating equal to the relief valve pressure setting. The pressure gauge between the rupture disk and the relief valve in service should be checked regularly. Whenever leakage is detected, turn the three-way valve to the alternate relief stack and replace the leaking rupture disk.

Tank Accessories

Anhydrous storage tanks should be fitted with the following accessory equipment (see Figures 5, 6 & 7):

1. Dip tube on liquid inlet line, extending to within 6 inches of tank bottom.
2. Tank bottom connection or dip tube on liquid exit line. A line from the tank bottom permits easier tank emptying for repairs.
3. Sampling valve on liquid exit line.
4. Manhole.
5. Heavily constructed sight gauge, such as Penberthy Type-X or Jerguson type.
6. Safety pressure relief system (see Figure 6).
7. Pressure gauge; steel or stainless steel construction (no brass or copper alloy). A high pressure and high level alarm feature is desirable.
8. Vent connection to process scrubber or to an absorber.
9. Suitable walkway and platform for operating valves and for servicing relief valve system.
10. Vapor-proof electric lights if night operation is contemplated.
11. Safety showers and eye wash fountains close to the tank, carspot, sampling and pump locations.
12. Clean-out nozzle on bottom of tank if there is no other bottom connection.
13. Electrical ground connections on all tanks.

In the following list, specific vendors are mentioned for illustrative purposes only. Similar equipment made by other manufacturers can also be used with satisfactory results except as noted. Keep in mind that copper, copper alloys, aluminum, galvanized metal and zinc alloys should not be used in direct contact with methylamines.

- TANKS—ASTM A-285, Type C Carbon Steel, horizontal cylindrical with dished heads; 90 psig operating pressure at 122 F. Design for 110 psig minimum at 450 F. If tank is to be heated, a higher design pressure must be specified. Hydrostatic test at 1½ times design pressure. Capacity should be 1½ times the volume of a normal shipment. Suggested outage allowance for expansion is 15 percent of tank capacity. Insulation not required. Tank accessories as listed previously.
- **TANK PRESSURE RELIEF SYSTEM**—Relief valves and rupture disks as shown in Figure 6.
- **RELIEF VALVES**—Crosby Valve; Style JO, Type A; two piece disks, O-ring seats of TEFLON®.
- **THREE WAY VALVES**—Rockledge Valve Division of Stellar Manufacturing Co.; Figure 302B transfer valve, non-closing; 300 psi cast carbon steel body; ASTM A-182, Class P6 stainless steel trim.
- **PIPING**—½ inch through 1½ inch, Schedule 40, ASTM A-106 seamless, Grade A or B; 2 inch through 4 inch, Schedule 40, ASTM A-53 seamless, Grade A or B.
- **FITTINGS**—Butt welded carbon steel, ASTM A-234. All brass, copper zinc and aluminum fittings must be avoided in methylamines service.
- **FLANGES**—300 psi (rather than 150 psi); this design permits better pull-down on gaskets, minimizing leaks.
- **GASKETS**—Johns-Manville No. 78, a high quality, graphite-filled, Buna-bonded, compressed asbestos gasket.
- **VALVES**—Jamesbury DF 30S (22-36) TT, carbon steel body, Type 316 stainless steel ball and stem, seat and seals of TEFLON®.
- **HOSES**, Liquid—Resistoflex hose lined with TEFLON® with Type 304 stainless steel braid outer cover with coil spring; 1⅛-inch diameter, 12 feet long or 1¼ inch diameter, 15 feet long, rating 1,000 psig working pressure.
- **HOSES**, Vacuum—Gates ammonia hose 73B-HB; 1-inch diameter, 25 or 50 feet long.
- **HOSE FITTINGS**—200-lb rating Huber-Yale unions.
- **VAPOR COMPRESSOR**—Corken Model 290; carbon steel, O-rings of TEFLON®; piston rings made of carbon—TEFLON®.
- **FLOWMETERS**—Fischer and Porter armored rotameters are recommended for safety reasons. Orifice-type meters can be as reliable as rotameters if the orifice run is located in a vertical position to insure degassing. Turbine and vortex type flowmeters also have been used successfully in anhydrous amine service. In any flow measuring system, flashing of the liquid into vapor must be avoided to maintain the accuracy of the instrument.

UNLOADING AND TRANSFER OF AQUEOUS METHYLAMINES

Du Pont ships aqueous methylamines in tank cars, tank trucks and 55-gallon drums. The U.S. Department of Transportation (DOT) classifies aqueous methylamines as flammable liquids.[5]

Tank Cars and Tank Trucks

Refer to the tank car unloading instructions on page 9 before making any connections to the tank car. Facilities should be in compliance with OSHA requirements (29 CFR 1910.106, Flammable and Combustible Liquids) and with applicable state and local regulations. The recommended method of unloading methylamine solutions is from the top of the tank car to a storage tank using a pump for transfer. Unloading by nitrogen pressure may also be used. DO NOT USE COMPRESSED AIR TO UNLOAD METHYLAMINES UNDER ANY CIRCUMSTANCES.

Unloading by Pump

Methylamine solutions are unloaded using the same general arrangement and procedure used for anhydrous amines (see Figure 1).

The advantages of using a pump to unload are less operator attention and lower cost per tank car unloaded. Any self-priming centrifugal pump of steel construction with good suction characteristics and a suitable mechanical seal may be used. A "canned," "seal-less" centrifugal pump is particularly useful since it avoids shaft sealing problems. The seal-less pump must be primed with nitrogen pressure on the tank car. ***A low level or low-flow cut-off is required as this type pump is easily damaged if run dry.***

The pump can be located either on the tank car unloading platform or on the ground. It is important to keep the pressure drop between the tank car and the suction of the pump as low as practical. This can be accomplished by keeping the suction line short and using as few valves and bends in the line as possible. Bends should be of the long radius variety. A 3-inch diameter suction pipe is recommended. To achieve lowest possible pressure drop, the valve on the suction line should be a ball or gate valve rather than the globe type.

Unloading by Nitrogen Pressure

Nitrogen pressure may be used to unload methylamine solutions but is not preferred because stopping the flow from an accidental leak is difficult. The number of cylinders required per unloading depends on the size of the tank car. A 10,000 gallon tank car normally requires 12 cylinders (224 cubic feet). A liquid nitrogen cylinder with suitable accessories also may be used.

The same general arrangement and procedure is used as for anhydrous amines (see Figure 3). The unloading rate will be determined by the nitrogen pressure on the car. Methylamine solutions are usually shipped in low pressure cars which have been tested to 60 psig. Nitrogen pressure should not exceed 25 psig during unloading. The test and relief valve pressures are stenciled on each tank car. A pressure relief valve set at 25 psig should be located in the nitrogen line between reducing valve and car.

Following is a suggested list of facilities and equipment necessary for unloading amine solution tank cars with nitrogen pressure:

1. Concrete pad or other suitable flooring for nitrogen cylinder storage area.
2. Chain support for safely holding nitrogen cylinders upright.
3. Nitrogen manifold and pressure reducer (purchased from a nitrogen supplier) to include:
   a. Flexible steel tubing pigtails; working pressure 2,000 psig; special adapters to fit nitrogen cylinders.
   b. Manifold steel valves; working pressure 2,000 psig.
   c. Standard nitrogen pressure reducing valve for maintaining constant pressure on tank car. Two pressure gauges are required to show cylinder and tank car pressure.
4. Check valve—¾-inch. Equipment must be all iron construction from this point to the tank car. (Avoid use of parts made from copper or aluminum alloys.)
5. Neoprene gas hose—¾-inch for connecting nitrogen line to vent valve on tank car. Hose should be able to withstand 100 psig pressure.
6. Flexible unloading hose—2-inch diameter, Gates Rubber Company, Type 73 HB for liquid solution.
7. 2-inch steel unloading line.
8. 2-inch gate valves or ball valves in the liquid piping.

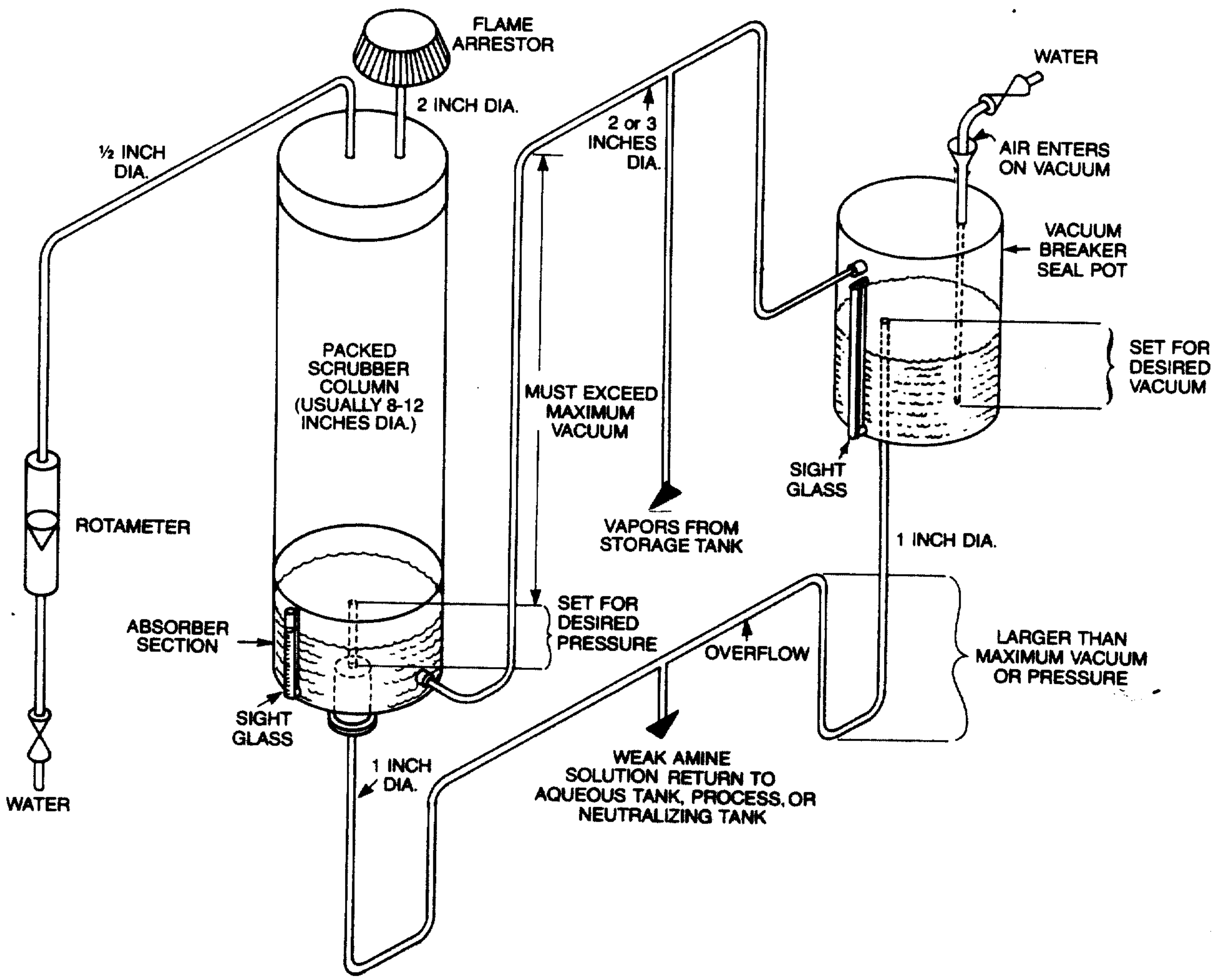
DRUM HANDLING

Receipt

Upon arrival, check the car or truck for the odor of methylamines and ventilate the vehicle if necessary before removing any drums. Remove any leaky drums to a safe location where the leak can be corrected or the drum immediately emptied.

Drums should be arranged in storage to facilitate stock rotation. Long term storage of any given drum is minimized by following a first-in, first-out schedule.

Figure 7
VENT SYSTEM



OPERATING NOTES

1. When pressure venting occurs over a sustained period of time, such as when a tank car is being unloaded, set the desired flow of water to the vent absorber to prevent escape of amine odor. The water will collect in the bottom seal pot and will overflow through the overflow seal leg to the aqueous storage tank or other vessel.

   Vent gas will bubble through the liquid in the bottom of the pot, and will be scrubbed by the fresh water before leaving the vent. The depth of water in the bottom determines the seal pressure—normally 4-8 inches is specified.

   The vacuum seal pot does not function under pressure except that the inlet line for water or air serves as a seal, and therefore must have sufficient height to avoid overflow. The exit overflow leg also is a seal and must be deep enough to hold the specified pressure without blow-through.
2. On vacuum, when the tank is being emptied, the pressure seal pot is sealed off by liquid backing up into the inlet line. Air is drawn into the vacuum seal pot through the water addition leg and flows into the tank.
3. Water level in both seal pots can be checked by inspection of the sight glass. The seal pot can be drained if desired by the usual drain valve on the bottom of the sight glass. In cold climates protection against freezing is required.
4. A valve in the tank vent line will allow the seal pot system to be closed off when the tank is not delivering or receiving aqueous methylamines.

Storage

Keep storage areas cool and dry. Protect the drums from direct heating by the sun, steam lines or other sources of heat. Methylamine drums should be stored at a temperature below the boiling point of the contents (see page 2) to prevent building positive pressure. No sources of sparks or flames should be allowed in storage areas. Use only vapor proof lighting fixtures and spark proof electrical equipment. Insure that the area is well-ventilated. A storage area containing aqueous trimethylamine, may require some safe heating equipment to avoid frozen drums in cold weather. DO NOT USE open flame, gas fired heaters.

Transfer

Before opening a drum, be sure that it is blocked, supported and electrically grounded. Drums should be opened with nonsparking tools and should not be struck with tools or other hard objects. Operators should wear chemical safety goggles, full face shield, protective clothing and rubber gloves when opening the drums. Where possible, transfer methylamine solutions from drums directly into a closed system.

Good ventilation must be provided since opening the drums will release some vapor to the atmosphere. Observe OSHA standards (see page 1).

Start the plug with a plug or bung wrench and slowly open one full turn. Allow any internal pressure which may be present to vent before removing the plug completely. Drums should be emptied by gravity or with a methylamine-resistant siphon. Never apply pressure or steam to the drum. After emptying a drum it should be rinsed thoroughly with water until free of all odor before disposal or re-use.

STORAGE OF METHYLAMINE SOLUTIONS

Storage tanks for aqueous methylamines (except 60% DMA) should be designed for an operating pressure of 15 psig. Minimum design pressure for tanks containing 60% DMA solution is 35 psig. Steel storage tanks are recommended. Tanks and vessels must be properly vented, taking into account normal breathing requirements, anticipated maximum filling and emptying rates and an emergency relief system in case of external exposure to fire. All vents should be piped to a safe location outside the building so that flammable vapors will not be trapped by eaves and other obstructions within the building.

Individual storage tanks of 10,000 gallons or greater capacity should be diked. State or local regulations may require diking of smaller tanks. Consult 29 CFR 1910.106 for applicable OSHA construction requirements for flammable and combustible liquid storage. Detailed recommendations on drainage dikes and walls for aboveground storage tanks appear in Section 2170 of NFPA Standard No. 30 "Flammable and Combustible Liquids Code."

Bubble type manometers, differential pressure level gauges or armored sight gauges with ball check and shut-off valves (e.g., Penberthy X-500 reflux type glass) may be used to measure the storage tank level.

Transfer from storage can be accomplished using a "canned" sealless pump. **A low level or low flow cut-off is required for sealless pumps because these pumps are easily damaged if run dry.** Centrifugal pumps with a mechanical seal are satisfactory.

Tanks, pumps and lines for 25% TMA should be insulated and heated in areas where freezing of these solutions may occur. Heating may be provided by steam heating panels on the tank and steam tracing of the lines. Temperature controls must be provided to prevent excessive pressure caused by overheating.

To minimize the obnoxious odor of methylamines from vents, all vents should pass through an absorber-scrubber before discharging to the atmosphere. Minimum atmospheric pollution is achieved by the installation of a vent absorber and seal pot as shown in Figure 7. For additional information on vent scrubber design, contact your nearest Du Pont sales office listed on the back cover.

Storage tanks should be grounded to avoid accumulation of a static charge. See Figure 8 for a satisfactory storage tank arrangement for methylamine-water solutions.

ON-SITE DILUTION OF ANHYDROUS METHYLAMINES

Many users of aqueous methylamines have installed facilities permitting them to dilute anhydrous amines at their site. This avoids the freight on water shipped with solutions. Attractive savings are often possible through purchase of anhydrous amine rather than the aqueous solution.

Diluting anhydrous methylamines produces substantial heat of solution. The necessary heat removal is usually accomplished by an external heat exchanger or by internal cooling coils in the storage tank. A simple, effective arrangement for preparing solutions is shown in Figure 9. This system includes a properly designed aqueous storage tank and a circulation loop through the heat exchanger. Anhydrous methylamine is fed into the circulating line directly upstream of the solution cooler. Other operating modes employing similar equipment have also been successfully used.

Sizing of the storage tank depends on the volume of anhydrous methylamine delivered and the required concentration of the methylamine-water solution. For example, 10,000 gallons of anhydrous dimethylamine (the smallest tank car) dilutes to approximately 12,500 gallons of 60% aqueous solution or to approximately 17,500 gallons of 40% aqueous solution.

Du Pont will assist customers in their design of methylamines dilution facilities. This assistance includes a review of alternate operating modes tailored to the customer's site. For additional information, contact your nearest Du Pont sales office listed on the back cover.

Figure 8
AQUEOUS METHYLAMINES STORAGE

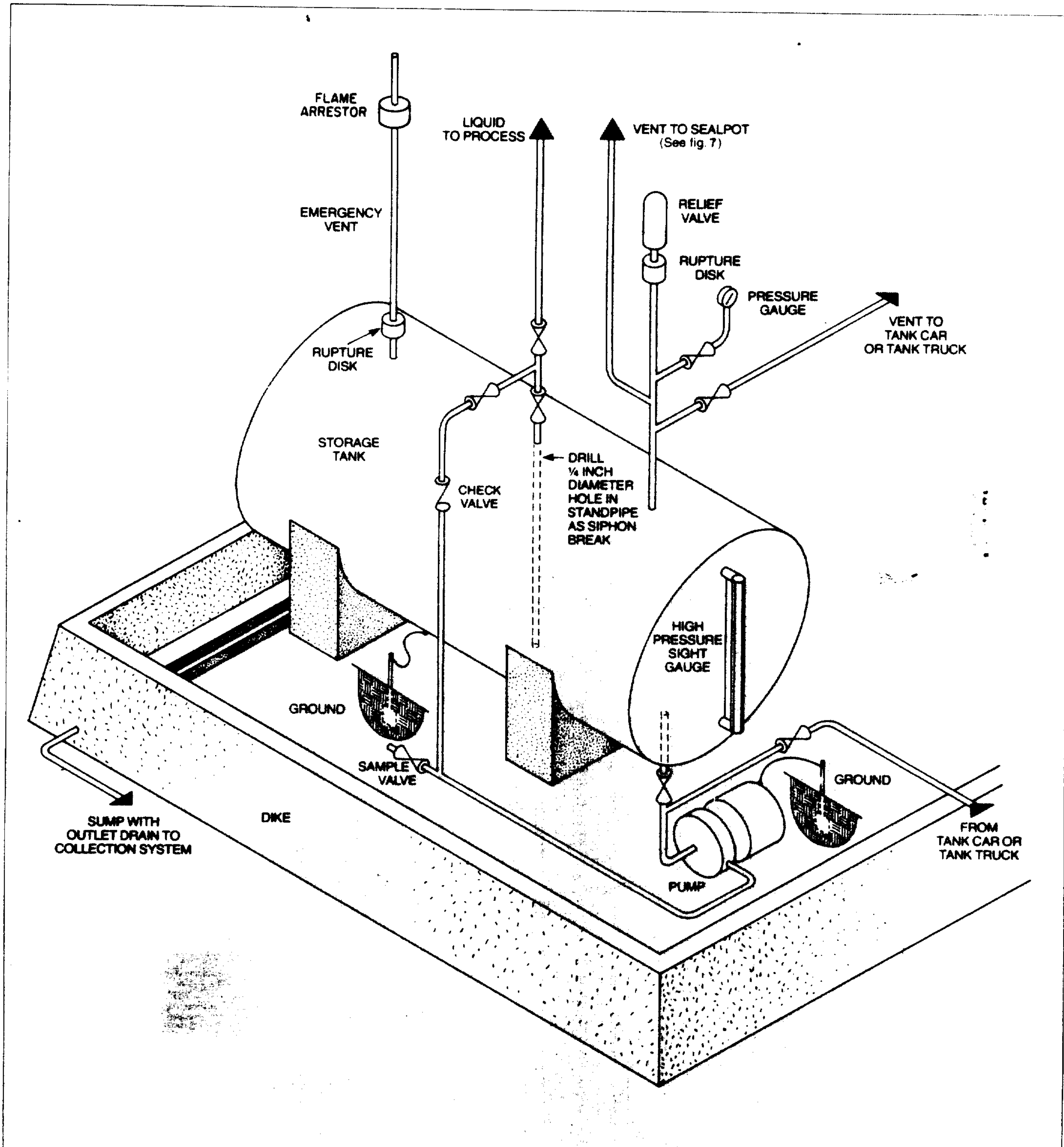
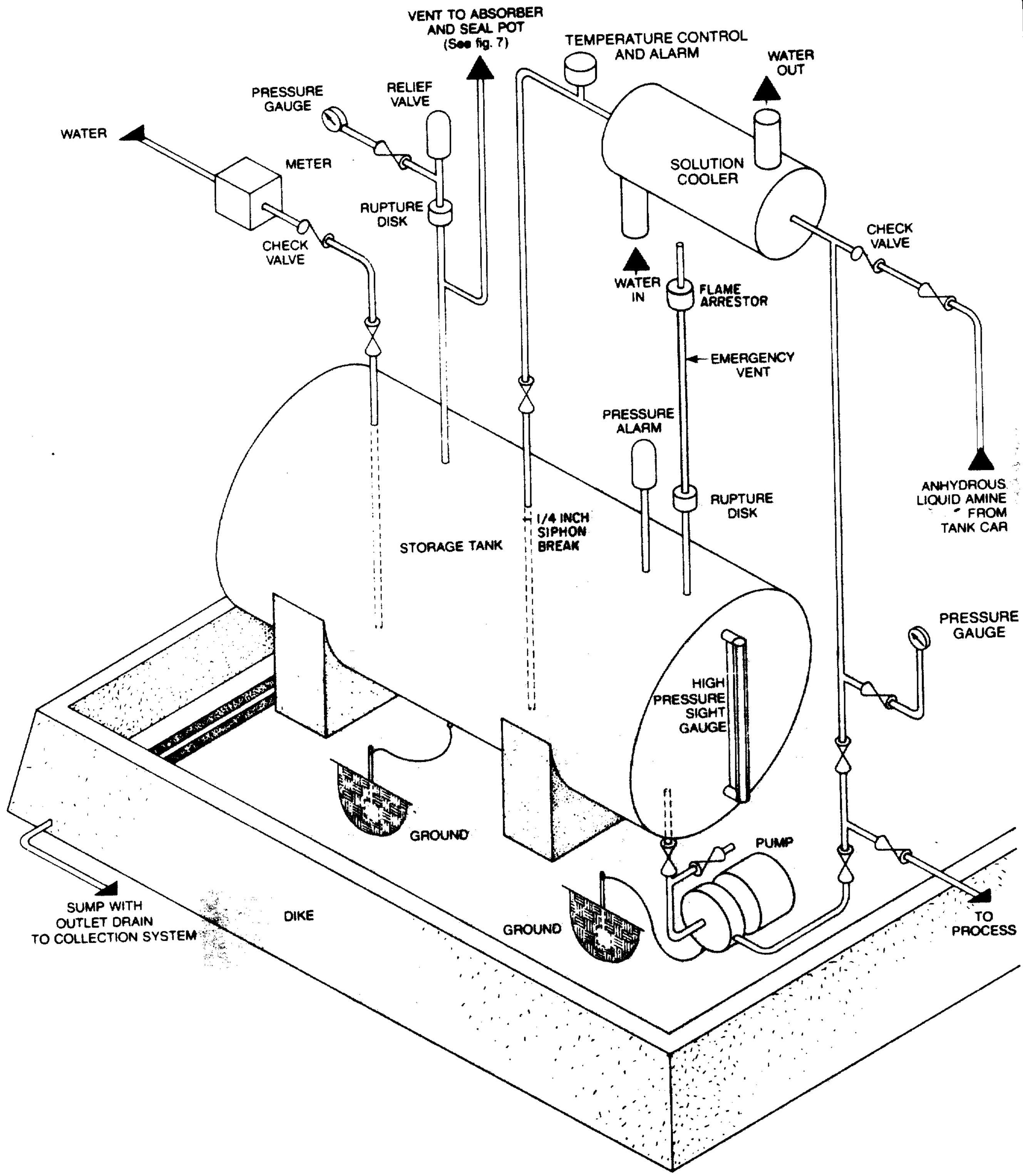


Figure 9
METHYLAMINE DILUTION SYSTEM



WASTE DISPOSAL

Handling Leaks and Spills

The potential for accidental leaks and spills of methylamines should be reviewed and plans made in advance for containment, drainage, collection and disposal.

Immediate steps should be taken to stop a methylamines leak provided it can be done without risking personal injury.

Water is particularly useful in handling methylamines leaks and spills. Properly applied, water will:

- reduce vapors (applied as a spray)
- protect personnel shutting off a leak (applied as a spray)
- flush spills away from hazardous exposures
- dilute the spill and raise the flash point.

It should be noted, however, that methylamines have high vapor pressures and even dilute aqueous solutions have relatively low flash points and are flammable.

Personnel must be kept upwind of leaks and evacuated from downwind areas. The affected area should be isolated until the vapor cloud (gas) has dispersed. All sources of ignition—open flame, sparks, vehicles—should be eliminated. The following personal safety precautions should be observed when handling leaks and spills

- Do not approach the vapor cloud until the danger of fire has passed
- Wear proper protective equipment
- Avoid contact of liquid or vapor with eyes, skin or clothing
- Use water or water spray to absorb or flush away small leaks

Small leaks should be located promptly and repaired before they intensify. The first indication of a leak in the system is usually the presence of the distinctive amine odor The source of the odor can be readily pin-pointed by using a sulfur dioxide (SO_2) lecture bottle fitted with a small ball valve and a three-foot length of stainles steel tubing Sulfur dioxide and methylamine vapor combine to produce a thick, white fog at the point of the leak.

Air Pollution Control

The control of air pollution in the manufacture and handling of methylamines is very important. To avoid odors and minor air pollution problems when disconnecting unloading hoses or when disconnecting piping for maintenance, care should be taken to prevent spills of liquid amines. Use nitrogen pressure to blow lines and hoses clear to the storage tank. Then, with the valves shut off, evacuate the lines by vacuum pump, steam jet or water jet eductor. A running water hose should be available when hoses or pipes are disconnected. The water will promptly absorb vapors and flush away drops of liquid. Decontaminate hoses, piping and accessory equipment by thoroughly flushing with water until no odor remains. (See Waste Water below).

Four air pollution control methods are currently in use at various locations among the producers and users of methylamines. The most successul and economical method involves the collection of all methylamine vapors into a vent system equipped with an absorber-scrubber unit. As shown in Figure 7, the vented vapors from a storage tank are contacted with cold water in a scrubber column. When large volumes of amine vapors are absorbed, it is often practical to recover the amines by distillation. Amines can also be recovered by using the absorber effluent as an amine solution.

A second method consists of feeding methylamine vapors to a small scrubber column packed with pall rings using a 5 percent sulfuric acid solution as the scrubbing medium. The recirculating scrubbing medium is maintained at pH 4 by the periodic addition of acid. When the acid solution becomes saturated with amine sulfate, it is trickled into a waste treatment sewer. Care must be taken that the saturated solution does not run into a heavy concentration of sodium hydroxide or other neutralizing solution which will liberate the amine.

Another method disposes of methylamine vapors by catalytic oxidation. A platinum catalyst supported on inlet wires is used in the presence of air as the oxidizing agent. A preheater must be used to bring the gases to the reaction temperature of approximately 310 C.

The fourth method consists of flaring the gathered amines with fuel gas. Total destruction of the methylamine vapors is accomplished in a properly designed flare stack.

Waste Water

Waste water containing small amounts of methylamines must be disposed of by procedures which comply with Federal, state and local water pollution regulations. Very dilute solutions have been successfully treated in biological oxidation waste treatment systems. It is sometimes economical to recycle or recover amines from scrubber effluents, evacuation systems or from waste water collected in washing down spills and leaks.

SOURCES OF EQUIPMENT

The following is a partial list of the manufacturers of equipment for methylamines storage and handling systems. Specifying these products does not imply an unqualified recommendation by the Du Pont Company; there are undoubtedly others of similar type which may be equally or better suited for the purpose.

AMINE DETECTION EQUIPMENT

Mine Safety Appliances Company
600 Penn Center Blvd.
Pittsburgh, PA 15235

FLOWMETERS

Fischer & Porter Company
51 Warminster Road
Warminster, PA 18974

The Foxboro Co.
86 Neponset Ave.
Foxboro, MA 02035

GASKETS

Garlock Inc.
Mechanical Packing Div.
1666 Division Street
Palmyra, NY 14522

Crane Packing Co.
6410 Oakton Street
Morton Grove, IL 60053

Manville Corp.
Industrial Products Div.
Ken-Caryl Ranch
Denver, CO 80217

GAUGES (PRESSURE)

Taylor Instrument Co.
Div. of Sybron Corp.
Olson and Ames Streets
Rochester, NY 14601

Meriam Instrument Div.
Scott & Fetzer
10978 Madison Avenue
Cleveland, OH 44102

Moeller Instrument Co.
Ivoryton Industrial Park
Ivoryton, CT 06442

GAUGES (SIGHT)

Penberthy Div.
Houdaille Industries, Inc.
P.O. Box 112
Prophetstown, IL 61277

Jerguson Gage & Valve Co.
15 Adams Street
Burlington, MA 01803

HOSE CONNECTORS (Huber-Yale Unions)

J. M. Huber Corp.
P.O. Box 2831
Borger, TX 79007

HOSES (Liquid)

Resistoflex Corp.
Woodland Road
Roseland, NJ 07068

HOSES (Vapor)

Gates Rubber Co.
999 South Broadway
Denver, CO 80217

PUMPS (Centrifugal)

Crane Company
Chempump Products Div.
Dept. TR, Warrington Industrial Park
Warrington, PA 18976

Kontro Co. Inc.
450-T W. River St.
Orange, MA 01364

Pacific Pumps Div.
Dresser Industries Inc.
5715-T Bickett St.
Huntington Park, CA 90255

PUMPS (Reciprocating)

Worthington Group
McGraw Edison Co.
270 Sheffield Street
Mountainside, NJ 07092

PUMPS (Self-Priming)

Duriron Co. Inc.
N. Findlay & Thomas Sts.
Dayton, OH 45401

RUPTURE DISKS

Black, Sivalls and Bryson, Inc.
BS&B Process Systems Div.
8303-T Southwest Frwy.
Houston, TX 77027

SAFETY VENTS

Oceco Div.
Pettibone Corp.
4720 W. Division St.
Chicago, IL 60651

The Protectoseal Co.
227 Foster Ave.
Bensenville, IL 60106

Varec Div.-Emerson Electric
11842 Monarch St.
Garden Grove, CA 90247

SIGHT FLOW INDICATORS

Jacoby-Tarbox Corp.
818 Nepperhan Ave.
Yonkers, NY 10703

Pressure Products Co., Inc.
P.O. Box 6656 Dept. TR-1
Charleston, WV 25302

SULFUR DIOXIDE LECTURE BOTTLES

Matheson Div.
Searle Medical Products, USA
P.O. Box 96
Joliet, IL 60434

VALVES

Jamesbury Corp.
640 Lincoln Street
Worcester, MA 01605

A. O. Smith Corp.
Dept. T. P.O. Box 484
Newark, CA 94560

Henry Vogt Machine Co. Inc.
PO Box 1918
Louisville, KY 40201

VALVES (Pressure Control)

Fisher Controls Co.
PO Box 900-TR
McKinney, TX 75069

VALVES (Three-Way)

Stellar Mfg. Co.
Rockledge Valve Div.
120-T Ferry Ave.
Collingswood, NJ 08108

VALVES (Relief)

Crosby Valve Div., Geosource Inc.
Dept. TR, PO Box 308
Wrentham, MA 02093

REFERENCES AND NOTES

(1) R. W. Gallant, "Physical Properties of Hydrocarbons, Part 33-Methylamines," Hydrocarbon Processing (April 1969)

(2) G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants," 14th Edition, (1973)

(3) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-3, (January 1968)

(4) Texas A&M University Thermodynamic Research Center, "Selected Values of Chemical Compounds," Volume I.

(5) Due to changing governmental regulations such as those of the Department of Transportation, Department of Labor, U.S. Environmental Protection Agency and the Food and Drug Administration, references herein to governmental requirements may be superseded. Each user should consult and follow the current governmental regulations, such as Hazard Classifications, Labeling, Food Use Clearances, Worker Exposure Limitations and Waste Disposal Procedures for the up-to-date requirements.

(6) "MSA" is a registered trademark of Mine Safety Appliances Company, 600 Penn Center Blvd., Pittsburgh, PA 15235.

(7) "A Guide to Industrial Respiratory Protection," HEW Pub. No. (NIOSH) 76-189.

(8) Available as NFPA No. 70 from National Fire Protection Association, 470 Atlantic Ave., Boston, MA 02210

(9) J. Nat. Cancer Instit., *49*, 1239 (1972)

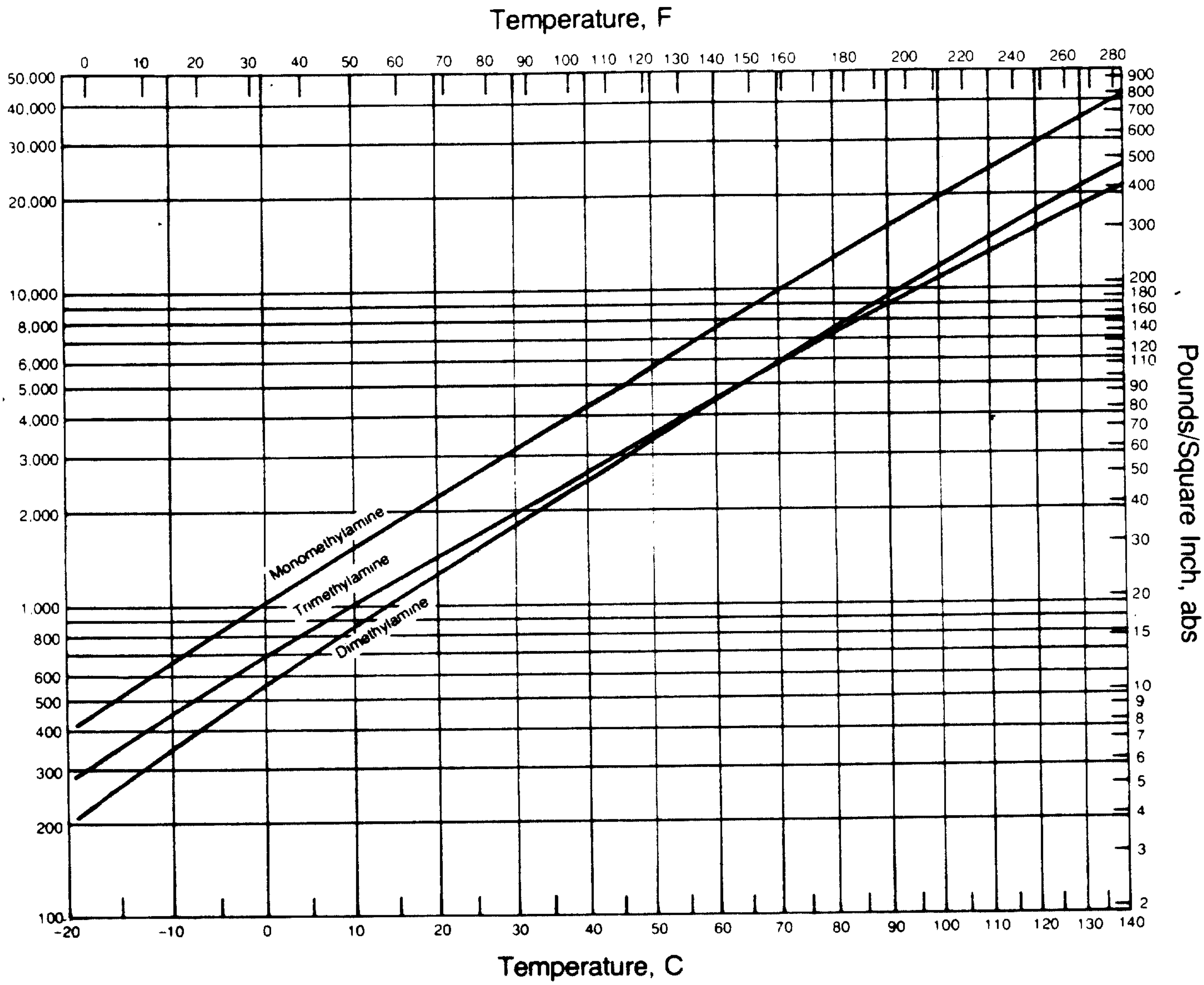
(10) Environmental Protection Agency Publication 600/6-77-001, "Scientific and Technical Assessment Report on Nitrosamines", EPA Office of Research and Development, (Nov. 1976)

(11) Compressed Gas Association, Inc., 500 Fifth Ave., New York, NY 10036

(12) "Chempump" is a registered trademark of Crane Company

(13) Available from National Foam System, Inc., Lionville, PA 19353

VAPOR PRESSURE OF ANHYDROUS METHYLAMINES



PHYSICAL PROPERTIES OF ANHYDROUS METHYLAMINES

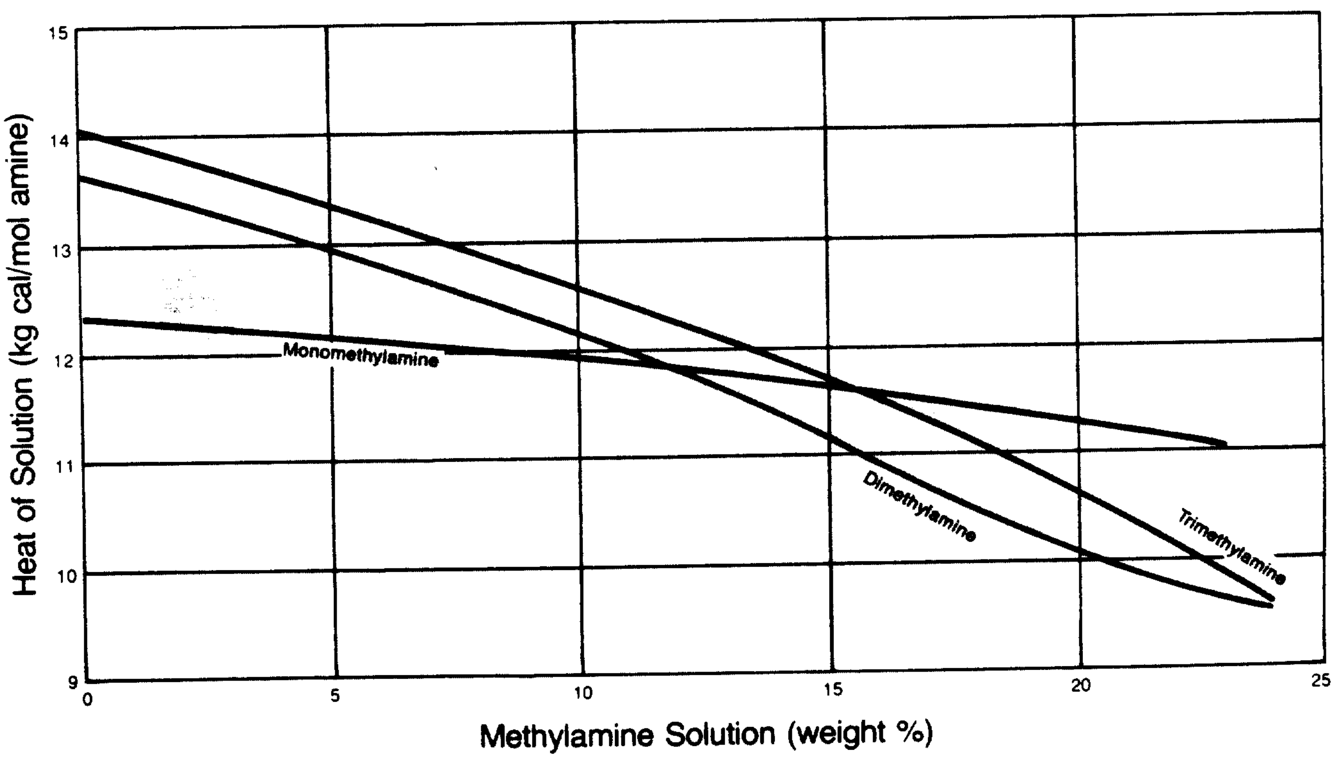
	Anhydrous Methylamine		
	MMA	DMA	TMA
Chemical formula	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
Molecular weight	31.06	45.08	59.11
Freezing point, C	−93.5	−92.2	−117.3
(in air at 1 atm) F	−136.2	−133.9	−179.1
Boiling point, C	−6.3	6.9	2.9
F	20.6	44.4	37.2
Vapor density at 1 atm (25 C, 77 F), g/liter	1.27	1.84	2.42
Vapor density relative to air (air = 1)	1.07	1.55	2.04
Liquid density at sat'n pressure (25 C, 77 F), g/mL (Mg/m^3)	0.6562	0.6496	0.6270
lb/gal	5.48	5.42	5.23
Refractive index at sat'n pressure, n_D^{25}	1.3491	1.3566	1.3443
Liquid viscosity (25 C, 77 F), cP(mPa•s)	—	0.190	0.175
Critical temperature, C	156.9	164.5	160.1
Critical pressure, atm	73.6	52.4	40.2
Enthalpy of formation, ΔH_f° (298.15 K, 25 C), kcal/mol			
—gas	−5.49	−4.41	−5.81
—liquid	−11.3	−10.5	−11.0
—solution (1000 moles H_2O)	−16.78	−17.3	−18.6
Gibbs energy, ΔG_f° (298.15 K, 25 C), kcal/mol			
—gas	7.67	16.35	23.65
—liquid	8.5	16.7	24.1
Heat capacity, C_p° (298.15 K, 25 C), cal/C•mol			
—gas	12.7	16.9	21.9
—liquid	—	32.9	32.31
Entropy, S° (298.15 K, 25 C) cal/C•mol			
—gas	58.15	65.24	68.6
—liquid	35.90	43.58	49.8
Heat of fusion (mp),			
cal/g	47.20	31.50	26.46
Btu/lb	84.96	56.70	47.63
kJ/kg	197	132	111
Heat of vaporization (bp),			
cal/g	198.6	140.4	92.7
Btu/lb	357.5	252.7	166.9
kJ/kg	831	587	388
Gibbs energy of solution, ΔG_f° (molality = 1; 25 C), kcal/mol	4.94	13.85	22.22
Entropy of solution, S° (molality = 1; 25 C), cal/C•mol	29.5	31.8	31.9
Autoignition temperature, C	430	400	190
F	806	752	374
Flammable limits, vol %			
—lower	4.9	2.8	2.0
—upper	20.7	14.4	11.6

SOLUBILITY OF ANHYDROUS METHYLAMINES

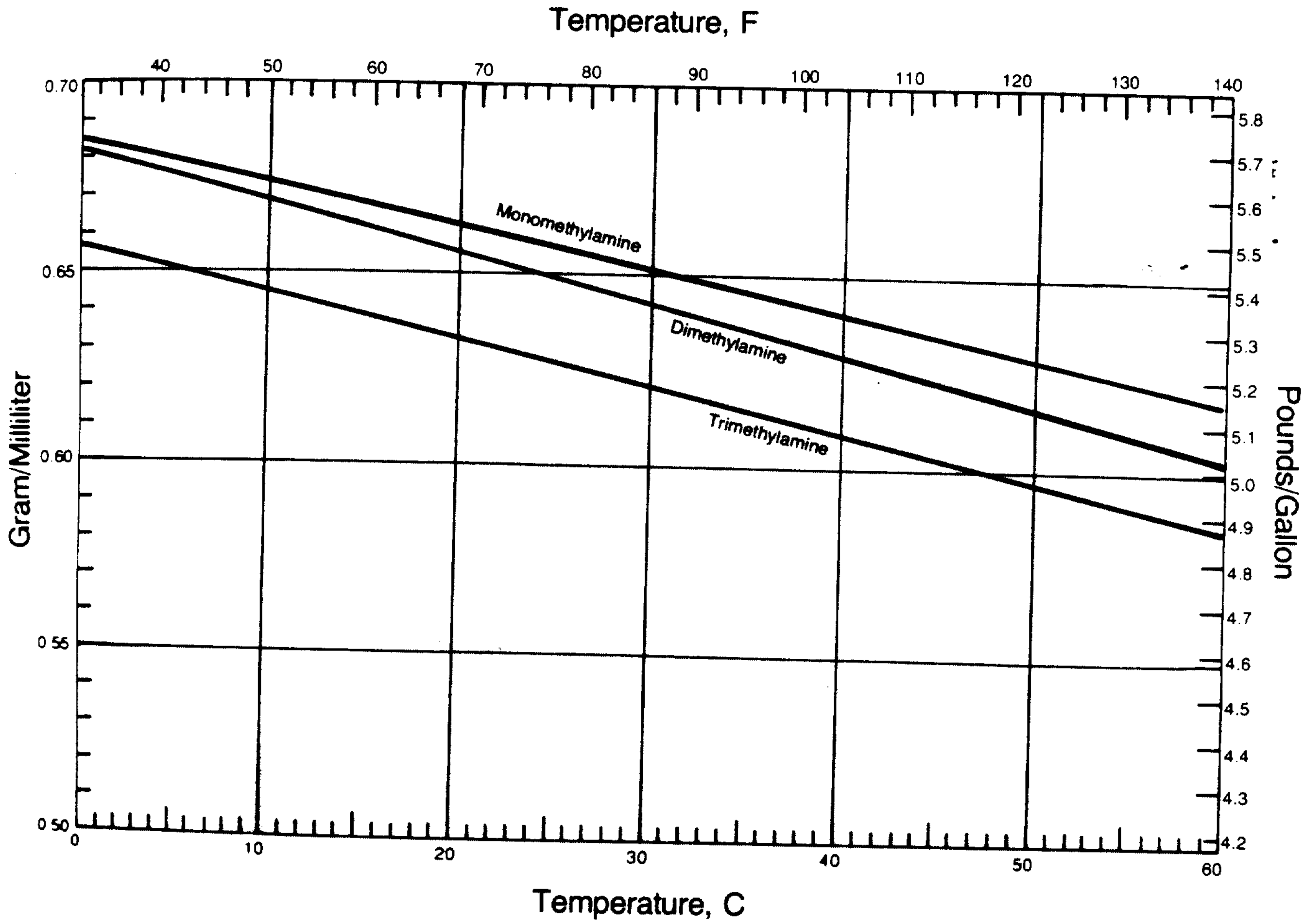
milliliters of gaseous amine per milliliter of solvent
measured at 1 atmosphere and 20 C (68 F)

Solvent	MMA	DMA	TMA
Aniline	228	516	330
Anisole	89	252	185
Benzyl alcohol	314	528	322
i-Butanol	298	598	405
n-Butanol	303	504	379
Cymene	48	182	177
Diacetone alcohol	420	457	345
Dibenzylether	115	154	120
o-Dichlorobenzene	64	252	240
Diethanolamine	313	497	74
Diethylaniline	60	180	134
Dimethylaniline	64	230	149
Dimethylcyclohexylamine	67	187	187
Dimethylformamide	132	298	78
Ethanol	440	727	600
Ethylene glycol	630	860	369
Furfuryl alcohol	413	679	410
Methanol	654	992	573
Methylcyclohexanol	219	439	256
Monoethanolamine	216	379	48
Monoethylaniline	113	324	228
Monomethylaniline	197	406	223
Morpholine	255	580	138
Nitrobenzene	88	226	154
o-Nitrotoluene	86	221	149
Pinene	34	156	176
n-Propanol	339	600	439
Quinoline	92	212	255
o-Toluidine	88	430	242
Triethylene glycol	316	488	164
Trimethylene glycol	480	722	307
Water	1,180	1,990	660

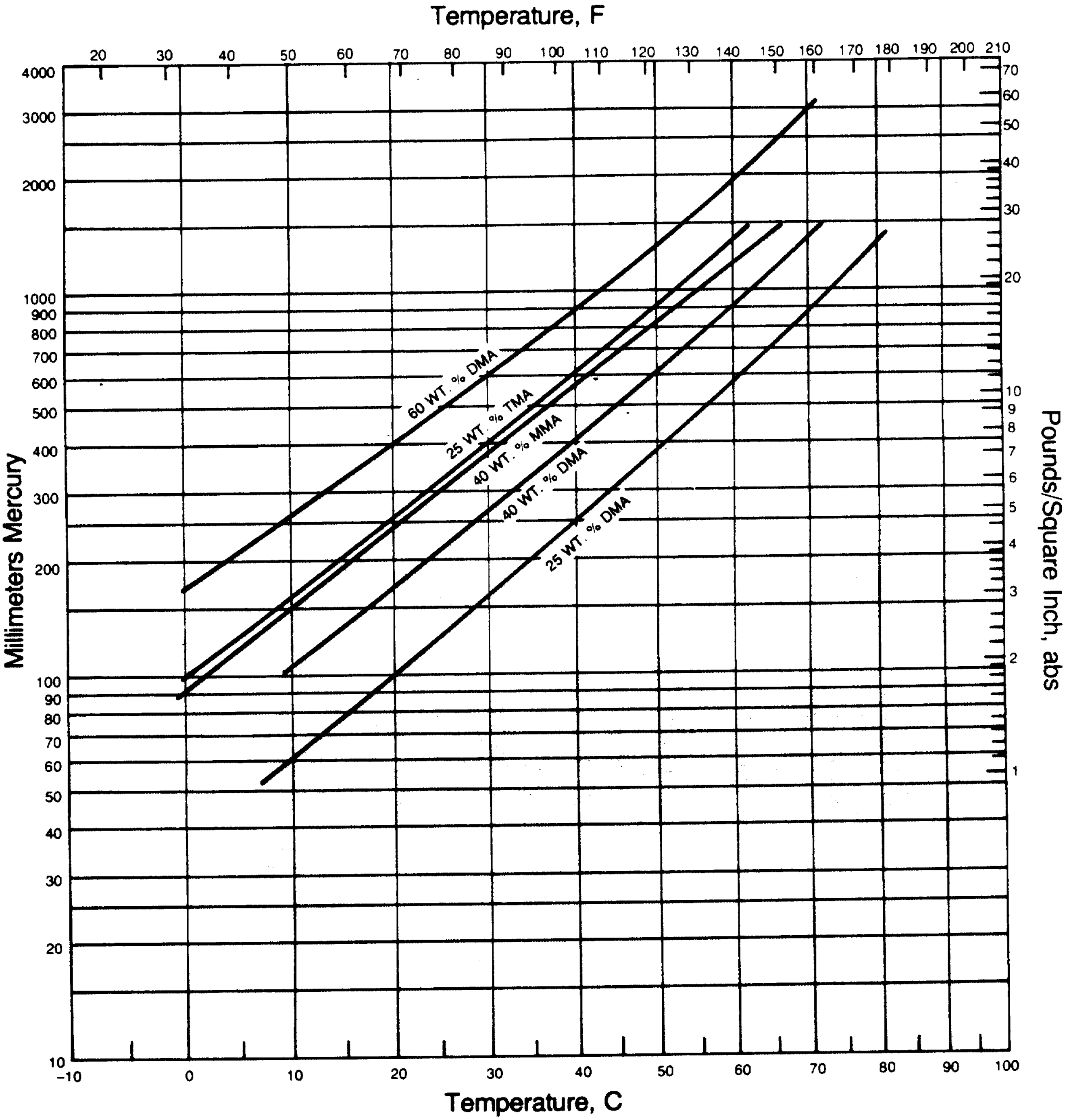
HEAT OF SOLUTION OF GASEOUS METHYLAMINES IN AQUEOUS SOLUTION AT 25 C



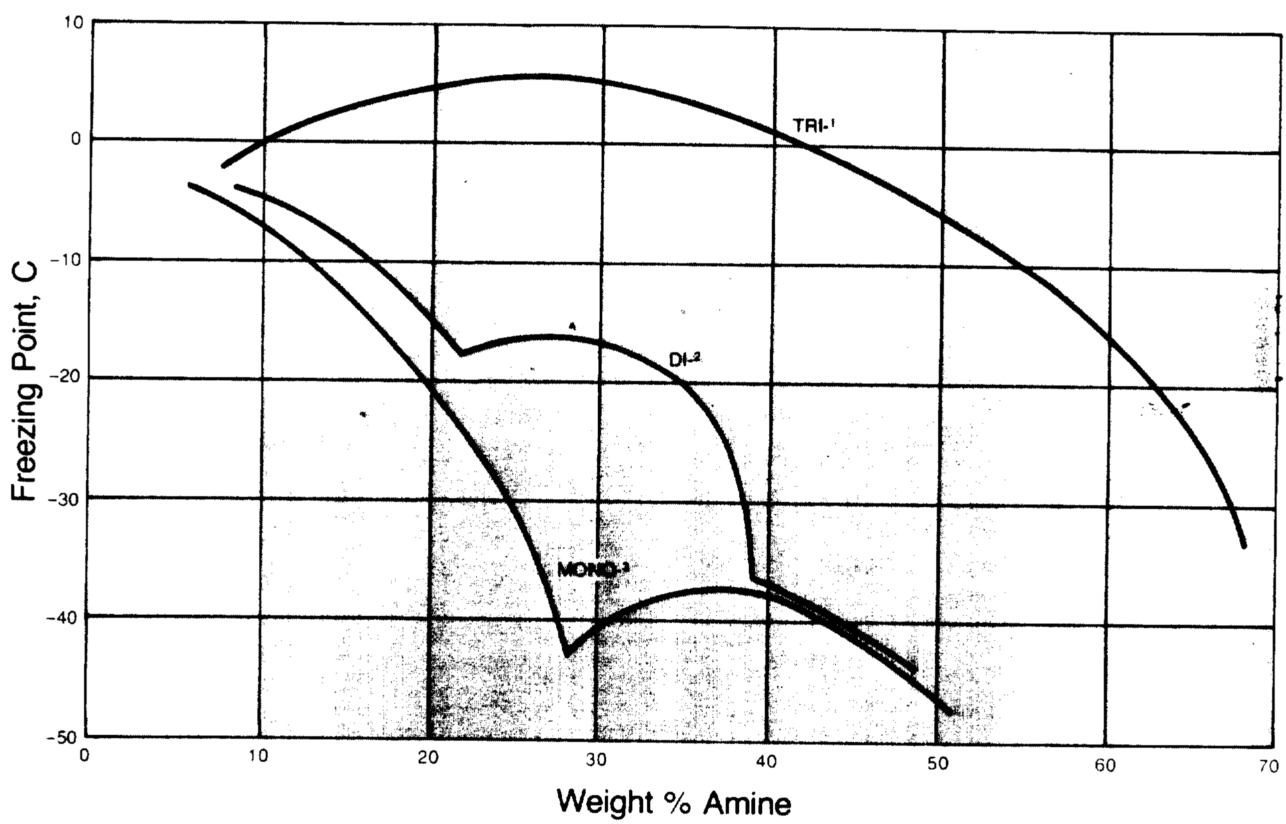
DENSITY OF LIQUID ANHYDROUS METHYLAMINES AT SATURATION PRESSURE



TOTAL PRESSURE OF METHYLAMINE-WATER SOLUTIONS



FREEZING POINT OF METHYLAMINE-WATER SOLUTIONS



[1] $(CH_3)_3N \cdot 10\ H_2O$ crystals above 8% conc.
[2] $(CH_3)_2NH \cdot 7\ H_2O$ crystals above 22% conc.
[3] $CH_3NH_2 \cdot 3\ H_2O$ crystals above 28% conc.

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Suite 255
Independence, OH 44131-2380
216-447-0868

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Suite 1620, Post Oak Tower
713-877-8859

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Saddle Brook, NJ 07662
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7YI-0794-00096

TOXICITY SUMMARY

METHYLAMINE

LIMITED DIST'

This review reflec'
literature, both publishe'
have not been evaluated for

Common Name: Methylamine

Chemical Name: Methanamine

Synonyms: Aminomethane
Monomethylamine

CAS Registry No.: 74-89-5

Chemical Structure:

```
H
|
N-CH3
|
H
```

Physical Properties: (15)

	GAS	40% SOLUTION
Description:	Colorless gas	Water-white to pale-straw liquid
Molecular Weight:	31.06	----
Boiling Point:	-6.3°C @ 760 mm Hg	48°C @ 760 mm Hg
Freezing Point:	-93.5°C	-38°C
Density/Specific Gravity:	0.6562 grams/mL @ 25°C (liquid)	0.897 grams/mL @ 25°C
Vapor Pressure:	2622 mm Hg @ 25°C	300 mm Hg @ 25°C
Flash Point/Flammability:	----	10°F (closed cup)
Explosive Limits:	4.9-20.7%	4.9-20.7%
Solubility:	Soluble in water	----
Conversion Factors:	1 mg/L = 878 ppm 1 ppm = 1.3 mg/m^3	

This literature search contains 10 pages of text and 80 references.

This search was prepared by R. C. Graham. See the last page of this document for its updating history.

Exposure Standards:

Du Pont AEL = 10 ppm (8- and 12-hour TWA) (14)
TLV® = 10 ppm (4)
OSHA PEL = 10 ppm (12a)

DOT Classification:

Flammable liquid or gas (12c)

EPA RCRA Status:

Listed as a hazardous substance under the Federal Water Pollution Control Act (12b)

FDA Status:

None

TSCA Inventory:

Yes

TOXICITY

Summary:

Methylamine has moderate acute oral toxicity with an LD50 in rats in the range of 100 to 200 mg/kg. Methylamine neutralized with HCl has slight acute oral toxicity. Contact of the skin of guinea pigs with a 40% solution caused necrosis. Similarly, instillation of a 40% solution into the rabbit eye produced severe irritation. By the acute inhalation route of exposure, methylamine has slight toxicity with a four-hour ALC in the rat of 4300 ppm. In a ten-day subchronic inhalation study, groups of ten rats were exposed six hours a day to 75, 250 or 750 ppm. At 750 ppm, five rats died and severe reductions in body weight occurred. At 250 ppm, erosion or ulceration of the nasal turbinate was observed following the last exposure. This lesion was not seen in rats given a two-week recovery period. No adverse effects occurred in the rats exposed to 75 ppm.

A. Acute

1. Oral

- LD50 (rats) = 100-200 mg/kg (16)
- LD50 (rats) = 1600-3200 mg/kg* (16)
- A single administration of 500 mg of methylamine hydrochloride had no effect in chickens; 1000 mg caused paralysis-like weakness that disappeared within 24 hours (32).
- The aim of this study was to determine whether the half-life of N-methylnitrosamine or one of the intermediates of its decay is long enough after formation *in vivo* to allow for a reaction with the DNA of the gastro-intestinal lining cells. Rats were given radiolabeled methylamine and a 50-fold molar excess of potassium nitrite by gavage. After 30 minutes, DNA of the stomach, the small intestines and liver was isolated, the purines removed by an acid hydrolysis and analyzed. 7-Methylguanine was found in the DNA of the stomach and the small intestines in about equal yield, while no radioactivity could be detected in the liver (23).
- Rats were administered 0.93 mg/kg of methylamine and 48 mg/kg of sodium nitrite. DNA isolated from the stomach and the first 15 cm of the small intestine was not methylated at the limit of detection (25).

*hydrochloride

2. Skin

- Application of 0.1 mL of a 40% aqueous solution did not kill a guinea pig but caused necrosis (16).

- Liquified methylamine gas produced necrosis and hemorrhage when applied to the clipped backs of guinea pigs (20).

3. Eyes

- Instillation of 0.1 mL of a 40% aqueous solution caused corneal damage of the eye of a rabbit (16).

- A drop of a 5% aqueous solution was found to cause hemorrhages in the conjunctiva, superficial corneal opacities and edema (17).

- Instillation of a 40% solution of the hydrochloride salt of methylamine into the rabbit eye produced mild irritation. The treated eye was normal 24 hours later (16).

- Slit lamp and ophthalmoscope examinations, determinations of visual acuity and central and peripheral vision field were carried out on workers exposed chronically to mono-, di- and trimethylamine and to DMF. No abnormalities were found that could be attributed to these agents (37).

4. Inhalation

- Four-hour ALC (rat) = 4300 ppm (14).

- Two-hour LC50 (mice) = 1889 ppm (27).

- Brief exposures of humans to 20-100 ppm produce transient eye, nose, and throat irritation. No symptoms of irritation are produced by longer exposures to 10 ppm (16).

- The odor of methylamine is faint but readily detectable at less than 10 ppm, becomes strong at from 20 to 100 ppm and intolerably ammoniacal at 100 to 500 ppm. Olfactory fatigue occurs readily (16).

- Odor Threshold = 0.021 ppm (34) and 3.2 ppm (5,6).

- See Related References 50-53 for additional information.

5. Injection Studies*

a) Intraperitoneal

- A single dose of methylamine did not produce methemoglobinemia in the rabbit, mouse and cat (38).
- Injection of methylamine followed by 5-hydroxytryptamine in rats produced stomach bleeding (22).

b) Subcutaneous

- ALD (rat) = 200 mg/kg (1).
- ALD (mouse) = 2500 mg/kg (9).
- ALD (rabbit) = 2000 mg/kg (11).
- Administration of 1000 mg/kg to rabbits was not fatal (21).
- ALD (guinea pig) = 200 mg/kg (1).
- In dogs, administration of 400 mg/kg of methylamine hydrochloride was ineffective. Administration of 280 mg/kg of methylamine caused a certain amount of agitation manifested by rolling about and persistent scratching with the forepaws. In addition there was a staggering gait, leaning against the wall and weakness in the hind legs; 600 mg/kg resulted in similar symptoms at first, but then the paralytic symptoms began to prevail. Short tetanic spasms were elicited a number of times by mechanical stimuli. With increasing paralysis, death ensued five hours after administration. Autopsy revealed slight gelatinous infiltration at the site of injection. No other changes were found (32).
- Methylamine, in concentrations above 0.067 M, produce acute gastric erosion and ulcer. The ulcerative effect is greater in animals with a chemically-induced damaged liver (28).
- Administration of methylamine to animals stimulates the erythropoietic apparatus, calling forth erythrocytes and polychromatophilic cells (33).

*See Related References 54-58 for additional information.

c) Intravenous

- ALD (rabbit) = 800-1000 mg/kg (9).

- The administration of 1000 mg/kg into dogs caused only a temporary increase in the pulse rate. Following infusion of 60 mL of a 16% aqueous solution of methylamine, a piglet repeatedly showed violent vomiting, inappetence and paralysis-like weakness; it died after three days with increasing paralytic symptoms. Autopsy revealed hemorrhagic gastroenteritis with erosion of the gastric mucosa. 500 or 1000 mg/kg of methylamine hydrochloride had no effect; 2000 mg/kg produced violent vomiting. In addition, the animal showed a tensed gait and rapidly increasing paralytic symptoms that resulted in death after seven hours. Autopsy was unrevealing (32).

- Administration of 150 to 200 mg/kg to rabbits was not fatal (21).

- In anesthetized dogs, methylamine produces a slight transitory fall of blood pressure without affecting respiration (3).

B. Extended Studies

1. Oral

- Five rats were administered 200 mg/kg, three times per day, for four days. All the rats died within five days. Autopsy revealed a duodenal ulcer in one rat. No evidence of adrenal necrosis was observed (45).

2. Inhalation

- Groups of ten rats were exposed six hours a day, five days a week, for two weeks to 75, 250 or 750 ppm of methylamine. No significant adverse effects were observed throughout the test in rats exposed to 75 ppm of methylamine. The 75 ppm level is considered a no-effect concentration under the conditions of this test. Compound-induced toxic effects in the 250 ppm exposure group were detected microscopically. Erosion or ulceration of the nasal turbinate mucosa was observed in all of the rats following the last exposure, but was not detected following the two-week recovery period. Rats from the 250 ppm group also excreted a more acidic urine than controls after the ninth exposure. After the recovery phase, the blood urea nitrogen values were elevated. In addition, absolute and relative kidney weights were significantly increased following the last exposure, but were similar to controls after the two-week recovery period. Exposure to the test compound at 750 ppm resulted in the morbidity or death of rats. Four rats died or were killed <u>in extremis</u> by the tenth day of exposure. One rat also died after 12 days of recovery. All rats that died or were killed had similar gross and microscopic findings. Pathological observations included a distended gastrointestinal tract, small spleen and thymus due to lymphocyte depletion, bone marrow hypoplasia with congestion, dark or dull red lungs and red nasal discharge. Severe reductions in body weight were noted in the 750 ppm group during both the exposure and recovery phases. The absolute weights of the liver and kidneys were decreased compared to controls after 14 days of recovery. Compared to controls, hematologic effects and significant changes in serum clinical chemical parameters were observed in rats exposed to 750 ppm. However, after a 14-day recovery period, hematologic effects were absent except blood urea nitrogen and serum glutamic-pyruvic transaminase values remained increased (14).

3. Subcutaneous Injection

- Rats were administered 324 mg/kg of methylamine hydrochloride, three times a day, for four days. Surviving animals were sacrificed on the next day and duodenal ulcers and/or adrenocortical necrosis evaluated. No adrenocortical necrosis occurred and the degree of duodenal ulcer was only slightly more than in controls (46).

C. Carcinogenic Potential

- The high incidence of stomach cancer in Japan and China is thought to be related to diet. Squid, a popular component of these diets, contains particularly high levels of dimethylamine (946-2043 ppm) and methylamine (38-255 ppm). Reaction of nitrite in acidic medium with aqueous extract of squid yielded appreciable amounts of nitrosamines (35).

- See Related References 59-64 for additional information.

D. Mutagenic Potential

- Alkylnitrosamines are known to be effective carcinogens. Under conditions found in the human stomach, secondary amines and nitrite could react to form dialkylnitrosamines. It has also been shown that tertiary amines are also able under similar conditions to give rise to dialkylnitrosamines. While primary amines do not react with nitrite to form dialkylamines, they do form the same reaction intermediates which according to current concepts are formed when dialkylnitrosamines are metabolically activated. In fact, the alkylation of DNA by a mixture of methylamine and nitrite at low pH has been observed. Biological tests were done on *Escherichia coli* for the mutagenic activity of primary amines alone or with nitrite. Mutations to streptomycin independence were studied. Methylamine in combination with nitrite was distinctly mutagenic while methylamine alone was not (26).

- See Related Reference 65 for additional information.

E.-F. Developmental and Reproductive Toxicity

- See Related References 66-69.

G. Aquatic/Environmental Studies

- The critical range for creek chub, a fish of average tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 10 to 30 mg/L (19).

- Rainbow trout (*Salmo irideus*) were tested at a methylamine concentration of 141 mg/L. The resulting pH was 10.2, and the temperature, 13.0-13.5°C. The fish showed their first reaction in about two minutes, turned over in five to eight minutes, and made their last movement in 19 to 23 minutes (13).

- 24-hour LC50 (killifish) = 1000 mg/L (47,48).

- The toxic threshold for methylamine hydrochloride occurred at a concentration of 4 mg/L for *Scenedesmus* and 50 mg/L for *Microregma* during a four-day exposure at 24°C. For *Daphnia* at 23°C for two days, the threshold was 480 mg/L, while for *Escherichia coli* at 27°C, concentrations up to 1000 mg/L had no deleterious effect (10).

- Methylamine inhibited photosynthesis and growth of *Scenedesmus obliquus*, a dominant species in high-rate sewage oxidation ponds (2).

- A 48-hour exposure of rainbow trout to 10 mg/L of methylamine did not impair the flavor of the fish (42).

- Methylamine imparts an unpleasant odor to water at a concentration of 1 mg/L or more. At 3 mg/L or less, methylamine does not affect the total sanitary system of the reservoir (BOD, the bacterial self-purification and nitrification) (40).

- The threshold odor concentration of methylamine in water is 1.82 mg/L (42).

- See Related References 70-73 for additional information.

H. Clinical Reports of Human Exposure

- Allergic or chemical bronchitis occurred in a worker exposed to 2 to 60 ppm of methylamine. Masks or respirators were worn during the greatest exposures. Some irritation was noted at about 25 ppm (36).

- In a plant processing dimethylamine, the ambient air contains less than 33.8 mg/m^3 of dimethylamine, 36.7 mg/m^3 of methylamine and 35 mg/m^3 of ammonia during a 12-hour period. The urine of workers contains 1.3 to 2.48 mg/L of methylamine during a 24-hour period (8).

I. Epidemiology

- No data found.

J. Metabolism

- Subcutaneous injection of methylamine in dogs results in its complete decomposition (18).

- In dogs fed fish containing methylamine, urinary excretion of methylamine was less than in controls, indicating complete metabolism (29). Almost complete destruction was also found when methylamine was fed by mouth to dogs (30).

- Methylamine is metabolized in the rat to CO_2 via the intermediate products formaldehyde and formic acid (49).

- In rats administered radiolabeled methylamine, the radiolabel was incorporated into dimethylamine (7).

- Perfusion of methylamine hydrochloride into dog liver results in a rapid removal of the methylamine from the circulation and probably a retention in the liver, since there was no immediate increase in urea output (31).

- See Related Reference 74 for additional data.

K. Biochemical Studies

- Methylamine inhibits the general secretion of proteins in isolated rat hepatocytes in suspension (41).

- Immunization of syngeneic mice with mouse sarcoma STU-D17 tumor cells, modified with dimethylsulfate, or acetic anhydride, or glutardialdehyde fixation followed by 1-ethyl-3(3-dimethylaminopropyl)-carbodiimide and methylamine treatment, gave best protection against challenge doses of viable cells at 1000 or 10,000 times LD100. Up to 40% of the mice remained tumor-free, and the remaining animals showed a greatly increased mean survival time. The postchallenge sera showed no detectable amounts of antibodies against the tumor cells (44).

- DNA was methylated by the reaction product of methylamine and nitrite (24). Methylated DNA also resulted from the oral gavage of rats with methylamine and sodium nitrite (25).

- Incubation of isolated rat hepatocytes with methylamine resulted in an inhibition of endogenous protein degradation and microscopically visible enlargement of the lysosomes (43).

- In slices of brain cortex or rat liver slices, deamination of methylamine was negligible. Guinea pig liver and kidney and rat kidney also had no effect (39).

- See Related References 75-80 for additional information.

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TOXICITY SUMMARY

DIMETHYLAMINE

LIMITED DISTRIBUTION

This review reflects the available toxicity literature, both published and unpublished. Studies have not been evaluated for scientific merit.

Common Name: Dimethylamine
Chemical Name: Methanamine, N-methyl-
Synonyms: DMA
CAS Registry No.: 124-40-3 (hydrochloride - 506-59-2)
Chemical Structure:

```
   CH3
   |
H-N
   |
   CH3
```

Physical Properties*: (30)

Description:	Gas or colorless liquid under pressure, ammonia-like odor, threshold = 0.047 (62) and 0.34 ppm (6)
Molecular Weight:	45.08
Boiling Point:	6.9°C @ 760 mm Hg
Freezing Point:	-92.2°C
Density/Specific Gravity:	0.65 (liquid @ 25°C)
Vapor Pressure:	1500 mm Hg @ 25°C
Flash Point/ Flammability:	Flammable
Explosive Limits:	2.8-14.4%
Solubility:	Completely soluble in water
Conversion Factors:	1 mg/L = 542 ppm 1 ppm = 1.8 mg/m^3

This literature search contains 18 pages of text and 130 references.

This search was prepared by Richard C. Graham. See the last page of this document for its updating history.

*DMA is also supplied as a 40 or 60% aqueous solution. See page 2 for their physical properties.

Aqueous Solutions

	40%	60%
Description:	Colorless liquid ammonia-like odor	
Boiling Point @ 760 mm Hg:	54°C	36°C
Freezing Point:	-37°C	-75°C
Density/Specific Gravity @ 25°C:	0.89	0.83
Vapor Pressure @ 25°C:	215 mm Hg	500 mm Hg
Flash Point/Flammability:	-1°F	-61°F

Exposure Standards:

TLV® = 10 ppm (4).
OSHA PEL = 10 ppm (22b).

DOT Classification (18):

Flammable gas or flammable liquid (22e)

EPA Status

Hazardous waste under RCRA (22d) and Hazardous Substance under the Federal Water Pollution Control Act (22c)

FDA Status:

Cleared for use in the production of ion-exchange membranes used in processing grapefruit juice (22a).

TSCA Inventory

Yes

TOXICITY

Summary

Dimethylamine (DMA) has slight acute oral toxicity with an LD50 in rats of 698 mg/kg. A neutralized DMA solution had very low acute oral toxicity with an LD50 in rats of 8100 mg/kg for DMA hydrochloride. Contact of the skin or eyes with DMA solutions produced a severe injury at concentrations greater than 6%. By the acute inhalation route of exposure, DMA is also slightly toxic with a four-hour LC50 in rats of 4700 ppm. As with skin and eye contact, the vapors of DMA also produce significant irritation of the exposed mucous membranes and respiratory tract. Extended inhalation studies show the nasal tissue to be most affected. DMA does not appear to be carcinogenic although the most definitive test is not completed. DMA can react with N-O compounds to form a potent carcinogen dimethylnitrosamine. DMA is not mutagenic in a number of tests. No information is available on its developmental potential. Subchronic inhalation exposure resulted in tubular degeneration of the testes in a rabbit and monkey. By the aquatic route, DMA is slightly toxic with a 96-hour LC50 in rainbow trout of 120 mg/L. DMA is easily biodegraded. In rats, DMA is excreted readily in the urine with most of an administered dose excreted unchanged.

TOXICITY

A. Acute

1. Oral

- LD50 (rats) = 698 mg/kg (31).
- LD50 (mice) = 316 mg/kg (31).
- LD50 (rabbits) = 240 mg/kg (31).
- LD50 (guinea pigs) = 240 mg/kg (31).

The clinical picture of poisoning was similar in all the species of animals investigated and included transient excitation, followed by sluggishness, a lateral position and disturbances of motor coordination. DMA also exerted a markedly irritant effect on the mucosae. Extensive hemorrhages in the stomach walls and in the intestinal tract were often found in animals which died or had been killed. When rats, guinea pigs, rabbits and mice were given short-term doses of a solution of DMA neutralized to pH 8.0 by HCl, the respective LD50's were 8100, 1070, 1600 and 1600 mg/kg. The role of the local action on the gastrointestinal tract was thus confirmed as the main role in acute DMA poisoning (31).

- Groups of 40 mice were fed dimethylamine hydrochloride at dose levels of 500, 1000, 2000 or 2500 mg/kg. None of the animals died during the three days following the study. Body weight changes and liver/body weight were slightly reduced only at the highest dose (8).

- Chickens infused with 500 and 1000 mg doses of dimethylamine in aqueous solution did not show any compound-related effects. Five grams produced paralytic symptoms and was lethal (59).

- Dogs administered oral doses of 1000 mg of dimethylamine vomited repeatedly but showed no other symptoms. If vomiting was prevented by administration of 20 mg of morphine hydrochloride, 1000 mg/kg of dimethylamine produced a strong drop in temperature, increase in the respiratory and pulse rate, discharge of watery stool, generally paralytic symptoms and death after sixteen hours. Autopsy did not reveal anything unusual (59).

- Oral doses of dimethylamine chloride at 350 and 500 mg/kg in water generally produced no effect in piglets. A 1000 mg/kg dose was lethal in one of several piglets tested (59).

- Groups of germ-free and conventional mice, deprived of food for six hours, were administered 2500 or 3500 mg/kg of DMA. Mortality occurred in both strains at 3500 mg/kg. No liver necrosis occurred in surviving animals after three days (75).

2. Skin

- A 6% solution of DMA when applied to rabbit skin caused reddening, then thickening and ulceration on single application. A 3% solution produced similar effects after five applications (56).

- DMA is corrosive and irritating to the skin and severe burns may result from direct contact (5).

- DMA was a skin sensitizer in the guinea pig closed epicutaneous test (49).

- Tails of white mice were immersed into 20% aqueous DMA for periods ranging from five to 30 minutes. After five minutes, the formation of numerous small hemorrhages under the skin was observed. Hemorrhages became massive after immersion for 10-15 minutes. After 30 minutes, disintegration of the skin had set in. When touched, the skin separated and exposed the bones. During the first day after a five-minute immersion, an exudative inflammation appeared. The inflammation increased in intensity for three to four days, began to disappear during the subsequent days, and a complete regeneration of the skin occurred within 13-14 days. Copious washing prevented the outbreak of inflammation only in the case of the five-minute immersion. Animals brought into skin contact with DMA did not exhibit general intoxication symptoms (71).

- The tails of mice were immersed for two hours in a 6% solution of DMA. Hyperemia and gangrene developed one to two days later. The affected part dropped off after two to four days (56).

3. Eyes

- A 3% solution of DMA produced edema of the eyelids of mice. Also produced was transient corneal clouding and pronounced dilation of blood vessels of the sclera (56).

- A 5% solution, dropped once on a rabbit eye, caused hemorrhages in the conjunctiva, corneal edema and superficial opacities (35).

- Instillation of a 6% aqueous solution into the rabbit eye caused sharp swelling of the eyelids and serous exudation (56).

- A drop of undiluted dimethylamine, placed on a rabbit's cornea, with the lids then closed and no irrigation performed, caused the cornea to become whitish-blue and translucent within a few seconds, then white as the sclera in one minute (70).

- DMA produced a very severe corneal injury in the rabbit eye (31).

- Slit lamp and ophthalmoscope examinations, determinations of visual acuity and central and peripheral vision field were carried out on workers exposed chronically to mono-, di- and trimethylamine and to dimethylformamide. No abnormalities were found that could be attributed to these agents (72).

4. Inhalation

- Four-hour LC50 (rats) = 4700 ppm (55).
- Six-hour LC50 (rats) = 4540 ppm (92).
- Two-hour LC50 (mice) = 7650 ppm (71,92)
- Two-hour ALC (mouse) = 2710 ppm (71).
- RD50 (rats) = 573 ppm (92).
- RD50 (mice) = 511 ppm (9,14,92).
- Groups of mice were given a single exposure to 3, 16, 37, 110-270, 1230-1340 or 1605-2140 ppm of DMA. At the two highest levels, all the mice died with severe respiratory and cutaneous effects. Similar, but less pronounced, effects occurred at 110-270 ppm with 19/32 mice dead. Mortality at 16 and 37 ppm was 4/12 and 11/22, respectively. At 3 ppm, all animals survived and only minor transient effects occurred (56).

- When mice were exposed to 813-1626 ppm of DMA, irritation of the lungs and eyes was observed. At 2710 ppm, tear flow was seen and at concentrations over 5420 ppm, cyanosis, convulsions and death occurred. Immediate autopsy of animals killed during exposure revealed hyperglycemia of all internal organs, numerous massive hemorrhages near the periphery of the lungs and peripheral emphysema. Autopsy of surviving animals, 20 days after exposure, revealed small hemorrhages in the lungs but no changes in the other organs (71).

- Histopathologic evaluation of the respiratory tract of rats exposed to a range of concentrations from 600 to 6000 ppm of dimethylamine revealed concentration-related changes ranging from ulceration and necrosis to rhinitis, tracheitis, and emphysema (92).

- The threshold concentration of DMA affecting the CNS in volunteers exposed while wearing protective clothing was 1.6 ppm (83).

- DMA and nitrogen dioxide reacted in air to produce a gaseous aerosol mixture of DMA, dimethylamine nitrate, N-nitrosodimethylamine and nitrogen dioxide. The combined action was essentially equal to the summing of their separate actions (76).

- See Related References 99-103 for additional information.

5. Injection Studies

a. Intravenous

- LD50 (mice) = 1210 mg/kg (1)

- In anesthetized dogs, DMA produced a brief increase in respiratory rate and a temporary drop in blood pressure immediately after administration (3).

- In piglets, administration of 60 and 100 mL of a 16% solution or 20 mL of a 33% solution immediately produced repeated vomiting and apathy and reduced appetite persisted for several days (59).

b. Subcutaneous

- LD50 (mice) = 2000 mg/kg (1)

- In piglets, subcutaneous injections of dimethylamine hydrochloride at 650 mg/kg produced increasing paralysis and death after 24 hours (59).

- In dogs, subcutaneous administration of 900 mg/kg of dimethylamine produced increasing general paralytic symptoms and eventual death within 15 hours of administration (59).

c. Intraperitoneal Injection

- LD50 (mice) = 1570 mg/kg (52)

B. Extended Studies

1. Oral

- Rats were administered 810 mg/kg/day for one month. An increase in the hemoglobin content, blood cholinesterase activity, serum-urea content and excretion of coproporphyrin and a decrease in ascorbic acid content of different organs occurred (31).

- Groups of 30 guinea pigs and 15 rabbits were fed 107 mg/kg/day and 160 mg/kg/day, respectively, of a hydrochloric acid neutralized DMA solution, for six weeks. There were rises in blood hemoglobin, increased activity of the blood cholinesterase, and an increased urea content in the blood serum and coproporphyrin excretion in the urine, with a rise in the weight coefficient of the liver and a fall in the vitamin C content of the organs (31).

- DMA (150 mg/kg in feed) added to the diet of rats for 3.5 months increased the liver demethylase activity even in the presence of the enzyme inducer casein (50,51).

- DMA (10 mg/day) added to the diet of rats for six months had no effect (58).

- Twenty female and 20 male mice were fed DMA hydro chloride in their diet for 28 weeks at a rate of 5.9 g/kg of food. This corresponds to approximately 47 mg/mouse/day. The mice were held for 12 weeks after the end of the study. The incidence of lung adenomas in these mice (13%) was approximately the same as in untreated control mice (14%). The incidence of other tumors was lower in the treated mice versus the untreated mice (3% versus 7%) (38).

- Groups of guinea pigs were fed doses of 3.5, 0.35 or 0.035 mg/kg/day for eight months. Groups of rats were similarly fed 0.35, 0.035 or 0.007 mg/kg/day. In the experiments on guinea pigs, the highest dose of dimethylamine resulted in increased coporporphyrin excretion in the urine, a rise in the blood urea, a fall in the vitamin C content in the supradrenals, and an increase in the weight coefficient of the liver. Rats that received 0.35 or 0.035 mg/kg, exhibited some CNS effects. In none of the other tests was any difference found between the experimental and control animals (31).

- Rats were administered drinking water containing 0.2% DMA for nine months. DMA caused significantly higher lipoperoxidation, free lysosomal enzyme activities and cytosolic superoxide dismutase activity in the liver (26)

- Groups of rats were fed diets containing 1600 mg/kg of DMA and/or 390 mg/kg of sodium nitrite or 33 mg/kg of dimethylnitrosamine (DMNA) for 2.5 years.

No tumors occurred in the DMA group of 27 rats. Tumors were found in 12 of 43 of the DMA-sodium nitrite group and in 15 of 27 DMNA rats (79,80).

2. Inhalation

- Mice were exposed to 510 ppm of DMA, six hours a day, for five days. Body weights were decreased 10 to 25% but in most cases returned to normal levels by three days postexposure. Three of the 24 exposed mice died during exposure. Nasal lesions were observed (14).

- Rats were exposed six hours a day for nine days to 175 ppm of DMA. The mucociliary function was inhibited with mucostasis being more variable in extent than ciliastasis. The dorsal surface of the nose was not affected (73).

- Groups of rats were exposed three hours a day for three weeks to 1-2 ppm of DMA. Effects were manifested on the tenth day of exposure and consisted of an increase in the latent period and duration of the motor reaction of the CNS to weak stimuli. This became less pronounced 17 days after cessation of exposure and completely disappeared 31 days thereafter (56).

- Groups of 20 rats were exposed six hours a day, five days a week, for 13 weeks to 10, 30 or 100 ppm of DMA. During the first week there were slight decreases in the mean body weights for both males and females in the 30 and 100 ppm groups. The mean body weight of the 100 ppm males remained significantly lower during the second week. From that time to the end of the study, all body weights were not significantly different than control body weights. No other compound-related changes were seen (21).

- Fifteen rats, 15 guinea pigs, three rabbits, two dogs and three monkeys were continuously exposed to 4.9 ppm of DMA for 90 days. The animals were killed at the end of the exposure. There were no deaths or signs of toxicity and all hematologic values were normal. On histopathological examination, interstitial inflammatory changes were noted in the lungs of all species. The three rabbits and two of three monkeys showed dilatation of the bronchi (23).

- Groups of ten rats, six guinea pigs and one rabbit of each sex plus five female mice and one monkey were given repeated seven-hour daily exposures, five days per week for 18-20 weeks to concentrations of either 97 or 183 ppm of dimethylamine. Corneal injury was observed in the guinea pigs and rabbits after nine days on the exposure regimen. Central lobular fatty degeneration and necrosis of the parenchymal cells of the liver was found in rats, guinea pigs, rabbits and mice. Tubular degeneration of the testes was observed in the male rabbit at the higher concentration and in the male monkey at the lower concentration (29).

- Chronic inhalation of 0.02 ppm by rats changed the ratio of the chronaxies of antagonistic muscles, decreased blood cholinesterase activity, decreased the blood serum content of SH groups, increased urinary excretion of coproporphyrins, disturbed immune reactions and decreased organ ascorbic acid. At 0.003 ppm DMA caused no changes (7).

- Groups of animals were exposed three hours a day, six days a week, for seven months to 1-4 ppm of DMA. During the fourth to fifth month of exposure, a significant decrease in hemoglobin concentration was observed. The blood picture returned to normal one month after conclusion of exposure (56).

- Exposure of rats, 24 hours a day, for one year to a mixture of dimethylnitrosamine (DMNA), DMA and NO_2 produced more tumors than exposure only to DMNA. Exposure of rats to either DMA or NO_2 in approximately the same concentrations, had no carcinogenic effects (10,77).

- Groups of 95 male and 95 female rats and mice were exposed six hours a day, five days a week, for two years to 10, 50 or 175 ppm of DMA. At the six month interim sacrifice, weight gain in both rats and mice exposed at 175 ppm was significantly reduced (5 to 15%) when compared to controls. The only other treatment-related effects were concentration-dependent lesions confined to the nasal passages, primarily in the olfactory mucosa. At both 50 ppm and 175 ppm, there was selective destruction of the olfactory epithelial sensory cells accompanied by degeneration of the olfactory nerves. Inflammation and epithelial hyperplasia were present in the respiratory mucosa of rats and mice exposed at 175 ppm and goblet cell hyperplasia was detected in the 175 ppm exposed rats only. No lesions were found in the 10 ppm exposed rats and only equivocal olfactory changes were detected in the 10 ppm exposed mice. At the 12-month interim sacrifice, the reduced weight gain and lesions of the nasal tissue continued to be seen. Slight lesions were now seen in the 10 ppm rat group. At the 18-month sacrifice, the reduced weight gain in the 175 ppm groups and the concentration-dependent nasal lesions continued to be observed. In both rats and mice the most notable lesion was seen at 175 ppm and was characterized by severe degeneration of the olfactory epithelium accompanied by atrophy of the olfactory nerves. Basal cell hyperplasia was found in the olfactory epithelium of rats and had an increased incidence compared to rats sacrificed at 12 months. Nasal lesions were much less severe in rats exposed at 50 ppm and were only minimal at 10 ppm (15,21).

3. Subcutaneous Injection

- Rabbits administered DMA for six days exhibited an increase in erythrocyte count by 18 to 30% and an appearance of polychromatophilia (61).

C. Carcinogenic Potential

- DMA did not produce an increase in the incidence of tumors found in controls in rats fed a diet containing 1600 mg of DMA per kg of diet for 2.5 years (79).

- DMA is currently being tested for its carcinogenic potential by the inhalation route. The exposure part of the two-year study has been completed. Final histopathological examinations are currently underway. At interim sacrifices at six, 12 and 18 months, no tumors were reported (21).

- Dimethylnitrosamine (DMNA) is a potent carcinogen in animal tests. DMNA can be produced by reaction of DMA and various N-O derivatives (e.g. sodium nitrite, nitrogen dioxide, etc.) under widely varying conditions. The formation of DMNA and its biological reactions in animals and in vitro has been extensively studied. These studies are not included in this review unless DMA has been used alone for comparison of its effect with that of DMNA. Also not included are studies where DMA and N-O sources are combined to produce DMNA and DMA is not used alone.

- See Related References 104 and 105 for additional information.

D. Mutagenic Potential

- DMA was weakly mutagenic in Salmonella typhimurium strain TA 1530 in the presence of a mouse liver activation system (37). No mutagenic activity occurred without activation (37,91). Additionally, no activity was found in a host-mediated assay in mice (37).

- DMA hydrochloride is not mutagenic in Salmonella typhimurium strains TA 98 and TA 100 and in the rec-assay with Bacillus subtilis. Additionally, DMA hydrochloride did not induce chromosomal aberrations or SCEs in hamster lung fibroblast cells (53,54)..

- In a host-mediated assay in mice, DMA was not mutagenic in Salmonella typhimurium strain LT2 (25).

- In a host-mediated assay in rats and mice with Salmonella typhimurium strain G46, DMA did not induce histidine reversions in the indicator organism recovered from the livers of either species. Simultaneous administration of DMA and sodium nitrite produced a significant increase in reversions (32). Although no attempt was made to study the kinetics, a doubling of the DMA dose resulted in a doubling of the revertants in both hosts (96).

- In rats administered 1000 mg/kg by gavage, the Ames test did not reveal any mutagenicity in either liver extracts or serum samples (27).

- Coupled with a rat liver S-9 activation system, DMA was not mutagenic in the CHO/HGPRT assay (39,40,81).

- DMA hydrochloride did not induce chromosomal aberrations in Chinese hamster cells (2,42,43).

- DMA is mutagenic in the CHO bioassay at high concentrations (82).

- DMA, when administered simultaneously with sodium nitrite and acetic acid to *Drosophila melanogaster*, produced a significant increase in the frequency of sex-linked recessive lethals relative to the frequency observed when sodium nitrite and acetic acid are omitted (12).

- Raising *Drosophila melanogaster* on an agar medium with 0.05M dimethylamine raised the frequency of abnormal morphogenesis from 1.48 to 15.85% (63).

- DMA did not induce petite mutants in *Saccharomyces cerevisiae* (65).

- DMA did not induce unscheduled DNA synthesis in primary cultures of rat hepatocytes (64).

- DMA did not inhibit mouse testicular DNA synthesis when administered orally to mice at doses of 1000 or 2000 mg/kg. When administered with sodium nitrite, inhibitions of 57 to 65% were observed (34).

- The oral administration of radiolabeled DMA to mice did not induce any radioactivity in the mouse liver DNA (33).

- DMA did not induce an increase in the percentage of DNA eluted from the liver of rats orally administered 698 mg/kg (13).

- DMA inhaled by rats at 0.27 and 0.54 ppm for three months induced an 18-24% frequency of aneuploid cells in the bone marrow, compared with 0.2% in untreated rats (41).

- See Related References 106-110 for additional information.

E.-F. Developmental and Reproductive Toxicity

- Tubular degeneration of the testes was observed in a male rabbit repeatedly exposed to 183 ppm and in a male monkey similarly exposed to 97 ppm (29).

G. Aquatic/Environmental Studies

- 96-hour LC50 (rainbow trout) = 120 mg/L (16-18)

- 96-hour LC50 (guppies) = 210 mg/L (95)

- 24-hour LC50 (guppies) = 55 mg/L (28).
- The critical range for creek chub, a fish of average tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 30 to 50 mg/L, i.e., all fish survived 30 mg/L but all died at 50 mg/L (36).
- Dimethylamine, because of high basicity, eroded the gills and mucous membranes of fish (74).
- 48-hour LC50 (killifish) = > 1000 mg/L (93,94)
- 48-hour LC50 (*Daphnia magna*) = 50 mg/L (95)
- 24-hour EC50 (immobilization, *Daphnia magna*) = 46 mg/L (16-18).
- Rainbow trout were exposed to 205 mg/L. The fish showed their first reaction in 33 to 40 seconds, turned over in three to four minutes and made their last movement at ten to 13 minutes (24).
- Rainbow trout were exposed for 30 days to 0.65-21.6 mg/L of DMA. No mortality, effect on weight or pathological effects were observed (16-18).
- Reproduction rate and survival of *Daphnia magna* were not affected during a 30-day exposure at concentrations as high as 10 mg/L. Exposure at 15 mg/L reduced fertility and survival (16-18).
- 96-hour EC50 (inhibition of growth, alga, *Selenastrum capricornutum*) = 6.2 mg/L (16-18)
- Toxicity threshold (alga, *Scenedesmus quadricauda*) = 7.4 mg/L (60)
- 96-hour EC50 (inhibition of respiration, alga, *Chlorella pyrenoidosa*) = 30 mg/L (95)
- Three-hour (minimum inhibiting concentration, bacterium *Nitrosomonas*/*Nitrobacter*) = 180 mg/L (95)

- 15-minute EC50 (reduction of bacterial luminescence, bacterium, *Photobacterium phosphoreum*) = 26.8 mg/L (95)

  BOD_5 = 1.3 g/g (69)

  BOD_{20} = 2.0 g/g (69)

  ThOD = 2.006 g/g (69)

- DMA is easily biodegradable at concentrations not exceeding 300 mg/L. The biodegradation rate is rather high and the time needed for microbiological acclimitization is short. In the treatment by activated sludge, DMA is easily removed from wastewaters and has little effect on the overall treatability of wastewaters (28).

- Wastewaters from an artificial leather plant containing DMF and DMA inhibited the growth of activated sludge. DMF had no effect on activated sludge microorganisms but DMA strongly inhibited their growth at higher concentrations (57).

- See Related References 111-127 for additional information.

H. Clinical Reports of Human Exposure

- DMA, generated in the small bowel during uremia, produces a serum DMA which may play an important role in the metabolic derangements that cause uremic symptomatology (85-90). DMA was also found in the breath of these patients (88).

I. Epidemiology

- See Related Reference 128.

J. Metabolism

- Rats were exposed for six hours to radiolabeled DMA. Respiratory and olfactory nasal mucosal tissue was dissected from these rats, pooled separately and homogenized. Fractions of DNA, RNA and protein isolated from these homogenates contained unextractable radioactivity. The concentration of ^{14}C appearing in macromolecules appeared to correlate with the concentration of ^{14}C deposited in the tissues after inhalation exposure. The results indicate that inhaled DMA is metabolized *in vitro* in the rat nasal mucosa to formaldehyde which can enter the one-carbon pool and be incorporated into macromolecules. Evidence suggests that much, if not all, of the ^{14}C in macromolecules is due to metabolic incorporation and not covalent binding (66,68). Seventy-two hours after termination of exposure, the disposition of recovered radioactivity was similar for each airborne concentration, with >90% in the urine and feces, 7 to 8% in selected tissues and the carcass, and 1.5% exhaled as carbon dioxide. Over 98% of the radioactivity in the urine was unmetabolized DMA. Analysis of tissue radioactivity immediately after exposure to DMA showed that the respiratory nasal mucosa contained the highest radioactivity followed by the olfactory nasal mucosa; concentrations of radioactivity in liver, lung, kidney, brain and testes were about two orders of magnitude less than in the nasal mucosal tissues. Radioactivity in plasma of rats exposed by inhalation to 175 ppm of DMA decayed in a biphasic manner. The terminal half-life for plasma radioactivity was similar to the half-lives of some plasma proteins, suggesting incorporation into proteins subsequent to metabolism. Thus, while most of the inhaled DMA is excreted unchanged, a small amount of oxidative metabolism of DMA occurs (67).

- In rats fed a diet containing 23.6 mg/kg of DMA, the highest concentration of DMA was found in the stomach and decreased from the upper region to the lower region. The half-lives of DMA in the ligated stomach, upper and lower small intestine, caecum and large intestine were 198, 8.3, 11.6 31.5 and 11.0 minutes, respectively. The DMA concentration in the blood increased from 0.3 mg/kg to 3.0 mg/kg, five minutes after injection of 0.25 mg/kg into the ligated upper small intestine. The half-life in the blood was 12.5 minutes when injected intravenously. Intestinal secretion was observed within 15 minutes. Urinary DMA increased from 17.3 mg/kg to 139 mg/kg within 30 minutes of injection (44, 46-84). Apparently after ingestion DMA is absorbed from the intestine into the blood, from which it disappears rapidly, the major part being excreted in the urine whereas a small proportion is excreted in the bile or secreted into the intestine, where it may be reabsorbed (46,48).

- Rats and guinea pigs were administered radiolabeled DMA by i.v. injection. The apparent volume of distribution and biological half-life did not show a species difference. In general, there were no marked differences in accumulation of radioactivity in tissues of guinea pigs and rats four hours after administration of DMA. Nucleic acid fractions prepared from liver and lungs of both species following DMA administration showed a much lower covalent binding with DMA than with dimethylnitrosamine (19,20).

- DMA, a precursor of dimethylnitrosamine, is normally found in rat and human urine. DMA is formed from TMA which in turn, is a breakdown product of dietary choline. Enzymes within gut bacteria catalyze both of these reactions. In control rats administered no choline, TMA and DMA urinary excretion was not significantly different than choline-supplemented rats. This shows that dietary choline was not the sole source of DMA (97,98).

- DMA is largely excreted via the kidneys (85%) and within 12 hours (84).

- DMA is excreted in the urine of humans. Of an administered 8g dose, 91.5% could be recovered in the urine (78).

  One hour after ingestion of 100 mg of DMA hydrochloride by human subjects, 1 ppm was found in the saliva. DMA remaining in the oral cavity after ingestion of DMA-HCl disappeared within 20 minutes. About 95% of the dose was presumed to be eliminated in the urine in 24 hours (45).

- In workers occupationally exposed to less than 18 ppm of DMA, 29 ppm of monomethylamine and 50 ppm of ammonia, urinary DMA increases slowly from 18 to 23 mg/L during the first five hours and then rapidly to about 60 mg/L during the last few hours. During the exposure-free hours the urinary DMA remains at more than 30 mg/L (11).

- Microsomes prepared from liver and from respiratory and olfactory nasal mucosa metabolized DMA to formaldehyde. Phenobarbital-induced microsomes metabolized DMA at a rate less than that of control (68).

K. Biochemical Studies

- See Related Reference 129.

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