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INIT 87/14/94



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Monsanto

DEPARTMENT OF MEDICINE &
ENVIRONMENTAL HEALTH

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63167
Phone: (314) 694-1000
November 21, 1984

RECEIVED
OPPT/CBIC
96 JUL 14 AM 9:23

Dr. Louis Borghi
Senior Scientist
Industrial Chemical Information Section
Dynamac Corporation
11140 Rockville Pike
Rockville, MD 20852

Dear Dr. Borghi:

Monsanto submits the following information on hexamethylenediamine (HMDA) (CAS No. 124-09-4) that you requested on behalf of the TSCA Interagency Testing Committee in your September 21, 1984 letter.

- Current annual production data and trends
- Technical product literature and material safety data sheets
- Use data
- Occupational exposure data
- Consumer exposure data
- Unpublished toxicological data

If you need further assistance, please contact me.

S. D. Paul, C.I.H.
Sr. Industrial Hygiene Specialist

Hexamethylenediamine

Effective Date: January 1, 1985

Product Codes: Anhydrous 5080-401-03-0799
Blended 5080-400-03-0799

General Information

The primary use for HMD is in the manufacture of polyamides, particularly nylon 6,6. Some HMD is converted to hexamethylene diisocyanate, which is used to manufacture polyurethanes. HMD has found minor applications as the hardener in epoxide polymers, a corrosion inhibitor, wet strength resins, and lubricating oil additive.

Specifications/Properties

Monsanto normally supplies hexamethylenediamine as an aqueous solution to facilitate transportation and unloading (75-90% HMD, controlled at $\pm 2\%$ of desired value). 100% HMD can be supplied if required.

Appearance	Clear, colorless liquid with a moderate but distinctive odor.
Color	APHA 20 maximum
Assay	99.9% minimum as HMD
Boiling Point^{1*}	199-200°C.
Freezing Point^{1*}	39.4°C.
Molecular Weight^{1*}	116.21

¹For pure HMD.

*Physical property based on tests in the laboratory; not guaranteed for all samples and not part of product specification.

NOTE: Product specifications are subject to change from time to time without notice. Please write us for our current product specifications.

Shipping Information

FOB	Monsanto plants at Decatur, Ala.; and Pensacola, Fla.
Freight Classification	Hexamethylene Diamine Solution CORROSIVE MATERIAL
Standard Containers	Pensacola Bulk: 4,000-gal. tanktruck and 20,000-gal. tankcar. Decatur Bulk: 4,000-gal. tanktruck and 20,000-gal. tankcar. 55-gal. steel drums; gross wt. 437 lbs., net weight 400 lbs., cubic ft. 10.175
Samples	16-oz. to a gallon via United Parcel Post

Handling Precautions

DANGER! EXTREMELY HAZARDOUS LIQUID. CAUSES SEVERE BURNS. COMBUSTIBLE. Do not get in eyes, on skin, on clothing. Do not breathe vapor. Keep away from heat and flame. Keep container closed. Use with adequate ventilation. Wear neoprene rubber gloves, chemical safety goggles and respirator approved by NIOSH for organic dust and vapors. Wash thoroughly after handling.

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 reuse.

In case of:

FIRE, use water, dry chemical or CO₂.

SPILL OR LEAK, flush area with water spray.

Labeling Requirements

Product label plus DOT Corrosive label required by law.

For More Information

For more information, contact Monsanto Fibers and Intermediates Co.,
800 N. Lindbergh Blvd., St. Louis, MO 63167. Phone: (314) 694-1000.

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MONSANTO FIBERS AND INTERMEDIATES CO.
800 N. Lindbergh Blvd., St. Louis, Mo. 63167
a unit of Monsanto Company

HEXAMETHYLENE DIAMINE

I. Preface

This document summarizes Monsanto toxicology data for hexamethylene diamine (CAS #124-09⁴4). Unless indicated otherwise, these tests were conducted on technical grade hexamethylene diamine produced by Monsanto. The typical composition of the product is:

Hexamethylene diamine 99 + %

Byproducts less than 1% total:

aminomethyl cyclopentylamine
1,5-diamino-2 methylpentane
Diaminocyclohexane
Tetramethylene diamine
Imines, NH
Ammonia
Diamine hydrolyzeable nitrogen

II. Summary of Toxicity Studies

A. Ninety Day Subchronic Aerosol Inhalation Study (BD-79-346)

Fifteen Sprague-Dawley derived (CD®) rats of each sex per group were exposed to hexamethylene diamine aerosols for six hours per day, five days per week for thirteen weeks. The target concentrations were 0.0, 12.5, 50 and 200 mg/m³. Hematology and clinical chemistry parameters were examined on five animals per sex per group prior to exposure, during week 5 and on all surviving animals at the termination of the thirteen week exposure period. Ophthalmoscopic examinations were performed on all animals prior to exposure and on all surviving animals after the termination of the thirteen week exposure.

Surviving animals from Group IV were sacrificed during week 7 after six weeks of test material exposure because of high mortality. Gross necropsy examinations were performed on all animals. Histopathological examinations were done on all animals in the control, mid and high dose groups.

Exposure to the test material caused signs of respiratory and ocular irritation at the 50 and 200 mg/m³ levels. The animals' fur became discolored and contaminated with the test material and was most prevalent at the high level. The animals in the 200 mg/m³ group displayed respiratory dysfunction, yellow ano-genital staining, general debilitation, weight loss and poor condition prior to death or sacrifice. Body weight gains were reduced throughout the study in both sexes receiving 200 mg/m³ and females at the mid-dose level; males at the mid-dose level were similarly affected in weeks 1-8. The body weights in the group receiving 12.5 mg/m³ were similar to the control group and did not indicate a response to treatment.

At the five week examination, high dose males and females showed elevations in blood urea nitrogen and females also had elevated SGPT levels. Evidence of RBC count elevation was noted for both sexes at the high dose.

At the 13 week examination the glucose levels in the females at the low and intermediate levels were significantly depressed and appeared to be dose related. All other clinical parameters were not effected by the 13 week exposure to 12.5 or 50 mg/m³ of hexamethylene diamine.

Squamous metaplasia of tracheal and nasal epithelia, acute rhinitis and interstitial pneumonia were seen at

the high level; no treatment-related micropathology was seen at the intermediate level.

Conclusion: Hexamethylene diamine administered by inhalation as an aerosol produced excess mortality in animals dosed at 200 mg/m³ within six weeks. At 50 mg/m³ exposure, the animals had reduced body weight gain and depression in glucose levels. Lesser depressions in glucose levels were seen in females at 12.5 mg/m³. No treatment-related lesions were observed at gross necropsy, but the high dose rats exhibited histopathological changes of the nasal and tracheal epithelium and the lungs.

B. **Teratology Study (IT-78-282)**

Twenty-two pregnant Sprague Dawley rats per group were dosed by oral gavage at levels of 0, 112, 184 and 300 mg/kg/day in a water solution on days 7-16 of gestation. These levels had been set on the basis of results from a prior pilot study in which maternal toxicity was observed at 225 mg/kg/day.

There was one maternal death in each of the 0, 184 and 300 mg/kg/day groups and another dam was sacrificed as moribund in the high dose group. The high dose group deaths were preceded by clinical signs including labored breathing which indicated the deaths resulted from test material administration. The other death appeared to have been caused by gavage accidents. At 300 mg/kg/day, common clinical signs of maternal toxicity were scruffy coat, red crusty stain on face, urine staining of anus and respiratory rattles. Significant depressions in body weight gain and food consumption were also noted in the high dose group. No significant findings of reduced body

weight, reduced food consumption or clinical signs were seen in the other test groups when compared to controls.

There were no differences in the mean number of viable fetuses, total implantations or corpora lutea between treatment and control groups. The controls had a greater rate of pre-implantation losses than treated dams which was within the historical laboratory data range for this strain of rats. Fetal body weight was reduced in the high-dose group, but fetal crown-rump length was not reduced by this or any other treatment level. External examinations did not reveal treatment-related morphological changes. Visceral examinations revealed changes which were considered to be associated with retarded fetal growth in the high dose group. These included liver spottiness, unfused components of the sacral and caudal vertebrae, and poorly ossified cervical vertebral centra. This latter finding was also noted at the mid-dose level.

Conclusion: Treatment with hexamethylene diamine at a dosage of 300 mg/kg/day on days 7-16 resulted in maternal toxicity as evidenced by reduced body weight gains, clinical signs and death of approximately 10% of the dams. Lower dosage levels did not produce maternal toxicity. Retarded development in fetuses of dams treated at 300 mg/kg/day was evidenced by reduced body weight, slight retardation of skeletal development and possibly liver spottiness. The dosage of 112mg/kg/day had no effect on fetuses and only slight retardation of cervical vertebral ossification precluded the 184 mg/kg/day as being the no effect level.

For the Sprague-Dawley rat, which is susceptible to teratogenic effects, hexamethylene diamine was not teratogenic when administered on days 7-16 of gestation via the oral route.

C. Metabolism Study (BD-79-347)

Six Sprague-Dawley rats (3 male and 3 female) received a single oral dose containing 1.84 mg hexamethylene diamine and an average of 11.96 uCi ^{14}C -hexamethylene diamine. Based on the body weights of the rats, this dose provided an average of 7.3 mg/kg for males and 8.5 mg/kg for females of hexamethylene diamine.

Urine, feces and expired air were collected at 0-8, 8-16, 16-24, 24-48 and 48-72 hours post-treatment. The level of ^{14}C -activity found in the urine of male rats ranged from 45.16 to 54.05% with an average of 49.75% of the administered dose. The total ^{14}C -activity found in the urine of female rats ranged from 47.34% to 64.81% with an average of 58.65% of the dose. The majority of ^{14}C -activity in the urine was excreted during the 0-8 hour post-treatment interval. The ^{14}C -activity found in the feces of male rats ranged from 21.31 to 32.54% and averaged 26.61% of the dose. The ^{14}C -activity found in the feces of female rats ranged from 8.46 to 28.77% and averaged 15.40% of the administered dose. The ^{14}C -activity found in expired air as carbon dioxide averaged 8.70% in the male rats and 13.35% in the female rats. The ^{14}C -activity found in expired air as volatiles was minimal, averaging 0.01% of the dose for both male and female rats.

The total ^{14}C -activity eliminated from male rats ranged from 84.56% to 85.93% with an average of 85.28% of the dose. The total ^{14}C -activity eliminated from female rats ranged from 85.71% to 90.92% and averaged 88.89% of the dose.

Conclusion: ^{14}C -hexamethylene diamine and its metabolites are quantitatively excreted 72 hours after oral administration, with the major route of elimination via the kidneys as urine and the secondary route was via gastrointestinal elimination in the feces.

D. Ames/Salmonella Assay (LF-76-206)

Hexamethylene diamine was assayed at 0.1, 1, 10, 100, 500 and 1000 $\mu\text{g}/\text{plate}$ with Salmonella typhimurium strains TA 1535, 1537, 1538, 98 and 100. The assay employed the plate incorporation method with and without S-9 metabolic activation.

Hexamethylene diamine showed no toxicity to any strain at the levels tested. The results of the study demonstrated that hexamethylene diamine did not produce any significant increases in reversion frequencies suggestive of mutagenic activity with or without metabolic activation for any of the five strains tested.

Conclusion: Hexamethylene diamine was considered non-mutagenic in the Ames/Salmonella assay under these test conditions.

E. In vivo Rat Bone Marrow Chromosome Study (HL-83-196)

Hexamethylene diamine was administered in a single oral dose to twenty four rats of each sex per group with a water vehicle control or at dose levels of 75, 250 or 750 mg/kg. One animal from each of the 250 mg/kg and 750 mg/kg groups died while on study. Abnormal clinical signs were observed in all treated groups. The mid and high dose groups showed significant body weight depressions as compared to controls.

Surviving animals from each group were sacrificed at 6, 12, 24, and 48 hours after the single administration of the test material. Two hours prior to sacrifice, the animals received a single intraperitoneal dose of colchicine (2.0 mg/kg). Femoral bone marrow was aspirated at sacrifice and underwent subsequent fixation, dispersion onto slides, air drying and staining with Giemsa. Sixty spreads per slide were read to determine numbers and types of chromosomal aberrations. Since no evidence of mitotic delay was seen after analysis of the mitotic indices, the slides from the 48-hour sacrifice were not analyzed for chromosomal aberrations.

No statistically significant increases in the frequency of chromosomal aberrations compared to control values were seen for any of the dose levels that were tested. No significant differences were seen in the mean modal numbers or mitotic indices of the test groups when compared to control values for the time periods examined.

Conclusion: Hexamethylene diamine administered by gavage at doses of 75, 250 and 750 mg/day did not produce clastogenic changes such as numerical or structural chromosomal aberrations in bone marrow cells of Sprague-Dawley rats. Hexamethylene diamine was considered non-mutagenic under these test conditions.

F. Aquatic Toxicity to Daphnia magna (ESC-EA6-84-8)
Acute 48 hr. LC50 - 50 ppm; slightly toxic.

HEXAMETHYLENEDIAMINE
IH MONITORING DATA
1979-1984

PLANT	NO. EXPOSED EMPLOYEES	NO. SAMPLES			DETERMINATION TYPE	RESULT, PPM	TYPICAL EXPOSURE PPM
		PERSONAL	AREA	OTHER			
Decatur, AL	14	10	0	0	10	0.02-0.26	0.10
Pensacola, FL	10	95	0	0	95	<0.01-1.34	<0.05

Monsanto Company produces 250-400 million pounds of HMDA annually in 2 U.S. plants.

Approximately 98% of the HMDA produced annually is used as an intermediate at 2 Monsanto sites to produce nylon polymer.

Monsanto MATERIAL SAFETY DATA

Page 1 of 4

MONSANTO PRODUCT NAME
**AQUEOUS
HEXAMETHYLENEDIAMINE**
(70-90% Solutions)

MONSANTO COMPANY
800 N. LINDBERGH BLVD.
ST. LOUIS, MO 63167
*Emergency Phone No.
(Call Collect)
314-694-1000*

PRODUCT IDENTIFICATION

Synonyms: 1,6-Hexanediamine, 1,6-Diaminohexane
Chemical Formula: Molecular $H_2N(CH_2)_6NH_2$
Empirical $C_6H_{16}N_2$
Chemical Family: Aliphatic Diamine
CAS Reg. No.: 124-09-4
DOT Proper Shipping Name: Hexamethylenediamine Solution
DOT Hazard Class/ I.D. No.: Corrosive Material/UN1783
DOT Label: Corrosive
Hazardous Substance(s)/ RQ(s): Not Applicable
U.S. Surface Freight Classification: Hexamethylenediamine Solution

MATERIAL SAFETY DATA

WARNING STATEMENTS

DANGER!
EXTREMELY HAZARDOUS LIQUID
CAUSES SEVERE BURNS TO EYES AND SKIN

PRECAUTIONARY MEASURES

Do not get in eyes, on skin, or clothing.
Avoid breathing vapor.
Keep container closed.
Use with adequate ventilation.
Wash thoroughly after handling.

Emptied container retains vapor and product residue. Observe all labelled safeguards until container is cleaned, reconditioned or destroyed. DO NOT CUT OR WELD ON OR NEAR THIS CONTAINER.

EMERGENCY AND FIRST AID PROCEDURES

FIRST AID: IF IN EYES OR ON SKIN, immediately flush with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse. Destroy contaminated shoes.

Aqueous Hexamethylenediamine (70-90% Solutions)

OCCUPATIONAL CONTROL PROCEDURES

Eye Protection: Wear chemical safety goggles to prevent eye contact. Have eye baths immediately available where eye contact can occur.

Skin Protection: Wear appropriate impervious gloves and impervious protective clothing to prevent skin contact. Wear face shields and impervious aprons and boots when splashing is likely to occur. Remove contaminated clothing promptly and launder before reuse. Provide safety shower at any location where skin contact can occur. Wash immediately when skin is contaminated.

Respiratory Protection: Use NIOSH approved equipment when airborne exposure is excessive. Consult respirator manufacturer to determine appropriate type equipment for given application.

Ventilation: Provide sufficient ventilation to minimize exposure. Local exhaust ventilation preferred.

Airborne Exposure Limits: Product: Hexamethylenediamine wt. % 70-90
ACGIH TLV/TWA/STEL and OSHA PEL/TWA not established.

FIRE PROTECTION INFORMATION

Flash Point: <200°F **Method:** Closed Cup

Extinguishing Media: Water spray, foam, dry chemical or CO₂ or any Class B extinguishing agent.

Special Firefighting Procedures: Firefighters exposed to material or products of combustion should wear full protective clothing and self-contained breathing apparatus. Firefighting equipment should be thoroughly decontaminated after use.

REACTIVITY DATA

Materials to Avoid: Oxidizing agents, acids, isocyanates, aldehydes, ketones, anhydrides, phenols, nitrates and halogenated compounds.

Hazardous Decomposition Products: Ammonia.

Hazardous Polymerization: Does not occur.

PHYSIOLOGICAL EFFECTS SUMMARY

The following information represents the results of tests conducted with animals to assess the physiological properties of Hexamethylenediamine. This information was used by qualified experts to develop the labeling statements and the recommended Occupational Control Procedures. Evaluation of the significance of the data from individual studies may require professional knowledge of toxicology.

Oral LD₅₀ (Rat): 980 mg/kg, Moderately Toxic
 Dermal LD₅₀ (Rabbit): >2,000 mg/kg, Slightly Toxic
 Eye Irritation (Rabbit): (FHSA) Corrosive
 Skin Irritation (Rabbit): (FHSA) Corrosive
 Inhalation (Rat): 10/10 rats survived exposure to 0.95 mg/l of hexamethylenediamine for 4 hours
 Microbial mutagenicity assay using five *Salmonella* strains and one yeast strain with and without mammalian microsomal activation did not reveal any mutagenic effect.

(Physiological Effects Summary Continued On Next Page)

Aqueous Hexamethylenediamine (20-30% solutions)

MATERIAL SAFETY DATA

Monsanto MATERIAL SAFETY DATA

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PHYSIOLOGICAL EFFECTS SUMMARY (Continued)

No adverse effects were observed when hexamethylenediamine was fed to rats at dietary levels of 0, 50, 150 or 500 mg/kg/day for 90 days.

In a subacute aerosol inhalation study, rats were exposed to hexamethylenediamine at 12.8, 51.0 and 215 mg/m³ for 6 hours/day, 5 days/week for 7 weeks. The study was terminated at the 7th week due to the high mortality rate at 215 mg/m³. Respiratory irritation was observed in both the high and mid dose groups. Microscopic changes in the lung were observed in the high exposure group only. The no effect level was 12.8 mg/m³.

Rats were orally dosed with 0, 112, 184 and 300 mg/kg hexamethylenediamine on days 7 through 16 of gestation. At the 300 mg/kg dose, maternal toxic effects were demonstrated by reduced body weight, decreased food consumption and 10% death of treated animals. Fetal toxicity was demonstrated by retarded fetal weight gain and skeletal development. No evidence of a teratogenic response was observed at any dosage.

PHYSICAL DATA

Appearance:	Colorless Liquid
Melting Point:	5°C (70% HMD) 25°C (90% HMD)
Boiling Point:	Starts at 113°C (pure HMD = 200.6°C)
Specific Gravity @ 25/4°:	0.9300 (70% HMD) to 0.8900 (40% HMD)
Viscosity @ 50°C, CENTIPOISE:	4.8 (90% HMD) to 5.8 (85% HMD)
Solubility in Water @ 25°C:	90% (HMD)

Note: These physical data are typical values based on material tested but may vary from sample to sample. Typical values should not be construed as a guaranteed analysis of any specific lot or as specification items.

SPILL, LEAK & DISPOSAL INFORMATION

Spill or Leak

Procedure:

Keep unnecessary people away. Stay upwind. Eliminate all sources of ignition. Shut off leak if without risk. Spray with water or foam to reduce fire and fume hazard.

If necessary to enter spill area, wear self-contained breathing apparatus and full protective clothing including boots.

Contain spill. Small spills can be collected on sand or other non-combustible absorbent material, then flush area with water. Sweep or shovel small dry spills into dry containers and cover. Remove containers then flush area with water. Collect large spills by pumping into drums, salvage tank or with vacuum truck. Residual soils may be contaminated, remove for disposal.

Guard against watershed, waterway, and water supply contamination. If not possible, notify health and pollution control authorities.

Waste Disposal: This material should not be dumped, spilled or flushed into sewers or public waterways.

Waste liquid should be disposed of in an approved hazardous waste incinerator. Contaminated soils and solid material should be disposed of in an approved hazardous waste landfill.

Applicable federal, state and local regulations should be followed when disposing of this material.

MATERIAL SAFETY DATA

Aqueous Hexamethylenediamine (70% solution)

Monsanto MATERIAL SAFETY DATA

Page 4 of 4

DATE: 3/1/84

REVISED:

SUPERSEDES:

MSDS NO.: S00010204

FOR ADDITIONAL NON-EMERGENCY INFORMATION, CONTACT:

Monsanto Company
800 North Lindbergh Blvd.
St. Louis, MO 63167
314-694-1000

Aqueous Hexamethylenediamine (75-90% solutions)

MATERIAL SAFETY DATA

Although the information and recommendations set forth herein (hereinafter "Information") are presented in good faith and believed to be correct as of the date hereof, Monsanto Company makes no representations as to the completeness or accuracy thereof. Information is supplied upon the condition that the persons receiving same will make their own determination as to its suitability for their purposes prior to use. In no event will Monsanto Company be responsible for damages of any nature whatsoever resulting from the use of or reliance upon information. NO REPRESENTATIONS OR WARRANTIES, EITHER EXPRESS OR IMPLIED, OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE OR OF ANY OTHER NATURE ARE MADE HEREUNDER WITH RESPECT TO INFORMATION OR THE PRODUCT TO WHICH INFORMATION REFERS.

This form has been approved by the Occupational Safety and Health Administration as "equivalent to" OSHA Form 20.

MONSANTO PRODUCT NAME
**HEXAMETHYLENEDIAMINE
(ANHYDROUS)**

MONSANTO COMPANY
800 N. LINDBERGH BLVD.
ST. LOUIS, MO 63167

Emergency Phone No.
(Call Collect)
314-694-1000

PRODUCT IDENTIFICATION

Synonyms:	1,6-Hexanediamine; 1,6-Diaminohexane
Chemical Formula:	Molecular $H_2N(CH_2)_6NH_2$ Empirical $C_6H_{16}N_2$
Chemical Family:	Aliphatic Diamine
CAS Reg. No.:	124-09-4
DOT Proper Shipping Name:	Hexamethylenediamine, Solid
DOT Hazard Class/ I.D. No.:	Corrosive Material/UN2280
DOT Label:	Corrosive
Hazardous Substance(s)/ RQ(s):	Not Applicable
U.S. Surface Freight Classification:	Hexamethylenediamine; Anhydrous or Molten

MATERIAL SAFETY DATA

WARNING STATEMENTS

DANGER!
CAUSES SEVERE BURNS TO EYES AND SKIN
COMBUSTIBLE

PRECAUTIONARY MEASURES

Keep away from heat and flame.
Do not get in eyes, on skin, or clothing.
Wear chemical goggles and rubber gloves.
Avoid breathing dust or vapor.
Handle only in areas with sufficient ventilation to prevent irritation or wear a suitable respirator.
Keep container closed.
Wash thoroughly after handling.

Emptied container retains vapor and product residue. Observe all labeled safeguards until container is cleaned, reconditioned or destroyed. DO NOT CUT OR WELD ON OR NEAR THIS CONTAINER.

EMERGENCY AND FIRST AID PROCEDURES

FIRST AID: IF IN EYES OR ON SKIN, immediately flush with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse. Destroy contaminated shoes.

Hexamethylenediamine (Anhydrous)

OCCUPATIONAL CONTROL PROCEDURES

Eye Protection: Wear chemical safety goggles to prevent eye contact. Have eye baths immediately available where eye contact can occur.

Skin Protection: Wear appropriate impervious gloves and impervious protective clothing to prevent skin contact. Wear face shields and impervious aprons and boots when splashing is likely to occur. Remove contaminated clothing promptly and launder before re-use. Provide safety showers at any location where skin contact can occur. Wash immediately when skin is contaminated.

Respiratory Protection: Use NIOSH approved full-face equipment when airborne exposure is excessive. Consult respirator manufacturer to determine appropriate type equipment for given application.

Ventilation: Provide ventilation to minimize exposure. Local exhaust ventilation preferred. Consult NFPA Standard 91 for design of exhaust systems.

Airborne Exposure Limits: Product: Hexamethylenediamine 100% by wt.
Although OSHA and ACGIH have not established specific exposure limits for this material, they have established limits for nuisance dusts:

OSHA PEL/TWA: Total 15 mg/m³; Respirable 5 mg/m³
ACGIH TLV/TWA: Total 10 mg/m³; Respirable 5 mg/m³

These limits are stated only to indicate the least stringent airborne dust exposure levels applicable to nuisance dusts. Hexamethylenediamine may be corrosive to the eye and skin at exposure concentrations below these limits.

FIRE PROTECTION INFORMATION

Combustible Solid

Flash Point: 200°F **Method:** Closed Cup

Flammable Limits, (In Air) % Vol.:
Lower Limit: 0.7
Upper Limit: 6.3

Extinguishing Media: Waterspray or any Class A extinguishing agent.

Special Firefighting Procedures: Wear full protective clothing including boots and self-contained breathing apparatus when exposed to products of combustion. Thoroughly decontaminate equipment after use.

REACTIVITY DATA

Materials to Avoid: Oxidizing agents, acids, isocyanates, aldehydes, ketones, anhydrides, phenols, Nitrates and halogenated compounds.

Hazardous Decomposition Products: Ammonia.

Hazardous Polymerization: Does not occur.

Hexamethylenediamine (Anhydrous)

MATERIAL SAFETY DATA

0019

PHYSIOLOGICAL EFFECTS SUMMARY

The following information represents the results of experiments conducted to assess the physiological properties of this material. This information was used by qualified experts to develop the Warning Statements and the recommended Occupational Control Procedures. Because dosages were intentionally chosen to induce toxic effects, evaluation of the significance of the data from individual studies may require professional knowledge of toxicology.

Oral LD₅₀ (Rat): 980 mg/kg, Slightly Toxic
Dermal LD₅₀ (Rabbit): >2,000 and <3,160 mg/kg, Slightly Toxic
Eye Irritation (Rabbit): (FHSA) Corrosive
Skin Irritation (Rabbit): (FHSA) Corrosive
Dust Inhalation (Rat): 10/10 rats survived exposure to 0.95 mg/l of hexamethylenediamine for 4 hours

Microbial mutagenicity assay using five *Salmonella* strains and one yeast strain with and without mammalian microsomal activation did not reveal any mutagenic effect.

No adverse effects were observed when hexamethylenediamine was fed to rats at dietary levels of 0, 50, 150 or 500 mg/kg/day for 90 days.

In a subacute aerosol inhalation study, rats were exposed to hexamethylenediamine at 12.8, 51.0 and 215 mg/m³ for 6 hours/day, 5 days/week for 7 weeks. The study was terminated at the 7th week due to the high mortality rate at 215 mg/m³. Respiratory irritation was observed in both the high and mid dose groups. Microscopic changes in the lung were observed in the high exposure group only. The no effect level was 12.8 mg/m³.

Rats were exposed to dust concentrations of hexamethylenediamine at 49 mg/m³ or 262 mg/m³, 6 hours per day, 5 days/week for 4 weeks. Ruffed fur, ptosis and hypoactivity but no evidence of target organ toxicity was observed at 49 mg/m³. Sneezing, rhinitis and rattled breathing were evidenced at 262 mg/m³. Discolored fur, ear and tail lesions indicative of burns and depressed body weight gain were also observed at this treatment level.

Rats were orally dosed with 0, 112, 184 and 300 mg/kg hexamethylenediamine on days 7 through 16 of gestation. At the 300 mg/kg dose, maternal toxic effects were demonstrated by reduced body weight, decreased food consumption and 10% death of treated animals. Fetal toxicity was demonstrated by retarded fetal weight gain at 300 mg/kg/day and retarded skeletal development at both 300 and 184 mg/kg/day. No evidence of a teratogenic response was observed at any dosage.

Single oral administration of C¹⁴ - hexamethylenediamine to rats indicated that the product and its metabolites were quantitatively excreted within 72 hours following administration. The major route of elimination was in the urine.

PHYSICAL DATA

Appearance:	Colorless, crystalline solid
Melting Point:	40.87°C
Solubility In Water:	Completely soluble
In Ethyl Alcohol:	Slightly soluble
In Benzene:	Slightly soluble
Boiling Point @ 760 mm Hg:	201.9°C
@ 90 mm Hg:	132°C
@ 10 mm Hg:	82°C

(Physical Data Continued On Next Page)

MATERIAL SAFETY DATA

Hexamethylenediamine (Anhydrous)

PHYSICAL DATA (Continued)

Specific Gravity ($H_2O = 1$), d_4^{25} g/cc:	0.8477
Critical Pressure, Atmosphere:	32.5
Critical Temperature:	390.4°C
Viscosity @ 50°C, Centipoise:	1.50

Note: These physical data are typical values based on material tested but may vary from sample to sample. Typical values should not be construed as a guaranteed analysis of any specific lot or as specification items.

SPILL, LEAK & DISPOSAL INFORMATION

Spill or Leak

Procedures:

Keep unnecessary people away. Stay up-wind. Eliminate all ignition sources. Spray with water or foam to reduce fire and fume hazard. Shut off leak if without risk. If necessary to enter the spill area, wear self-contained breathing apparatus and full protective clothing including boots.

Contain spill. Small spills can be collected on sand or other non-combustible absorbent material. Flush area with water. Small dry spill - sweep or shovel into clean dry containers and cover. Remove containers then flush area with water.

Collect large spills by pumping into drums, salvage tank or with vacuum truck. Residual soils may be contaminated. Remove for disposal.

Guard against watershed, waterway and water supply contamination. If not possible notify health and pollution control authorities.

Waste Disposal:

This material should not be dumped, spilled or flushed into sewers or public waterways.

Contaminated soils and solid material should be disposed of in an approved hazardous waste landfill or incinerator.

Applicable federal state and local regulations should be followed when disposing of this material.

DATE: 3/1/84

REVISED:

SUPERSEDES:

MSDS NO.: 000124094

FOR ADDITIONAL NON-EMERGENCY INFORMATION, CONTACT:

Monsanto Company
800 North Lingbergh Blvd.
St. Louis, MO 63167
314-694-1000

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This form has been approved by the Occupational Safety and Health Administration as "equivalent to" OSHA Form 20.

Hexamethylenediamine (Anhydrous)

MATERIAL SAFETY DATA

MONSANTO TEXTILES COMPANY

DMEX No. 2006

PENSACOLA, FLORIDA

DATE: December 15, 1979
REVISION: Original

CODE: ASD-4751

SPECIAL PROCEDURE BRIEF
HEXAMETHYLENEDIAMINE IN AIR

HMD (4751)

Standard Preparation and Calibration:

Prepare a blend of approximately 7 mg/ml by weighting about 0.1 g of 85% HMD into a 100-ml volumetric flask and diluting to the mark with MeOH containing 6% KOH. Transfer 0.25 ml of this stock solution to a 50-ml volumetric flask and dilute to the mark with MeOH containing 6% KOH.

$$\text{HMD in standard, } \mu\text{g/ml} = \text{g sample} \times \frac{\% \text{ HMD}}{100} \times 10^4 \times .005$$

OR

$$= \text{g sample} \times \frac{\% \text{ HMD}}{100} \times 50$$

Sampling

Using a molecular sieve collection tube and a personal sampling pump, collect a sample noting the volume of air sampled. (The pump should be calibrated as given in STM 2002). As a guideline, when HMD vapors are at 12 mg/m³ a sampling rate of 0.5 l/minute for 8 hours will give about 2.4 mg HMD.

Analysis

Carefully wipe off the outside of the molecular sieve tube and place the contents of the tube and the pieces of the tube into a reaction vessel. Add, by pipette, 2 ml of 6% KOH in methanol and tightly close the vessel. Place on a wrist action shaker and shake for 30±1 minutes.

With GC set at conditions listed, inject a 3 µl sample.

Typical Instrument Conditions

Column: 8" x 2 mm glass, 4% carbowax 20M plus 0.8% KOH on Carbopack B

Amplifier Range: 100 Attn: XI

N₂: Rotameter, 40(11 lbs. back pressure)

Air: 30 lbs.

N₂: 24 lbs.

Temp: 130°C hold for 3 minutes
155°C @ 40°/min. hold for 2 minutes
190°C @ 40°/min. hold for 1 minute

Injection: 3 µl

Calculation

$$\mu\text{g HMD in sample} = \frac{\text{area sample}}{\text{area standard}} \times \mu\text{g HMD in standard}$$

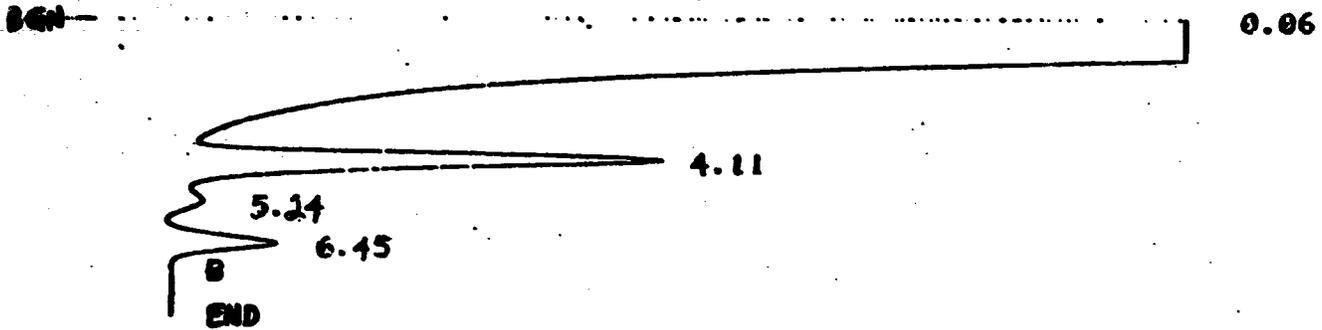
$$\text{HMD, mg/m}^3 = \frac{\mu\text{g HMD in sample}}{\text{liters of air sampled at NTP}}$$

PERKIN ELMER SIGMA SYSTEM FID DETECTOR

(3120 GC)

COL: 8' X 2MM GLASS
 48 CARBOWAX 20M PLUS 0.8% KOH ON CARBOPACK B
 AMPLIFIER RANGE 100; ATTN X 1
 N₂ - ROTOMETER, 40 .81 LBS. BACK PRESSURE)
 AIR - 30 LBS.
 H₂ - 24 LBS.
 TEMP: 130°C HOLD FOR 3 MIN.
 155°C @ 40/MIN HOLD FOR 2 MIN
 190°C @ 40/MIN HOLD FOR 1 MIN
 BLEND: 1.15 MG HMD IN 2 MLS 6% KOH IN METHANOL
 INJECTION - 3.0 µl

SENSITIVITIES 400



MMH 1 DFT 2 METH .20 FILE 30
 RUN 1 12; 30.2 4 / 16 / 79

TIME	AREA	BC	RRT	PF	C	NAME
0.07	366.5497	T	0.017	1.000	4332.7488	!
4.11	2.4753	TS	1.000	0.079	0.9778	MG HMD:
5.24	0.1541	TS	1.274	1.000	0.7705	!
6.44	0.7262	S	1.566	1.000	3.4310	!

PERKIN-ELMER

Analyte : BMDA

Matrix : AIR

**Procedure: COLLECT VAPORS ON SILICA
GEL, DESORB INTO AQUEOUS
BUFFER, ANALYZE BY HPLC/
PCR W/FLUORESCENCE DETEC.**

Validation Date: 12-16-82

Range: 0.008-18 PPM IN AIR

**Author(s): J M WARNER
R K BFASLEY**

1.0 PRINCIPLE OF METHOD

1.1

Described in this method is an HPLC/PCR (Post Column Reactor) procedure for the selective and sensitive determination of HMDA (1,6-diaminohexane, hexamethylenediamine, triethylenediamine, or HMD) in air.

1.2

An accurately measured volume of air is drawn through a silica gel sampling tube which adsorbs HMDA vapors. The loading of silica gel in the tube is 150 mg in the front section and 75 mg in the back. The two sections are separated by a small foam plug.

1.3

The front and back silica gel sections are separately desorbed into an aliquot of HPLC mobile phase (pH 4.0 potassium hydrogen phthalate aqueous buffer with 0.08% triethylamine modifier) containing 5 ug/mL propylamine as internal standard. The resulting solution is analyzed by HPLC/PCR using an ion exchange column. The primary amines are reacted after chromatography with o-phthalaldehyde in the presence of 2-mercaptoethanol to form the isoindoles and are assayed with a fluorescence detector.

1.4

Quantitation is based on peak areas which are measured by an electronic integrator.

2.0 SAFETY

2.1

Some of the chemicals and solvents used are hazardous and should be used only with proper precautions and adequate ventilation.

3.0 RANGE AND SENSITIVITY

3.1 Range

Laboratory validation for the method was for the range of 0.008 - 18 ppm (HMDA in air) based on a 20 liter air sample.

3.2 Sensitivity

The lower limit of validation of the method is 0.008 ppm based on a 20 liter air sample.

4.0 INTERFERENCES

4.1

No interferences were observed in the chromatograms from samples collected during field testing at the [REDACTED] plant.

4.2

The pH of the post column reaction must be carefully adjusted. A pH too low (acidic) does not allow the reaction to occur and no isoimidazole peaks will be observed. A pH which is too high (basic) will cause non-linearity in the calibration curve. The optimum pH at the detector outlet is 10.

4.3

Three week storage of silica gel tubes used for air sampling under conditions of both low (<10%) and high (96.5%) relative humidity indicated no adverse effects.

4.4

No adverse effects on collection, chromatography, post column derivatization, or quantitation of HMDA were observed in this method under conditions of high humidity (96.5% RH).

5.0 PRECISION AND ACCURACY

5.1 Precision

The summary report in Attachment 1 lists the VALMET [1] data analysis by NIOSH-type statistical testing of the validation results. The Pooled Coefficient of Variation (relative standard deviation) for HMDA was 0.079 for the six levels of validation. Bartlett's test shows a direct correlation between the validation levels and the relative variance of their data.

5.2 Accuracy

A TSI Model 3050 Berglund-Liu Vibrating Orifice Monodisperse Aerosol Generator (VOG) was used to generate air standards. Spiking and air sampling experiments showed that the VOG produced HMDA in air standards as vapors rather than aerosols [4]. The HMDA used to generate the standard atmospheres was labeled with carbon-14 and all HPLC analyses were corroborated by liquid scintillation counting (LSC). Attachment 2 shows good correlation between the two methods (R squared = 0.985). Five spiked samples from field tests showed an overall average recovery of 88% and a range of 69-103%. Eight spiked samples from laboratory tests showed an average recovery of 91%.

6.0 ADVANTAGES AND DISADVANTAGES

6.1 Advantages

The sampling apparatus is compact, readily portable, easy to use, and involves no liquids. Interferences are considerably below the claimed limit of detection. Sample analysis is accomplished rapidly by an instrumental method.

The equipment and chemicals are commercially available.

The isoindole derivatives of HMDA and the internal standard (propylamine, PA) are highly fluorescent and permit low detection limits. The use of post column derivatization avoids time-consuming sample preparation steps needed in precolumn derivatization.

6.2 Disadvantages

Two separate buffer or buffered reagent systems are required for the chromatography and post column reaction. These systems require some degree of user preparation.

7.0 APPARATUS

7.1

High Pressure Liquid Chromatograph. A DuPont 8800 high pressure liquid chromatograph pump module, Waters WISP 710B autosampler, Varian PCR-1 postcolumn reactor system, and Varian Fluorichrom [tm] fluorescence detector, or equivalent.

7.2

Cation Exchange Liquid Chromatographic Column. A 25.0 cm x 4.60 mm I.D. Whatman Partisil 10 SCX column. The column is preconditioned by flushing with charcoal filtered deionized water at 1.1 mL/min for one hour followed by the pH 4.0 potassium hydrogen phthalate aqueous buffer mobile phase (Section 8.0) at 1.1 mL/min until a stable baseline is achieved.

The lifetime of a given column is somewhat limited (approximately three months under heavy use). However, its life can be extended by following a number of practices. When the column is not to be used for an extended period of time (five days or more) it is best to flush the column with deionized water and then methanol. This prevents the crystallization of buffers in the column and inhibits the growth of bacteria. When retention times and resolution start to decrease significantly some limited column regeneration may be accomplished by following the column-washing technique suggested by the manufacturer. Pass 50 mL of each of the following mobile phases through the column:

1. Buffer wash - 5 x as concentrated as that used previously.
2. Distilled water.
3. Acid wash - 0.1M sulfuric acid.
4. Distilled water.
5. Complexer wash - 0.1M disodium EDTA.
6. Distilled water.
7. Methanol wash.
8. Distilled water.
9. Buffer for separation.

Mobile phases of basic pH must be avoided to preserve the integrity of the Partisil column packing.

7.3

Recording Integrator. An in-house computerized recording integration system (Monsanto Chromatographic Data System) was used. A Hewlett Packard 3390A recording integrator was used as backup and is recommended for field use.

7.4

Personal Sampling Pumps. Calibrated battery-powered pumps capable of drawing an accurate and reproducible flow of approximately 0.5 L/min through the silica gel tubes are required. Recommended are DuPont P4000 pumps.

7.5

Soap Film Bubble Flowmeter. A Mast Development Co. Series 823-Bubble flowmeter was used and is recommended. Mast Development Co., Air Monitoring Division, 2212 East 12th Street, Davenport, IA 52803.

7.6

Stopwatch.

7.7

Glass Vials. Waters Associates, Inc., Maple Street, Milford, MA 01757, 1 dram vials (Part Number 72710) are used for desorption and sample analysis. Also used were Waters H-style vial caps (Part Number 72711) and Waters PTFE septa (Part Number 73005).

7.8

Charcoal Developer. Occupational Health Associates, 310 Sovereign Ct., Manchester, ND 58011, Catalogue Number 226D-03-115.

7.9

Micropipettes. Eppendorf Digital Pipettes, Fisher Scientific Co., 711 Forbes Avenue, Pittsburgh, PA 15219, 100 - 1000 microliters, Catalogue Number 21-278-43C; 10 - 100 microliters, Catalogue Number 21-278-43B. Tips, 100 - 1000 microliters, Catalogue Number 21-371-1; 1 - 100 microliters, Catalogue Number 21-371.

7.10

Macropipette. Oxford Laboratories Macro-Set Pipette. Fisher Scientific Co., 1 - 5 mL, Catalogue Number 21-195. Tips, 1 - 5 mL, Catalogue Number 21-195-3.

7.11

Assorted Laboratory Glassware. Pipettes, volumetric flasks, graduated cylinders, etc.

7.12

Tygon Tubing. 1/8" I.D. x 1/4" O.D. x 1/16" wall, Fisher Scientific Co., Catalogue Number 14-169-1E.

7.13

Silica Gel Sampling Tubes. SKC, Inc., R.D. 1, 395 Valley View Road, Eighty Four, PA 15330, 6 x 70 mm, 75/150 mg silica gel, Catalogue Number 226-10.

7.14

Membrane Filter Assembly. Acrodisc-CR [tm], Gelman Instrument Co., Ann Arbor, MI 48106, Product Number 4219, Non-Sterile, 0.45 micron pore size.

7.15

Disposable Syringes. 5 cc, Becton-Dickinson and Co., Rutherford, NJ 07070, Luer Slip Tip, without needle.

7.16

Aerosol Generator (Optional). Used for the generation of the air standard concentrations used in laboratory validation. Berglund-Liu Monodisperse Aerosol Generator (Model 3050) equipped with a Model 3054 Aerosol Neutralizer (Both obtained from ISI, Inc., 500 Cardigan Road, P.O. Box 43394, St. Paul, MN 55164) and a Model 475 Accurate Infusion Pump (Syringe Pump) obtained from New England Medical Instruments, Inc., Medway, MA 02053.

7.17

Solvent Filter Apparatus. All glass, for filtering HPLC mobile phase. Millipore Corporation, Bedford, MA 01730, Catalogue Number XX15 047 00.

7.18

Solvent Clarification Membranes. Millipore Corporation, 0.22 micron pore size, type GS, Catalogue Number GSWP 047 00.

8.0 REAGENTS**8.1**

Methanol, OmniSolv [tm] prefiltered distilled in glass, Matheson, Coleman, and Bell, Catalogue Number MX0488-1.

8.2

Iso-propyl alcohol, OmniSolv [tm] prefiltered distilled in glass, Matheson, Coleman and Bell, Catalogue Number MX1843.

8.3

Deionized water, filtered through ion exchange resin and charcoal, Continental Deionized Water Service, 4338 Bridgeton Industrial Dr., St. Louis, MO.

(8.4

1,6-Hexanediamine (1,6-diaminohexane, HMDA) Aldrich Chemical Company, Inc., Milwaukee, WI 53233, Catalogue Number H1,169-6.

8.5

Triethylamine, Fisher Scientific Co., Fisher Reagent, Catalogue Number 0-4885.

8.6

Internal Standard.

Propylamine, Fisher Scientific Co., Reagent, Catalogue Number 1216.

8.7

(2-Mercaptoethanol, Fisher Scientific Co., Fisher Reagent, Catalogue Number 0-3446.

8.8

Phthalaldehyde (o-phthalaldehyde), Fisher Scientific Co., Fisher Reagent, Catalogue Number 0-4241.

8.9

Potassium Hydrogen Phthalate Primary Standard, Fisher Scientific Co., Fisher Certified ACS, Catalogue Number P-243.

8.10

(Buffer Solution, pH 10.00, potassium carbonate-potassium borate-potassium hydroxide, Fisher Scientific Company, Fisher Certified, Catalogue Number So-8-116.

8.11**Preparation of Mobile Phase.**

Into a clean four liter bottle measure three liters of charcoal filtered deionized water. Add 30.00 g potassium hydrogen phthalate and stir magnetically until dissolved. Using a solvent filter apparatus (Section 7.17) and a solvent clarification membrane (Section 7.18) filter the solution to remove any particles which may clog the chromatographic column. Add 150 mL of methanol and with an Oxford pipette add 3.6 mL of triethylamine. Stir until homogeneous. This solution contains 0.08% (w/w) triethylamine as a mobile phase modifier.

8.12**Preparation of Propylamine Internal Standard Solution.**

In a 1000 mL volumetric flask place approximately 995 mL of mobile phase. Using an Eppendorf micropipette inject subsurface 69.7 microliters (50 mg) of propylamine. Dilute the solution to volume with more mobile phase. This primary standard contains 50 micrograms/mL of propylamine. Using a volumetric pipette transfer 100 mL of this primary standard solution to a second 1000 mL volumetric pipette. Dilute the solution to the mark with more mobile phase. This internal standard solution contains 5.0 micrograms/mL of propylamine.

8.13**Preparation of OPA Post Column Reaction Buffer Solution.**

Dissolve 1.00 g of OPA in 100 mL of methanol. Using a volumetric pipette transfer 50 mL of the OPA/methanol solution to a one liter amber glass bottle. Add to it 950 mL of pH 10.0 borate buffer solution. Using an Oxford macropipette add to this 2.0 mL of 2-mercaptoethanol. Mix well.

9.0 CALIBRATION AND STANDARDIZATION

The composition of standards used for calibration is as follows:

- Solution A.** Into a 100 mL volumetric flask accurately weigh approximately 0.03465 g HMDA. Dissolve and dilute to the mark with the internal standard solution prepared above in Section 8.12. This solution contains 347 micrograms/mL of HMDA.
- Solution B.** In a 100 mL volumetric flask dilute 25 mL of Solution A to 100 mL with internal standard solution. This solution contains 86.8 micrograms/mL.
- Solution C.** In a 100 mL volumetric flask dilute 10 mL of Solution A to 100 mL with internal standard solution. This solution contains 34.7 micrograms/mL.
- Solution D.** In a 100 mL volumetric flask dilute 2 mL of Solution A to 100 mL with internal standard solution. This solution contains 6.94 micrograms/mL.
- Solution E.** In a 100 mL volumetric flask dilute 0.5 mL of Solution A to 100 mL with internal standard solution. This solution contains 1.7 micrograms/mL.
- Solution F.** In a 100 mL volumetric flask dilute 0.1 mL of Solution A to 100 mL with internal standard solution. This solution contains 0.347 micrograms/mL.

Instrument Calibration.

Make three injections of Solution A (347 micrograms/mL, prepared above) into the high pressure liquid chromatograph [2] to assure that the system is conditioned and that detector response is consistent.

Analyze aliquots of Solutions A-F on the high pressure liquid chromatograph to prepare a standard curve of the detector response (peak area) of HMDA divided by the detector response of internal standard vs. micrograms/mL of HMDA. A typical calibration curve is shown in Attachment 3.

Attachment 4 shows typical chromatograms for standards prepared and analyzed as described above.

Method Calibration (Optional).

Standard concentrations of HMDA in air were produced using a TSI Model 3050 Berglund-Liu Monodisperse Aerosol Generator (vibrating orifice generator, VOG) equipped with a TSI Model 3054 Aerosol Neutralizer and a New England Medical Instruments, Inc. Accurate Infusion Pump (syringe pump). Feed solution was delivered to the

VOC using a Hamilton Gas Tight Syringe (50 mL capacity, Model Number 1050TLL, Catalogue Number 81920), Hamilton Co., 1410 Valley Lake Dr., Suite 303, Schaumburg, IL 60195. The feed solution from the syringe pump to the VOC was filtered using a Gelman Acrodisc-CR [tm] membrane filter (0.45 micron pore size).

Dispersion Air - 1500 cc/min

Dilution Air - 16.67 L/min

Total Air Flow - 18.17 L/min

Syringe Pump - Setting of 3 (24 cc/min) to start stream
- Setting of 19 (0.11 cc/min) for operation.

Function Gen. - Range: 10K Hz
- Frequency: 46
- Function: Smooth Wave

Amplitude and DC offset at Midrange

Micro Orifice - Model 10353, Nominal Diameter of 20 microns

Different concentrations of solutions were used in generation of HMDA air standards and this was found to be the best method. For the range of 0.008 - 18 ppm in air the concentrations of the HMDA feed solutions were 0.060 - 10.01 mg/mL HMDA in isopropyl alcohol. Each HMDA feed solution was spiked with an aliquot of carbon-14-labeled HMDA (prepared in-house) to bring the activity of each solution to approximately 2500 DPM/microliter. Calculation of ppm output of the generator [3] gave approximate values for HMDA in air but these were not sufficiently accurate to use as corroboration of the method under development. The HPLC analysis was corroborated instead by liquid scintillation counting (LSC) of 100 microliter aliquots of the desorbed sample solutions and comparing these results to those for the mother feed solutions. By use of a five-port sampling manifold on the VOC outlet it was possible to use four ports for air standard sampling and one port to prevent back pressure build-up. This back pressure release port was vented to a triple cascade of sparge traps filled with 10% sulfuric acid to remove remaining carbon-14-labeled HMDA.

Early experiments with spiked samples and air samples collected from the VOC showed that this instrument produced HMDA air standards as vapors rather than as aerosols [4]. One possible reason for this is that once the HMDA aerosol particle is formed, the high vapor pressure of the compound allows it to quickly vaporize. Since this same process seems likely to occur for HMDA particles in the air of a plant environment, this method was developed using the VOC in this capacity.

The air standards were generated as per the instructions of the VOC manufacturer for the production of aerosol standards [4]. Filtered, distilled-in-glass isopropyl alcohol was used to

(initiate the stream through the vibrating orifice. Once this was accomplished the feed solution was switched to a standard solution of HMDA in filtered, distilled-in-glass isopropyl alcohol. At least fifteen minutes was allowed at this point for system equilibration. It was convenient during this time to adjust and calibrate the personnel sampling pumps (with silica gel sampling tubes attached) to approximately 500 mL/min. The pumps and sampling tubes were then attached to the sampling manifold with short pieces of Tygon [tm] tubing. Care was taken to assure that the manifold port and silica gel sampling tube were "butted". That is, there was no Tygon [tm] exposed to the air stream. Stream sampling proceeded for 40 min (for a 20 L air sample) and the sampling tubes were then detached from the pump, desorbed, filtered, and analyzed (see Section 10).

Some minor cautions are necessary for proper operation of the VOC. Attempts to increase the vapor-in-air concentration by increasing the pump rate of the feed solution give poor results; high back pressure causes poor flow characteristics and deflection of the droplet stream from the vibrating orifice. Further, high pressures can damage the pump mechanism. Leakage of feed solution around the Teflon [tm] plunger of the syringe can also be a problem when operating above the recommended pump rate. Consequently it is best to use different feed solution concentrations to generate different vapor-in-air standards.

(Partial or complete orifice blockage is a common problem. This results in a diminution or stoppage of standard generation. Due to the solubility of HMDA, flushing with filtered water and acetone usually resolves the problem. If this procedure fails it is best to simply replace the orifice with a spare kept on hand for the purpose. It should be noted that the manufacturer recommends against the use of sonic equipment for the cleaning of the orifices.

Chromatograms are reproduced in Attachment 5 which exemplify those obtained from the method calibration and validation.

10.0 PROCEDURE

10.1 Cleaning Of Equipment

10.1.1

(It is necessary to clean all glassware carefully and scrupulously before use to avoid possible sources of contamination and cross-contamination. Use of standard good laboratory practices for cleaning glassware is encouraged.

10.2 Collection And Shipping Of Samples

10.2.1

Extra silica gel sampling tubes must be used as blanks when collecting samples. The blanks are handled in the same manner as the sample filters (transport, desorb), except that no air is sampled. These tubes must be labeled as blanks.

10.2.2

In order to drain off the over-charge and to allow equilibration it is important to allow the fully charged pumps to run for at least 15 minutes prior to calibration.

10.2.3

Before pump calibration score (scratch) both ends of the silica gel sampling tube with a glass scoring tool and carefully snap off the tips. Embossed on the silica gel tube is an arrow indicating the direction of air flow. Attach the sampling tube to the personnel pump with a short piece of Tygon [tm] tubing so that the arrow is pointing toward the pump. Use a stopwatch and a bubble flow meter to calibrate the pump. An approximate flow rate of 0.5 L/min should be used and the accurate rate must be recorded.

10.2.4

After placing the pump in the area of interest or attaching to a person, allow the pump to run sufficiently long to sample 20 L of air. For a flow rate of 0.5 L/min the sampling time would be 40 minutes.

10.2.5

After collecting the sample, the pump must be recalibrated as described above and the accurate value must be recorded for later use in sample volume calculations.

10.2.6

Mark the used sampling tube for later identification and proceed to Sample Preparation (Section 10.3). The silica gel tubes used for sample collection are stable to storage three weeks before work-up and analysis.

10.3 Sample Preparation

10.3.1

If necessary use the glass scoring tool to scratch the front end of the sampling tube (the end toward which the arrow does not point) and break off enough of the tip to allow easy access to the contents with a forceps.

10.3.2

Use a forceps to remove the glass wool plug and transfer this plug to a 1 dram sample vial. Carefully add to this all the silica gel in the front section of the sampling tube. Label the vial.

10.3.3

Use the forceps or a hooked piece of wire to remove the separating sponge from the tube and transfer it to a second 1 dram sample vial. Carefully add the silica gel from the back section of the sampling tube. Finally, transfer the back sponge plug from the tube to the sample vial. Label the vial.

10.3.4

Add 3.0 mL of the internal standard solution (Section 8.12) to both of the sample vials and desorb using a Charcoal Developer [tm] for one hour.

10.3.5

Attach a Gelman Acrodisc-CR [tm] filter (0.45 micron pore size) to the tip of a 5 cc Becton-Dickinson disposable syringe from which the plunger has been removed. Decant the liquid contents of one of the desorbed sample vials into the syringe body, replace the plunger, and filter the sample into a second 1 dram sample vial. Cap the vial tightly and label it. Repeat this procedure with the second desorbed sample vial using a fresh filter assembly. The samples are now ready for analysis.

10.4 Analysis Of Prepared Sample

10.4.1

To assure a high degree of stability in the chromatographic system, make several injections of a high level standard. Follow the procedure in Section 9 for preparation of a calibration curve.

10.4.2

Using the conditions described in Sections 10.4.6 and 10.4.7 make at least three injections into the high pressure liquid chromatograph. To avoid carry-over between samples it is useful to have wash vials positioned between standards and samples.

10.4.3

Results are calculated from peak areas of HMDA and PA internal standard as described in Section 11 (Calculations).

10.4.4

This same procedure is used for the preparation and analysis of samples and blanks.

10.4.5

Frequent standards of the appropriate levels must be injected during analysis of samples to monitor consistency of detector response. One standard analysis following three sample analyses is recommended once the standard curve has been established.

10.4.6

High Pressure Liquid Chromatographic Conditions.

Flow rate	- 1.1mL/min.
Mobile Phase	- pH 4.0 potassium hydrogen phthalate aqueous buffer containing 3.8% methanol and 0.08 % (w/w) triethylamine (see Section 8.11).
Detector	- Fluorescence with 360 nm excitation and bandpass above 420 nm emission.
Spectrophotometer Attenuation	- 5

Spectrophotometer Gain	- Lo.
Spectrophotometer Lamp Power	- Lo.
Integrator Attenuation	- Between 2 to the 4th and 2 to the 7th.
Chart Speed	- 0.3 cm/min.
Column Pressure	- 75-90 bar.
Analysis Time	- 14 min.
Post Column Reagent	- pH 10.0 aqueous borate buffer containing OPA and 2-mercaptoethanol.
PCR Pump Micrometer Setting	- 1.06.

10.4.7

Analysis is performed by the injection of 100 microliter aliquots into the liquid chromatograph. The highest validation level (18 ppm) overloaded the fluorescence detector so at this level 50 microliter injections were made. No peaks are observed to have retention times in the chromatogram longer than 11 minutes. The strip chart recorder is set at a speed of 0.3 cm/min. It is necessary to make triplicate injections of each sample and standard in order to obtain good quantitation.

10.5 Special Comments

10.5.1

In some of air monitoring methods glass fiber filters are attached to the front end of silica gel sampling tubes to trap particulate analyte [5]. However, spiking and air standard collection experiments showed early in the validation that no airborne HMDA is retained by such a filter. Consequently none is used in this method.

10.5.2

The pump rate of the OPA/borate buffer (pH 10) into the PCR module must be carefully adjusted. If the rate is too slow the pH of the reaction medium is too low (acidic) and the post column derivatization reaction does not occur. If the rate is too fast, the detector response is observed to be extremely nonlinear. A

ATTACHMENT 1

**SUMMARY REPORT
FOR
HADA**

Run processed on: 4-Jan-83

Level	Samples Tot	Rej	Mean	Standard Deviation (Sigma)	Coeff. of Variation (Sigma/Mean)	Outlying Measurement	Grubbs Test
8.720E+02	7	0	7.424E+02	2.854E+01	3.844E-02	7.000E+02	1.49
1.310E+02	7	0	1.129E+02	7.559E+00	6.698E-02	1.300E+02	2.27
1.830E+04	8	0	1.786E+04	1.434E+03	8.029E-02	1.570E+04	1.51
2.440E+03	8	0	1.761E+03	1.492E+02	8.473E-02	1.980E+03	1.47
7.400E+00	6	0	6.900E+00	7.975E-01	1.156E-01	8.000E+00	1.38
7.420E+01	6	0	7.442E+01	5.368E+00	7.213E-02	8.210E+01	1.43

GLP Sample Sufficiency

All levels have sufficient samples to be (95%) confident that the true mean is within +/- 20% of the calculated mean.

Bartlett's Test for Equality of Variances

Type Variance	Pooled Coefficient	X ²	DF	P(X ²)	Constant Coeff.?
Sigma [Std.Dev.]	6.360E+02	2.006E+02	5	1.000	No
Sigma / Sqrt(Mean)	5.018E+00	8.006E+01	5	1.000	No
Sigma / Mean [CV]	7.888E-02	6.011E+00	5	.695	--
Sigma x Sqrt(Mean)	8.457E+04	3.245E+02	5	1.000	No
Sigma x Mean	1.130E+07	4.486E+02	5	1.000	No

>>> Due to Non-constant Variance(s) 1/Mean²
>>> factors were used as weighting coefficients
>>> in the least squares calculation:

Least-Squares Solution to: Ymeas = a + b(Ylevel)

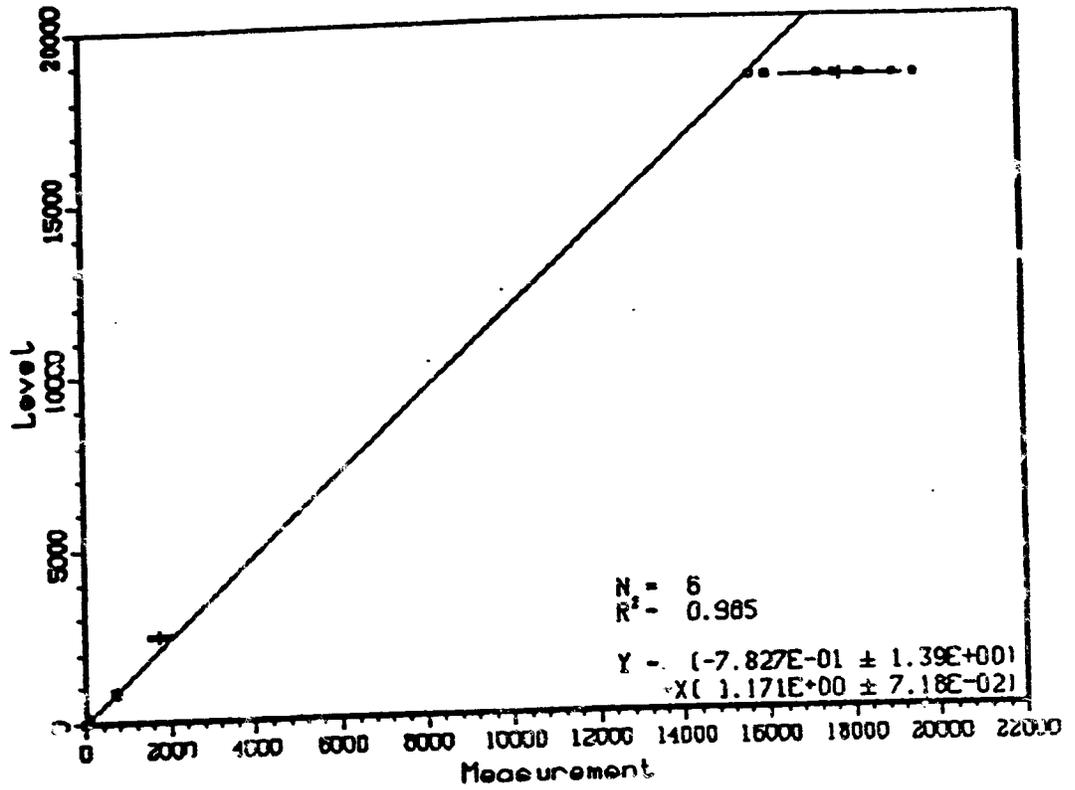
Intercept	+/- Sigma	Slope	+/- Sigma	Std. Error	Corr ²
6.682E-01	1.01E+00	8.537E-01	5.23E-02	1.313E-01	.9852

Equation of Prediction: Ylevel = c + d(Ymeas)

Intercept	+/- Sigma	Slope	+/- Sigma
-7.827E-01	1.39E+00	1.171E+00	7.18E-02

0 0 4 2

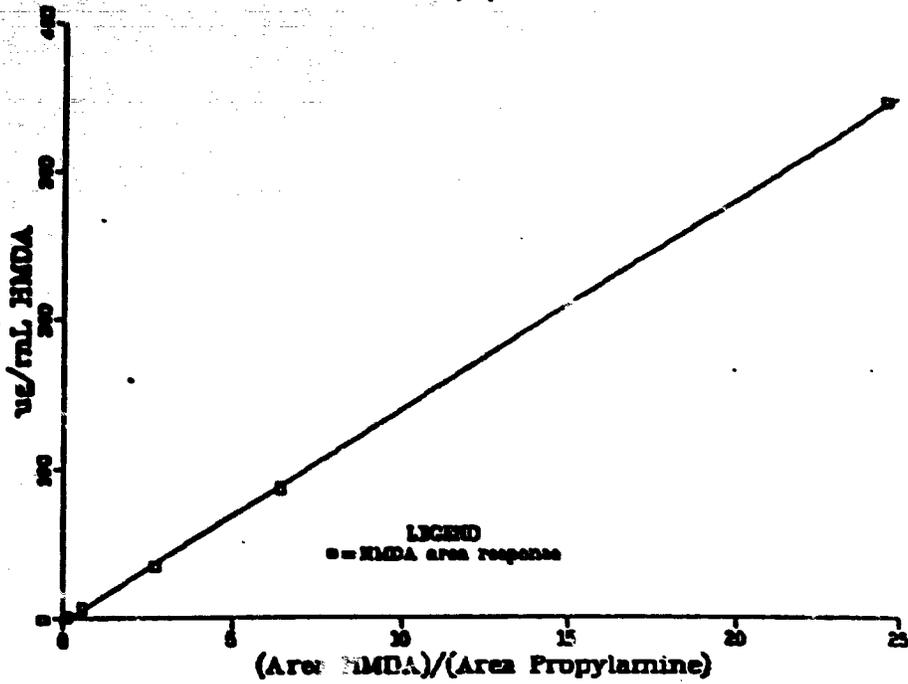
ATTACHMENT 2
HMDA



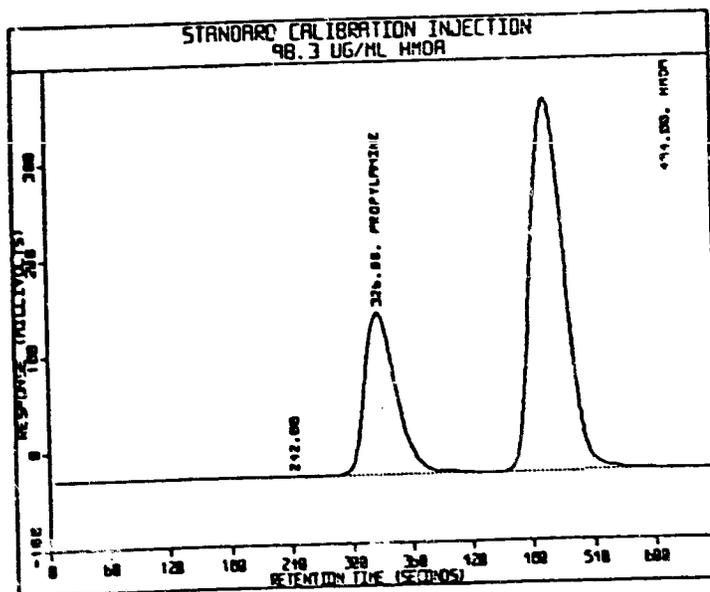
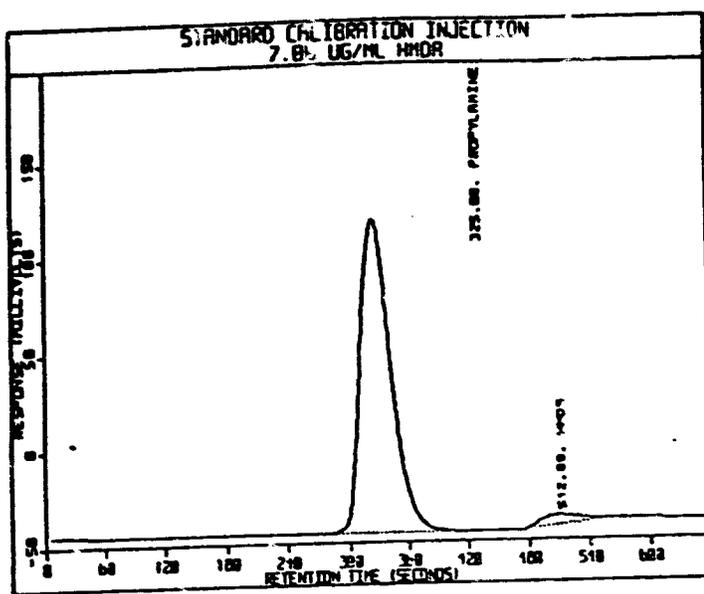
N = 6
R² = 0.985

Y = (-7.827E-01 ± 1.39E+00)
+ X(1.171E+00 ± 7.18E-02)

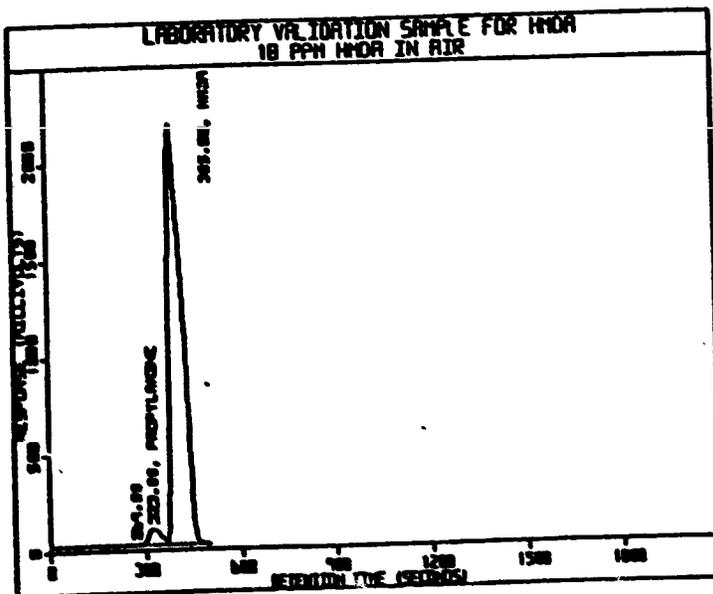
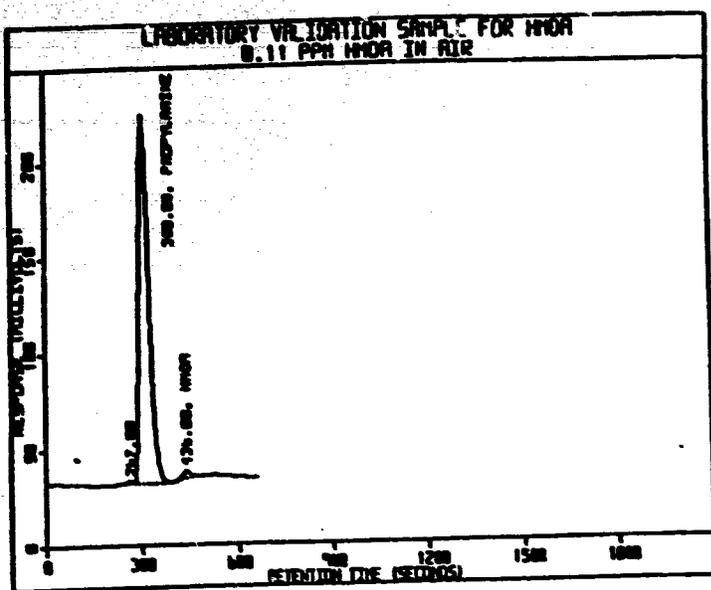
Calibration Curve for OPA-PCR Analysis
of HMDA
10/7/82



ATTACHMENT 4



ATTACHMENT 5



Hexamethylenediamine

1,6-HEXANEDIAMINE

(HMD)

$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$

MW 116.21

Pub. No. 167

Monsanto

Hexamethylenediamine
1,6-HEXANEDIAMINE
(HMD)

$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$

MW 116.21

Pub. No. 167

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Monsanto Fibers & Intermediates Co.
800 N. Lindbergh Blvd., St. Louis, Mo. 63167
a unit of Monsanto

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I. Introduction

Hexamethylenediamine ($H_2N(CH_2)_6NH_2$) is perhaps the best known and commercially one of the most extensively used aliphatic diamines having two terminal primary amine groups. The amine groups undergo chemical reaction at one or both groups and lend themselves to a number of important chemical intermediates. It provides the backbone structure of a large variety of polymers.

The major use of hexamethylenediamine (HMD) is in the production of polyamide resins for fibers and plastics. The most important of the polyamides derived from hexamethylenediamine is nylon 6,6—the product of the polycondensation of hexamethylenediamine with adipic acid. The presence of the amine group provides a site for interchain bonding by secondary forces, resulting in the formation of crystalline structures. Polyamides are important commercially as resins and plastics because of their great range of physical and mechanical properties.

Hexamethylenediisocyanate is an important intermediate using hexamethylenediamine. Polyurethanes are produced through the addition of hexamethylenediisocyanate with polyhydroxy compounds. Polyureas are produced when hexamethylenediisocyanate adds to hexamethylenediamine or other diamines. Polyureas also can be made from hexamethylenediamine and other diisocyanates.

Monsanto is a producer of hexamethylenediamine in the U.S. and in Europe and has the proven capability of meeting customers' international requirements. Monsanto is the largest U.S. supplier of hexamethylenediamine to the non-nylon market. Extensive and ongoing research programs help assure Monsanto's advanced position in HMD technology. Technical expertise, backed by Monsanto's considerable production and technical know-how, is available to help customers with processing and handling problems.

Monsanto hexamethylenediamine meets specifications for polymer and fiber uses. It is supplied as aqueous solutions of concentrations between 70-99.9% HMD. Hexamethylenediamine can be shipped in railcars, tanktrucks, 55-gallon steel drums or 55-gallon lined drums.

A computerized system minimizes order handling, helping promote prompt shipments and timely deliveries. All orders are placed through a special order representative assigned to the customer's account.

II. Specifications

Monsanto normally supplies hexamethylenediamine, $H_2N(CH_2)_6NH_2$, as an aqueous solution to facilitate transportation and unloading. Concentration during mid-April thru mid-October (summer conditions) is 90% HMD and mid-October thru mid-April (winter conditions) is 85% HMD. Concentrations of 70%, 75% and 100% (anhydrous) HMD are available on request provided the plant has advance notification of shipping date requirements.

	Aqueous*	Anhydrous*
Appearance	Clear, colorless liquid	
Hexamethylenediamine: HMD %		99.7 min.
Summer	87.0-93.0	—
Winter	82.0-88.0	—
Color: APHA	10.0 max.	—
Water: H_2O %	—	0.3 max.
Hydrolyzable Nitrogen: D/N. mpm**	30.0 max.	30.0 max.
Ammonia: NH_3 . mpm	60.0 max.	60.0 max.
Imines: NH . mpm	25.0 max.	25.0 max.
1,2-Diaminocyclohexane: DCH. ppm	70.0 max.	70.0 max.

*Analysis—on a dry basis except for concentration, color, and water content.

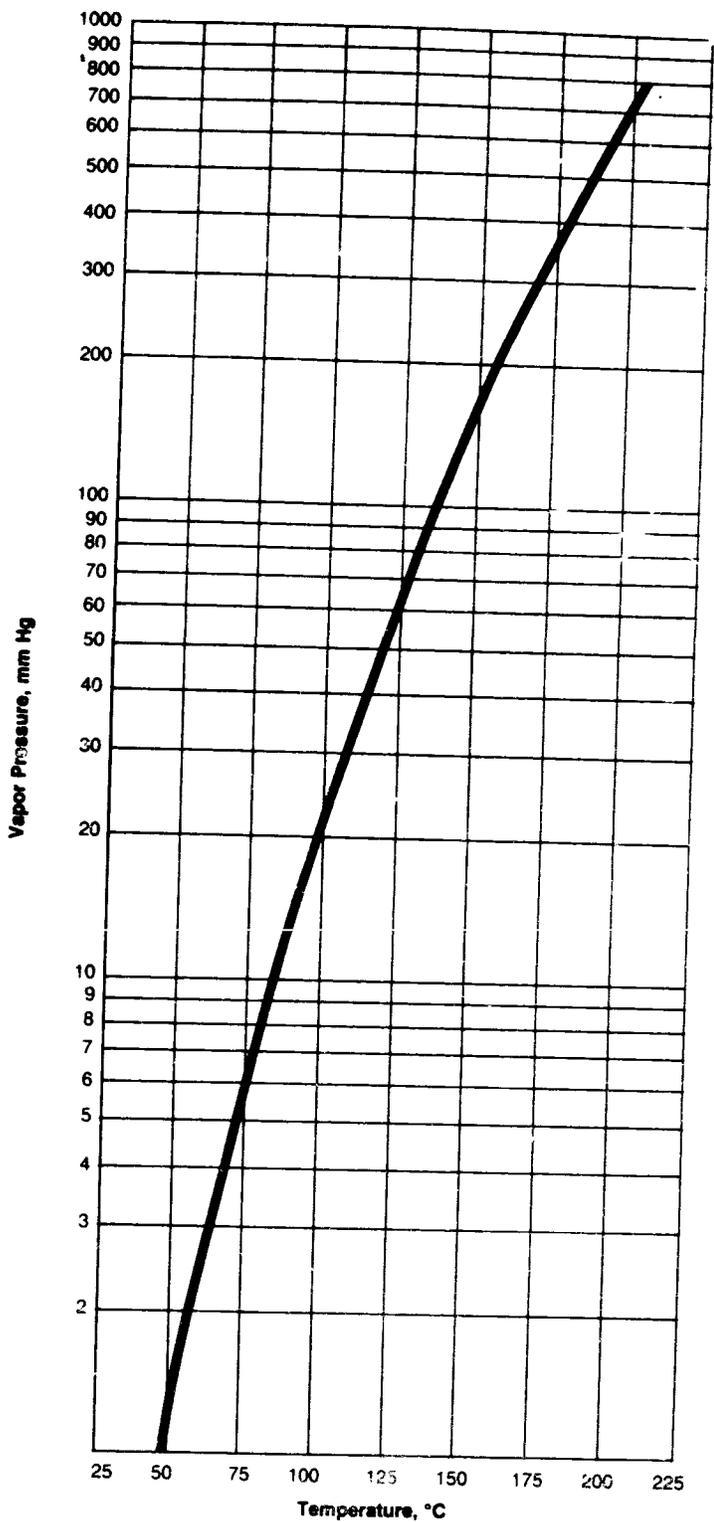
** mpm = moles per million moles

NOTE: Product specifications are subject to change from time to time without notice. Please write us for our current product specifications.

III. Physical Properties (Anhydrous Hexamethylenediamine)

	$H_2N(CH_2)_6NH_2$ 1,6-Hexanediamine
Formula	
Chemical Abstract Name	124-09-4
Chemical Abstract Registration No.	116.21
Molecular Weight	40.87
Melting Point, °C	200.6
Boiling Point, °C, at 760 mm Hg	132
at 90 mm Hg	82
at 10 mm Hg	
Specific Gravity ($H_2O = 1$) d_{41}^{41}	0.8477
Weight, pounds per gallon at 120°F	7.01
Flammable Limits (lower limit), Vol. %	0.7
(upper limit), Vol. %	6.3
Flash Point, Closed Cup, °F	178
Open Cup, °F	185
Critical Pressure, atmospheres	32.5
Critical Temperature, °C	390.4
Refractive Index, n_D^{41}	1.4498
Specific Heat of Liquid, Cal./gm/°C at 50°C	0.530
Surface Tension in Air at 60°C, dynes/cm.	34.64
Viscosity at 50°C, centipoises	1.50
Heat of Combustion, K Cal./gm. mol.	1059.6
Solubility in Water	See Graph 2
Benzene	Slightly soluble
Acetone	Completely soluble

1. Vapor Pressure of Hexamethylenediamine* (Anhydrous)



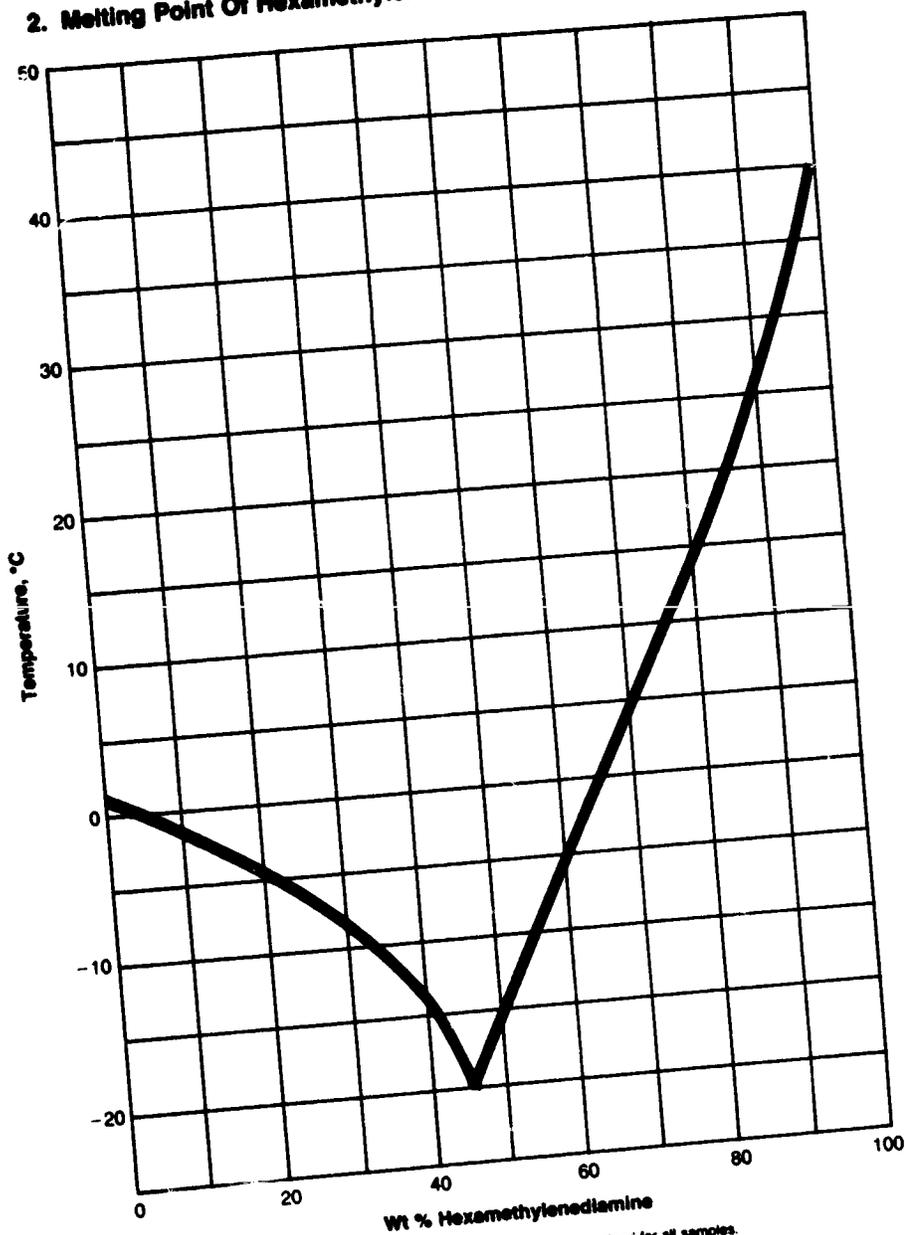
*This data based upon samples tested in the laboratory and is not guaranteed for all samples.

Physical Properties of Aqueous Hexamethylenediamine Solutions

Chemical Name
Melting Point, °C
Weight, pound per gallon
Flash Point, Closed Cup, °F
Solubility in Water, Wt. %

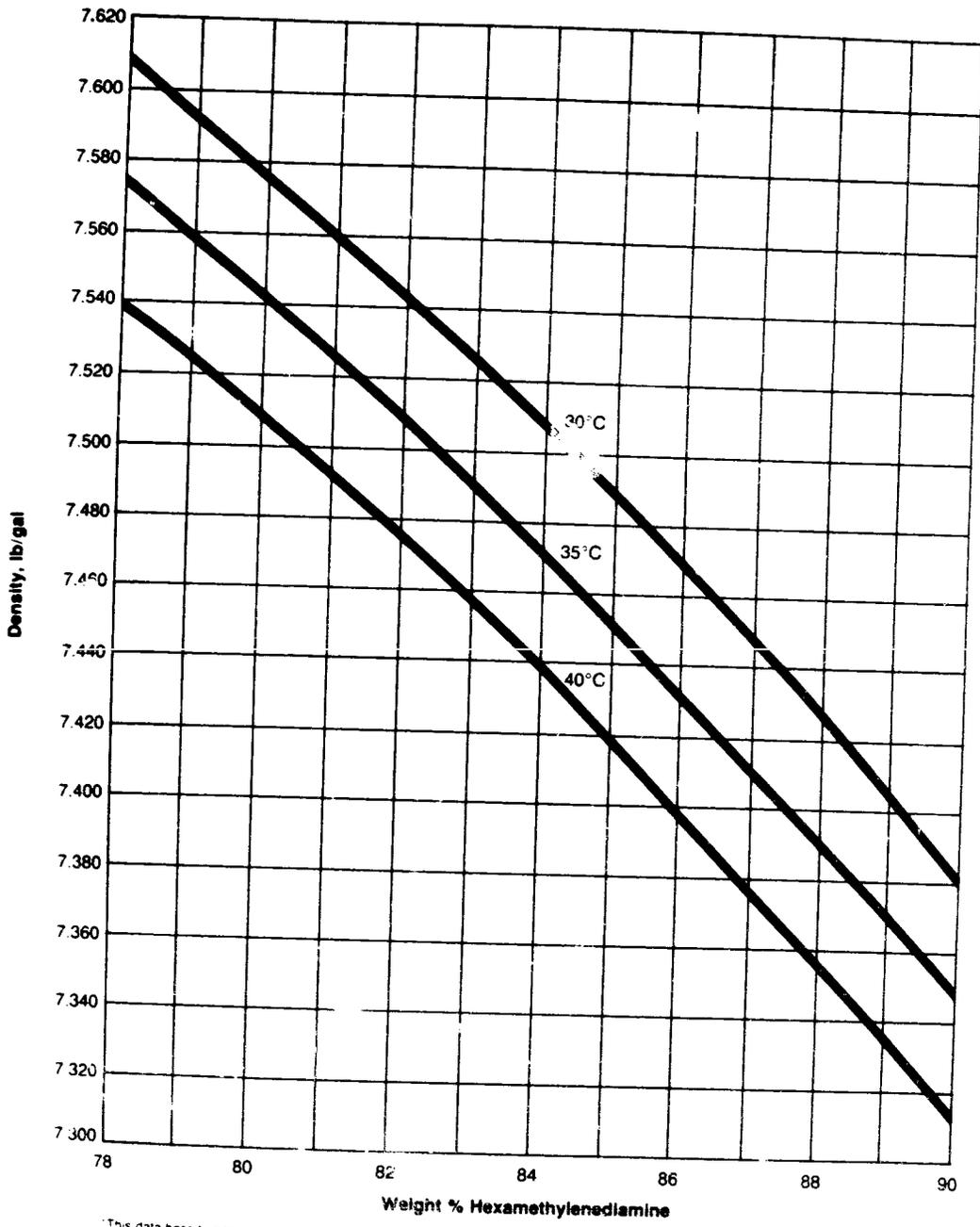
Hexamethylenediamine Solution
See Graph 2
See Graph 3
>212
See Graph 2

2. Melting Point Of Hexamethylenediamine-Water Solutions*



*This data based on samples tested in the laboratory and is not guaranteed for all samples.

3. Density of Hexamethylenediamine-Water Solutions*



*This data based upon samples tested in the laboratory and is not guaranteed for all samples

IV. Shipping Information

D.O.T. Shipping Name Hexamethylenediamine Solution
D.O.T. Classification Corrosive Material, UN1783 ONM
Freight Classification Hexamethylenediamine, Corrosive Material

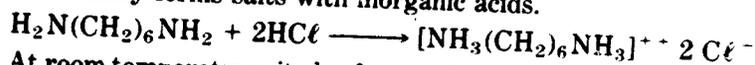
D.O.T. Shipping Name Hexamethyl-nediamine, Solid
D.O.T. Classification Corrosive Material, UN2280
Freight Classification Hexamethylenediamine, Solid
F.O.B. Monsanto Plants at Decatur, Ala; and Pensacola, Florida

Standard Containers: PENSACOLA
Bulk: 6,000-gal. tank truck and 20,000 and 25,000 gal. tank cars
DECATUR
Bulk: 6,000-gal. tank truck and 20,000 and 25,000 gal. tank cars
55-gal. steel drums (with sprayed phenolic lining); gross wt. 425 lbs., net weight approx. 385 lbs.; cubic ft. 10.175

Samples: 16 oz. to a gallon via United Parcel Service

V. Chemical Reactions

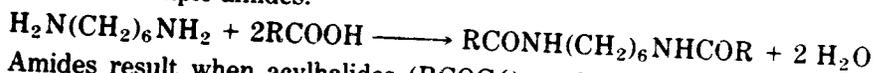
1. *Salt Formation.* Hexamethylenediamine is a strong base and readily forms salts with inorganic acids.



At room temperature, it also forms salts with carboxylic acids. Salts with dicarboxylic acids are intermediates for forming polyamides.

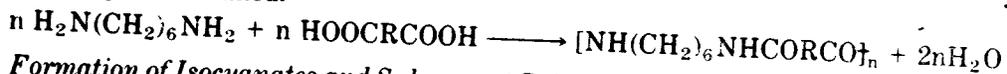


2. *Formation of Amides.* The heating of hexamethylenediamine with a monocarboxylic acid and removing the resulting water yields the simple amides.



Amides result when acylhalides (RCOCl), carboxylic anhydride (ROCOCOR) or esters (RCOOR') are reacted with HMD, and the resulting hydrogen halide, carboxylic acid or alcohol respectively is removed from the reaction system.

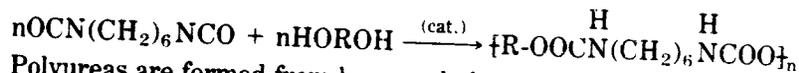
3. *Formation of Polyamide.* Heating hexamethylenediamine with a dicarboxylic acid and the removal of the water from the reaction system yields the polyamide. The ratio of reactants and reaction conditions have an important bearing on the final polymer obtained.



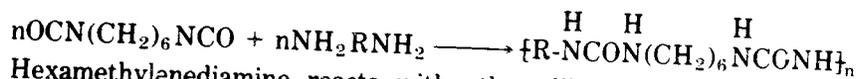
4. *Formation of Isocyanates and Subsequent Polyurethanes and Polyureas.* Hexamethylenediamine or its hydrochloride salt reacts with phosgene to yield the mono or diisocyanate. Hexamethylenediisocyanate is made from two equivalents of phosgene.



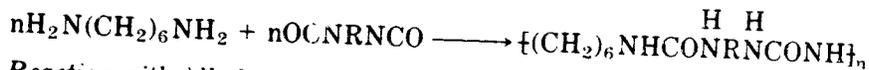
The addition of di or polyhydroxyl compounds to hexamethylenediisocyanate yields polyurethanes.



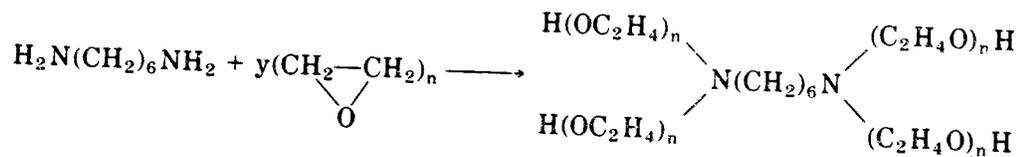
Polyureas are formed from hexamethylenediisocyanate and di or polyamines.



Hexamethylenediamine reacts with other diisocyanates to yield polyureas.



5. *Reaction with Alkylene Oxides.* Hexamethylenediamine reacts with alkylene oxides, such as ethylene oxide or propylene oxide. The ratio of the reactants and the reaction conditions have an important bearing on the amounts of mono, di-, tri-, and tetraoxyalkylated products obtained.



VI. Preparations and Applications

1. Polyamides

The principal use of hexamethylenediamine is as an intermediate in the formation of polyamides, nylon 6,6 being the main polymer produced. The hexamethylenediamine forms a salt with any of a number of polybasic acids and the resultant salts are heated to form the polymers^{1,2,3,4}.

This polycondensation also can be carried out at low temperature in solution by using an interfacial formation technique with a dibasic acid chloride⁵. Condensation occurs between dibasic acid chlorides and aqueous solutions of hexamethylenediamine at the interface of the two liquid phases. Types of polyamides formed using this technique with hexamethylenediamine include adipamides^{6,7} furamides⁸ and sulfonamides and mixed polymers^{10,11}. Dibasic acid chlorides of succinic¹², glutaric¹³, terephthalic¹⁴ and other aromatic diacids¹⁵, have been reacted with hexamethylenediamine to give the various linear polyamides.

Reaction of hexamethylenediamine with alkyl¹⁶ and aromatic diesters¹⁷ and diamides^{18,19} lead to the various polyamides²⁰. Mixed polyamides have been formed using mixed acids with HMD or when caprolactam^{1,22,23,24} or its polymer^{25,26,27} are added to these polyamide components. Different polymer properties result when part of the hexamethylenediamine is replaced by other diamines such as ethylenediamine²⁸, tetramethylenediamine, pentamethylenediamine²⁹, or aromatic diamines²⁰. Alternation of properties can also be done by grafted copolymers in which chain blocks are grafted to the polyamide backbone at specific intervals^{30,31}.

Polyamides offer perhaps a greater range of physical and mechanical properties than is possible with any other simple chemical type of synthetic resin. The dominant role of polyamides in the field of industrial fibers is related to an exceptionally high toughness index, an ability to absorb high-velocity impact, exceptional strength with high elongation, and elastic recovery and low specific gravity. In addition, the general compatibility of nylon with common adhesives is a significant economic factor³².

Nylon has had a major role as a safety fiber; specifically in automobile seat belts, in parachute cloth and shrouds, in industrial slings, in seagoing tow lines because of its extensibility and resilience when stressed by wave impact, in fishing nets, and in a large variety of high-strength cordage and tape, where wear and strength are as important as the ability to accept shock³².

Nylon in fiber form has been used in the manufacturing of strapping, weaving, belts, sewing thread, surgical silk, tire cord and glider tow ropes. A major use of nylon is in home furnishings such as carpets, and the silk-like nature of polyamides has always put

them in great demand for women's apparel. Texturizing by crimping, false twist, knife end and a wide variety of specialized cross sections to optimize comfort and ease of care factors have increased the use of nylon in the wearing apparel field^{33,34}. Nylon monofilaments are used in flexible hoses, corrosion resistant screens, and bristles.

These polyamides are widely used as molding and extrusion compounds. They are used in applications for their flame resistance, chemical resistance, toughness, low coefficient of friction, stiffness, outstanding wear resistance, good electrical insulating properties and high temperature resistance³⁵.

High melting nylon molding powders are characterized by unusual toughness, rigidity, abrasion resistance and fatigue resistance; low melting powders are characterized by flexibility. Nylon molding powders can be handled by most molding and extrusion techniques, and are characterized by their ability to be molded in thin sections and to flow around complicated inserts. They have low coefficient of friction and thus are used for bearings and bushings. They are also used for hubs for hypodermic needles, electrical-coil forms, valve seats, gears, cams and other machine parts, automotive doorlock mechanisms and dome light lenses, wristwatch straps and protective jacketing over primary insulation on electrical cables³⁶. Specially prepared finely divided polyamide powder can be sintered and has good dimensional stability. These specially prepared powders can be compounded with such additives as molybdenum disulfide, and can be made in a range of porosities to hold lubricating oils or inks and are used for rollers, bearings, bushings, valve seats and general wear-resistant machine parts³⁷.

The excellent mechanical and formability properties of nylon make it highly suitable for nonwoven fabrics. Nylon in nonwoven fabrics has the advantage of good wrap strength, soil resistance, quick drying, chemical resistance, high elasticity, and good heat-setting properties³⁸.

Films of polyamides made from HMD may be cast from solution or dispersions or extruded and cast from melts³⁹. Polyamide resin films are very glossy and pleasing in appearance, and are usually flexible even without plasticizers. Their moisture-vapor transmission resistance is excellent, they are resistant to alkalines, dilute acids, oils, greases and solvents. One of their most outstanding properties is their ability to form strong bonds under the application of heat. They are used as heat-sealing adhesives for bonding a wide variety of surfaces including paper, label stock, kraft paper, glassive paper, waxed papers, metal foil, metals, glass, cork, cloth, asbestos, leather, wood and coated cellophane⁴⁰. Polyamides that can be processed as solutions can be produced in the form of copolyamides. These materials have a major application

in textile coatings⁴¹. Interfacial deposition of a polyamide enhances grease proofing of natural^{42, 43, 44, 45, 46, 47} or synthetic fibers^{12, 48}. Glass fibers have been coated by interfacial deposition also⁴⁹.

Nylon insulating enamel may be applied to magnet wire by means of molten polymer⁵⁰, dispersion⁵¹, or a solution⁵² in a suitable solvent. It offers unusual chemical resistance, solvent resistance, toughness and abrasion resistance. Flexibility of the enamel may be modified by means of plasticizers.

Mixed polyamides having properties intermediate between the properties of the individual homopolymers are used in fibers, films and plastic resins^{53, 54}. Thixotropic agents for paint include mixed polyamides^{55, 56}.

A methoxylated polyamide made using HMD serves as a printing surface on paper⁵⁷ and when foamed is used as an artificial leather⁵⁸. An ethoxylated copolyamide is used in paper manufacturing⁵⁹ and stabilizes wool against shrinking^{42, 43, 44, 45, 46, 47}.

Phosphorous containing polyamides are used to encapsulate insecticide or other liquid, solid and gaseous material⁶⁰.

2. Polyurethanes

Polyurethanes using hexamethylenediamine are principally produced by condensation with 1,4 butanediol bis(chloroformate)^{61, 62, 63}, but 1, 6 hexanediol bis(chloroformate)⁴⁷ as well as the chlorothioformate have been used⁶⁴. Hexamethylenediisocyanate, made from hexamethylenediamine by reaction with phosgene, is reacted with 1,4 butanediol or other glycols to produce various polyurethanes⁶⁵. A mixed polyurethane-urea is formed from hexamethylenediisocyanate, a glycol and urea⁶⁶.

These polyurethanes are characterized by their extreme toughness abrasion resistance and can withstand attack by many chemicals and solvents^{54, 67}. They appear to be the only plastic that can be simultaneously polymerized and expanded into massive shapes. Examples are the flexible and rigid foams.

A large outlet for flexible polyurethane foam is for furniture cushions which are lightweight and have high strength. Another flexible foam use is in the automotive industry for seat cushioning, instrument-panel trim, safety pods, arm rests, floor mats, sun visors, roof insulation, weather stripping, air filters, etc. Flexible foam is used in carpet underlaying for cushioning, nonskidding properties and does not mat down⁶⁸.

Rigid polyurethane foam is used in home refrigerators, all types of refrigerated trucks such as milk trucks, ice cream trucks, and trailers. Besides having particularly good insulating properties, rigid foams contribute to the structural strength of the body of the truck, have low moisture pick up and can withstand solvents

such as gasoline and temperatures up to 100°C. Rigid polyurethane foam is also used in the building industry in curtain-wall construction, preformed rigid panels, spray-applied wall construction and roofing insulation (either sprayed or in preformed panels). Most boats built today utilize rigid foam in some manner to help support the boat in the water and larger boats use rigid foam as void fillers and in lifeboats.

Polyurethane fiber is used in drive belts, ropes; low abrasion, high coefficient of friction and low noise level are advantageous^{67,68}. One of the earliest uses of polyurethanes was in the field of coatings. Polyurethanes have been used for flat surface coatings as well as wire coatings⁶⁹. Wool can be stabilized against shrinking by the interfacial deposition of polyurethane^{42,49}.

Isocyanates made from hexamethylenediamine are used in adhesives for bonding synthetic textile fibers to elastomers, elastomers to wood or metal, wood to wood or to metal or porcelain, or many plastics to any of these materials⁶⁹.

Mixed polyurethanes have much lower softening temperatures and generally better solubility in certain organic solvents⁵⁴ than any of the separate polyurethanes used to make up the mixed polymers. One mixed polyurethane reminds one of skin⁵⁴.

Because of the excellent resistance to most oils, modified polyurethanes derived from HMD are used for such specialty products as sealants, air filters, wiper rings and valve seats⁶⁷. Polyurethanes are also used as binders for rocket propellants.

3. Polyureas

Polyureas are prepared from the bis(carbamyl) chloride made from hexamethylenediamine and reacting this with additional HMD or another diamine. Alternatively, the bis(carbamyl) chloride of another diamine can be reacted with hexamethylenediamine to form the polyurea^{70,71,72}. Similarly, the diisocyanate of HMD, when added to more HMD or another diamine, produces the polyureas^{73,74,75}. An interfacial polycondensation technique has been used to prepare linear polyureas using a solution of the diisocyanate in an organic solvent immiscible in water and an aqueous solution of HMD or another diamine bis hydrochloride at low temperature^{76,77}. These methods allow for block copolymers to be prepared.

Polyureas have suitable melt viscosities, good mechanical and electrical properties and outstanding resistance to hydrolysis⁷⁸.

Mixtures of polyurea fiber and wool have been blended into staple fiber for wearing apparel. Wool immersed in HMD has been treated with diisocyanates by interfacial polycondensation which leads to formation of a polyurea on the surface of the wool fiber,

giving it dimensional stability during laundering. Wool coated with this polyurea has good weather resistance⁷⁹.

An insulation lacquer for magnet wire is made from a mixed polyurea derived from HMD. Coating of metal parts with a layer of polyurea has been done using a fluidized-bed technique. Polyurea coatings are particularly good in their adhesion to copper⁸⁰.

Water-soluble polyureas with tertiary amino groups in the carbon chain are claimed to be useful for the flocculation of coal suspensions⁸¹.

4. Polyamines

A wide variety of polyamines of varying molecular weights are produced by reaction of HMD with the preferred 1,2 dichloroethane, but other alkylene dihalides have been used. Reaction with epichlorohydrin leads to polyamines containing hydroxyl groups^{82,83,84,85,86}.

These polyamines may generally be described as hydrophilic, polar substances, owing to the multiplicity of nitrogen groups. Polyamines derived from HMD are highly functional substances, and because of the variety of reactions they can undergo, often have been used as chemical intermediates. These include being hydroxythylated, hydroxypropylated⁸⁷, and converted to polyureido compounds by reaction with alkali metal cyanates⁸⁸ or urea⁸⁹. Polyamines may be acylated, reacted with various aldehydes and are frequently crosslinked with epichlorohydrin although there are numerous other crosslinking agents⁹⁰.

Because of their potentially high charge, polarity and molecular size, polyamines are frequently used in aqueous solution as flocculants. This is especially true when the suspended matter to be treated is negatively charged (anionic) as in the case of aqueous colloidal suspensions. Examples of which are treated in commercial operations are cellulose fiber suspension and dispersions of mineral ores⁹¹.

Polyamines made from HMD are reacted with epichlorohydrin to produce wet-strength resins for paper⁹². These polyamines are used also as aids for filters and fines retention in paper mill operation⁹³.

These polyamines have been reacted with long-chain fatty acids so that hydrophobic groups are introduced into the chain. These have been used as fuel additives⁹⁴. A salt of a polyamine and an alkylated phenol has been used as a diesel fuel additive⁹⁵, and a lube oil detergent is based on a polyamine salt of thiophosphoric acid⁹⁶. Burner oils are stabilized for storage by polyamines reacted with epichlorohydrin and then condensed with simpler polyamines⁹⁷.

These polyamines increase the dye receptivity of polyolefins⁸⁵ and polynitriles⁸⁶. Cationic polyelectrolyte made polyamines have been used as coagulant aids, antistatic agents, anticorrosive agents and conductive polymer coatings⁸⁸. Rubbery epoxy polymers have resulted when a polyamine or its carbamate was used as a curing agent⁸⁹. Crosslinked polyamines have been used as anion-exchange material¹⁰⁰.

5. Other Uses of Hexamethylenediamine

Various properties of polymers can be purposely modified by reaction with hexamethylenediamine. The bonding of polyethylene-terephthalate film and yarns to rubber can be greatly improved by treatment with aqueous hexamethylenediamine. The strength of yarns made of poly-(4-methyl-1-pentene) are increased after treatment with aqueous hexamethylenediamine¹⁰¹. The thermal stability of trioxane-styrene copolymer was increased after reaction with hexamethylenediamine¹⁰². Copolymers of methacrylic acid and methylacrylates have increased strength and thermal stability after treatment with hexamethylenediamine¹⁰³.

Hexamethylenediamine can be used to introduce crosslinking in such polymers as polyvinylchloride¹⁰⁴ and polyvinylesters¹⁰⁵, and copolymers such as ethylene with methacrylic acid and vinyl acetate¹⁰⁶, butadiene and methacrylates¹⁰⁷, fluorosubstituted nitrosoalkanes with halogenated olefins¹⁰⁸, butylacrylate with acrylonitrile¹⁰⁹, and acrylonitrile with glycidylmethacrylates¹¹⁰. The thermal stability of yarns made of acrylonitrile and methacrolein are increased by crosslinking with hexamethylenediamine¹¹¹.

Polyamides crosslinked with hexamethylenediamine show good dye properties¹¹². Nylon 6 containing small amounts of hexamethylenediamine has increased dyeability with acid dyestuffs^{113,114}. Nylon 12 when modified with hexamethylenediamine and ϵ -caprolactam is readily dyed and has reduced shrinkage¹¹⁵. Polypropylene shows improved dyeability when modified with an unsaturated polyester and hexamethylenediamine¹¹⁶.

The HCl and H₂SO₄ salts of hexamethylenediamine are used as regulators for the viscosity of polyamides, such as Nylon 6¹¹⁷.

Natural fibers, such as cotton, show decreased shrinkage after treatment with a diester and hexamethylenediamine, and then heated¹¹⁸. Woolen yarns and fabrics also show decreased shrinkage after treatment with a solution of hexamethylenediamine and a urethane copolymer¹¹⁹. Hexamethylenediamine has been grafted onto cellulose, and fabrics of natural silk have been treated with hexamethylenediamine and a diacid chloride using an interfacial polycondensation technique¹¹⁷.

Mixtures of hexamethylenediamine with phenol¹²⁰, hexamethylenimine^{121,122,123}, dibutylphthalate¹²⁴ or polyaminophenylene meth-

ylene are used as coating strengtheners for epoxide polymers. Resistance to radiation is increased by treating some epoxide resins with hexamethylenediamine¹²⁵. Acetone-formaldehyde plastics are strengthened by treatment with hexamethylenediamine, and are characterized by their high mechanical strength, thermal stability and resistance to frosts¹²⁶.

Hexamethylenediamine is used as a polymerization catalyst for ϵ -caprolactams^{127, 128, 129}, β -lactams¹³⁰, δ -lactones¹³¹, and epimulpaides¹³², and the copolymerization of N-carboxyanhydride of α -aminoacids with lactones¹³³. Complexes of CoCl_2 with hexamethylenediamine are used with diethylchloraluminum in the suspension polymerization of butadiene¹³⁴.

Hexamethylenediamine is used in the vulcanization of fluoro-containing rubbers¹³⁵, and in the production of polymeric latexes made from chloroprene¹³⁶.

The corrosion of aluminum alloys in aqueous caustic, boiling tetrachloride and liquid hydrocarbons is inhibited by hexamethylenediamine^{137, 138}. Pistons, micrometers, ball bearings and roller bearings, and fuel pump valves were inhibited from atmospheric corrosion by an aviation oil containing hexamethylenediamine chromate¹³⁹.

The depth of color is increased with insoluble vat dyestuffs in strong alkaline solution when hexamethylenediamine is added¹⁴⁰.

Reacting polyvinylchloride and hexamethylenediamine produces an aminized polyvinylchloride useful as an anionic exchange resin for the separation of uranium from solution¹⁴¹.

To reduce yellowing and formation of volatile bases in ϵ -caprolactam in the presence of air, hexamethylenediamine is added as a stabilizer¹⁴². Polymerization can be carried out without removing the stabilizer and the poly- ϵ -capoamide is stabilized by the hexamethylenediamine.

A patching material for repairing break and shrinking cracks in highway concrete is made up of hexamethylenediamine, bituminous coal pitch, chloroprene polymer, petroleum distillate, lead dioxide and three different diesters. This patching material is stable to degradation by light and air, and shows good cohesion¹¹⁷.

A bleaching solution of sodium chlorite containing 0.5+% hexamethylenediamine is stable in storage, and can be rapidly activated by heating rather than by the addition of an excess of acid¹⁴³.

Carbon dioxide and hydrogen sulfide can be removed from gaseous mixture by passing the gas over packing coated with hexamethylenediamine¹⁴⁴.

A press board material is produced by hot pressing wood shavings, hexamethylenediamine and polyvinylchloride¹¹⁷.

VII. Product Handling Information

1. Toxicity and Hazards

WARNING: Hexamethylenediamine in liquid form is corrosive to eyes, skin and mucous membranes, and dust and vapors are extremely irritating to the nose, eyes and respiratory tract.

Hexamethylenediamine can cause pulmonary irritation after inhalation of excessive amounts. The prickly or stinging sensation caused by this compound to the nose and throat should act as a warning before excessive exposure.

Hexamethylenediamine is a severe skin irritant and in more dilute solutions can cause dermatitis. This compound is a skin sensitizer and persons who have exhibited a previous history of skin allergies or sensitivity should not work with it.

Hexamethylenediamine is corrosive to eyes. Serious damage can result to the eye tissues from contact with the pure compound or its solutions.

This material has a low vapor pressure. Therefore, exposures to vapors at ambient temperatures are not a major concern. Contact with liquid hexamethylenediamine is the predominant hazard.

2. First Aid Measures

- a. *Inhalation.* Remove person from contact with fumes and immediately summon a physician. If oxygen is available, it should be administered. Treatment for shock should be initiated as soon as it is practicable. **WARNING:** If a person has been exposed to sufficient vapor to cause irritation to upper respiratory tract or shows signs of pulmonary distress, he probably has suffered eye exposure as well. The eyes should be irrigated with large quantities of running water for a period of at least 15 minutes.
- b. *Skin Contact.* In case of skin contact, remove any contaminated clothing (including shoes) and flush material from the skin with water followed by washing with soap and water. Contact physician if skin irritation develops. Launder contaminated clothing before reuse.
- c. *Eye Contact.* In case of contact with the eyes, the eyes should be irrigated with large quantities of running water for at least 15 minutes. The eyelids should be held apart during the irrigation to ensure contact of water with all surfaces of the eyes and lids. Immediately summon a physician.

3. Handling Precautions

Although hexamethylenediamine is a colorless solid melting at about 41°C, it is commonly handled as a liquid (aqueous solution). In either case, hexamethylenediamine is a corrosive, caustic material. Chemical safety goggles and full face shield, impervious protective gloves and boots, and long-sleeved clothing should be

worn by workers when handling hexamethylenediamine. In atmospheres containing hexamethylenediamine of unknown concentration, a NIOSH approved full-faced air supplied respirator should be worn.

Have eye baths immediately available where eye contact can occur.

Hexamethylenediamine is not considered a flammable material, but it has a flash point of 200°F (closed cup) and is combustible. Buildings and equipment should be designed so that no sources of ignition are present in areas where hexamethylenediamine is handled. Avoid contact of hexamethylenediamine with strong acids, oxidizing agents, isocyanates, aldehydes, ketones, anhydrides, phenols, nitrates and halogenated compounds.

In the event of a spill, inspect for and protect against any ignition sources. Evacuate spill area and keep unnecessary personnel out of the area. Leaks and small spills can be diluted with water and collected via pumping into drums or a vacuum truck; guard against storm sewer or water supply contamination. Large spills can be diked and covered with a medium or high expansion foam as protection against fire and for fume protection before being removed. Disposal of spilled material should be carried out in compliance with federal, state and local regulations regarding health, air and water pollution. Slippery surfaces result from spills of liquid hexamethylenediamine or its aqueous solutions and persons working in and around spill areas should be particularly aware of their footing.

4. Tank Car and Tank Truck Unloading Procedure

Measure the storage tank to be sure adequate room is available for the contents of the tank car or tank truck. Chemical safety goggles, impervious gloves and boots, and long-sleeved impervious protective clothing should be worn by the workers taking part in the unloading operation. Care should be taken to prevent water and foreign matter from entering tank car or tank truck. An inert gas should be used to blanket the hexamethylenediamine to insure no contact with air during the unloading. It is recommended that tank cars be unloaded from the top by pumping (or blowing with inert gas) through a standpipe. Unloading from a bottom outlet is hazardous because the leakage at the bottom connection might cause burns to workmen exposed to mists or fumes as well as loss of material.

The practices described in the Manufacturing Chemist Association, Inc.* Manuals, TC-8, "Recommended Practices For Bulk Loading And Unloading Flammable Liquid Chemicals To And From Tank Trucks", and TC-29, "Loading And Unloading Flammable Liquid Chemicals—Tank Cars", are recommended as guidelines for handling hexamethylenediamine. The unloading procedure should comply with "General Industrial Standards (OSHA), 29CFR1910.106 Tank Vehicle and Tank Car Loading And Unloading Flammable And Combustible Liquids".

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