



ASCEND

PERFORMANCE MATERIALS

Hexamethylenediamine (HMD)  
Product Stewardship Summary  
April 12, 2017

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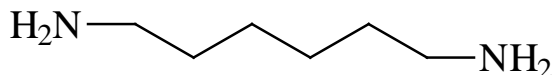
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## Hexamethylene Diamine Product Stewardship Summary

*Chemical Family:* Organic di-amine  
*Chemical Name:* 1,6-Hexanediamine  
*Synonyms:* HMD; Diamine  
*CAS. Number:* 124-09-4  
*EC Number:* 204-679-6  
*Formula:* H<sub>2</sub>N(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>



### Introduction

HMD is a high production volume chemical, with more than 2 billion pounds produced annually worldwide. Ascend Performance Materials LLC is one of the world's leading producers of HMD. Ascend produces this material in our Cantonment, FL, USA and Decatur, AL, USA facilities, for distribution to our customers worldwide. Ascend provides HMD in a variety of package sizes (55 gallon drums, Totes, Tank Truck, ISO Container, Rail Car and Bulk Ship Compartment), and in several grades which vary in water content, from anhydrous to 70% HMD.

### Conclusion of Safety for Use

HMD is safe for industrial and limited commercial uses, when used with proper care and responsibly. This includes adherence to Safety Data Sheet and labeling guidance, along with good industrial hygiene, process safety and waste disposal practices. It is up to the customer to determine fitness for use in their facility, handling systems, reaction processes and in their reacted or formulated products.

### Chemical Inventory Listings

HMD is allowed for commerce in every world area, and is listed on the following Chemical Inventories:

| Country/World Area      | Listed Name                             | Other Designation    |
|-------------------------|---|----------------------|
| Australia (AICS)        | 1,6-Hexanediamine                       |                      |
| Canada (DSL)            | 1,6-Hexanediamine                       |                      |
| China (IECSC)           | 1,6-Hexanediamine                       | 1,6-己二胺              |
| European Union (EINECS) | Hexamethylenediamine                    |                      |
| European Union (REACH)  | Hexamethylenediamine                    | Registered by Ascend |
| Japan(ENCS, IHSL)       | 1,6-Hexanediamine, Hexamethylenediamine | (2)-153              |
| Korea (ESL)             | Hexamethylenediamine                    | KE-18611             |
| New Zealand (NZIoC)     | 1,6-Hexanediamine                       | HSR002749            |
| Philippines (PICCS)     | 1,6-Hexanediamine                       |                      |
| Switzerland (ChemO)     | Hexamethylendiamin                      | G-1682               |
| Turkey                  | Hekzametilen diamin                     |                      |
| United States (TSCA)    | 1,6-Hexanediamine                       |                      |

Please contact Ascend for more information regarding REACH registration and applicability for EU/EEA customers

## Uses for HMD

HMD is used in a variety of ways, to make industrial and consumer products. Typical uses include:

### Use as an industrial intermediate:

HMD is reacted with other chemicals to form reactive coating components, scale and corrosion inhibitors and other chemical products. These include:

- HMD Isocyanate – Reactive coating additive
- 1,6-Hexanediol – A monomer in the manufacture of polyurethanes and polyesters

### Use as a monomer:

HMD's largest use is as a monomer in the formation of various polymers. These include

- Nylon 6,6 – The reaction product of HMD and Adipic Acid (Such as Ascend's Vydyne<sup>®</sup> and Ascend<sup>®</sup> resins)
- Other polymers, such as Nylon copolymers, and Wet Strength Resins for paper manufacture

### Use as a formulation ingredient:

- HMD salts may be useful as ingredients in oil/gas extraction fluids.

## Properties of HMD

### Physical Properties

Commercially, 100% HMD is a white crystalline solid. It is also available as a 70 to 98% water solution. HMD has a very high thermal expansion coefficient at its melt point. Below its melt point, HMD molecules are very tightly packed together. When anhydrous HMD melts, the change from the tightly packed structure to a liquid structure results in a volume increase of about 17%; the reverse of this is true when HMD freezes.

For this reason, containers of HMD should be vented during heating or cooling. Permanent handling systems should contain process vents to prevent damage or leakage from an unexpected change in temperature.

The volume change for HMD solutions is not as dramatic, but is still substantial. Once either anhydrous or aqueous HMD is above its melt point, volume expansion is more gradual, and is in line with what is expected for organic fluids.

### Chemical Properties

Available chemical information is below. This data is a combination of Ascend historical data, and data submitted as a part of the joint REACH registration. The REACH data may differ slightly, and is the result of consensus among many producers of HMD. Differences may be due to crystal properties or measurement methods.

| Parameter           | Ascend Data                                    | REACH Consortium Data   |
|---------------------|--|-------------------------|
| Appearance:         | White Crystalline Solid                        | White Crystalline Solid |
| Crystalline Density | 0.8477 g/cm <sup>3</sup>                       | 0.815 at 25°C           |
| pH at 25°C:         | Wt% 0.1 1.0 10<br>pH 11.45 11.94 12.52         | No Data                 |
| Viscosity           | Solid at Room Temperature;<br>1.5 mPa.s @ 50°C | 0.95 mPa.s at 80°C      |
| Melting Point:      | 40.87°C  | 39.9 °C at 1013 hPa     |

|   |   |   |
|---|---|---|
| Boiling Point:                                    | 200°C @ 760 mmHg with decomposition<br>132°C @ 90 mmHg<br>82°C @ 10 mmHg  | 201 °C at 1013 hPa  |
| Flash point:                                      | 85°C (185°F) Cleveland open cup   | 85°C (185°F) Closed Cup   |
| Flammability:                                     | US-OSHA – Flammable Cat. 4  | Non flammable by GHS/CLP  |
| Upper-lower<br>flammability/ Explosive<br>limits: | Data Set 1    Data Set 2    Data Set 3<br>LEL : 0.9        LEL: 0.7%        LEL : 0.9<br>UEL : 4.1        UEL:6.3%        UEL : 7.6 | No Values Established; Classified as<br>non-explosive by GHS/CLP  |
| Vapor Pressure:                                   |   | 1000 Pa at 78.5°C   |
| Relative Density:                                 |   | 815.7 kg/m <sup>3</sup> at 80°C (Molten)  |
| Solubilities:                                     | Completely Miscible with water at 25°C  | Water - 637 g/L at 20 °C (63.7%)  |
| Partition Coefficient:                            |   | Log Kow (Pow): 0.04 at 25 °C<br>Log Kow = 0.4 (un-ionized form, pH ><br>13)<br>Log D = 3.75 at pH = 7.5 |
| Autoignition<br>temperature                       |   | 315°C   |
| Dissociation constant                             |   | pKa = ca. 10.7  |

## Combustion Properties

Under the 2012 revision of the OSHA Hazcom standard (GHS), HMD is considered as Flammable Category 4 by OSHA. HMD meets the US Department of Transportation (DOT)'s combustible criteria; however, in the Hazardous Materials Table, DOT has chosen to classify HMD only as a Corrosive material.<sup>1</sup> HMD has a flashpoint of 185°F (85°C), and if HMD burns in a fire event, it will release water and carbon dioxide, along with ammonia, nitrogen oxides, carbon monoxide and possibly other low molecular weight nitrogen containing hazardous materials.

HMD has had a variety of autoignition values measured and published. The value which Ascend considers the most scientifically valid is 315°C at 1027 hPa.<sup>2</sup>

## Corrosion and Material Properties

Under certain conditions, HMD may be corrosive to steels, and is corrosive to copper and copper alloys. Copper, Brass and Bronze should never be used for HMD service. Anhydrous and Aqueous HMD are commonly stored in unlined Carbon Steel storage tanks.

Upon prolonged exposure, HMD can soften, swell and weaken various polymeric materials, such as natural and synthetic rubber. Proper engineering determinations should be made for designing pressurized handling systems for HMD, and selecting gasket and sealant materials for HMD service.

## Carbamate Formation

HMD is a strong base, and will spontaneously react with Carbon Dioxide (a weak acid) in the air. The reaction product of these two chemicals is hexamethylenediamine carbamate, CAS 143-06-6. Since HMD is a semi-volatile material, this reaction will take place in the air any time liquid HMD is exposed to air. It appears as a thin, hazy, white "smoke," although it is not smoke at all. With time, HMD Carbamate will settle out onto surfaces as a fine powder.

Although HMD Carbamate is a safe material (as a neutralized form of HMD), its spontaneous formation is important for a variety of health and safety reasons. HMD Carbamate can accumulate in tank or process vents, or any place where HMD may be leaking from a process or storage facility. If process or storage vents become plugged with HMD Carbamate, the integrity of the process may be challenged, as

over (or under) pressurization can occur in a system with plugged vents. The HMD customer should have a system of vent inspection and cleaning, along with a preventive maintenance program which addresses vent issues.

HMD Carbamate can serve an important warning function, as it is an indicator of leaking or venting HMD. While HMD carbamate is a lower acute hazard than HMD, care should be taken in its removal, as it is possible for pockets of unreacted HMD to be present within it, and it may be serving as a plug for a pressurized system.

Figure 1 – HMD Carbamate collected on a leaking rail car filling valve, and surrounding surfaces



Figure 2 – HMD Carbamate collected on surface of a drum after a nearby spill. HMD Carbamate is the white haze on the upper portions of the drums.



## Health Affects Overview

HMD has been extensively studied by manufacturers, governmental agencies and researchers around the world. Hundreds of studies have been conducted, and these studies have shown that:

- HMD is safe as industrial reactant or monomer when handled and used responsibly in the manner intended.
- HMD must be carefully controlled through engineering and protective equipment and safe work practices combined with personal protective equipment.
- Like most caustic materials, HMD is corrosive to the skin, eyes and mucous membranes. If not quickly and thoroughly removed, permanent damage may occur. Opportunity for these effects can be minimized through good industrial practice and personal protective equipment.
- HMD is biodegradable, and poses no risks to the environment from industrial use.

## Established Occupational Exposure Limits

In many jurisdictions, occupational exposure limits have been established. While many of these are identical some variance does exist. These are limits above which it is deemed necessary to have employees protected from inhalation exposure. The current established limits are:

| Jurisdiction or Authority    | Value                            | Type of Value              |
|------------------------------|----------------------------------|----------------------------|
| ACGIH TLV:                   | 0.5 ppm                          | 8-hr TWA                   |
| Argentina OEL                | 0.5 ppm                          | 8-hr TWA                   |
| Austria                      | 0.5 ppm<br>2.3 mg/m <sup>3</sup> | 8-hr TWA                   |
| Bahrain                      | 0.5 ppm<br>2.3 mg/m <sup>3</sup> | 8-hr TWA                   |
| Belgium: OEL                 | 0.5 ppm<br>2.3 mg/m <sup>3</sup> | 8-hr TWA                   |
| Bulgaria                     | 1.0 mg/m <sup>3</sup>            | 8-hr TWA                   |
| Canada: Alberta OEL          | 0.5 ppm<br>2.4 mg/m <sup>3</sup> | 8-hr TWA                   |
| Canada: British Columbia OEL | 0.5 ppm                          | 8-hr TWA                   |
| Canada: Manitoba OEL         | 0.5 ppm                          | 8-hr TWA                   |
| Canada: Ontario OEL          | 0.5 ppm                          | 8-hr TWA                   |
| Canada: Quebec OEL           | 0.5 ppm<br>2.3 mg/m <sup>3</sup> | 8-hr TWA                   |
| Canada: Saskatchewan OEL     | 0.5 ppm<br>1.0 ppm               | 8-hr TWA<br>15 minute STEL |
| Columbia OEL                 | 0.5 ppm                          | 8-hr TWA                   |
| Denmark : OEL                | 0.5 ppm<br>2.3 mg/m <sup>3</sup> | 8-hr TWA                   |
| Hungary: AK Value            | 2.3 mg/m <sup>3</sup>            | 8-hr TWA                   |
| Iceland: OEL                 | 0.5 ppm<br>2.3 mg/m <sup>3</sup> | 8-hr TWA                   |
| Indonesia: OEL               | 0.5 ppm                          | 8-hr TWA                   |
| Ireland : OEL                | 0.5 ppm<br>2.3 mg/m <sup>3</sup> | 8-hr TWA                   |
| Israel                       | 0.5 ppm                          | 8-hr TWA                   |
| Italy : OEL                  | 0.5 ppm                          | 8-hr TWA                   |
| Latvia: AERs)                | 0.1 mg/m <sup>3</sup>            | 8-hr TWA                   |

|                                  |  |                            |
|----------------------------------|--|----------------------------|
| Malaysia: OEL                    | 0.5 ppm<br>2.3 mg/m <sup>3</sup>               | 8-hr TWA                   |
| Norway OEL                       | 0.5 ppm<br>1.0 ppm                             | 8-hr TWA<br>15 minute STEL |
| Peru OEL                         | 0.5 ppm<br>2.4 mg/m <sup>3</sup>               | 8-hr TWA                   |
| Portugal : OEL                   | 0.5 ppm  | 8-hr TWA                   |
| Romania: OEL                     | 1.0 mg/m <sup>3</sup><br>5.0 mg/m <sup>3</sup> | 8-hr TWA<br>15 minute STEL |
| Russian Federation: OEL          | 0.1 mg/m <sup>3</sup>                          | Ceiling Limit, Vapor       |
| Serbia and Montenegro: MAC Value | 1.0 mg/m <sup>3</sup><br>0.2 ppm               |                            |
| Singapore: PEL                   | 0.5 ppm<br>2.3 mg/m <sup>3</sup>               | 8-hr TWA                   |
| Spain : VLA-ED                   | 0.5 ppm<br>2.4 mg/m <sup>3</sup>               | 8-hr TWA                   |
| United Arab Emirates             | 0.5 ppm<br>2.3 mg/m <sup>3</sup>               | 8-hr TWA                   |
| United States - OSHA             | 0.5 ppm  | 8-hr TWA                   |
| United States - California       | 0.5 ppm<br>2.3 mg/m <sup>3</sup>               | 8-hr TWA                   |
| Uruguay                          | 0.5 ppm  | 8-hr TWA                   |
| Venezuela – CAP                  | 0.5 ppm  | 8-hr TWA                   |

## ***Details on Health Effects***

### **Acute Effects**

In the workplace, acute effects from HMD exposure may occur via skin, eye and mucus exposure to the eyes, or inhalation of HMD containing mist.

**Skin Corrosion – HMD is a severe skin corrosive material, and its effects should not be underestimated.** HMD causes caustic burns to the skin, resulting in permanent scarring, pain and long lasting physical effects. The GHS classification of HMD is “Causes severe skin burns and eye damage,” H314.

Caustic materials such as HMD literally dissolve skin. HMD saponifies fats from skin cells and denatures proteins; the fats become water dispersible, and this effect causes cell walls to break down, allowing the chemical to penetrate deeper into the skin. This type of damage is known as liquefaction necrosis. Such action persists until the chemical is neutralized.

If HMD gets on the skin, intense burning will be felt, as skin nerves are affected. The skin area will feel “soapy” and slick; this effect is due to the breakdown of the cell walls, and the liberation of water and fats from the cells. HMD should be immediately and thoroughly removed from the skin. Medical care should be sought.

**Eye Corrosion – Similar to skin effects, HMD is a severely corrosive material to the eyes.** The GHS classification of HMD is “Causes severe skin burns and eye damage,” H314. HMD will cause the cornea to become cloudy, and affect cell walls of eye cells in the same fashion as skin cells. While detailed studies of HMD eye effects do not exist, other highly caustic materials (such as sodium hydroxide) can completely penetrate the eye in 40 seconds<sup>3</sup>.



**Oral Toxicity** – HMD is classified under GHS as harmful if swallowed (H302). In animal studies, the LD<sub>50</sub>(rat) value for HMD is 1160 mg HMD/kg of body weight. As HMD is a caustic material, it will cause painful and harmful burns to the mouth and throat. The oral toxicity value is based on a gavage study, where the substance is placed directly into the stomach. While this information is valuable, the health effects of permanent burns to the mouth and upper digestive tract, including complete destruction of tissue, would be seen from any amount of HMD entering the mouth.

**Inhalation Toxicity** – There is no available inhalation toxicity value for HMD. Based on available data, HMD is classified under GHS as “may cause respiratory irritation,” H335. This classification is based on a 13 week inhalation study. The No Observed Adverse Effect Concentration (NOAEC) is 10 mg/m<sup>3</sup>, with the effects seen including cellular irritation in the nose and larynx. Inhalations of large quantities of HMD containing mist would likely cause chemical burns to the nasal passages.

**Dermal Toxicity** – HMD is considered as moderately toxic by dermal exposure, and is classified under GHS as “Harmful in contact with skin,” Category 4. When HMD was applied to rat skin, the LD50 value is 1900 mg HMD/kg of body weight. The dose/response curve shows no mortality at 1400 mg/kg, and completely mortality at 3000 mg/kg.

While this information is valuable for evaluation of whole body toxicity, we wish to stress that any amount of HMD on the skin will result in painful skin burns. In the dermal study mentioned above, doses which were fatal to most of the test animals (2000 mg/kg and higher) resulted in skin lesions which were unable to heal; lower doses resulted in wounds which healed prior to the end of the study, characterized by scabbing and scarring.

## **Chronic Effects**

In the workplace, chronic effects from HMD exposure may occur via skin, eye and mucus exposure to the eyes, or inhalation of HMD containing mist.

**Sensitization** – HMD has not been tested for sensitization properties. Since it is a skin corrosive material, protection from the corrosive effects of HMD should protect against any sensitization concern.

**Oral Exposure** – Many repeat dose feeding studies have been conducted on HMD, by many different organizations, of varying quality and relevance to risk assessment. Two week animal feeding studies have shown that ingestion of HMD had a No Observed Adverse Effect Level (NOAEL) of 335 mg/kg/day in male rats, and 390 mg/kg/day in female rats. This was the highest dose tested, which means that no statistically significant effects were seen.

**Inhalation Exposure** – In a 13 week study of rat exposure to chloride salt of HMD, effects were seen in the nose and larynx of the tested animals at the higher concentrations tested (31 and 100 mg HMD salt/m<sup>3</sup>). The No Observed Adverse Effect Concentration (NOAEC) was judged to be 10 mg HMD salt/m<sup>3</sup>. Similar findings were found in mice, also with a NOAEC of 10 mg HMD salt/m<sup>3</sup>.<sup>4</sup> The toxicity observed for HMD results primarily from the irritant properties of the chemical

**Cancer** – Several studies have shown that HMD does not cause genetic mutations in bacteria or animal cells. No long term animal cancer studies exist for HMD, as they are considered scientifically unjustified, due to:

- Lack of systemic toxicity at low levels of exposure
- Negative results in genetox studies
- Corrosive nature of HMD, leading to need for tight industrial controls on its use.

## REACH Registration

In 2010, HMD was registered for continued, large scale use in Europe. Ascend was part of the consortium which helped assemble the registration dossier. This comprehensive review contained hundreds of studies, and narrowed the available dataset down to the most scientifically valid studies. The following data was used for regulatory assessment:

### Acute Animal Toxicity, Sensitization and Corrosion Data

| Exposure Route         | Type of Test   | Species            | Value  |
|------------------------|--|--------------------|--|
| Oral                   | LD50 oral gavage   | Sprague-Dawley rat | 1160 mg/kg bw (male/female)  |
| Inhalation             | Not applicable   |                    |  |
| Dermal                 | LD50 occlusive   | Sprague-Dawley rat | 1900 mg/kg bw (male/female)  |
| Skin irritation        | In vitro membrane barrier test method (corrositex test)  | in vivo            | corrosive  |
| Eye irritation         | equivalent or similar to 92/69/EEC, B.5  | New Zealand rabbit | Highly irritating, induced irreversible effects  |
| Respiratory irritation | subchronic (inhalation: aerosol) (whole body)  | Fisher 344/N Rat   | Irritating; STOT SE3<br><br>NOAEC: 10 mg/m <sup>3</sup><br><br>Target organs: nose, larynx |
| Exposure:              | 13 weeks (6 hours plus T90 (30 minutes) per day, 5 days per week)                                    |                    |  |
| Skin Sensitization     | No reliable information (key study or weight of evidence) was available for sensitisation assessment |                    | not sensitising  |

### Repeat Dose/Chronic Toxicity Data

| Exposure Route          | Type of Test  | Species          | Value   |
|-------------------------|---|------------------|---|
| Repeat dose Oral:       | subacute (oral: drinking water)   | Fisher 344/N Rat | NOAEL: 335 mg/kg bw/day<br><br>Target organs: other: all gross lesions and masses |
| Exposure:               | Drinking water solutions ad libitum on a continuous basis for 15 days (Continuous basis (ad libitum)) (OECD 408)                          |                  |   |
| Repeat dose Dermal:     | The study is scientifically unjustified considering animal welfare since HMD is classified as corrosive; at non-irritating concentrations |                  |   |
| Repeat dose Inhalation: | subchronic (inhalation: aerosol) (whole body)   | Fisher 344/N Rat | NOAEC: 10 mg/m <sup>3</sup><br><br>Target organs: nose, larynx                    |
| Exposure:               | 13 weeks (6 hours plus T90 (30  |                  |   |

minutes) per day, 5 days  
per week) (OECD 413)

**Carcinogenicity/ Mutagenicity Data**

|   |   |                        |  |
|---|---|------------------------|--|
| Mutagenicity – In Vitro                 | mammalian cell gene mutation assay (gene mutation) (OECD 476)   | Chinese hamster ovary  | negative   |
|   | bacterial reverse mutation assay (e.g. Ames test) (gene mutation) (OECD 471)  | Salmonella typhimurium | negative   |
| Mutagenicity – In Vivo                  | oral: gavage  | Sprague-Dawley Rat     | Genotoxicity: negative (male/female); toxicity: yes        |
|   | chromosome aberration assay (chromosome aberration) (OECD 475)  |                        |  |
|   | inhalation: aerosol   | Mouse                  | Genotoxicity: negative (male/female); toxicity: no effects |
|   | micronucleus assay (chromosome aberration) (OECD 474)   |                        |  |
| Carcinogenicity                         | The substance is classified as corrosive and irritant for respiratory tract. HMD is only used in industrial area. Hence, there is no evidence or long-term human exposure. Moreover, studies showed a lack of genotoxicity together with a lack of systemic toxicity for HMD. |                        |  |
| Reproductive and developmental toxicity | Oral, in feed, 2 generation (equivalent to OECD 416)  | Sprague-Dawley Rat     | NOAEL = 500 mg/kg bw/day                                   |
| Developmental toxicity (Teratogenicity) | oral: gavage Prenatal Developmental Toxicity Study (OECD 414)   | Sprague-Dawley Rat     | NOAEL = 300 mg/kg bw/day                                   |

**Specific Target Organ Toxicity (STOT)**

HMD was classified as specifically toxic to the respiratory tract. Exposure to HMD mist or vapor may cause irritation.

**Derived No Effect Levels**

The REACH Risk Assessment process requires that Derived No Effect Levels (DNEL's) be calculated for likely exposure routes. These values were derived from the available best data, and by using ECHA's methodology for risk assessment.

| Exposure pattern                           | DNEL  |                              |
|--|---|------------------------------|
|  | Workers   | General population           |
| Acute – inhalation, systemic effects *     | Not relevant  |                              |
| Acute – dermal, systemic effects           | Qualitative risk assessment based on corrosivity of HMD | Exposure unlikely            |
| Acute – oral, systemic effects             | n.a.  | No peak exposure is expected |
| Acute – inhalation, local effects          | 1.62 mg/m <sup>3</sup>                                  | 1.2 mg/m <sup>3</sup>        |
| Acute – dermal, local effects              | Qualitative assessment based on corrosivity of HMD      | Exposure unlikely            |
| Long-term – dermal, systemic effects       | Qualitative assessment based on corrosivity of HMD      | Exposure unlikely            |
| Long-term – inhalation, systemic effects * | Not relevant  |                              |
| Long-term – oral, systemic effects         | No information available                                | 0.56 mg/kg bw/day            |
| Long-term – dermal, local effects          | Qualitative assessment based on corrosivity of HMD      | Exposure unlikely            |
| Long-term – inhalation, local effects      | 0.54 mg/m <sup>3</sup>                                  | 0.4 mg/m <sup>3</sup>        |

\* No inhalation study is needed since HMD is classified as corrosive

Use of this data for Risk Assessment should be performed by qualified risk management professionals.

In addition to basic physical, chemical and toxicological data, REACh registration requires that the registrant proves the HMD is safe when used properly, in the types of end uses seen within Europe. Since all major uses of HMD occur in Europe, this health assessment has relevance for the rest of the world. It was successfully shown that for 6 different types of Exposure patterns, the risk to human health and the environment was sufficiently controlled, and HMD may continue to be used in current applications. The typical end uses for HMD were covered, with the exception of food, drug and cosmetic use; these are not within the scope of REACh. Please see Ascend's [Extended Safety Data Sheet](#) for registration details<sup>5</sup>.

## ***Environmental Affects Overview***

HMD has been extensively studied by manufacturers, governmental agencies and researchers around the world. Hundreds of studies have been conducted, and these studies have shown that:

- HMD is not Persistent, Bioaccumulative or Toxic in the environment.
- HMD is readily biodegradable in water.
- HMD is readily broken down in both aerobic and septic waste disposal systems
- While HMD is shows low or moderate toxicity to aquatic in laboratory studies, these are not reflective of real world conditions. HMD is a strong organic base acid, and raises the pH of water. These toxic effects seen are negated when the pH of the test medium is adjusted back to an environmentally relevant level. Further explanation is below.
- HMD undergoes photo and chemical degradation.
- Ultimate chemical and biodegradation products are carbon dioxide and water.

## **Details on Environmental Effects**

HMD's primary uses do not result in substantial releases into the environment. In almost all cases HMD is an intermediate or monomer, used within a chemical facility, and converted to another chemical substance. Proper use and disposal practices will minimize releases to the environment from all uses of HMD.

### **Biodegradation**

HMD has been shown to be readily biodegradable in aerobic and freshwater conditions in the environment. HMD was shown to be 82% degraded in a GLP compliant study.

### **Aquatic Toxicity**

The acute toxicity of HMD to aquatic organisms has been extensively studied. It has been concluded that through normal use, disposal and waste treatment, HMD should not adversely affect freshwater or marine organisms. As with any base, if HMD is placed in a pure water environment, it will raise the pH of the water. Any organisms which are in the water will be affected by such a pH change. Studies have shown that a pH change of 3-4 units will be fatal to 50% or more of organisms which are present in the water.<sup>6</sup> Aquatic toxicity data for HMD is shown below.

If a large spill of HMD was to occur, and this spilled material would enter surface water, clearly there may be acute toxic effects. HMD, when properly controlled and treated, poses no hazard to the aquatic environment.

### **Wastewater Treatment Facilities**

No specific wastewater treatment data exists for HMD. Based on the readily biodegradable status of HMD, no negative effects on wastewater treatment processes are expected from normal use and disposal.

## **REACH Dossier for HMD – Environmental Health Effects**

In 2010, HMD was registered for continued, large scale use in Europe. Ascend was part of the consortium which helped assemble the registration dossier. In addition to basic physical, chemical and toxicological data, REACH registration requires that the registrant proves the HMD is safe when used properly, in the types of end uses seen within Europe. Since all major uses of HMD occur in Europe, this health assessment has relevance for the rest of the world. In preparation of the dossier for HMD's REACH registration, all available data (through June 2010) was reviewed<sup>7</sup>. This comprehensive review contained hundreds of studies, and narrowed the available dataset down to the most scientifically valid studies. The following data was used for regulatory assessment:

### **Aquatic Toxicity**

| Exposure Route                       | Type of Test                                  | Species                                   | Value     |
|--------------------------------------|---|---|-----------|
| Fish, Short Term                     | LC50, freshwater, static, 96 hr<br>(OECD 203) | Pimephales promelas                       | 1825 mg/L |
| Fish, Long Term                      | Study waived – scientifically unjustified     |   |           |
| Aquatic Invertebrates,<br>Short Term | EC50, freshwater, static, 48 hr<br>(OECD 202) | Daphnia magna                             | 31.5 mg/L |
| Aquatic Invertebrates,<br>Long Term  | NOEC, Freshwater, 21 day                      | Daphnia magna                             | 4.2 mg/L  |
| Algae and aquatic<br>plants          | NOEC, Freshwater, static, 72 hour             | Pseudokirchnerella<br>subcapitata (algae) | 10 mg/L   |

Aquatic micro-organisms                      EC10, freshwater, static, 20 hr                      Pseudomonas putida                      12.5 g/L

### **Persistence and degradability**

Biodegradation                      Hexamethylene was found to be readily biodegradable meeting the 10-day window in a OECD 301D closed bottle test (van Ginkel, 2009).

### **Bioaccumulative potential**

Based on its Log Kow < 3.0 the substance is not believed to bioaccumulate, moreover, due to the ready biodegradability of the substance with discharge only via STP, exposure via the aquatic environment is expected to be low.

### **Mobility in soil**

Based on readily biodegradability and to very low Log Kow, the substance is not expected to adsorb.

### **Results of PBT and vPvB assessment**

The screening assessment of the available data for Hexamethylene diamine indicates that the data show that the properties of the substance do not meet the specific criteria detailed in Annex XIII, i.e. it is not P/vP, not B/vB, and not T.

Thus, the Hexamethylene diamine is not considered a PBT/vPvB.

### **Predicted No Effect Concentrations**

The REACH Risk Assessment process requires that Predicted No Effect Concentrations (PNEC's) be calculated for likely exposure routes. These values were derived from the available best data, and by using ECHA's methodology for risk assessment.

| Exposure pattern                  | PNEC                    |
|-----------------------------------|-------------------------|
| PNEC aqua (freshwater)            | 0.42 mg/L               |
| PNEC aqua (marine water)          | 0.04 mg/L               |
| PNEC aqua (intermittent releases) | 0.32 mg/L               |
| Freshwater Sediment               | 1.44 mg/kg sediment dw  |
| Marine Sediment                   | 0.144 mg/kg sediment dw |
| Soil                              | 0.0541 mg/kg soil dw    |
| PNEC STP                          | 12.5 g/L                |
| PNEC (oral, secondary poisoning)  | Irrelevant              |


Use of this data for Risk Assessment should be performed by qualified risk management professionals.

### **REACH Exposure Scenarios and Proof of Safe Use**

Within REACH, once the PNEC's are calculated, a registrant must prove that the uses of the substance result in exposures which are less than the PNEC. In 6 different exposure scenarios, using data provided by downstream users, safe use was proven for each condition. The typical REACH regulated end uses for HMD were covered; please see Ascend's [Extended Safety Data Sheet](#) for details<sup>8</sup>.

## GHS Classification and Labeling

Under the Global Harmonized Standard for Hazard Communication (GHS), Version 4, Adipic Acid is classified as follows:

| Category  | Sub-Category  | Classification  |
|---|---|---|
| Physical Hazards                                      | Flammable Liquids   | Category 4, Combustible Liquid                        |
| Acute Health Hazards                                  | Serious Eye Irritation/<br>Eye Damage   | Category 1, Causes Serious Eye Damage                 |
|   | Skin Corrosion/Irritation   | Category 1B, Causes sever skin burns and eye damage   |
|   | Acute Toxicity – Oral   | Category 4, Harmful if swallowed                      |
|   | Acute Toxicity - Dermal   | Category 4, Harmful in contact with skin              |
| Chronic Health Hazards                                |   | Not classified for any Chronic Health hazard          |
| Specific Target Organ Toxicity (STOT), Acute Exposure | Respiratory Tract Irritation  | Category 3, May Cause Respiratory Irritation          |
| Acute Environmental Hazards                           | Toxicity to Algae, Invertebrates  | Category 3, Harmful to Aquatic Life                   |
| Long-term Environmental Hazards                       |   | Not classified for any long term environmental hazard |
| Signal Word   | Danger  |   |
| Pictogram   |  |   |

## References

- <sup>1</sup> [49CFR 172.101](#), accessed May 4, 2012
- <sup>2</sup> Vibert, Martine, Determination of the flash point, explosion properties and, the auto-ignition temperature of Hexamethylene diamine, Rhodia CRTL, 2007. Unpublished study, summarized in the REACh registration for HMD
- <sup>3</sup> Spöler & al., Dynamic analysis of chemical eye burns using OCT-HR, J of Biomedical Optics, 2007,12 (4), 041203
- <sup>4</sup> Hebert, 1993, NTP Technical Report on Toxicity Studies of 1,6-Hexanediamine Dihydrochloride (CAS No. 6055-52-3). [http://ntp.niehs.nih.gov/ntp/htdocs/st\\_rpts/tox024.pdf](http://ntp.niehs.nih.gov/ntp/htdocs/st_rpts/tox024.pdf) (Accessed on July 16, 2012)
- <sup>5</sup> Ascend Performance Materials e-SDS, 2011
- <sup>6</sup> S.E. Belanger and D.S. Cherry, Journal of Crustacean Biology, Vol. 10, No. 2 (May, 1990), pp. 225-235
- <sup>7</sup> Ascend Performance Materials, REACh Dossier for CAS 5064-31-3, November 2010.
- <sup>8</sup> Ascend Performance Materials e-SDS, 2011