WRITE – UP ON Aldehydes India "CUTTING EDGE STATE OF THE ART PROCESS TECHNOLOGY" FOR HEXA METHYLENE TETRA AMINE (H.M.T. / HEXAMINE / UROTROPINE) MANUFACTURE

1.0 PREAMBLE

1.1 **Aldehydes India offers the entire range of "State of Art" process technologies for production of Hexa Methylene Tetra Amine (H.M.T. / HEXAMINE)** products.

1.2 This short note presents an overview of Aldehydes India Cutting Edge Technologies for manufacture of **Hexamine**.

2.0 Aldehydes India "ADVANCED CUTTING EDGE STATE OF THE ART TECHNOLOGIES" FOR MANUFACTURE OF HEXA METHYLENE TETRA AMINE (H.M.T. / HEXAMINE)

Aldehydes India possesses the complete technological know-how and basic design / detailed engineering expertise to build **Hexamine Plants** based on both **Liquid Phase Ammoniation** and **Vapour Phase Ammoniation** variants of the manufacturing process.

3.0 Aldehydes India HEXAMINE PROCESS TECHNOLOGIES

3.1 THE PRODUCT

"Hexamine" is the short form of **Hexa Methylene Tetramine ($C_6H_{12}N_4$).** It has also other names like Urotropin, Methenamine, Aminoform, Crystamin, Formin, Uritone etc. Hexamine is a solid crystalline or granular white powder generally having an average particle size of 40 to 60 mesh per linear inch. It is soluble in water, spirit, chloroform etc.

Hexamine sublimes at about 263 deg. C without melting and with partial decomposition. When in contact with a fire it readily burns with a smokeless flame. The Aqueous solution has a pH about 8.4.

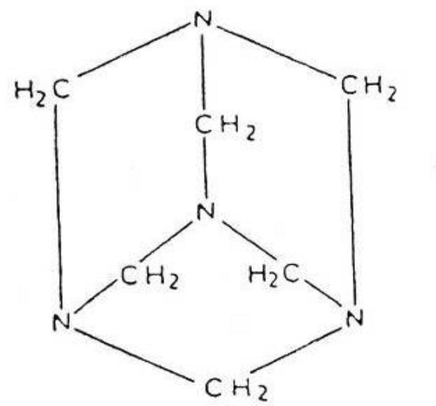
Hexamine is the **amino – analogue** of **Trioxane**. Since hexamine contains no oxygen, water is not liberated when it is employed as a **Methylenating agent**.

In addition it has neither the odour nor the chemical reactivity of Formaldehyde only in the presence of a catalyst under the influence of heat, or when brought in contact with an active

Formaldehyde acceptor. Due to this reason the reactions with Hexamine are more readily controlled than those of Formaldehyde.

Hexamine is produced by reaction of Aqueous Formaldehyde (AF 37) and anhydrous Ammonia in liquid phase or gaseous phase.

Hexamine was first prepared in 1859 by Butlerov by reaction of gaseous Ammonia and Paraformaldehyde. As a result of further studies Butlerov later identified the compound as possessing the empirical formula $C_6H_{12}N_4$ and suggested the structural formulae as shown below:



HEXAMETHYLENETETRAMINE
(HEXAMINE)

3.2 MANUFACTURING PROCESSES

There are quite a few variants of the manufacturing process of hexamine starting from Formaldehyde and Ammonia. It can be made from both aqueous Formaldehyde as well as aqueous Ammonia and can also be synthesized by using one of the reactant or both the reactant in gaseous / vapor state. It is formed as per the following reaction:-

$$\mathbf{6\ HCHO + 4\ NH_3 \longrightarrow {}_6H_{12}N_4 + 6\ H_2O}$$

The reaction is **exothermic** in nature and is also instantaneous. However, when 37% Aqueous Formaldehyde is used as a reactant, the product of synthesis is 25 to 30% solution of Hexamine in water. This **liquid phase process** requires large quantity of steam to evaporate the water before the crystalline product is produced.

In a process variant where the **Formaldehyde** is directly taken after the **reactor of Formaldehyde** PLANT (along with other by products and inerts such as Nitrogen etc,) the exothermicity of Hexamine reaction increases to such an extent that the water of reaction formed can be evaporated without external source of heat. Such a takes the advantage of this and produces Hexamine without any necessity of steam for evaporating water. (However a small quantity of steam is required for final drying of the product before bagging).

This however requires appropriate tapings to be taken from an existing Formaldehyde PLANT after the Reactor for production of Hexamine in gaseous phase.

Alternatively, an integrated PLANT of Formaldehyde along with Hexamine can be installed wherein the gaseous product after the Formaldehyde reactor is taken for synthesis of Hexamine and reacted in Hexamine Reactor along with Ammonia.

Since gaseous product from Formaldehyde **PLANT** is along with by products such as carbon dioxide, Formic acid etc., Hexamine reactor also needs to handle these gases depending upon the original composition of these gases. Therefore, the final off gases after the Hexamine **PLANTS** may require further treatment such as incineration, in the gaseous phase Process.

Aldehydes India can design, engineer and supply Hexamine PLANTS based on both the "Liquid Phase Process" and the **"Vapour Phase Process".** A brief description of each of these processes follows:

A. "LIQUID PHASE AMONIATION OF FORMALDEHYDE" PROCESS

The formation of Hexamine from aqueous Formaldehyde and Amonia is indicated by the following equation, for which the heat of reaction has been calculated from accepted thermochemical values:

$$6\ HCHO + 4\ NH_3 \dashrightarrow C_6H_{12}N_4 + 6H_2O + 81Kcal$$

At ordinary temperature this reaction is rapid and proceeds quantitatively to completion. When Formaldehyde of 37% wt/wt strength is used, the reaction is instantaneous and exothermic yielding about 25% wt/wt solution of Hexamine in water. Preferred temperature for the reaction are in the range of about 50 deg. C., since at higher temperature some resinous by-product forms which imparts a yellowish tinge to the final product.

The main process consists of the following steps – the entire route is non catalytic:

- **SYNTHESIS**

The aqueous Formaldehyde 37% wt/wt is continuously fed to a circulating 25% wt/wt Hexamine solution. Anhydrous liquid Ammonia, is also fed to this circulating solution at a point where Formaldehyde has already been added. The reaction thus takes place in presence of the Hexamine solution which helps in absorbing the heat of reaction.

The synthesis loop is equipped with coolers which removes the heat of reaction and maintains the required temperatures.

In order to control the reaction, aqueous Formaldehyde and Ammonia is charged in measured quantities maintaining a small excess of Ammonia over the Stoichiometric requirement.

- **EVAPORATION CUM CRYSTALLISATION**

The Hexamine solution overflowing from the synthesis loop requires concentration so that Hexamine crystallizes upon achieving the saturation point.

The solubility of Hexamine in water is about 45%wt/wt and therefore deteriorates the quality of Hexamine the evaporation is done at low temperatures by boiling the water under vacuum.
The equipment design also takes care to generate larger sized crystal which helps in subsequent operations.

- **CENTRIFUGING**

In order to have uniform production a continuous pusher type centrifuge has been selected which provides a product with about 5% moisture to the dryer.

In order to provide continuous feed to each pusher centrifuge an intermediate tank after the evaporator cum crystallizer has been designed which acts as a surge tank.

The centrifuge separates the mother liquor collected along with the fitness escaping through the filter media of the centrifuge is recycled back to the evaporator.

The impurities and by-products formed during the evaporation cum crystallization stage impart a yellowish colour to the mother liquor. The mother liquor, therefore, is decolorized in pressure leaf filters and recycled to the system.

- **DRYING**

The wet cake from the Centrifuge is fed to the drying system through a hopper and a screw conveyor.

The dryer system comprises of a continuous fluidized bed type dryer wherein hot air acts as a fluidizing cum drying media for the product. The air is separated in the cyclone separator and is sent to the scrubber for fines recovery.

The product collected is bagged or pulverized to a finer mesh before bagging, depending upon the requirements.

A basic process flow diagram (**Figure 1**) for Hexamine production is shown below:

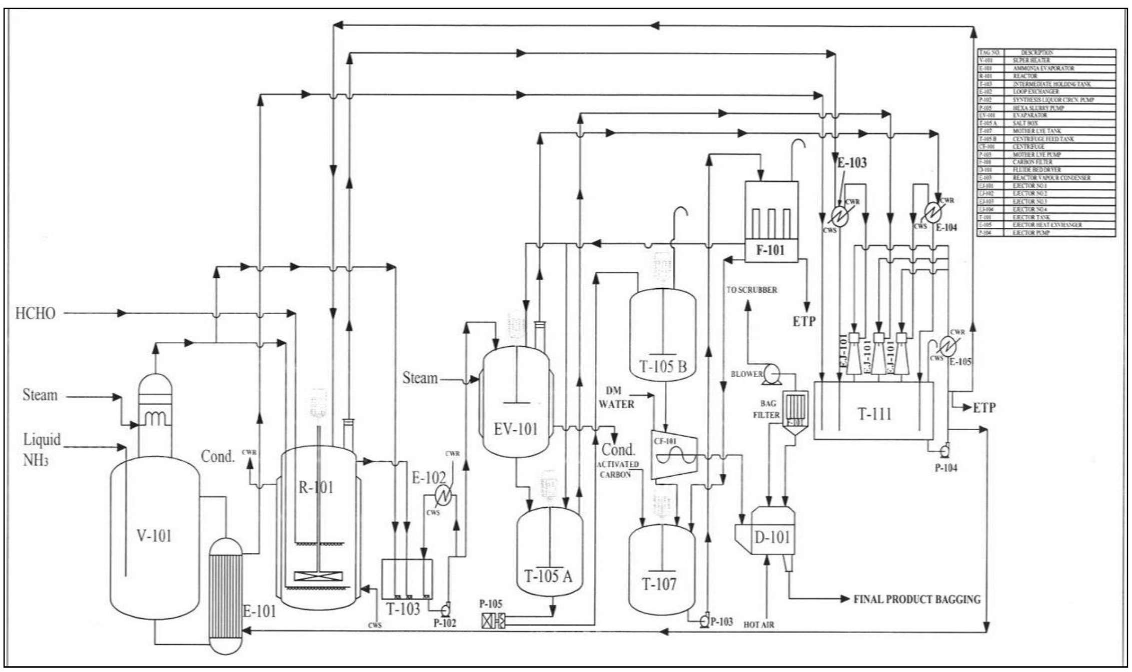


FIGURE 1 : Basic Process Flow diagram: Hexamine Production liquid phase

B. GASEOUS PHASE AMMONIATION PROCESS

- **SYNTHESIS CUM CRYSTALLIZATION**

Anhydrous liquid Ammonia stored in Ammonia tank is fed to an **Ammonia vaporizer**. Ammonia is vaporized utilizing the heat available in the off gases after Hexamine reaction is completed. **Gases** containing **Formaldehyde** from Formaldehyde manufacturing Facility along with **vaporized Ammonia** are reacted in a specially designed Reactor. The Reactor contains partly crystallized slurry of Hexamine in water. The water balance is so maintained that the crystal growth is achieved directly in the Reactor and Reactor contents (slurry) are handled further for centrifuging.

- **CENTRIFUGING / DRYING**

Hexamine slurry from the reactor is drawn to a Holding tank by maintaining the level in the reactor. The slurry is thereafter centrifuged in a **Continuous Centrifuge** which is washed with process water to achieve required purity of Hexamine. The wet product after the centrifuge is dried in a specially designed Dryer with hot air.

The mother liquor from the centrifuge is treated in an activated carbon Filter for removal of certain bi-product impurities formed during synthesis and recycled back to the reactor. Some process water is also added to the reactor to maintain water balance. The off gases from the reactor after transferring heat to evaporate Ammonia is taken to a Scrubber along with off gases from the Dryer. The scrubber circulates the process water which helps clean the off gases before letting it out to either atmosphere or for further off gas treatment.

The Reactor is maintained under **vacuum** using the **water jet ejector system** provided after the scrubber. A **Basic Process flow diagram (Fig. 2)** is placed below:

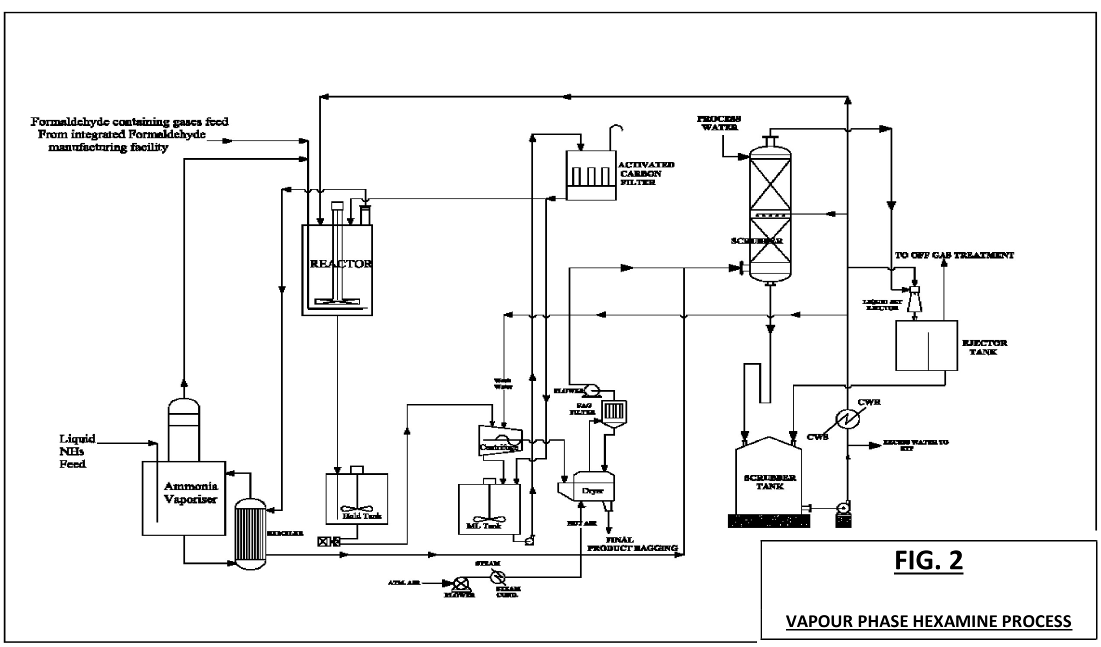


FIGURE 8 : Basic Process Flow diagram : Hexamine Production vapour phase

- **SUMMARY OF CHEMICAL REACTIONS**

As previously mentioned, Hexamine is produced by reacting Formaldehyde and Anhydrous Ammonia.

Chemical Reaction:

$$6\ HCHO + 4\ NH_3\ (g) \rightarrow C_6H_{12}N_4\ (s) + 6\ H_2O\ (l)$$

Heat of Reaction = -178 Kcal /g mole

Aldehydes India will work out the said Techno - Commercial Proposal based on the liquid phase Hexamine process due to sevaral advantages.

4.0 PRODUCT SPECIFICATIONS

As mentioned in the Power Point template above, **two different grades** of **Hexamine** are generally marketed, specifications of which are reproduced below:

Constituent	Composition (wt%)	
	(Stabilized)	(Un-stabilized)
Purity	98.2	99.2 min
Ash Content	1.0 max	0.05 max
Moisture	0.3 max	0.3 max
Free Ammonia	0.01 max	0.01 max
Chlorides	0.001 max	0.001 max
Sulphates	0.005 max	0.005 max
Heavy Metals	N.T.	N.T.

5.0 SPECIFICATIONS OF RAW MATERIALS / UTILITIES

5.1 FORMALDEHYDE FEEDSTOCK

CONSTITUENT	UNITS	COMPOSTION
Formaldehyde	HCHO (Min.)	37% w/w
Methanol	CH_3OH (Max.)	1% w/w
Acidity as Formic Acid	HCOOH (Max.)	0.02% w/w
pH	Units	3 to 4
Ash	(Max.)	20 ppm
Iron	(Max.)	0.5 ppm

5.2 ANHYDROUS AMMONIA FEEDSTOCK

Ammonia	:	99.8% w/w (Minimum)
Oil	:	5 ppm w/w (Maximum)
Water	:	Balance
Pressure	:	Atmospheric
Temperature	:	-33°C

5.3 REQUIRED UTILITIES

Electric Power

Voltage	440 V ±10%
Frequency	50 Hz,

Cooling water:

Pressure	5 Bar G,
Temperature	max. 30 °C
Temperature rise allowed	10 °C,

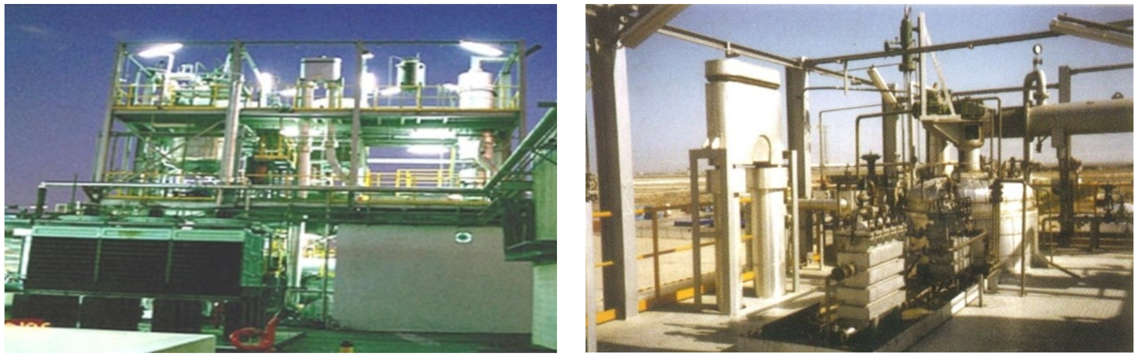
Instrumental air

Pressure	5 Bar G,
Dew point	no more than -40 °C

6.0 PHOTOGRAPHS OF Aldehydes India "STATE OF THE ART" HEXAMINE PLANTS

6.1 Some Photographs of Aldehydes India "State of The Art" Hexamine Plants shown below:

10 TPD HEXAMINE PLANT



15 TPD HEXAMINE PLANTS

27 TPD HEXAMINE PLANT

7.0 SUMMARY

Aldehydes India offers "Cutting Edge State of the Art Process Technologies" for production of Hexamine products on a most **cost effective basis.** The Plants are based on **proven design / engineering** conforming to the best international standards and are tailor-made to render smooth, trouble free and sustained operations over long periods.