WRITE – UP ON Aldehydes India PARAFORMALDEHYDE PROCESS TECHNOLOGIES

1.0 GENERAL

1.1 Aldehydes India is in possession of technologies to produce all types of Paraformaldehyde products in varying concentration ranges and polymerization degree spans. It can offer PLANTS for:

(89-91)% FLAKED PARAFORMALDEHYDE PRODUCTION

Multi stage evaporation and chilled conveying process.

(91-96)% GRANULAR / PRILLED PARAFORMALDEHYDE PRODUCTION

Multi stage evaporation and rotary vacuum drying.

(91-96)% PRILLED PARAFORMALDEHYDE PRODUCTION

Multi stage evaporation and spray cum fluidized bed drying.

PLANTS for production of flakes are relatively inexpensive, whereas the processes for production of **prills/ granules** are fairly elaborate and such PLANTS involve a much larger investment.

2.0 THE PRODUCT – TECHNOLOGICAL ASPECTS

2.1 **Paraformaldehyde** is a **polymer of Formaldehyde** in **solid form**, containing a percentage of water, readily soluble in order to obtain an aqueous solution or to be used as a reactant by dissolving it in the reaction medium.
In chemical terms, Paraformaldehyde is a Polymer which is obtained by **Polycondensation of Formaldehyde** in aqueous solution. It is formed by mixture of Polyoxymethylene Glycols.

The formula is represented by:
$HO\ (CH_2O)n\ H)$
Where n= 6 (minimum)

The Polymeric Value (**n**) grows as the concentration increases, and depends, among other factors, on the way in which the Polymerization is carried out, the product ageing, etc. Through heating Paraformaldehyde in aqueous medium Formaldehyde Solutions are obtained. The solution rate is increased by adding small quantities of diluted Acids or Alkalies.

Paraformaldehyde is a mixture of polyoxy- methylene glycols containing from 8 to 100 Formaldehyde units per molecule. The number of CH_2O units is indicated by the chain length "n" also named as the "DEGREE OF POLYMERIZATION". However, the formation of Paraformaldehyde starting from aqueous Formaldehyde solution is not a polymerization process but rather one of polycondensation.

To the end of such a chain one molecule of water is attached being characterized as combined water. The average chain length (DEGREE OF CONDENSATION) can, therefore be deduced form the contents of Formaldehyde and of free and combined water.

The smaller the portion of combined water, the higher are the Formaldehyde content and the chain length. The types of Paraformaldehyde produced by production processes contain between 2 to 6.5% of combined water so that the average chain length lies between 8 and 30.

2.2 Typical **characteristics** of various **Paraformaldehyde grades** known to be manufactured are given below:

FREE FLOWING WHITE GRANULES WITH TYPICAL FORMALDEHYDE ODOUR (Granules)				**WHITE POWDER**
89%	91%	93%	96%	97%
FORMALDEHYDE CONTANT (%)				
89 ± 1	91 ± 1	93 ± 1	95.5 ± 1	96.5 ± 1
METHANOL CONTENT (%Max.)				
1	0.5	0.5	0.5	0.5
pH (10% AQUEOUS SUSPENSION				
3-5	3.5-6.5	3.5-6.5	5-7	5-7
ACIDITY (AS FORMIC ACID (%) Max.)				
0.03	0.03	0.03	0.03	0.03
REACTIVITY (RESORCINOL TEST) (Minutes)				
2-3	2-4	2-4	2-4	3-5
FLASH POINT (OPEN CUP) (^oC)				
93	93	93	93	93
FLASH POINT (CLOSED CUP) (^oC)				
71	71	71	71	71
IRON CONTENT (PPM Max.)				
2	2	2	2	2
ASH CONTENT (PPM Max.)				
100	100	100	100	100
MELTING POINT (^oC)				
120-170	120-170	120-170	120-170	120-170
BULK DENSITY (kg / m^3)				
750-750	750-850	750-850	750-850	500-800
GRAIN SIZE (MIN. 80%) (mm)				
0.2-1.0	0.2-1.0	0.2-1.0	0.2-1.0	Min. 90% < 0.100 DIN 60

Paraformaldehyde cannot be regarded as a chemical compound of exactly defined molecular weight. It therefore, follows that Paraformaldehyde cannot be precisely characterized by the regular chemical and physical methods, because its properties are changing over the course of time. The reason for this is that Paraformaldehyde as produced, still contains a certain amount of residual moisture and exhibits the properties of a hydrogel of low water content in the release and recapture of this free water.

Paraformaldehyde has the appearance of a **colorless solid**. Commercial grades have different degrees of sub division, ranging from **flakes, granules to a fine powder**. Its odor is the characteristic pungent odor of monomeric Formaldehyde.

As mentioned the chemical composition of PARAFORMALDEHYDE is best expressed by the type formula HO. $(CH_2O)_n$.H. Depending on conditions of preparation it may contain 91% to 99% Formaldehyde. Paraformaldehyde is a mixture polyoxy-methylene glycols containing from 8 to 100 Formaldehyde units per molecule. The chain length "n", also named as a "degree of polymerization" indicates the number of CH2O units.

Different kinds of Paraformaldehyde are produced according to variety of conditions for manufacture such as period of the condensation process, temperature, effect of catalysts, pressure for further dehydration and final Formaldehyde concentration.

It follows from the above that Paraformaldehyde is a mixture of polymeric hydrates having the average formula $(CH_2\ O)_8$. H2O and is formed by the condensation of methylene glycol as indicated by the equation:

$$\mathbf{nCH_2(OH)_2 \rightarrow (CH_2O)_n\ H_2O + (n\text{-}1)\ H_2O.}$$

The number of CH_2O units in commercial Paraformaldehyde is however generally higher.

3.0 PRODUCTION TECHNIQUE

3.1 Production of Paraformaldehyde usually starts from 37% or 55% by weight **aqueous** solutions of Formaldehyde. It is concentrated at temperatures below 100°C often done by vacuum distillation and mainly water distills of at first. The concentration of Formaldehyde present chiefly as hydrate is increased. The solutions can be concentrated in this way up to Formaldehyde content of above 80% at which point the greater part of the Formaldehyde is already present in the form of oligo – oxymethylene glycols. On cooling, gels with colloidal properties are obtained which are at first waxy but later on becomes brittle which consist of **Paraformaldehyde**.

As mentioned previously different kinds of **Paraformaldehyde** are produced according to the variety of conditions for manufacture such as period of condensation process, temperature, affect of liquid catalyst, pressure for further dehydration and final Formaldehyde concentration.

These **Paraformaldehydes** differ in such properties as the content of Formaldehyde, the content of water, the reactivity and the rate of depolymerization.

Therefore, it is possible to obtain powdered products after extensive dehydration in which the content of Formaldehyde is some 95% or more. However by reducing particularly the content of water very drastically, the products are of reduced rate of depolymerization and reactivity.

Since Paraformaldehydes having high reactivity, high rate of depolymerization and good stability on storage are desired in many fields of use, techniques for earlier arrest of the dehydration process have also been developed. Consequently, the Formaldehyde content of these products is lower, being generally below 96%.

4.0 Aldehydes India PARAFORMALDEHYDE PRODUCTION PROCESSES

Brief description of the three manufacturing process technologies for Paraformaldehyde production follows:

4.1 Aldehydes India FLAKED PARAFORMALDEHYDE TECHNOLOGY

Paraformaldehyde in flake form is produced by this process. The raw material for the said Paraformaldehyde production is freshly manufactured high concentration (52-55%) Formaldehyde solution.

The Paraformaldehyde, which is represented by typical formula HO $(CH_2O)_n$ H is also termed as mixture of Polyoxymethylene Glycols. It is controlled polymerized product of Formaldehyde in solid form. The presence of Formaldehyde unit per molecule is more than 6.

Salient Features

Salient features of Aldehydes India modified process for manufacture of flaked Paraformaldehyde are enumerated below:

1) Simple in Operation
2) Free flowing, dustless white flakes. Dust is a big problem for the workers handling Para
3) 100% utilization of Formaldehyde with almost '0%' loss in the process.
4) 100% pollution free
5) Highest safety measures
6) Easy solubility and simple to dissolve
7) Low power consumption

DESCRIPTION OF Aldehydes India FLAKED PARAFORMALDEHYDE PROCESS:

The production process is based on the concentration of freshly prepared Formaldehyde solution (52-55%) under vacuum.

After concentration of Formaldehyde to a certain high strength in concentrators and evaporators, it is solidified in flake form on flakers. The solidification is achieved through cooling on the stainless steel band of the flaker. The solidified flakes are then conveyed by belt conveyors to the maturation tanks for achieving desired concentration. Flake in specific sizes is then stored in silos before weighment and bagging. During Paraformaldehyde production process, lean formaldehyde is also obtained which may be used in other PLANTS like Hexa Methylene Tetramine PLANT, if existing in client's existing chemical complex. Otherwise, some lean formaldehyde is recycled back, after treatment, in the integrated formaldehyde-Paraformaldehyde PLANT as proposed above by ATEC.

A basic Process flow diagram is placed below in **Figure 1**:

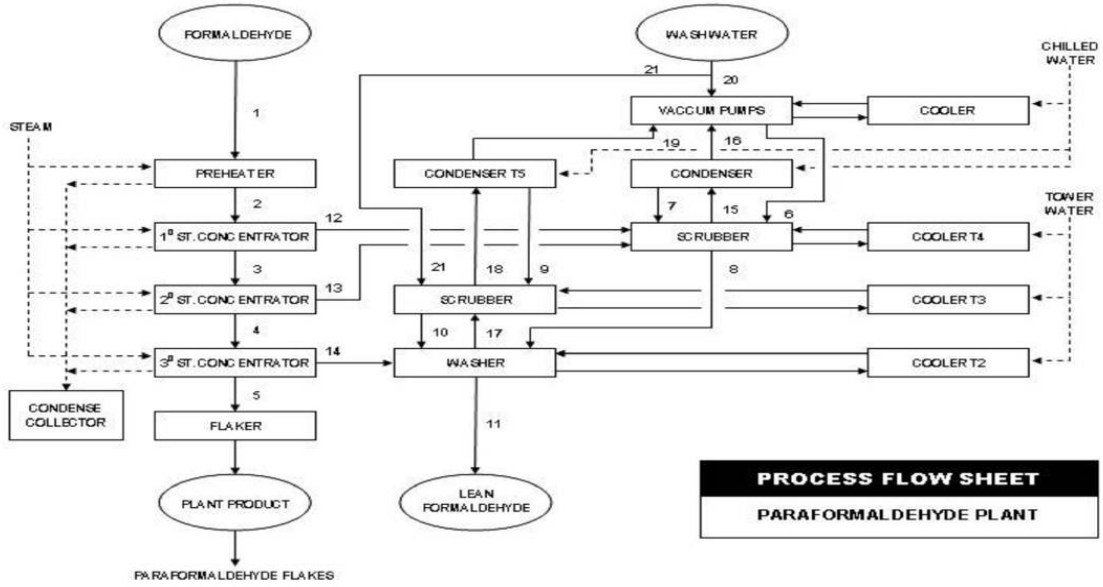
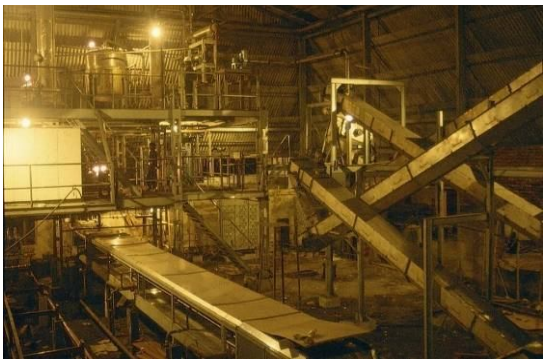


FIGURE 1



FLAKED PARAFORMALDEHYDE PLANTS

4.2 GRANULAR / PRILLED PARAFORMALDEHYDE PRODUCTION TECHNOLOGY BY ROTARY VACUUM DRYING

A unique process based on **Vacuum Concentrated and Drying of Product** to produce various (91% to 96%) concentration grades of Paraformaldehyde would be applied. A brief description is placed below:

CONCENTRATION UNIT

In the Aldehydes India process Paraformaldehyde is manufactured from aqueous (37%) Formaldehyde solutions by the process involving distillation and concentration at a point at which solidification or precipitation of polymer takes place. The process of concentration is carried out by vacuum evaporation.

The main sections of the PLANT are:

Concentration of aqueous Formaldehyde (AF 37 / AF 55)
Polymerization and drying
Concentration of distillates for recycling.
Conveying, pulverization and storage / packaging of the Product.

Concentration of aqueous Formaldehyde (37% or 55% with predecided Formic acid content) to (65-75)% is carried out by feeding the material from a storage tank to **proprietary concentration equipment (Evaporator – I).** The distillate containing (10-20) % Aldehyde content is condensed, sub cooled in heat exchangers and collected in an **Intermediate Tank**. **Polymerization and Drying** up to **96%** Formaldehyde concentration is carried out in proprietary **special drying equipment** which operates in a cyclic manner for polymer precipitation, cooling and unloading formed Paraformaldehyde lumps.

EVAPORATION

The (20-20) % Formaldehyde Concentration distillate obtained from the **Evaporator – I** and the distillate from the **drying section** are fed to concentration **Evaporator – II** for concentration and recycling. Functionally Evaporator II is similar to Evaporator I with certain differences in construction features. Use of secondary evaporation step helps in achieving the following:

a) Recovery of Formaldehyde to improve overall yield.
b) Facilitation of continuous operation of the PLANT by feed recycle.

c) Recovery of final distillates below (3-4) % Formaldehyde concentration grade which can be recycled to the Formaldehyde PLANT supplying AF-37 / AF-55 feed stock thereby virtually eliminating liquid effluents.

Depending on the Paraformaldehyde grade to be produced the solubility of the product, reactivity and pH requirements, a proprietary **Liquid Catalyst** is added before the polymer precipitation process.

Dilute Formaldehyde solution can be sent to Formaldehyde PLANTS for recovery and to avoid effluent generation.

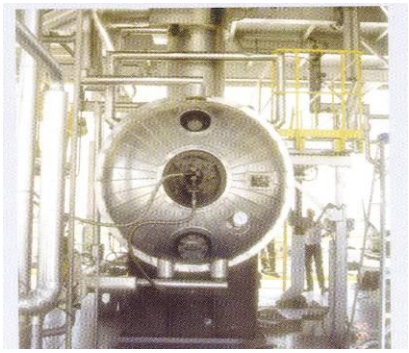
A Process Steam generation Boiler Package, D.M. Water unit, Chilled Water unit, Instrument Air system and Cooling Tower shall be required as Utilities.

Product from Drying Equipment is dumped onto the **Belt Conveyor** from where it is conveyed to a **Precrusher**. Crushed product is pneumatically conveyed to a **Cyclone** through a rotory air lock valve. The product from the cyclone is taken to a **Sieve Shaker** in which particles below **1mm size** are separated and sent to mixed Product Silo via pneumatic conveying system. The oversize material from sieve shaker goes to a **Pin Pulverizer** for further grinding and then through same pneumatic conveying system to **mixed Product Silo**. The mixed product is separated in **II Sieve Shaker** and transferred to **separate silos** for powder and granular products.

Typically about **40% product** is in **powder form** (particle passing through 65 mesh) and remaining **60% particles** are in **granular form** (retaining on 65 mesh). In case required, almost **100% product** can be in **granular form**, by compacting finer powder.

Two independent Dust Collection Systems are provided for the two conveying, and pulverizing sections. An Aspirator System with third bag filter and blower is installed for keeping the whole material handling system under slightly negative pressure. The aspirator system helps in collecting fine dust particles during conveying, crushing and sieving operations thus improving recovery and reducing pollution. The dust handling systems provide dust collecting for each set of cyclones / bag filters / blowers. Air from the three bag filters is passed through scrubbers for further cleaning before venting into open atmosphere.

GRANULAR PARAFORMADEHYDE PLANT



ROTARY VACUUM DRYER

ADVANTAGES OF Aldehydes India GRANULAR / PRILLED PARAFORMALDEHYDE PROCESS:

- Excellent Quality of Product results from the process utilizing specially designed concentration equipment evaporators which ensure no deterioration of product. The final product has low Reactivity Test Value (i.e. higher reactivity), high solubility, low ash content and low insoluble content.

- Any desired concentration of the product between 91% and 96% Aldehyde content can be produced in the PLANTS. "Dust Free" free flowing prills / granules as well as powder grades can be produced simultaneously.

- The p-H of final product can be adjusted as required by the ultimate consumer, which helps in achieving the flexibility of product application, envisaged.

- High Conversion Efficiency and low specific Consumptions of raw materials and utilities are obtained from the optimized process layout. Nearly theoretical conversion of Formaldehyde based on recycle Formaldehyde credit, is achieved along with lower energy consumption for evaporation and concentration step. Lower emergency power requirements in case of main power supply failure, result from the optimized energy distribution.

- Totally environmentally friendly process in which all vents are contained and the dust is scrubbed prior to venting any gaseous stream.

- Fast change over to different concentration grades and very low hold up of concentrated formaldehyde within the PLANTS.

- Lower capital and operating costs due to lower Formaldehyde consumption and lower energy requirements as well as lower manpower requirement.

- Proven process, **developed** in **1978**, commercialized and **operated** for more than **28 years**.

The **Process** has been over the years **upgraded** based on actual **operational experience** obtained in PLANTS of different optimal production level from 5 M.P.D through 15 M.T.P.D. upto 30 M.T.P.D. and beyond. The upgradation carried out was in terms of optimization of equipment / machinery sizing and more compact lay out at individual floor level of the PLANTS.

Indicative **Process flow diagram** for the Granular / Prilled Paraformaldehyde processes is shown in **Figures 2**, placed below:

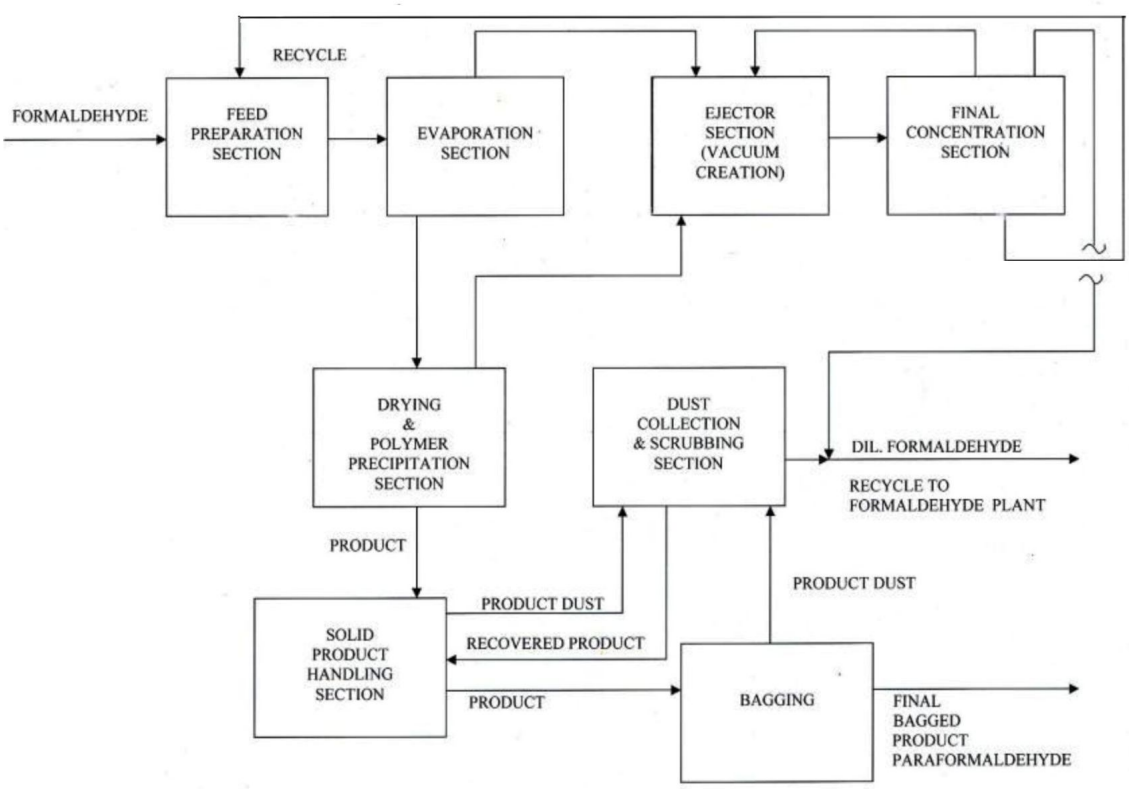


FIGURE 2: GRANULAR / PRILLED PARAFORMALDEHYDE PROCESSES BASED ON ROTARY VACUUM DRYING

4.3 PRILLED PARAFORMALDEHYDE PRODUCTION PROCESS BASED ON SPRAY CUM FLUIDIZED BED DRYING

The process essentially consists of the following steps:

- Concentration of Aqueous Formaldehyde
- Vacuum Spray Drying
- Fluidized Bed Drying
- Product Handling

Concentration of Aqueous Formaldehyde (AF-37) to AF (75 – 85) is carried out in a falling film evaporation and thin film evaporation (side stream) system.

(75 – 85) % concentrated Aqueous Formaldehyde is fed to a conical bottom NIRO vacuum Spray Dryer.

Spray dried powder is further concentrated in a Fluidized Bed Dryer before being sent to the product handling system. A liquid catalyst is used.

Three different grades (89%, 92% and 96%) of Paraformaldehyde are produced by under for end use application in resins, agro chemicals (Herbicides / Pesticides), Disinfectant / Medical intermediates sectors.

Basic block diagrams of the Process are shown in **Figures 3 and 4** below:

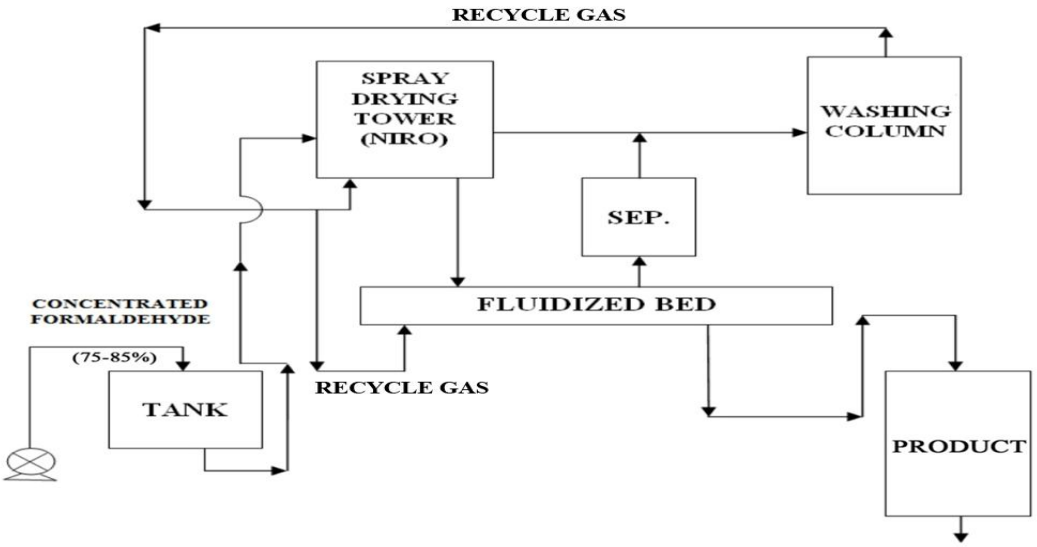


Figure 3 : PROCESS BLOCK DIAGRAM

An alternative process for production of **prilled Paraformaldehyde** products using the **"Prilling Tower Concept"** is also available. A schematic block diagram of this Process is shown in **Figure 4** below:

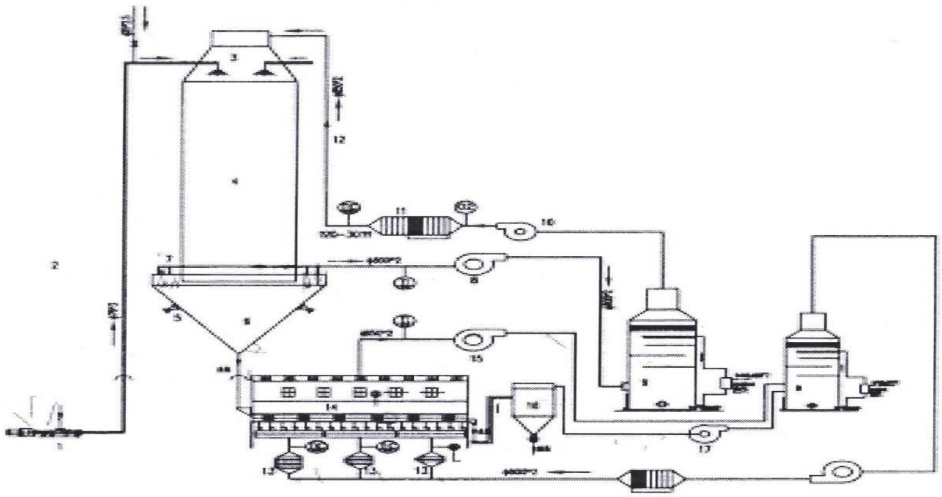


FIG. 4: SCHEMATICS OF PRILLED PARAFORMALDEHYDE PRODUCTION

COMBINED SPRAY AND FLUIDIZED BED DRYING FOR PARAFORM

- **PRODUCT'S SPECIFICATIONS**

The granular Paraformaldehyde manufacturing processes offered by Aldehydes India will produce **Paraformaldehyde** of the following **specifications**:

Aldehyde content (as HCHO % by mass)	:	(91-96 ± 1) for individual grades
Ash Content, ppm (max.)	:	100
Free Moisture content Percent by mass, (max.)	:	1
Acidity (as HCOOH) Percent by mass (max.)	:	0.03
Iron (ppm by mass max)	:	2
p-H	:	4 – 7
Methanol (% by mass max.)	:	1
Melting Point	:	120º - 170º C

- **RAW MATERIAL SPECIFICATIONS**

FORMALDEHYDE FEEDSTOCK

CONSTITUENT	**UNITS**	**COMPOSTION**
Formaldehyde	HCHO (Min.)	37% to 55% w/w
Methanol	CH3OH (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

Notably the PLANTS can be **designed** at **Formaldehyde Concentration** upto 50%

Note: Aldehydes India Paraformaldehyde Process can operate with higher Methanol content Aqueous Formaldehyde (AF – 37) feedstock as well.

- **SPECIFIC CONSUMPTION OF RAW MATERIALS / UTILITIES PER UNIT PARAFORMALDEHYDE**

RAW MATERIAL / UTILITIES	**SPECIFIC CONSUMPTION (PER M.T. 96% PARAFORM)**
Formaldehyde (AF – 37)	2.8 MT
L.P. Steam	5.0 M.T. (Av), 8.25 M.T. (Peak)
Electrical Power	300 KWH
Cooling Water	25 m^3
Process Water	0.18 M.T. (Av) 0.72 M.T. (Peak)
Chilled Water	88 m^3 (Average 156 m^3)
Instrument Air	250 N m^3 / Hour

- **EQUIPMENT MACHINERY FOR PARAFORMALDEHYDE PLANT (GRANULAR PARAFORM PROCESS)**

MAIN EQUIPMENT / MACHINERY

Item No.	Description	Nos	MOC	Remarks
T-02	Feed Mixing Tank	1	SS304	
T-03	Ejector Tank	1	SS304	
T-07	Distillate Collection Tank	1	SS304	
V-01	Evaporator Distillate Receiver	1	SS304	
V-02	Seal tank for Dryer Vapour Scrubber	1	SS304	
V-03	Recycle Concentrate Receiver	1	SS304	
V-04	Recycle Distillate Receiver	1	SS304	
V-06	Drier Vap. Scrubber	1	SS304	
V-09	Recycle Tank with Agitator	1	SS304	
V-17	Dust scrubber Tank	1	SS304	
V-26	Condensate Recovery Drum	1	CS	
V-27	Effluent Drain vessel	1	SS304	
V-32	Condensate Vessel for Evaporator	1	CS	
V-12	Vibratory Hopper with Vibrators	1	SS304	
V-13A	Silo for PF product with Vibrators	1	SS304	
V-13B	Silo for PF product with Vibrators	1	SS304	
V-15	Reject Hopper	1	SS304	
V-16	Intermediate Hopper for Fines +Vibrator	1	SS304	
V-22A/B	Undersize Feed Hopper		SS304	
V-25A	Bagging Silo	1	SS304	
V-25B	Bagging Silo	1	SS304	
E-01*	**Evaporator alongwith Associated items**	**1**	**SS316**	**Proprietary**
E-02	Evaporator overhead condenser	1	SS316	
E-03*	**Recycle Evaporator**	**1**	**SS316**	**Proprietary**
E-07	Recycle Distillate condenser	1	SS316	
E-10	Condensate Tank Vent Condenser	1	CS	

E-05A/B	Combined PHE (Plate heat exchanger)		SS316	
E-08	Ejector Tank Chiller - PHE	1	SS316	
E-09	Dust scrubber HE-PHE	1	SS316	
D-1/23/4/5*	**Drying System**	**5**	**SS316**	**Proprietary**
VF-1/2/3/4/5	Vibratory Feeders	5	SS304	
EJ-01	Evaporator Jet Ejector	1	SS304	
EJ-02	Drier Scrubber Jet Ejector	1	SS304	
EJ-04	Recycle Evaporator Jet Ejector	1	SS304	
EJ-05	Reactor Evacuater	1	SS304	
P-01A/B	Pump for T-01	2	SS316	
P-02A/B	Evaporator Feed Pump	2	SS316	
P-04A/B	Ejector Tank Pump	2	SS316	
P-05A/B	Vapour Scrubber Circulation pump	2	SS316	
P-12A/B	Weak Distillate Transfer Pumps	2	SS316	
P-13A/B	Dust Scrubber circulate pump	2	SS316	
P-16A/B	Condensate Transfer Pumps	2	CS	
P-19	Drain Pit Pump	1	SS316	
FT-01A/B	Basket filter	2	SS304	
BC-01	Belt Conveyor	1	SS304	
DFV-01A/B	Double Flap Valves	2	SS304	
BC-02	Belt Conveyor for Metal detector	1	SS304	
ME-01	Metal Detector	1	Plastic	
DV-01	Diverter Valve	1	SS304	
VF-11	Vibratory Feeder	1	SS304	
CR-01	Precrusher with Hopper	1	SS304	
SC-01	Screw Conveyor for Precrusher	1	SS304	
BE-01	Bucket Elevator to Sieve	1	SS304	
X-01	Sieve	1	SS304	
CR-02	Pin Pulverizer	1	SS304	
RV-01	Rotary valve at inlet of pin crusher	1	SS304	
RV-02	Rotary valve at outlet of pin crusher	1	SS304	
RV-03	Rotary valve at outlet of Silo	1	SS304	

- **MATERIALS**

(a) PIPING MATERIALS

Piping elements
Valves
Gaskets
Spring Supports

(b) INSTRUMENTATION

Control Valves
Flow Measurement Devices
Safety valves, Rupture discs
Thermo elements
Transmitters
Analytical Instruments
Manometers
Pneumatic Control Panel
Level Switches

(c) ELECTRICAL INSTALLATION

Motor Control Centre
Electrical Motor Drives for Pumps / Blowers

The above list is indicative only and the actual equipment / machinery / material list shall be finalized during engineering stage.

5.0 SUMMARY

Aldehydes India "Cutting Edge State of the Art Process Technologies" for production of a wide spectrum of **Formaldehyde and derivative products** on a most cost effective basis. The Plants are based on proven design / engineering confirming to the best international standards and are tailor-made to render smooth, trouble free and sustained operations over long periods. The company offers **highly reliable Paraformaldehyde Plants** based on its own Technologies.