

HYDRAZINE

Hydrazine, $\text{NH}_2\text{-NH}_2$, is the simplest diamine. Lobry de Bruyn first prepared anhydrous hydrazine in 1894. In 1953 Arch Hydrazine (formerly Olin Chemical) pioneered U.S. production of hydrazine to fuel the first Titan rocket.

Hydrazine is a clear, hygroscopic fuming liquid with the odor of ammonia. It is a mild base that is miscible in polar solvents such as water, ammonia, amines and alcohols. Additional properties are shown in Table 18.1¹³⁵.

TABLE 18.1. Physical Properties of Hydrazine

Molecular weight	
Anhydrous	32
Hydrate	50
Boiling point (°C)	113.5
Melting point (°C)	1.4
Specific gravity (g/ml)	
0°C	1.025
15°C	1.014
25°C	1.004
50°C	0.982
Critical temperature (°C)	380
Critical pressure (atm)	145
Vapor pressure (mm Hg)	
25°C	14
31°C	20
36°C	100

TABLE 18.1. Physical Properties of Hydrazine - Continued

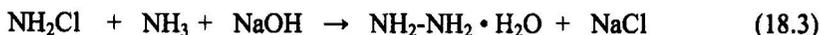
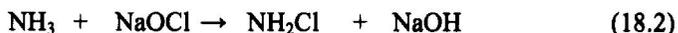
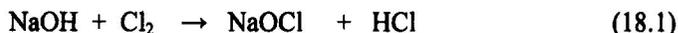
Viscosity (cp)						
5°C				1.2		
25°C				0.9		
Heat of vaporization (kcal/mol)				9.6		
Heat of solution (kcal/mol) @ 25°C				-3.9		
Heat capacity (J/mol °K) @ 25°C				98.87		
Heat of combustion (kcal/mol)				- 146.6		
Heat of formation (kcal/mole)						
Liquid				12		
Gas				23		
Flash point (°C)				52		
Explosive limits in air by vol. (%)				4.7 to 100		
Azeotrope Boiling Point (68% Hydrazine) (°C)				120.5		
		<u>Hydrazine Concentration (wt %)¹³²</u>				
	<u>100</u>	<u>64</u>	<u>51.2</u>	<u>35.2</u>	<u>22.4</u>	<u>15.4</u>
Melting Point, °C	2.0	-51.7	-59.8	-64.6	-26	-14
Boiling Point, °C	113.5	120.5	117.2	108	107	103
Density (25°C), g/ml	1.0045	1.0320	1.0281	1.0209	1.0132	1.0083
Viscosity (20°C), $\mu\text{Pa} - \text{s}$	0.974	1.5	1.44	1.10	1.08	1.04
pH		12.75	12.10			10.5

18.1. PROCESSES

Commercial production of hydrazine from its elements has not been successful. However three processes are available for the commercial production of hydrazine: 1) The Raschig Process, 2) The Raschig/Olin Process, 3) The Hoffmann (urea) Process, 4) Bayer Ketazine Process, and 5) the Peroxide process from Produits Chimiques Ugine Kuhlmann (of France).

18.1.1. Raschig Process

The Raschig process was discovered in 1907 and then modified into the Olin process. The chemical reactions take place in the liquid phase and involve three steps:



Hydrazine is produced in the hydrated form with one mole of water added. Although a significant fraction of hydrazine is used as the hydrate, numerous applications (such as rocket propulsion) require anhydrous hydrazine. Because of the azeotrope at 68% hydrazine, reactive distillation or extractive distillation must be used to produce pure hydrazine.

In Eq. (18.1), sodium hypochlorite is produced by feeding chlorine into a 30% aqueous caustic solution in a circulating reactor/cooler system. To avoid sodium chlorate formation, the reaction temperature is kept below 30°C and NaOH concentration is kept below 1 g/liter. Typical reaction temperature is 5 °C¹³².

In Eq. (18.2), the reaction rate for chloramine (NH_2Cl) formation is rapid relative to the formation of hydrazine in Eq. (18.3). In this step dilute ammonia solution (5% to 15%) is added to the NaOCl at a ratio of 3:1. Use of NaOCl is estimated to be 3.5 pounds per pound of hydrazine.

Because the decomposition rates are relatively insensitive to temperature, Eq. (18.3) is operated at 130°C to 150°C and 3.0 MPa¹³² to speed up the rate-determining step. Excess ammonia, at a ratio of 40:1, is used to minimize the hydrazine-chlorine decomposition. Synthesis efficiency favors a dilute system although the increase in operating cost due to the low concentration may ultimately become inhibiting. The Raschig process is shown in Figure 18.1¹³².

At the reactor outlet, the reaction liquor contains 1% hydrazine hydrate and 4% NaCl. The pressure is reduced to atmospheric in a battery of evaporators. Ammonia is condensed, concentrated and recycled. The liquor from the bottom of the stripping columns is freed from salt in a conventional, forced-circulation salting evaporator. The distillate is then concentrated to 100% hydrazine hydrate¹³².

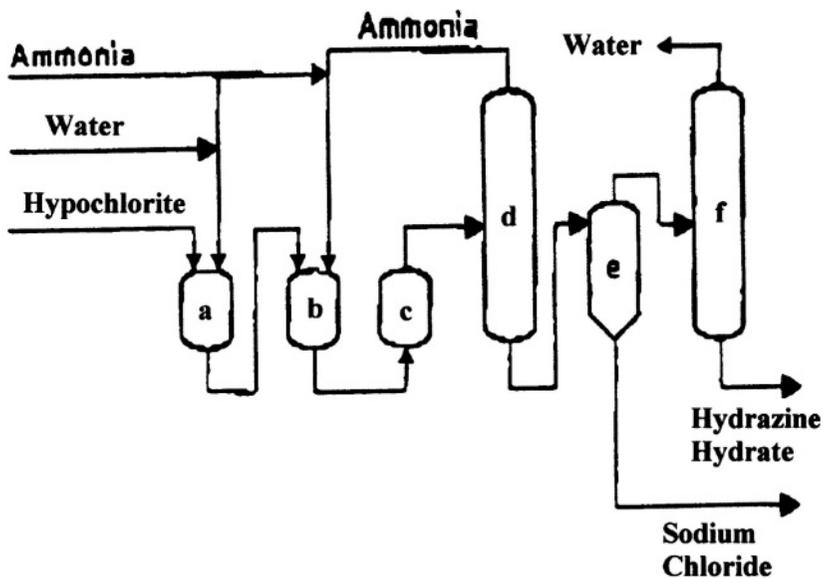
The Raschig process can also be used to react amines with chloramine to make monosubstituted or unsymmetrical disubstituted hydrazines.



18.1.2. Raschig/Olin Process

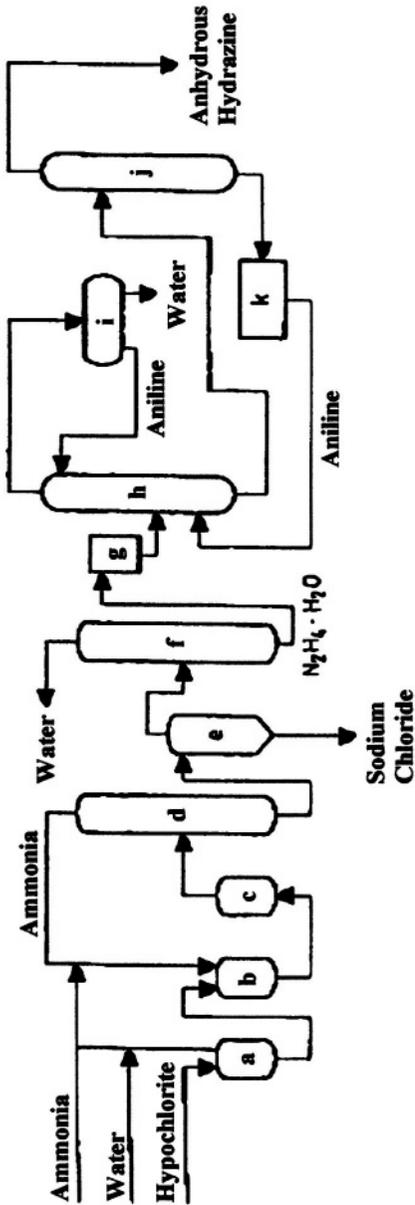
The Raschig/Olin process (see Figure 18.2) is used to make anhydrous hydrazine. In this process the NaOCl production occurs at a low temperature to prevent decomposition and chlorate formation. The excess NaOH is kept to a low level¹³².

The NaOCl solution is mixed with a threefold excess of ammonia at 5°C to form chloramine, which is then rapidly added to a 30-fold molar excess of anhydrous ammonia under pressure (20-30 MPa) and heated to 130°C¹³².



- a. Chloramine Reactor**
- b. & c. Hydrazine Reactors**
- d. Ammonia Evaporator**
- e. Hydrazine-Sodium Chloride Separator**
- f. Hydrazine Hydrate Concentrator**

Figure 18.1. Raschig Process for Hydrazine Production.
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- a. Chloramine Reactor
- b. & c. Hydrazine Reactors
- d. Ammonia Evaporator
- e. Hydrazine-Sodium Chloride Separator
- f. Hydrazine Hydrate Concentration
- g. Hydrazine Hydrate Storage
- h. Hydrazine Hydrate Dehydration
- i. Aniline-Water Decantation
- j. Anhydrous Hydrazine Distillation
- k. Aniline Storage

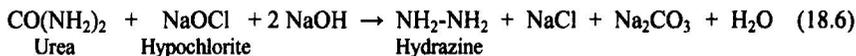
Figure 18.2. Raschig / Olin Process for Hydrazine Production.
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The refining area has five steps: 1) ammonia removal, 2) NaCl concentration and removal, 3) hydrazine-water distillation to reach azeotropic concentration, 4) extractive distillation with aniline to break the azeotrope and 5) distillation to separate hydrazine from aniline. Sometimes 50% caustic replaces aniline in the extractive distillation. If ultra pure hydrazine is needed, freeze crystallization is used to remove the supernatant fluid. Assays between 99.5% and 99.99% have been achieved.

The overall yield based on chlorine is 65%. The combined yield for Eqs. (18.1) and (18.2) is about 95%, whereas the yield for Eq. (18.3) is 70%. Japanese patent SHO-62-83308 claims to increase hydrazine yield by almost 10% by high frequency heating immediately after the reactants are mixed in Eq. (18.2).

18.1.3. Hoffmann (Urea) Process

The overall reaction for the Hoffmann process is:



As in the Raschig process, aqueous caustic reacts with chlorine to make sodium hypochlorite solution. The urea solution is prepared by dissolving urea in water with the addition of steam to provide the heat needed for the endothermic dissolution. The temperature is kept at about 5°C for 43 percent urea solution. Glue is added at a ratio of 0.5g/liter of solution to inhibit side reactions. The urea and hypochlorite solutions are added to the hydrazine reactor at a ratio of 1:4, and the reaction temperature is allowed to rise to 100°C. The crude product contains approximately 35 g N_2H_4 /liter and can be refined in the same steps as used for the Raschig process.

This process is not being operated in 2001 although it has operated commercially in the past. Compared with the standard Raschig process, it was the most economical method for low production levels. However rapid growth in plant size made it obsolete¹³².

18.1.4. Peroxide Process

This process (see Figure 18.3) was invented by PCUK and is operated by AtoFina in France. The reaction is carried out in the presence of methyl ethyl ketone (MEK) at atmospheric pressure and 50°C. The molar ratio in the feed of hydrogen peroxide (H_2O_2): MEK: NH_3 is 1:2:4.

The reaction pathway involves the formation of an intermediate that is able to oxidize ammonia to a hydrazine derivative. The methyl ethyl ketazine is insoluble in the reaction mixture and is separated by decantation and is then purified by distillation. The purified ketazine is hydrolyzed under pressure (0.8 to 10 MPa) to give concentrated aqueous hydrazine and MEK that is recycled¹³².

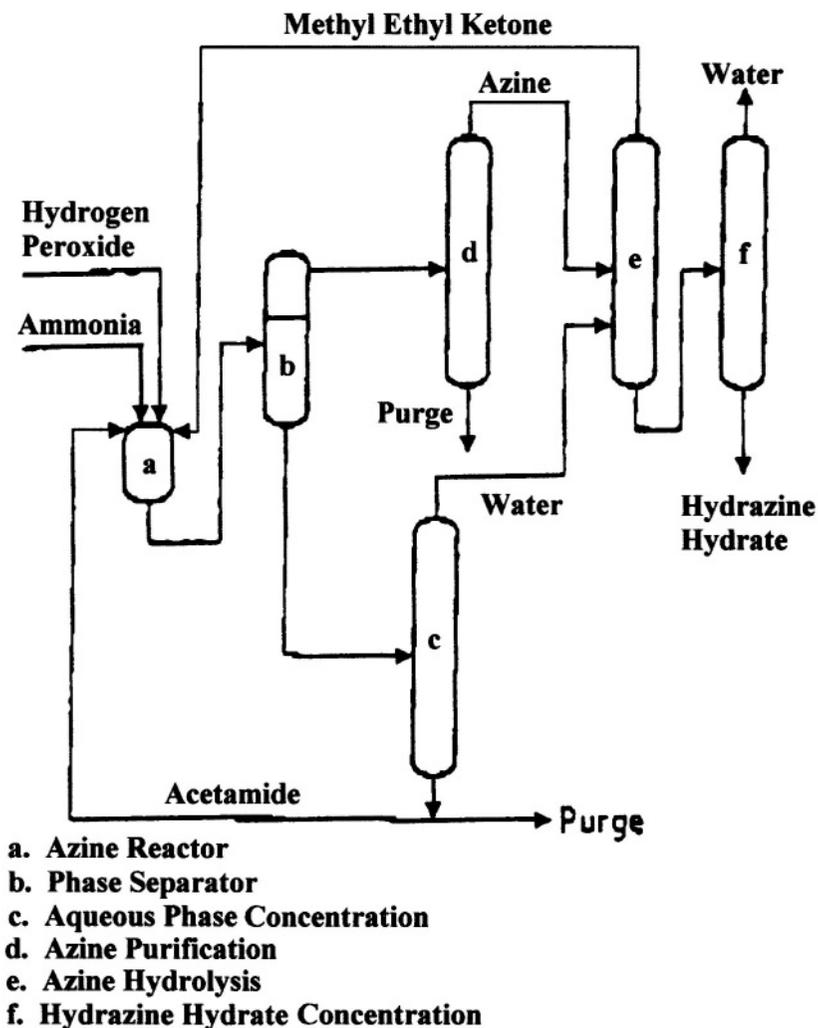


Figure 18.3. Peroxide Process for Hydrazine Production.¹³²
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The Peroxide process has many advantages compared to other processes: no salt by-product, high yields, low energy consumption, low molar excess and no aqueous effluent treatment¹³².

18.1.5. Bayer Ketazine Process

The Bayer Ketazine process is based on the reaction of chloramine with ammonia in the presence of acetone at pH 12 to 14. NaOCl, acetone and a 20% aqueous solution of ammonia (at a mole ratio of 1:2:20, respectively) are fed to a reactor at 35°C and 200 kPa to make the aqueous dimethyl ketazine solution. Excess ammonia and acetone are removed in a series of columns and recycled to the reactor. The ketazine solution is distilled to make a hydrazine hydrate containing 64% hydrazine. A sketch of this process is shown in Figure 18.4¹³². Use of NaOCl is estimated to be 3.5 pounds per pound of hydrazine.

18.1.6. Materials of Construction

Hydrazine is thermally stable and storable for years without adverse effects either to the product or the storage container. However the recommended materials must be used; all systems must be clean; and an inert gas (such as nitrogen) must be maintained over the system at all times. Suitable materials of construction for handling hydrazine are given in Table 18.2²⁵³.

TABLE 18.2. Materials of Construction for Aqueous Hydrazine Solutions^a

Material	Hydrazine Concentration (wt %)			
	<10	35	54.4	64
Stainless Steel	S	S	S	S
304L	S	S	S	S
347	S	S	S	S
316 ^b	S	S	S	S
Cold-Rolled Steel	S	NR	NR	NR
Copper	NS	NS	NS	NS
Brass	NS	NS	NS	NS
Aluminum	NS	NS	NS	NS
PTFE ^c	S	S	S	S
Polyethylene	S	S	S	S
Polypropylene	S	S	S	S

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^a S = generally satisfactory; NR = not recommended; NS = not suitable owing either to decomposition or to adverse effects of the solution on the material of construction.

^b Only up to 65°C

^c PTFE = poly(tetrafluoroethylene)

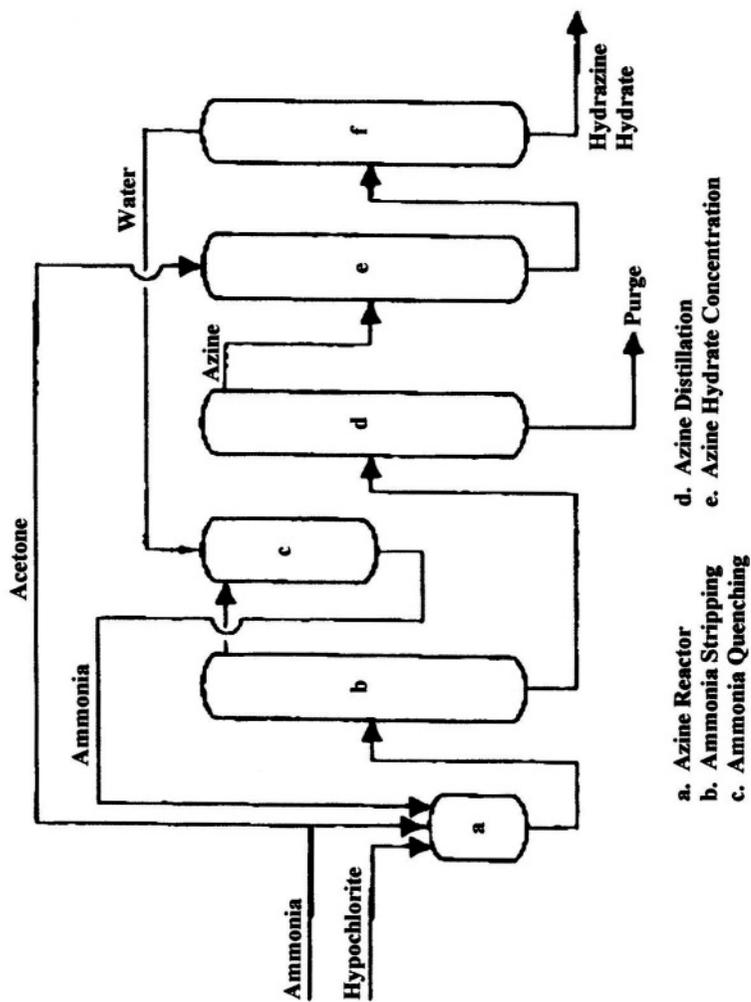


Figure 18.4. Bayer Hydrazine Process.
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For solutions that contain less than 10% hydrazine, cold-rolled steel is satisfactory. PVC is not recommended. Ethylene-propylene-diene monomer (EPDM) rubber, polyketones and polyphenylene sulfides are suitable for use with anhydrous hydrazine²⁵³.

In some cases testing may be needed to identify a suitable material. For example, low concentrations of CO₂ (250 ppm) in anhydrous hydrazine accelerate the decomposition of hydrazine in stainless steel. Long-term storage tests of hydrazine propellants in 17-7 PH stainless steel and AM350 precipitation-hardened stainless steel at 50°C for about three years showed no pressure rise or hydrazine decomposition²⁵³.

18.2. PRODUCTION

Hydrazine is marketed as anhydrous hydrazine, as the monohydrate (64% hydrazine), and as a 54.5% aqueous solution (85% hydrazine monohydrate). The largest U.S. producers of hydrazine based on a 2000 report¹³⁴ are: Arch Chemical (23 Million Pounds per Year), Bayer (17 Million Pounds per Year), and Fairmont Chemical (1 Million Pounds per Year).

Total U.S. Production averages around 36 million pounds per year. About 29 million pounds are sold commercially while the manufacturers retain the remainder for internal use. The space industry uses only 5% of all hydrazine produced in the U.S.¹³⁴. Total capacity in the western world in 1988 was estimated to be about 130 million pounds per year¹³².

The Permissible Exposure Limit (PEL) for hydrazine hydrate on an 8 hour, time-weighted average (TWA) is 0.1 ppm. The ammonia-like odor of hydrazine hydrate normally can be detected at concentrations above 3 to 5 ppm, which does not provide adequate warning of potentially hazardous concentrations¹³⁵.

18.3. USES

Hydrazine is used directly as an oxygen scavenger and as an energy source. As an intermediate, it is used in the production of a number of important chemicals and polymers. Hydrazine is consumed in the following applications: Blowing Agents (33%), Pesticides (32%), Water Treatment (18%) and Miscellaneous (17%). The miscellaneous applications include Pharmaceuticals, production of urethanes, lubricant additives, in anti-oxidant compounds, as a reducing agent for noble metals, in the production of mirrors, in the recovery of precious metals, as a raw material for flame-retardants, in the purification of muriatic acid and in the production of iodine compounds¹²⁸.