HYDRAZINE AND ITS DERIVATIVES

1. Introduction

Hydrazine [302-01-2] (diamide), N_2H_4, a colorless liquid having an ammoniacal odor, is the simplest diamine and unique in its class because of the N–N bond. It was first prepared in 1887 by Curtius as the sulfate salt from diazoacetic ester. Thiele (1893) suggested that the oxidation of ammonia (qv) with hypochlorite should yield hydrazine and in 1906 Raschig demonstrated this process, variations of which constitute the chief commercial methods of manufacture in the 1990s.

The first large-scale use of hydrazine was as fuel for the rocket-powered German ME-163 fighter plane during World War II. Production in the United States began in 1953 at the Lake Charles, Louisiana plant of the Olin Corp. (now Arch Chemicals), a facility then having a capacity of 2040 metric tons. In 2004, world capacity is ~46,2100 metric tons, reported as N_2H_4. Most of this is in the form of hydrazine hydrate.

Hydrazine and its simple methyl and dimethyl derivatives have endothermic heats of formation and high heats of combustion. Hence, these compounds are used as rocket fuels. Other derivatives are used as gas generators and explosives (see EXPLOSIVES AND PROPELLANTS; PROPELLANTS). Hydrazine, a base slightly weaker than ammonia, forms a series of useful salts. As a strong reducing agent, hydrazine is used for corrosion control in boilers and hot-water heating systems; also for metal plating, reduction of noble-metal catalysts, and hydrogenation of unsaturated bonds in organic compounds. Hydrazine is also an oxidizing agent under suitable conditions. Having two active nucleophilic nitrogens and four replaceable hydrogens, hydrazine is the starting material for many derivatives, among them foaming agents for plastics, antioxidants (qv), polymers, polymer cross-linkers and chain-extenders, as well as fungicides (see FUNGICIDES, AGRICULTURAL), herbicides (qv), plant-growth regulators (see GROWTH REGULATORS, PLANT), and pharmaceuticals (qv). Hydrazine is also a good ligand; numerous complexes have been studied (see COORDINATION COMPOUNDS). Many heterocyclics are based on hydrazine, where the rings contain from one to four nitrogen atoms as well as other heteroatoms.

The many advantageous properties of hydrazine ensure continued commercial utility. Hydrazine is produced commercially primarily as as aqueous solutions, typically 35, 51.2, 54.4, and 64 wt% N_2H_4 (54.7, 80, 85, and 100% hydrazine hydrate). Anhydrous hydrazine is produced for rocket propellant and limited commercial applications.

2. Physical Properties

Anhydrous hydrazine is a colorless, hygroscopic liquid having a musty ammoniacal odor. It fumes in air owing to the absorption of water and perhaps also of carbon dioxide, forming carbazic acid [471-31-8], $CH_4N_2O_2$. Hydrazine is miscible with water, alcohol, amines, and liquid ammonia, but has only limited solubility in other nonpolar solvents. Its physical properties are more like the

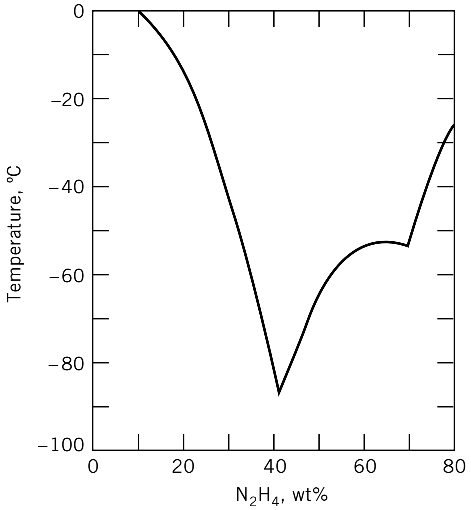


Fig. 1. Freezing-point diagram for hydrazine–water mixtures.

isoelectronic hydroxylamine or hydrogen peroxide (qv) rather than ethane, owing to hydrogen bonding, which is exemplified in relatively high melting (2°C) and boiling (113.5°C) points, as well as an abnormally high [39.079 kJ/mol (9.340 kcal/mol)] heat of vaporization as compared to 14.64 kJ/mol (3.50 kcal/mol) for the isoelectronic ethane.

The freezing point diagram for the hydrazine–water system (Fig. 1) shows two low melting eutectics and a compound at 64 wt% hydrazine having a melting point of −51.6°C. The latter corresponds to hydrazine hydrate [7803-57-8] that has a 1:1 molar ratio of hydrazine to water. The anomalous behavior of certain physical properties such as viscosity and density at the hydrate composition indicates that the hydrate exists both in the liquid as well as in the solid phase. In the vapor phase, hydrazine hydrate partially dissociates.

$$N_2H_5OH \rightleftharpoons N_2H_4 + H_2O \qquad K = \frac{pH_2OpN_2H_4}{pN_2H_5OH} \tag{1}$$

where p_x represents the partial pressure of substance x.

Equation 2 gives the temperature dependence of the equilibrium constant K when p is in kPa and T in kelvin (1). Dissociation of the hydrate is extensive at elevated temperatures.

$$\log K = 10.56 - 3054/T \tag{2}$$

Hydrazine forms a high (120.5°C) boiling azeotrope with water that has a composition of 58.5 mol% (71.48 wt%) N_2H_4 at 102.6-kPa (1.02-atm) pressure. This complicates the separation of hydrazine from water in the manufacturing process because it necessitates the removal of a large amount of water in order to approach the azeotropic composition.

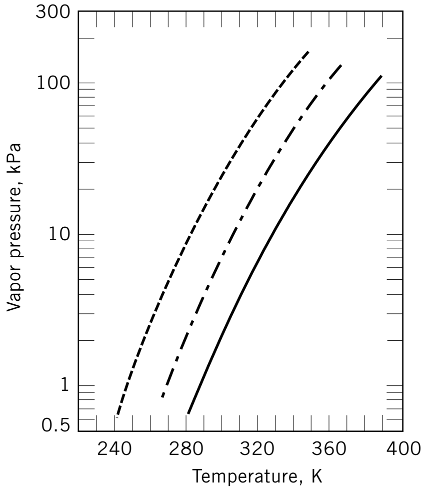


Fig. 2. Vapor pressure of (—) anhydrous hydrazine (AH), (– - –) monomethylhydrazine (MMH), and (– – –) unsymmetrical UDMH.

Figure 2 shows the vapor pressures of anhydrous hydrazine (AH), monomethylhydrazine [60-34-4] (MMH), and unsymmetrical dimethylhydrazine [57-14-7] (UDMH) as a function of temperature (2). The partial pressures of N_2H_4 over aqueous solutions of various concentrations are plotted in Figure 3.

Hydrazine has a gauche conformation, ie, one NH_2 group is rotated from the cis or trans positions. Maximum rotational energy barriers are 46.23 and 25.98 kJ/mol (11.05 and 6.21 kcal/mol), respectively (3,4). The high dipole moment, $6.17 \times 10^{-30} \mathrm{C \cdot m}$ (1.85D), supports this conformational assignment. The N–N bond length is 0.145 nm; the N–N–H bond angle is 112° (5), indicating

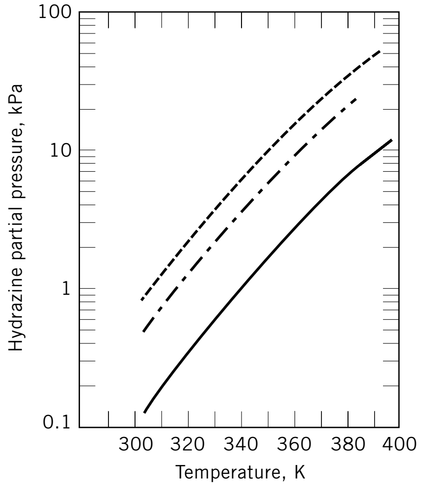
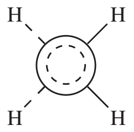
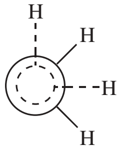


Fig. 3. Hydrazine partial pressure over aqueous solutions containing (– – –) 64, (– - –) 54.4, and (—) 35 wt % hydrazine.

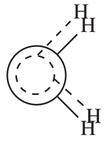
sp^3 hybridization. The vacant tetrahedral positions are occupied by lone electron pairs, which are the source of the basic and nucleophilic character of the hydrazine molecule.



trans or chair form



gauche



cis or boat form

Table 1 summarizes some of the physical properties of anhydrous hydrazine, hydrazine hydrate, monomethylhydrazine, and unsymmetrical dimethylhy-

Table 1. **Physical Properties of Commercial Hydrazines**

Property	Hydrazine	Hydrazine hydrate	MMH	UDMH
formula	N_2H_4	$N_2H_4 \cdot H_2O$	CH_3NHNH_2	$(CH_3)_2NNH_2$
molecular weight	32.0453	50.0607	46.0724	60.0986
CAS Registry Number	[302-01-2]	[7803-57-8]	[60-34-4]	[57-14-7]
freezing point, °C	2.0	−51.6	−52.4	−57.2
boiling point, °C	113.5	119.4	87.6	62.3
vapor pressure, 25°C, kPa[a]	1.92	1.2	6.62	22.3
critical constants				
P_c, MPa[b]	14.69		8.24	5.42
T_c, °C	380		312	250
d_c, g/mL	0.231		0.290	0.23
liquid density, 25°C, g/mL	1.004	1.032	0.874	0.786
surface tension, 25°C, mN/m(= dyn/cm)	66.45	74.3	33.83	24.09
liquid viscosity, 25°C, mPa·s(= cP)	0.913	1.5	0.775	0.492
refractive index, $n_{25}{}^{D}$	1.4683	1.4644	1.4284	1.4053
heat of vaporization, kJ/mol[c]	39.079	47.7	37.212	32.623
heat of fusion, kJ/mol[c]	12.66		10.42	10.07
heat capacity, 25°C, J/(g·K)	3.0778		2.9296	2.945
heat of combustion, kJ/mol[c]	−622.1		−1304.2	−1979
heat of formation, kJ/mol[c]	50.434	−242.71	54.83	51.63
free energy of formation, kJ/mol[c]	149.24		179.9	206.69
entropy of formation, J/(mol·K)	121.21		165.9	197.99
flash point, COC,[d]	52	72	1.0	−15

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] To convert MPa to atm, divide by 0.101.
[c] To convert J to cal, divide by 4.184.
[d] COC = Cleveland open cup. °C.

Table 2. **Lower Explosive Limits of Hydrazine in Other Gases**

Mixture	N_2H_4 composition, vol%	Pressure, kPa[a]	Temperature, °C
hydrazine–air	4.7	100.9	92–102
hydrazine–nitrogen	38.0	100.5	109–112
hydrazine–helium	37.0	100.9	105–118
hydrazine–water	30.9	91.8–118.5	130–135
hydrazine–water	37.4	28.5–35.3	98–100
hydrazine–heptane	86.8	53.9–110.2	104–133

[a] To convert kPa to mm, Hg, multiply by 7.5.

Table 3. **Hydrazine Standard Electrode Potentials, 25°C**

Half-reaction	*E*°, *V*	Equation
As reductant		
$N_2H_4 + 4\,OH^- \longrightarrow N_2 + 4\,H_2O + 4\,e^-$	+1.16	3
$N_2H_5^+ \longrightarrow N_2 + 5\,H^+ + 4\,e^-$	+0.23	4
As oxidant		
$2\,NH_4^+ \longrightarrow N_2H^+{}_5 + 3\,H^+ + 2\,e^-$	−1.275	5
$2\,OH^- + 2\,NH_3 \longrightarrow N_2H_4 + 2\,H_2O + 2\,e^-$	−0.1	6

drazine (6–8). A comprehensive review of the physical and thermodynamic properties of the hydrazines is available (9).

The explosive limits of anhydrous hydrazine in air are 4.7–100 vol%, the upper limit (100 vol%) indicating that hydrazine vapor is self-explosive. Decomposition can be touched off by catalytic surfaces. The presence of inert gases significantly raises the lower explosive limit (10) (Table 2).

The hydrazine molecule represents an intermediate valence state for nitrogen, suggesting that hydrazine can function both as an oxidizing and reducing agent. Table 3 lists the standard electrode potentials for acidic and basic solutions (11). In basic solution, hydrazine is a powerful reducing agent (eq. 3). It is much less so, however, in an acidic medium (eq. 4). In fact, hydrazine solutions may be stabilized against air oxidation by acidification. The reduction of hydrazine to ammonia is thermodynamically favored in acid solution (eq. 5), but ordinarily the rate of this reaction is slow.

3. Chemical Properties

3.1. Thermal Decomposition. Hydrazine is a high energy compound having a high positive heat of formation; however, elevated (>200°C) temperatures are needed before appreciable decomposition occurs. The decomposition temperature is lowered significantly by many catalysts, particularly copper, cobalt, molybdenum, ruthenium, iridium, and their oxides. Iron oxides (rust) also catalyze decomposition. Hydrazine, especially in high concentrations, should be handled with care using scrupulously clean systems. Reviews are available covering the kinetics and mechanisms of the thermal decomposition of hydrazine liquid and vapor (12,13). A detailed discussion of literature on this topic is in Ref. (9). Simple gas-phase decomposition to nitrogen and hydrogen is seldom observed alone. Alternative, more energetic routes lead to the formation of some ammonia.

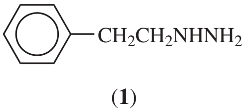
3.2. Acid–Base Reactions. Anhydrous hydrazine undergoes self-ionization to a slight extent, forming the hydrazinium, $N_2H_5^+$, and the hydrazide, $N^2H_3^-$, ions:

$$2\ N_2H_4 \leftrightarrows N_2H_5^+ + N_2H_3^- \qquad K_i = 10^{-25} \tag{7}$$

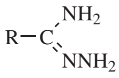
Hydrazinium salts, $N_2H_5^+X^-$, are acids in anhydrous hydrazine, metallic hydrazides, $M^+N_2H_3^-$, are bases. Neutralization in this solvent system involves the hydrazinium and hydrazide ions and is the reverse of equation 7. Metal hydrazides, formally analogous to the metal amides, are prepared from anhydrous hydrazine and the metals as well as from metal amides, alkyls, or hydrides. (The term hydrazide is also used for organic compounds where the carboxylic acid OH is substituted with a N_2H_3.) Sodium hydrazide [13598-47-5] is made from sodium or, more safely, from sodium amide (14):

$$2\ Na + 2\ N_2H_4 \longrightarrow 2\ NaN_2H_3 + H_2 \tag{8}$$

The ionic hydrazides are extremely sensitive and explode on contact with air or upon heating. The alkaline-earth hydrazides, which have the general formula $M(N_2H_2)$, appear to be less sensitive (15). Hydrazides such as aluminum hydrazide [25546-96-7], $Al(N_2H_3)_3$, have also been made (16). The hydrazide anion is more nucleophilic than hydrazine and undergoes reactions not possible using hydrazine itself (17). Thus, styrene in ethyl ether solution at 0°C is converted in good yield to phenethylhydrazine [51-71-8] (**1**) and nitriles give amidrazones (**2**) which are useful in the synthesis of heterocycles. Such reactions probably proceed more safely using barium hydrazide [28330-62-3], BaN_2H_2, (18); however, little work has been carried out using the alkaline-earth hydrazides.



(**1**)



$$R-C\begin{matrix}NH_2\\NNH_2\end{matrix}$$

(**2**)

In water, hydrazine is a slightly weaker base than ammonia and ionizes in two steps:

$$N_2H_4 + H_2O \longrightarrow N_2H_5^+ + OH^- \qquad K_b\ (25°C) = 8.4 \times 10^{-7} \tag{9}$$

$$N_2H_5^+ + H_2O \longrightarrow N_2H_6^{2+} + OH^- \qquad K_b\ (25°C) = 8.9 \times 10^{-16} \tag{10}$$

Hydrazinium salts form by simple neutralization using the corresponding acid. Two series of salts are possible, containing the hydrazinium(1+) ion, $N_2H_5^+$, and the hydrazinium(2+) ion, $N_2H_6^{2+}$. The second ionization constant is so small,

Table 4. **Properties of Hydrazinium Salts**

Compound	CAS Registry number	Mp, °C	Solubility, 25°C, g/100 g water	Comments
$N_2H_4{\cdot}HN$	[14662-04-5]	75.4 dec	very soluble	explosive
$N_2H_4{\cdot}HBr$	[13775-80-9]	86.5	282.0	
$N_2H_4{\cdot}2HBr$	[23268-00-0]	195	86.4	
$N_2H_4{\cdot}HCl$	[14011-37-1]	92.6	179	
$N_2H_4{\cdot}HCl$	[5341-61-7]	198 dec	104.8	
$N_2H_4{\cdot}HI$	[10039-55-1]	127	soluble	
$N_2H_4{\cdot}HNO_3$	[37836-27-4]	70.71[a]	327.5	explosive
$N_2H_4{\cdot}HClO_4$	[13762-80-6]	137		explosive
$N_2H_4{\cdot}2HClO_4$	[13812-39-0]			explosive
$N_2H_4{\cdot}H_2SO_4$	[10034-93-2]	254	3.41	low solubility
$2N_2H_4{\cdot}H_2SO_4$	[13464-80-7]	85	202	

[a] Value is for α form. A β form also exists having mp = 62.09°C.

however, that salts containing the $N_2H_6^{2+}$ cation are extensively hydrolyzed in water. The $N_2H_6^{2+}$ cation is formed only with strong acids and exists only in strongly acidic solutions or in the solid state (19). Table 4 lists a few of the many known hydrazinium salts. Thermodynamic properties for most of these are available (20).

3.3. Hydrazine as Nucleophile.

Reaction of hydrazine and carbon dioxide or carbon disulfide gives, respectively, hydrazinecarboxylic acid [471-31-8], $NH_2NHCOOH$, and hydrazinecarbodithioic acid [471-32-9], $NH_2NHCSSH$, in the form of the hydrazinium salts. These compounds are useful starting materials for further synthesis. For example, if carbon disulfide reacts with hydrazine in basic medium with an alkyl halide, an alkyl dithiocarbazate ester is obtained in a one-step reaction:

$$N_2H_4 + CS_2 + KOH + R'X \longrightarrow NH_2NHCSSR' + HOH + KX \tag{11}$$

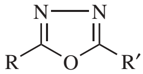
Such esters can be acylated on the amine nitrogen using acyl halides,

$$R\overset{O}{\overset{\|}{C}}X$$

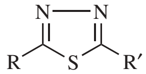
to give (**3**), which can be cyclized under appropriate conditions to yield 1,3,4-oxadiazoles (**4**) or thiadiazoles (**5**):

$$R\underset{O}{\underset{\|}{C}}NHNH\underset{S}{\underset{\|}{C}}SR'$$

(**3**)



(**4**)



(**5**)

Using thionyl chloride, and calcium oxide as HCl acceptor, hydrazine gives the calcium salt of hydrazinemonosulfinic acid, $Ca(NH_2NHSO_2)_2$, an extremely strong reducing agent (21). The monosulfonic acid (**6**) is formed from hydrazine and sulfur trioxide. Sulfuryl chloride gives sulfuryl dihydrazide (**7**); phosphorus oxychloride yields the corresponding trihydrazide (**8**). The phosphoric acid hydrazides have been reviewed (22).

NH_2NHSO_3H (**6**) $O_2S(NHNH_2)_2$ (**7**) $O{=}P(NHNH_2)_3$ (**8**)

Hydrazine–borane compounds are made by the reaction of sodium borohydride and a hydrazinium salt in THF (23,24). The mono-($N_2H_4(BH_3)$) and di-($N_2H_4 \cdot 2BH_3$) Lewis adducts are obtained, depending on the reaction conditions. These compounds have been suggested as rocket fuels (25) and for chemical deposition of nickel–boron alloys on nonmetallic surfaces (see METALLIC COATINGS, SURVEY) (26).

3.4. Reductions. Hydrazine is a very strong reducing agent. In the presence of oxygen and peroxides, it yields primarily nitrogen and water with more or less ammonia and hydrazoic acid [7782-79-8]. Based on standard electrode potentials, hydrazine in alkaline solution is a stronger reductant than sulfite but weaker than hypophosphite; in acidic solutions, it falls between Sn^{2+} and Ti^{2+} (27).

Metal Reductions. Essentially all the metals of the transition, lanthanide, and actinide series have been reduced using hydrazine to either a lower valence state or to the metal. The advantage of using hydrazine in these applications is that it is completely consumed and leaves no residue. Such reductions can be used to make silver mirrors (28); for electroless plating (qv) of nickel (29,30), gold (31), cobalt, iron, chromium on metal or plastic (32); and for the preparation of noble-metal catalysts. It is possible to obtain exceedingly small and uniform metal particles by this technique, eg, gold particles having an average diameter of 6.8 nm (33), silver–palladium alloy having a specific surface area of 19 m^2/g (34), and ultrafine copper particles (35). The lanthanides and actinides are generally reduced to a lower valence state, not to the metals themselves (36). Chromate, an undesirable pollutant in waste water streams from electroplating shops, is readily reduced by hydrazine in basic solution to the insoluble chromium(III) hydroxide, which can then be removed by filtration (37). The final chromate concentration is below the limit detectable by standard procedures, ie, 2 ppb.

Hydrogenations. Reduction of organic compounds with hydrazine and its derivatives is covered in several reviews (39). These procedures have some advantages over conventional pressure hydrogenations in being more selective in their attack, sometimes stereospecific (cis addition), and in not requiring the use of hydrogen gas and high pressure equipment.

Carbonyl Reductions. The classical Wolff-Kishner reduction of ketones (qv) and aldehydes (qv) involves the intermediate formation of a hydrazone, which is then decomposed at high temperatures under basic conditions to give the methylene group, although sometimes alcohols may form (40).

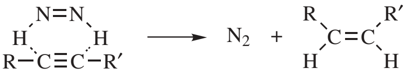
$$R_2C{=}O + N_2H_4 \longrightarrow R_2C{=}NNH_2 \xrightarrow[\text{heat}]{\text{base}} R_2CH_2 + N_2 \qquad (12)$$

This reaction is discussed extensively in an earlier review (41). In the Huang-Minlon modification of the Wolff-Kishner reaction, a high boiling solvent such as diethylene glycol is used to achieve the required high temperatures (180–210°C) without the use of pressure equipment (42). The base is generally alkali hydroxide or an alkoxide (43).

Catalytic Hydrogenations. Nitro compounds, primarily aromatics, are reduced using hydrazine in the presence of standard hydrogenation catalysts such as Raney nickel or ruthenium on carbon. The products are generally the corresponding amines (qv), but in some cases partially hydrogenated intermediates, such as azo-, azoxy-, hydrazo-, and hydroxylamino aromatics, have been isolated (see AMINES BY REDUCTION). [Some aromatic hydroxylamines may be sensitive and one explosion has been reported when 2-chloro-5-methylphenylhydroxylamine formed in an attempt to reduce the corresponding nitro compound to 2-chloro-5-methylaniline (44)]. This method of hydrogenation has also been applied to nitroso compounds, nitriles, oximes, nitrites, nitrates, and carbon–halogen compounds. In some cases, no catalyst is required (45), and yields may be better than in conventional hydrogenations. In the presence of several reducible bonds, the procedure is often selective. For example, dinitroarenes may be reduced in good yields to nitroanilines in the presence of Raney nickel (46). This catalyst is also effective for the selective reduction of nitro groups to amines in the presence of carbonyls and other reducible groups (47) and also for the reduction of nitriles to hydrazones . Dehalogenation of aromatics with hydrazine is favored by palladium on carbon.

Diazene Reductions. Olefins, acetylenes, and azo compounds are reduced by hydrazine in the presence of an oxidizing agent. Stereochemical studies of alkene and alkyne reductions suggest that hydrazine is partially oxidized to the transient diazene [3618-05-1] (diimide, diimine) (**9**) and that the cis isomer of diazene is the actual hydrogenating agent, acting by a concerted attack on the unsaturated bond:

$$N_2H_4 \xrightarrow{o} HN{=\!=}NH + H_2O \qquad (13)$$



(14)

(**9**)

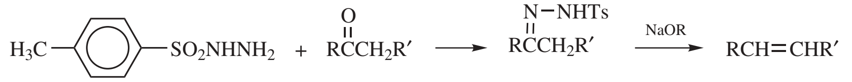
Suitable oxidants for the generation of diazene are oxygen, hydrogen peroxide, iodine, iodate, ferricyanide, and the cupric ion. Diazene is also formed by acidification of dipotassium azodicarboxylate [4910-62-7], KOOCN=NCOOK, or by thermolysis of *p*-toluenesulfonylhydrazide [1576-35-8]. Reductions with diazene are both selective and stereospecific: olefins (qv), acetylenes, and azo compounds are reduced easily; unsymmetrical bonds such as C=N,C≡N,C=O, NO_2, and NO are not attacked. Disulfides are not cleaved, nor are haloaromatics dehalogenated. This technique has been applied extensively to unsaturated fatty acids (49). Polybutadiene and its copolymers in xylene solution are hydrogenated to >99% using diazene generated thermally from *p*-toluenesulfonylhydrazide (50). Reduction of the double bond in acrylonitrile–butadiene rubber latices is efficiently achieved with hydrazine and hydrogen peroxide in the presence of Cu(II) as catalyst (51). Reductions using diazene have been reviewed (52).

Aldehyde Syntheses. Aromatic (Ar) carboxylic acids are reduced to the corresponding aldehydes by a sequence of steps known as the McFadyen-Stevens reaction. The acid is converted to the hydrazide, derivatized with benzenesulfonylchloride, then decomposed to the aldehyde in hot glycol in the presence of a base:

$$\mathrm{ArCOOH} \xrightarrow{N_2H_4} \mathrm{ArCONHNH_2} \xrightarrow{C_6H_5SO_2Cl} \mathrm{ArCONHNHSO_2C_6H_5} \xrightarrow{\text{base}} \mathrm{ArCHO} \qquad (15)$$

Aliphatic aldehydes can also be prepared in moderate yields by distilling the aldehyde from the mixture rapidly to avoid aldol addition or a Cannizzaro reaction (53).

Olefin Syntheses. Conversion of aldehydes and ketones to olefins by the base-catalyzed decomposition of *p*-toluenesulfonic (Ts) acid hydrazones (**10**) is known as the Bamford-Stevens reaction (54,55).



(**10**)

(16)

3.5. Alkylhydrazines.

Mono- and higher substituted alkyl hydrazines can be made by alkylation of hydrazine using alkyl halides. For monoalkylhydrazines, however, the procedure is often unsatisfactory, producing a mixture of higher substituted hydrazines, including trialkylhydrazinium salts:

$$N_2H_4 \xrightarrow{RX} RNHNH_2 \xrightarrow{RX} R_2NNH_2 \xrightarrow{RX} R_3NNH_2^{+}X^{-} \qquad (17)$$

A large excess of hydrazine or bulky alkyl groups favor monosubstitution. For example, a 60–70% yield of monoisopropylhydrazine [2257-52-7] is achieved by reaction of isopropyl bromide and a fivefold excess of hydrazine (56).

In a variation of the Raschig process for making hydrazine, amines rather than ammonia are reacted with chloramine to give the corresponding alkyl hydrazine:

$$\begin{array}{ccc} RNH_2 & \nearrow & RNHNH_2 \\ R_2NH + NH_2Cl & \longrightarrow & R_2NNH_2 \\ R_3N & \searrow & R_3NNH_2C^{+}1^{-} \end{array} \qquad (18)$$

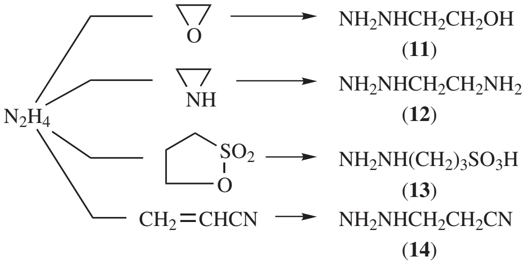
Both MMH and unsymmetrical UDMH are produced commercially by this route for use as fuels in missiles and in the U.S. space program as well as for several commercial applications. Hydroxylamine-*O*-sulfonic acid [2950-43-8] can serve as a convenient aminating agent in place of chloramine, but it has no cost advantage. Monoalkylhydrazines have also been made by the reaction of hydrazine and alcohols in the presence of phosphoric and hydrochloric acid at elevated temperatures in an autoclave (57). Unsymmetrical dialkylhydrazines, $RR'NNH_2$, can be prepared by nitrosation of dialkylamines followed by catalytic hydrogenation of the resulting nitrosamine, $RR'NNO$. UDMH was made commercially by this route (58), but this process has since been abandoned in the United States because the nitrosamine is such a potent carcinogen. UDMH can also be obtained by the catalytic reductive alkylation of acethydrazide [1068-57-1] using formaldehyde and hydrogen over Pd or Pt, followed by basic hydrolysis of the acetic acid dimethylhydrazide [6233-041-1] to remove the acetyl group (59,60) (eq. 19):

$$CH_3CONHNH_2 \xrightarrow[\text{catalyst}]{CH_2O/H_2} CH_3CONHN(CH_3)_2 \xrightarrow[H_2O]{\text{base}} CH_3COO^- + (CH_3)_2NNH_2 \quad (19)$$

Reduction of hydrazones, $R_2C{=}NNH_2$, and azines, $R_2C{=}NN{=}CR_2$, with hydrogen (qv) or hydrides (qv) as hydrogenating agents provides another approach to mono and disubstituted hydrazines (61,62). Complete hydrogenation leads to rupture of the N−N bond to yield primary amines (63). Alkylation of azines is also possible on the nitrogen, using alkylating agents such as alkyl sulfates.

Branched-chain alkenes react with hydrazine under acidic conditions to give the corresponding alkyl hydrazine. For example, isobutylene bubbled through an aqueous solution of hydrazine and HCl gives *tert*-butylhydrazine in reasonably good yields (64).

Substituted Alkylhydrazines. Substituted alkyl hydrazines are prepared from suitable alkylating agents. Epoxides yield hydroxyalkylhydrazines such as [109-84-2] (**11**) (65); aziridines, β-aminoalkylhydrazines, eg, β-aminoethylhydrazine [14478-61-6] (**12**) (66,67); sultones, ω-sulfoalkylhydrazines, eg, ω-sulfopropylhydrazine [6482-66-2] (**13**) (68–70); and acrylonitrile, β-cyanoethylhydrazine [353-07-1] (**14**) (71). These compounds are all potentially useful in further syntheses as each contains an active substituent on the alkyl group yet has an intact hydrazine moiety that can undergo many of the reactions of hydrazine itself.



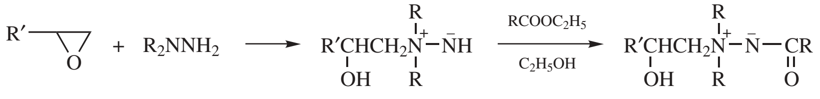
(**11**)

(**12**)

(**13**)

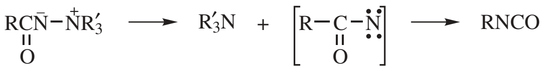
(**14**)

Hydroxyethylhydrazine (**11**) is a plant growth regulator. It is also used to make a coccidiostat, furazolidone, and has been proposed, as has (**14**), as a stabilizer in the polymerization of acrylonitrile (72,73). With excess epoxide, polysubstitution occurs and polyol chains can form to give poly(hydroxyalkyl) hydrazines which have been patented for the preparation of cellular polyurethanes (74) and as corrosion inhibitors for hydraulic fluids (qv) (75). Dialkylhydrazines, R_2NNH_2, and alkylene oxides form the very reactive amineimines (**15**), which react further with esters to yield aminimides (**16**):



(**15**) (**16**)

The preparation and properties of these tertiary aminimides, as well as suggested uses as adhesives (qv), antistatic agents (qv), photographic products, surface coatings, and pharmaceuticals, have been reviewed (76). Thermolysis of aminimides causes N−N bond rupture followed by a Curtius rearrangement of the transient nitrene (**17**) intermediate to the corresponding isocyanate:



$$\underset{\substack{\|\\ O}}{RC}\bar{N}-\overset{+}{N}R'_3 \longrightarrow R'_3N + \left[R-\underset{\substack{\|\\ O}}{C}-\ddot{N}:\right] \longrightarrow RNCO$$

(**17**)

Bisaminimides form Diisocyanates. This reaction and its application in polymer chemistry have been reviewed (77). A review of the general subject of aminimide monomers and polymers is available (78).

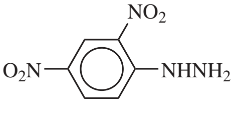
Aromatic Hydrazines. A general synthesis for arylhydrazines is via diazotization of aromatic amines, followed by reduction of the resulting diazonium salt (**18**):

$$ArNH_2 \xrightarrow[HCl]{NaNO_2} \underset{(\mathbf{18})}{(Ar—N\equiv N)C^{+}l^{-}} \xrightarrow[NaOH]{[H]} ArNHNH_2 \qquad (22)$$

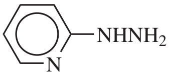
In the industrial synthesis of phenylhydrazine [100-63-0], the reducing agent is sodium bisulfite. It is also possible to react aniline with chloramine as in the Raschig process (79):

$$C_6H_5NH_2 + NH_2Cl + NaOH \longrightarrow C_6H_5NHNH_2 + NaCl + H_2O \qquad (23)$$

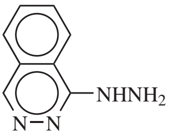
Generally, aromatic hydrazines are not made from haloaromatics and hydrazine, unless the halo substituent is activated by neighboring electronegative groups. For example, 2,4-dinitrochlorobenzene reacts with hydrazine to give 2,4-dinitrophenylhydrazine [119-26-6] (**19**), which is used as an analytical reagent for the identification of aldehydes and ketones. Other haloaromatics that exchange halogen for hydrazine are 2-chloropyridine to give the 2-hydrazinopyridine [4930-98-7] (**20**) and 1-chlorophthalazine to form hydrazinophthalazine [86-54-4] (**21**), an antihypertensive drug (see CARDIOVASCULAR AGENTS). The preparation and properties of arylhydrazines are covered in some earlier reviews (80,81).



(**19**)



(**20**)



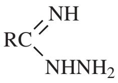
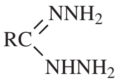
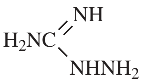
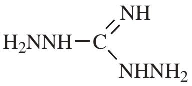
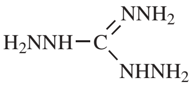
(**21**)

3.6. Hydrazides and Related Compounds.

Substitution of the hydroxyl group in carboxylic acids with a hydrazino moiety gives carboxylic acid hydrazides. In this formal sense, a number of related compounds fall within this product class although they are not necessarily prepared this way. Table 5 lists some of the more common of these compounds (82).

Carboxylic acid hydrazides are prepared from aqueous hydrazine and the carboxylic acid, ester, amide, anhydride, or halide. The reaction usually goes poorly with the free acid. Esters are generally satisfactory. Acyl halides are particularly reactive, even at room temperature, and form the diacyl derivatives (**22**), which easily undergo thermal dehydration to 1,3,4-oxadiazoles (**23**). Diesters give dihydrazides (**24**) and polyesters such as polyacrylates yield a polyhydrazide

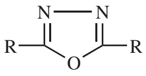
Table 5. **Hydrazides and Related Compounds**

Type	CAS Registry number	Structure
carboxylic hydrazides		 $\mathrm{R}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHNH_2}$
thiohydrazides		 $\mathrm{R}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{NHNH_2}$
sulfonylhydrazides		$\mathrm{RSO_2NHNH_2}$
semicarbazide	[57-56-7]	 $\mathrm{H_2N}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHNH_2}$
thiosemicarbazide	[79-19-6]	 $\mathrm{H_2N}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{NHNH_2}$
carbohydrazide	[479-18-7]	 $\mathrm{H_2NNH}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHNH_2}$
thiocarbohydrazide	[2231-57-4]	 $\mathrm{H_2NNH}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{NHNH_2}$
amidrazones		
hydrazidines		
aminoguanidine	[79-17-4]	
diaminoguanidine	[4363-78-7]	
triaminoguanidine	[2203-24-9]	

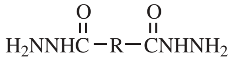
(**25**). The chemistry of carboxylic hydrazides has been reviewed (83,84).

$R\overset{O}{\overset{\|}{C}}-NHNH-\overset{O}{\overset{\|}{C}}R$

(**22**)

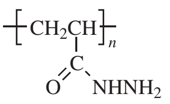


(**23**)



$H_2NNH\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}NHNH_2$

(**24**)



(**25**)

Thiohydrazides

$R\overset{S}{\overset{\|}{C}}-NHNH_2$

are best prepared from hydrazine and dithioesters, RCSSR′. These are useful for the formation of heterocyclics and have been studied for their pharmacological and pesticidal properties. Several somewhat older reviews of the chemistry of thiohydrazides are available (85,86).

Sulfonic acid hydrazides, RSO_2NHNH_2, are prepared by the reaction of hydrazine and sulfonyl halides, generally the chloride RSO_2Cl. Some of these have commercial applications as blowing agents. As is typical of hydrazides generally, these compounds react with nitrous acid to form azides (**26**), which decompose thermally to the very reactive, electron-deficient nitrenes (**27**). The chemistry of sulfonic acid hydrazides and their azides has been reviewed (87).

$$RSO_2NHNH_2 \xrightarrow{HONO} \underset{(\mathbf{26})}{RSO_2N_3} \xrightarrow{-N_2} \underset{(\mathbf{27})}{RSO_2N} \tag{24}$$

Hydrazinecarboxamides (semicarbazides) (**28**) and hydrazinecarbothioamides (thiosemicarbazides) (**29**) are starting materials for many useful products. They are generally prepared from hydrazine and either isocyanates or isothiocyanates. The unsubstituted parent semicarbazide (**28**, R = H) is best made from urea and hydrazine; using excess urea, hydrazodicarbonamide [110-21-4] is formed. Methods have been reported for the preparation of all positional isomers of thiosemicarbazide (85), with substituents in the 1, 2, and/or 4 positions (**30**):

$RNH\overset{O}{\overset{\|}{C}}NHNH_2$

(**28**)

$RNH\overset{S}{\overset{\|}{C}}NHNH_2$

(**29**)

$\underset{4}{H_2N}\overset{S}{\overset{\|}{C}}\underset{2}{NH}\underset{1}{NH_2}$

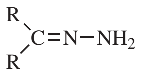
(**30**)

A process for heating alkyldithiocarbamate salts (**31**) in the presence of hydrazine hydrate to produce 4-alkylthiosemicarbazides (**32**) has been described (88).

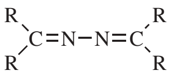
$$CH_3NH_2 + 2\,NH_3 + CS_2 \longrightarrow \underset{(\mathbf{31})}{CH_3NH—CS—S^-NH_4^+} \xrightarrow{N_2H_4} \underset{(\mathbf{32})}{CH_3NH—CS—NHNH_2} \tag{25}$$

Thiosemicarbazides are useful in forming 1,3,4-thiadiazoles, a class of compounds having herbicidal activity.

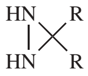
3.7. Hydrazones and Azines. Depending on reaction conditions, hydrazines react with aldehydes and ketones to give hydrazones (**33**), azines (**34**), and diaziridines (**35**), the latter formerly known as isohydrazones.



(**33**)



(**34**)



(**35**)

Hydrazones are formed from mono- and N,N-disubstituted hydrazines. Hydrazine itself can give either hydrazones or azines, depending mainly on the ratio of carbonyl component to hydrazine. The ease of formation of these compounds depends on the nature of the carbonyl constituent:

aldehydes > dialkyl ketones > alkylaryl ketones > diaryl ketones

Many of these compounds are highly colored and have found use as dyes and photographic chemicals. Several pharmaceuticals and pesticides are members of this class. An extremely sensitive analytical method for low hydrazine concentrations is based on the formation of a colored azine. They are also useful in heterocycle formation. Several reviews are available covering the chemistry of hydrazones (80,89) and azines (90).

3.8. Heterocyclics. One of the most characteristic and useful properties of hydrazine and its derivatives is the ability to form heterocyclic compounds. Numerous pharmaceuticals, pesticides, explosives, and dyes are based on these rings. A review of the application of hydrazine in the synthesis of heterocyclics is available (91). For further information in the field of heterocyclic chemistry, see the *General References*.

4. Manufacture

The direct fixation of nitrogen and hydrogen to hydrazine is thermodynamically unfavorable. Ammonia is the preferred product of that reaction. Instead the commercially feasible processes involve partial oxidation of ammonia (or urea) using hypochlorite or hydrogen peroxide. Most hydrazine is produced by some variation of the Raschig process, which is based on the oxidation of ammonia using alkaline hypochlorite. Ketazine processes are modifications in which the oxidation is carried out in the presence of a ketone such as acetone or butanone. Bayer first commercialized such a process, using acetone, and hypochlorite as oxidant. A process developed by Produits Chimiques Ugine Kuhlmann (PCUK) and practiced by Atofina (France) and Mitsubishi Gas (Japan) involves the oxidation of ammonia by hydrogen peroxide in the presence of butanone and another component that apparently functions as an oxygen-transfer agent. The oxidation of benzophenoneimine has received much attention, but is not commercial.

4.1. Raschig Process. The Raschig process (92) is based on the oxidation of ammonia with hypochlorite according to the following overall reaction:

$$2\,NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O \tag{26}$$

This is a stepwise process in which chloramine [10599-90-3] is first formed from ammonia and hypochlorite in a rapid reaction at low temperature:

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH \tag{27}$$

The chloramine then reacts with excess ammonia to form hydrazine:

$$NH_2Cl + NH_3 + NaOH \longrightarrow N_2H_4 + NaCl + H_2O \tag{28}$$

This reaction is slow and requires elevated temperatures of 120–150°C under pressure. The kinetics (93,94) and mechanism (95,96) of these reactions have been studied. An undesirable competing reaction is the further oxidation of hydrazine by chloramine:

$$N_2H_4 + 2\,NH_2Cl \longrightarrow 2\,NH_4Cl + N_2 \tag{29}$$

This reaction is also slow but catalyzed by metal-ion impurities, especially copper(II). It is minimized by avoiding metal contamination or by adding chelating agents (qv) to complex the metal ions (Raschig used glue or gelatin). Reaction 28 is favored over reaction 29 by using a large molar excess of ammonia over chloramine (30:1) and by keeping the hydrazine concentration low (~1–2%). Under these conditions, yields up to 80% (based on hypochlorite) can be achieved; the penalty for this favorable yield is an energy-intensive process involving large ammonia recycle and evaporative load.

Olin Raschig Process. One process used by Arch Chemicals Corp. in its Lake Charles, Louisiana, facility is an adaptation of the basic Raschig process (Fig. 4). Liquid chlorine is continuously absorbed in dilute sodium hydroxide to form sodium hypochlorite, cooled by an external brine recirculating loop to prevent hypochlorite decomposition and chlorate formation. The chlorination is automatically monitored by measuring the oxidation potential of the recirculating stream. Excess sodium hydroxide in the sodium hypochlorite is kept low (<1 g/L) to avoid caking in the salt crystallizer and to improve yields somewhat (97). The sodium hypochlorite is mixed with about a threefold molar excess of aqueous ammonia in the chloramine reactor; chloramine formation is almost instantaneous at ~5°C. To this chloramine-containing stream is added immediately a 20–30 molar excess of anhydrous ammonia under sufficient pressure to keep ammonia in the liquid phase. The heat of dilution raises the temperature rapidly to about 40°C. Further heating with steam to 120–130°C favors the hydrazine-forming reaction 28 and minimizes the competing destructive reaction 29. The nitrogen that is formed (eq. 29) is scrubbed with water to remove ammonia and is then used as an inert pad to prevent decomposition of hydrazine during the concentration steps.

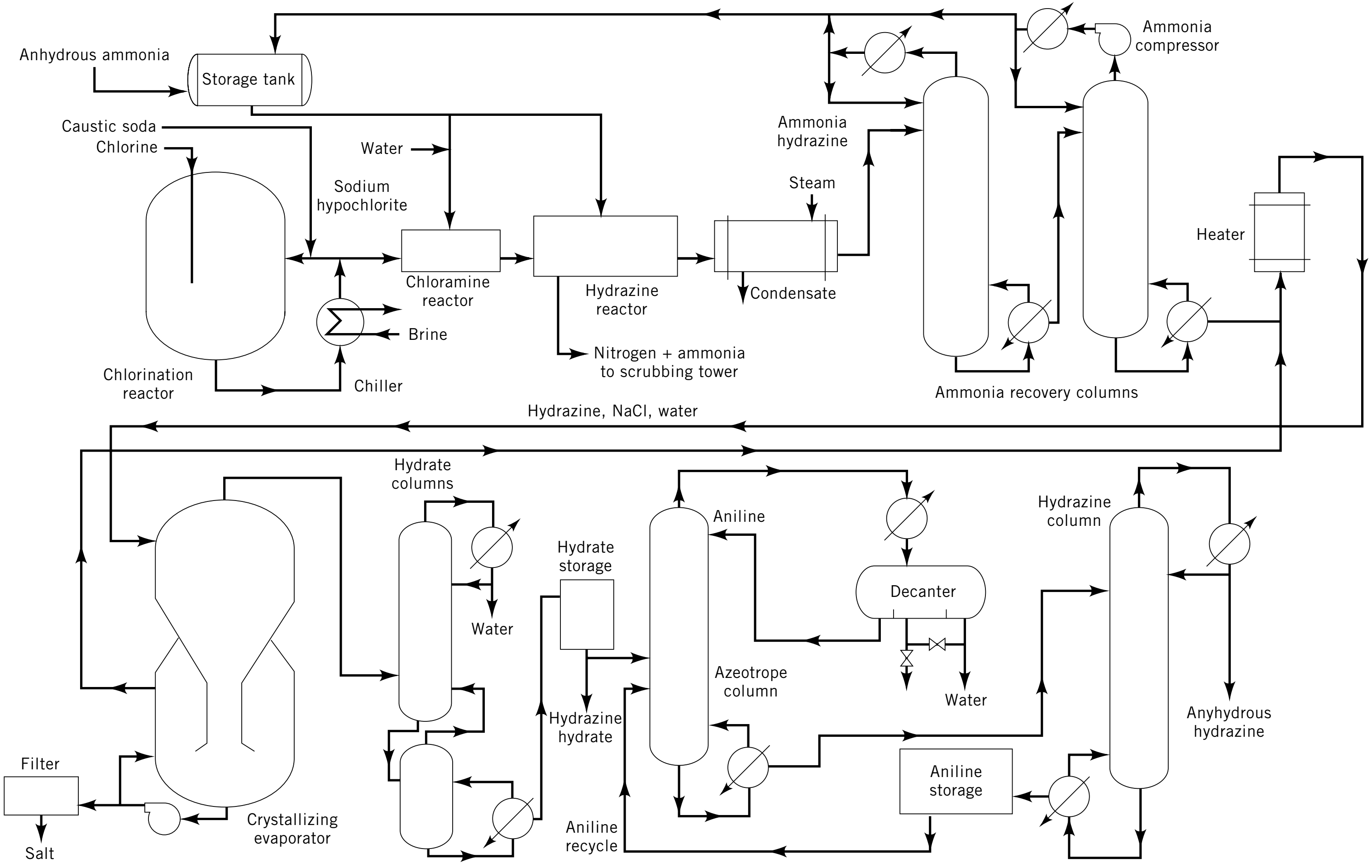


Fig. 4. Arch Raschig process flow sheet.

The reactor effluent, containing 1–2% hydrazine, ammonia, sodium chloride, and water, is preheated and sent to the ammonia recovery system, which consists of two columns. In the first column, ammonia goes overhead under pressure and recycles to the anhydrous ammonia storage tank. In the second column, some water and final traces of ammonia are removed overhead. The bottoms from this column, consisting of water, sodium chloride, and hydrazine, are sent to an evaporating crystallizer where sodium chloride (and the slight excess of sodium hydroxide) is removed from the system as a solid. Vapors from the crystallizer flow to the hydrate column where water is removed overhead. The bottom stream from this column is close to the hydrazine–water azeotrope composition. Standard materials of construction may be used for handling chlorine, caustic, and sodium hypochlorite. For all surfaces in contact with hydrazine, however, the preferred material of construction is 304-L stainless steel.

Anhydrous hydrazine, required for propellant applications and some chemical syntheses, is made by breaking the hydrazine–water azeotrope with aniline. The bottom stream from the hydrate column (Fig. 4) is fed along with aniline to the azeotrope column. The overhead aniline–water vapor condenses and phase separates. The lower aniline layer returns to the column as reflux. The water layer, contaminated with a small amount of aniline and hydrazine, flows to a biological treatment pond. The bottoms from the azeotrope column consist of aniline and hydrazine. These are separated in the final hydrazine column to give an anhydrous overhead; the aniline from the bottom is recycled to the azeotrope column.

The small amount of aniline remaining in the anhydrous hydrazine can be objectionable in some monopropellant applications, such as in thruster engines used for the control of satellites and spacecraft; carbon containing impurities may foul the decomposition catalyst or cause metal embrittlement. These and similar applications require an even purer grade of anhydrous hydrazine. At one time Martin-Marietta Corp. practiced a process of fractional crystallization to remove aniline. A variation, zone freezing, has also been described (98). Another approach is to break the hydrazine–water azeotrope without the addition of an organic azeotroping agent. The ternary system, N_2H_4–NaOH–H_2O has a two-phase liquid region above 60°C (99). Addition of sufficient NaOH to hydrazine hydrate causes phase separation into a hydrazine-rich upper phase with a N_2H_4 content above that of the azeotrope. The lower phase contains the bulk of the water and caustic. The upper phase can then be distilled to obtain anhydrous hydrazine. Process variations based on this ternary system are described for the preparation of anhydrous hydrazine of ultrahigh purity by vacuum distillation (100). Arch Chemicals produces such a product under the name Ultra Pure.

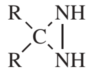
MMH and UDMH. Monomethylhydrazine and *unsym*-dimethylhydrazine are manufactured by Arch Chemicals using the same Raschig process and equipment employed for anhydrous hydrazine. Chloramine, prepared as described above, reacts with methylamine or dimethylamine instead of with ammonia. These products are used primarily as propellants for rockets and missiles.

4.2. Ketazine Processes.

The oxidation of ammonia by chlorine or chloramine in the presence of aliphatic ketones yields hydrazones (**36**), ketazines (**37**), or diaziridines (**38**), depending on the pH, ketone ratios, and reaction conditions (101).

$R_2C{=}N{-}NH_2$ (36)

$R_2C{=}N{-}N{=}CR_2$ (37)


(38)

The hydrazones and diaziridines (isohydrazones) form ketazines with excess ketone. The advantage of these intermediate hydrazine derivatives lies in resistance to further oxidation compared to the behavior of hydrazine itself (eq. 29). Higher chemical yields are possible than in the Raschig process. After complete consumption of the oxidizing agents (Cl_2, NaOCl, NH_2Cl), intermediates can be concentrated and then hydrolyzed to hydrazine or its salts. Many patents describe embodiments of this reaction scheme (102–109).

Bayer Ketazine Process. Chlorine reacts continuously with dilute sodium hydroxide to form sodium hypochlorite and sodium chloride (Fig. 5). This hypochlorite solution reacts at 30–40°C under slight pressure with aqueous ammonia and acetone (qv). With good mixing and a molar ratio of 1 hypochlorite:2 acetone:20 ammonia, a high yield based on chlorine is obtained. This dilute synthesis stream goes to the pressure ammonia stripper to remove excess ammonia, which is then absorbed in water and returned to the ketazine reactor. The bottoms from the ammonia recovery system, consisting of aqueous hydrazone, ketazine, and salt, go to the ketazine column where acetoneazine (**37**, $R = CH_3$) is taken overhead as a low boiling azeotrope with water (95°C, 55.5 wt% acetoneazine at 101.3 kPa) (110). In order to favor the ketazine equilibrium, additional

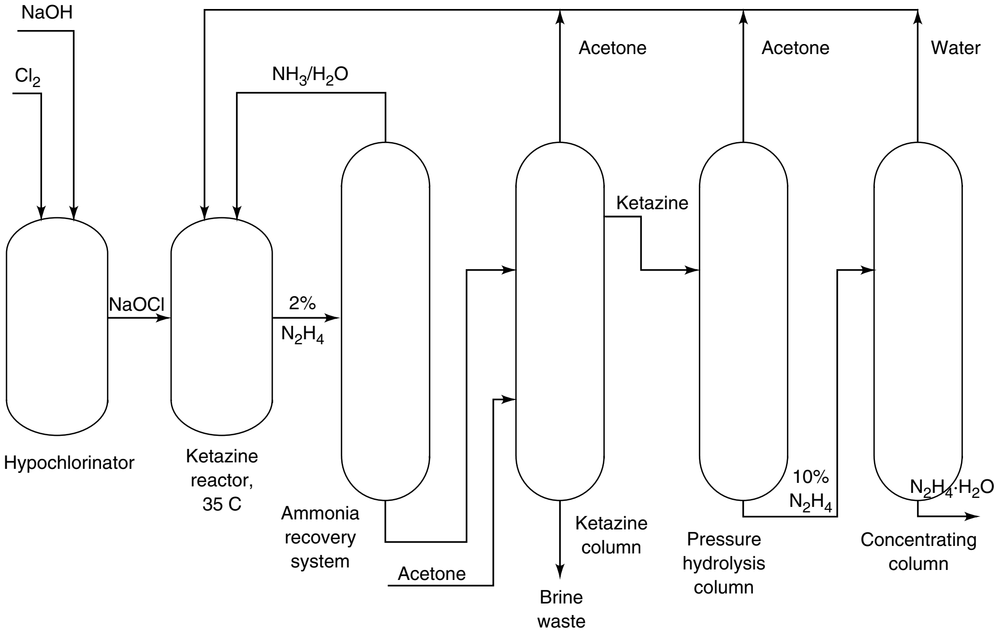


Fig. 5. Hypochlorite–ketazine process flow sheet.

acetone is added to this column so that all the hydrazine is present as ketazine (111).

$$(CH_3)_2C{=}N{-}NH_2 + (CH_3)_2C{=}O \longrightarrow (CH_3)_2C{=}N{-}N{=}C(CH_3)_2 + H_2O \qquad (30)$$

The overhead acetoneazine from the ketazine column hydrolyzes in the pressure hydrolysis column at ~1 MPa (10 atm) to form acetone and hydrazine:

$$(CH_3)_2C{=}N{-}N{=}C(CH_3)_2 + 2\ H_2O \longrightarrow 2\ (CH_3)_2C{=}O + N_2H_4 \qquad (31)$$

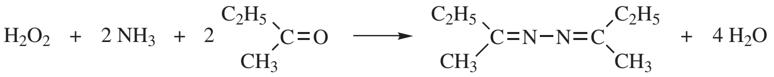
It is largely the pressure hydrolysis step that makes this ketazine process economic. Previous methods involved acid hydrolysis of ketazine to give the corresponding hydrazine salt. Because hydrazine, rather than a salt, is usually the desired product, an additional equivalent of base is needed in these processes to liberate the free hydrazine. Such processes require both one equivalent of acid and one of base to produce free hydrazine and this makes them uneconomical. When a salt such as hydrazine sulfate is the desired product, acid hydrolysis of the ketazine could become an option.

Acetone is withdrawn as overhead product from the pressure hydrolysis step and returned to the ketazine reactor. Excess acetone is also taken from the top of the ketazine column for recycle. The bottom stream from the ketazine column is essentially a sodium chloride solution with minor amounts of hydrazine and organic by-products. Before discharge this stream can be subjected to a clean-up chlorination treatment (112). The bottoms product from the pressure hydrolysis column is a 10–12% hydrazine solution. This is further fortified in a concentrating column where water is taken overhead, leaving essentially 64 wt% hydrazine, ie, 100% hydrazine hydrate, as a bottom product.

4.3. Comparison of the Raschig and Hypochlorite–Ketazine Processes. The formation of ketazine in the reaction step avoids destruction of hydrazine by chloramine, because the ketazine is not attacked by chloramine. The result is a synthesis yield (based on hypochlorite) that is substantially higher than that realized in the Raschig synthesis. Furthermore, the evaporative load is less because the hydrazine is removed from the bulk of the water as a low boiling ketazine–water azeotrope in the ketazine column. In the Raschig process, a much larger amount of water must be vaporized because hydrazine forms a high boiling azeotrope with water. This makes the ketazine process less energy intensive, an important consideration as energy costs escalate. Disadvantages of the ketazine process are the need to dispose of organic by-products, the loss of acetone, and the problem of handling acetone vapors. Also, it is difficult to remove all the organics from the final product so the total organic carbon (TOC) may be 500–1500 ppm. For some applications, this level of TOC may be objectionable and require further treatment, such as an additional distillation or adsorption on active carbon or other adsorptive surface (113). This is not a problem with hydrazine hydrate made by the standard Raschig process, and for most applications is not a problem at all.

4.4. Urea Process. In a further modification of the fundamental Raschig process, urea (qv) can be used in place of ammonia as the nitrogen source (114–116). This process has been operated commercially. Its principal advantage is low investment because the equipment is relatively simple. For low production levels, this process could be the most economical one. With the rapid growth in hydrazine production and increasing plant size, the urea process has lost importance, although it is reportedly being used, eg, in the People's Republic of China (PRC).

4.5. Peroxide–Ketazine Process. Atofina in France operates a process patented by Produits Chimiques Ugine Kuhlmann (PCUK). Hydrogen peroxide (qv), rather than chlorine or hypochlorite, is used to oxidize ammonia. The reaction is carried out in the presence of 2-butanone (MEK) at atmospheric pressure and 50°C. The ratio of H_2O_2/MEK:NH_3 used is 1:2:4. Hydrogen peroxide is activated by acetamide and disodium hydrogen phosphate (117). Figure 6 is a simplified flow sheet of this process. The overall reaction results in the formation of 2-butanone [5921-54-0] (**39**) and water:



$$H_2O_2 + 2\,NH_3 + 2\,(C_2H_5)(CH_3)C{=}O \longrightarrow (C_2H_5)(CH_3)C{=}N{-}N{=}C(C_2H_5)(CH_3) + 4\,H_2O \qquad (32)$$

(**39**)

The mechanism of this reaction involves an activation of the ammonia and hydrogen peroxide because these compounds do not themselves react (118–121). It appears that acetamide functions as an oxygen transfer agent, possibly as the iminoperacetic acid (**41**), which then oxidizes the transient Schiff base

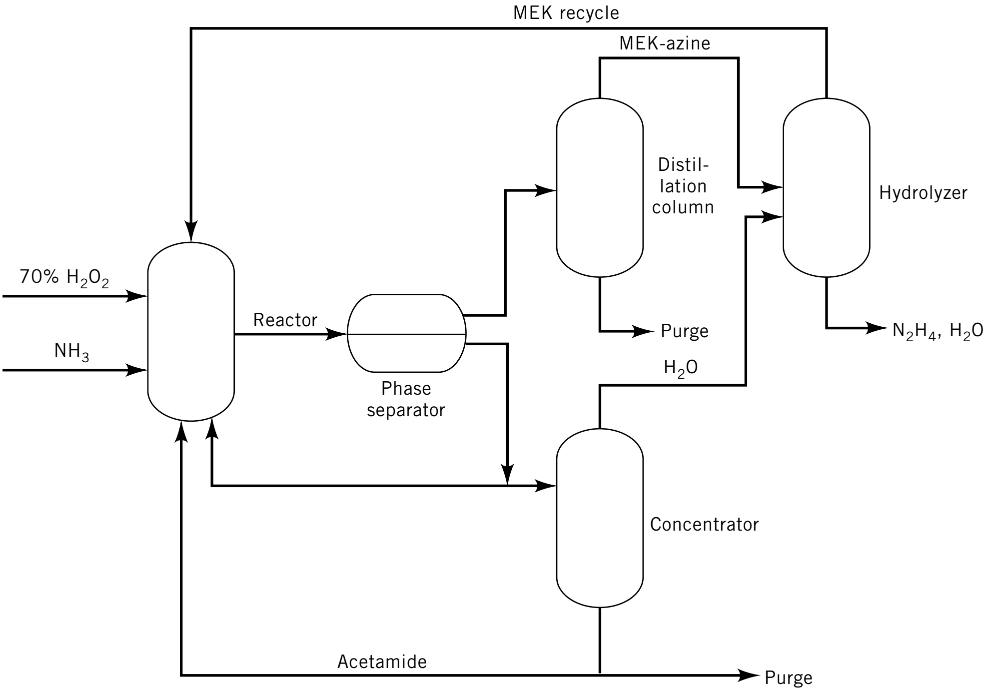
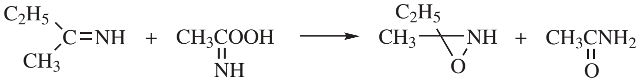


Fig. 6. Peroxide–ketazine process flow sheet. (MEK = ethyl ketone).

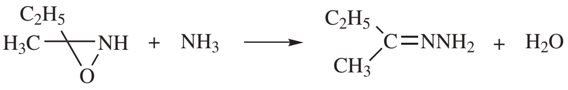
formed between MEK and ammonia (**40**) to give the oxaziridine (**42**), with regeneration of acetamide:



(33)

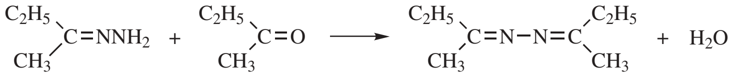
(**40**) (**41**) (**42**)

The oxaziridine oxidizes a second molecule of ammonia to form a hydrazone (**43**) which, with excess ketone, forms the azine (**39**).



(34)

(**43**)



(35)

(**39**)

The methyl ethyl ketazine (2-butanone) forms an immiscible upper organic layer easily removed by decantation. The lower, aqueous phase, containing acetamide and sodium phosphate, is concentrated to remove water formed in the reaction and is then recycled to the reactor after a purge of water-soluble impurities. Organic by-products are separated from the ketazine layer by distillation. The purified ketazine is then hydrolyzed under pressure (0.2–1.5 MPa (2–15 atm)) to give aqueous hydrazine and methyl ethyl ketone overhead, which is recycled (122). The aqueous hydrazine is concentrated in a final distillation column.

Comparison to the Raschig Process. The economics of this peroxide process in comparison to the Raschig or hypochlorite–ketazine processes depend on the relative costs of chlorine, caustic, and hydrogen peroxide. An inexpensive source of peroxide would make this process attractive. Its energy consumption could be somewhat less, because the ketazine in the peroxide process is recovered by decantation rather than by distillation as in the hypcochlorite process. A big advantage of the peroxide process is the elimination of sodium chloride as a byproduct; this is important where salt discharge is an environmental concern. In addition to Atofina, Mitsubishi Gas (Japan) uses a peroxide process.

4.6. Benzophenone Process. Benzophenone, $(C_6H_5)_2C{=}O$, reacts with ammonia to form diphenylmethanimine, $(C_6H_5)_2C{=}NH$. In the presence of copper catalysts, this is oxidized with oxygen to benzophenone azine, $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$. The formation of the imine and its further oxidation can be accomplished in a single step by passing ammonia and air through benzophenone at elevated temperature and pressure in the presence of zinc chloride and cuprous chloride. Acid hydrolysis of the azine gives hydrazine and regenerates the benzophenone. This process has been thoroughly reviewed (123); however, it is not commercial.

Table 6. **2004 Hydrazine Solutions Production Capacity, N_2H_4, t**

Country	Producer	Process	Capacity
United States	Arch	hypochlorite–ketazine	9,100
	Bayer	hypochlorite–ketazine	7,750
Germany	Bayer	hypochlorite–ketazine	7,750
France	Atofina	peroxide–ketazine	7,750
Japan	Mitsubishi Gas	peroxide–ketazine	5,000
	Nippon Carbide	Raschig	1,000
Korea	Otsuka	hypochlorite–ketazine	4,100
PRC	Several small plants	Raschig/urea (?)	1,400
Russia	Runs in termittanly	Raschig	3,500
Total			*47,350*

5. Economic Aspects

The estimated world production capacity for hydrazine solutions is 47,350 t on a N_2H_4 basis (Table 6). About 60% is made by the hypochlorite–ketazine process, 25% by the peroxide–ketazine route, and the remainder by the Raschig and urea processes. In addition there is anhydrous hydrazine capacity for propellant applications. In the United States, one plant dedicated to fuels production (Arch Chemicals, Raschig process), has a nominal capacity of 3200 t. This facility also produces the two other hydrazine fuels, monomethylhydrazine and unsymmetrical dimethylhydrazine. Other hydrazine fuels capacity includes AH in the PRC, Japan, and Russia; MMH in France and Japan; and UDMH in France, Russia, and the PRC.

World demand for hydrazine solutions is ~25,000 t N_2H_4, excluding Eastern Europe, Russia, and mainland China, down from the 1992 estimate of 31,000 t. The demand is nearly equally divided between captive use and merchant business. Table 7 shows an estimated breakdown by use and by region for hydrazine solutions. Synthesis of chemical blowing agents (CBAs) for the foaming of plastics accounts for ~30% of demand; another 25% goes into agricultural chemicals (pesticides). Water treatment represents nearly 25% of the market. Pharmaceu-

Table 7. **2004 Hydrazine Solutions Applications, N_2H_4, t**

Country	CBAs	Agriculture	Water treatment	Others[a]	Total
United States/Canada	1,815	2,495	910	2,040	7,260
Western Europe	1,590	3,860	1,905	1,315	8,670
Japan		1,135	1,950	365	3,450
Korea					
Indonesia					
Taiwan	680		90		770
Singapore	270		270	320	860
Australia/New Zealand			45		45
Africa/Middle East		180	410	365	955
Central and South America	545		500	180	1,225
Total	*49,00*	*7,670*	*6,080*	*4,585*	*23,235*

[a] Pharmaceuticals, photography, polymers, metal reduction, etc.

tical applications are significant but difficult to quantify; the remaining applications are fragmented among many industries.

Hydrazine is a mature product likely to grow worldwide in step with the gross national product at best. The use of hydrazine in chemical blowing agents in southeast Asia has dropped significantly due to the adoption of non-hydrazine routes to azodicarbonamide, the major compound in this application. In water treatment, the growth might be somewhat less, perhaps 2–3%.

6. Shipment and Specifications

Shipment of hydrazine solutions is regulated in the United States by the Department of Transportation (DOT), which classifies all aqueous solutions between 64.4 and 37% N_2H_4 as “Corrosive” materials with a subsidiary risk of “Poison”. Hydrazine has been identified by both the Environmental Protection Agency and the DOT as a hazardous material and has been assigned a reportable quantity (RQ) of 0.450 kg (1 lb) (on a N_2H_4 basis) if spilled. Drums for the shipment of these solutions must bear both the DOT specification “Corrosive” and “Poison” labels in association with the markings “RQ Hydrazine Aqueous Solution UN 2030”. Aqueous solutions of 37% concentration or less are a hazard Class 6.1, UN 3293, Packing Group III and require “Keep Away From Food” placards and labels.

The aqueous grades of hydrazine are packaged in 208-L (55-gal) plastic drums, 1304-L (345-gal) stainless steel returnable tote tanks and tank trucks. Anhydrous hydrazine (AH) and MMH are available in 114- and 208-L returnable drums made of 304 low Mo stainless steel. UDMH ships in 208-L mild steel drums. Returnable stainless steel cylinders are also widely used for AH, MMH and UDMH. They can be filled to customer specified volumes and can be pressurized.

Table 8. **Specifications for Propellant Hydrazine Grades**[a]

Parameter	Regular[b]	Monopropellant[c]	High purity[c]	Ultra pure
assay, wt%[d]	98	98.5	99.0	99.5
water, wt%	1.5	1.0	1.0	0.5
particulates, mg/L	10	1.0	1.0	1.0
ammonia, wt%			0.3	0.3
aniline, wt%	0.5	0.50	0.003	[e]
carbon dioxide, wt%		0.003	0.003	0.003
chloride, wt%	0.005	0.0005	0.0005	0.0005
iron, wt%	0.003	0.002	0.0004	0.0004
nonvolatile residue, wt%		0.005	0.001	0.001
other volatile carbonaceous matter, wt%		0.02	0.005	0.005

[a] All values are maximum allowed unless otherwise specified.

[b] Military Specification MIL-PRF-26536 E, Sept. 24, 1997.

[c] Military Specification MIL-PRF-26536 E, Sept. 24, 1997.

[d] Values are minimum allowed.

[e] Not detectable.

Table 9. **Aqueous Hydrazine Specifications**[a]

	Hydrazine, wt%			
Specification	64	54.4	51.2	35
assay,[b] wt%	64.0–64.8	54.4–55.1	51.2–51.8	35.0–35.7
water,[c] wt%	36.0	45.6	48.8	65.0
iron, ppm	3	3	3	2
sodium, ppm	4	4	4	3
chloride, ppm	3	3	3	2
fluoride, ppm	1	1	1	1
sulfate, ppm	1	1	1	1

[a] All values are maximum unless otherwise noted.

[b] Values are minimum to maximum.

[c] By difference.

Table 8 summarizes specifications for anhydrous grades of hydrazine. Propellant grades meet all requirements of the most recent Military Specification MIL-PRF-26536 E. Military specifications covering the other propellant hydrazines are MMH (Mil-PRF-27404 C, Oct. 1, 1997; UDMH (Mil-PRF-25604 E, Oct. 24, 1997; Aerozine-50 (Mil-P-27402 C, Oct. 1, 1997; H-70 (Mil-PRF-87930 A, USAF, Oct. 24, 1997).

Table 9 lists specifications for the common aqueous hydrazine products available in the United States (124).

Whereas there is sometimes confusion in how concentrations of aqueous solutions of hydrazine are expressed, concentrations of wt% N_2H_4 are used herein. In many parts of the world, however, concentrations are often expressed in terms of wt% hydrazine hydrate, $N_2H_4 \cdot H_2O$. Hydrazine hydrate is 64 wt% N_2H_4, 36% H_2O. The correlation between the two systems is therefore:

wt% N_2H_4	64	54.4	51.2	35
wt% $N_2H_4 \cdot H_2O$	100	85	80	54.7

7. Handling and Storage

Hydrazine is a base, a reducing agent, and a high energy compound; it is also volatile and toxic. These properties determine its proper handling, storage, use, and disposal. Inadvertent contact with acids or oxidizing agents must be avoided because extremely exothermic reactions and evolution of gases may result. Flash points, however, of aqueous and anhydrous hydrazine are relatively high compared to common combustibles such as alcohol or gasoline. It is much easier and safer to handle aqueous solutions than the anhydrous product; aqueous solutions containing $<40\%$ hydrazine have no flash point, ie, they cannot be ignited. Liquid hydrazine is not sensitive to shock or friction. In the absence of decomposition catalysts, liquid anhydrous hydrazine has been heated to $>200^\circ C$ without appreciable decomposition. Hydrazine fires are effectively combated using water because hydrazine is miscible with water in all proportions.

The broad explosive range of hydrazine vapor is a concern. An inert gas blanket helps avoid formation of explosive mixtures. Even for dilute aqueous solutions, a nitrogen pad prevents gradual loss of hydrazine by air oxidation. Because acid solutions of hydrazine are not readily oxidized, air oxidation can be minimized or prevented by acidification, which also serves to reduce the vapor pressure. Hydrazine may ignite wood, rags, paper, or other common organic materials. Thus these should not be used near hydrazine. Use protective clothing to avoid body contact and provide adequate ventilation to reduce inhalation danger.

7.1. Materials of Construction. In choosing the proper materials of construction for storing and using hydrazine, it is necessary to consider both the effects of the material on the stability and quality of the hydrazine as well as the effect of the hydrazine on the material of construction. Hydrazine is thermally stable, storable for years without adverse effects either to the product or the storage container provided the recommended materials are used, all systems are clean, and an inert gas, ie, nitrogen, is maintained over the system at all times. Table 10 is a brief listing of materials compatibility (125).

As shown, materials generally considered satisfactory for all N_2H_4 concentrations, including anhydrous, are 304 L and 347 stainless steels having <1.0 wt% molybdenum, a catalyst for the decomposition of hydrazine. For concentrations <10%, cold-rolled steel is satisfactory. Among the nonmetallic materials, poly(tetrafluoroethylene), polyethylene, and polypropylene are suitable; PVC is not recommended. Ethylene–propylene–diene monomer (EPDM) rubber (126) and polyketones and polyphenylene sulfides (127) are reportedly suitable for use with anhydrous hydrazine. Many factors are involved in materials compatibility; a final choice may require some testing. For example, low (<250 ppm) concentrations of CO_2 in anhydrous hydrazine accelerate the decomposition of hydrazine in stainless steel (128). Long-term storage tests of

Table 10. **Materials Compatibility for Aqueous Hydrazine Solutions**[a]

	Hydrazine concentration, wt% N_2H_4			
Material	<10	35	54.4	64
stainless steel				
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

[a] S = generally satisfactory; NR = not recommended; and 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 = polytetrafluoroethylene.

hydrazine propellants in 17–7 pH stainless steel [12742-98-2] and AM350 precipitation-hardened stainless steel [12731-98-5] at 50°C for ∼3 years showed no pressure rise or N_2H_4 decomposition (129). Extensive information and bibliographies are available on suitable materials of construction for AH, MMH, and UDMH (7,130).

7.2. Disposal. Spills and wastewater containing hydrazines must be contained and treated. Proper disposal methods for the hydrazines make use of their reductive properties. Fuel-grade hydrazines may be burned, but aqueous solutions <50% may require supplementary fuel (131). Chemical destruction of dilute (preferably 5% or less) solutions can be achieved with various oxidants such as NaOCl, $Ca(OCl)_2$, H_2O_2, and acidified permanganate; however MMH and UDMH, may form mutagenic nitrosamines (132). A method is described for treating contaminated wastewater in which N_2H_4, MMH, UDMH, and *N*-nitrosodimethylamine [62-75-9] are effectively decomposed at a controlled pH of ∼5 by an (uv)-induced chlorination (133) (see also PHOTOCHEMICAL TECHNOLOGY, SURVEY). Ozonation of these three hydrazines yields a variety of products, including methanol, formaldehyde monomethylhydazone [36214-48-9], and formaldehyde dimethylhydrazone [2035-89-4]; and tetramethyl tetrazene [6130-87-6] from the oxidative coupling of two molecules of UDMH (134). Methyldiazene [26981-93-1] was also found as an oxidation product of MMH (135). The rates of decomposition from aqueous solutions are greatest at pH 9.1 in the presence of uv light (136). Blowdown from boilers treated with hydrazine for corrosion control is effectively treated by neutralization with lime and chlorination (137). A vapor suppressant foam system (ASE95 polyacrylic/MSAR combination) has been evaluated for covering hydrazine fuel spills to minimize the release of toxic fumes (138). An excellent review covering disposal methods for hydrazine, MMH, and UDMH is available (139). Although laboratory methods of decontamination are emphasized, these could easily be adapted for large-scale disposal.

8. Analytical Methods

As a strong reducing agent, hydrazine can be determined quantitatively using a variety of oxidants. Most convenient, perhaps, is an iodometric titration (140):

$$N_2H_4 + 2\ I_2 \longrightarrow N_2 + 4\ HI \tag{36}$$

The pH must be kept at 7.0–7.2 for this method to be quantitative and to give a stable end point. This condition is easily met by addition of solid sodium bicarbonate to neutralize the HI formed. With starch as indicator and an appropriate standardized iodine solution, this method is applicable to both concentrated and dilute (to ∼50 ppm) hydrazine solutions. The iodine solution is best standardized using monohydrazinium sulfate or sodium thiosulfate. Using an iodide-selective electrode, low levels down to the ppb range are detectable (see ELECTROANALYTICAL TECHNIQUES) (141,142). Potassium iodate (143,144), bromate (145), and permanganate (146) have also been employed as oxidants.

Dilute hydrazine solutions may be determined colorimetrically by the formation of highly colored azines with salicylaldehyde or, preferably, *p*-dimethylaminobenzaldehyde. This is the basis for a qualitative spot test for hydrazine and some of its derivatives (147). Ammonia and hydroxylamine do not interfere. Using *p*-dimethylaminobenzaldehyde, the method is suitable for the quantitative determination of ppm levels or less of hydrazine (ASTM D1385–88). It is used for the analysis of hydrazine residuals in boiler water or wastewater, and in air by absorption of hydrazine from a known volume of air in an acidified solution of the aldehyde reagent. Reagents, color chips, color comparators, and spectrophotometers are available for these applications, eg, from Hach Chemical Co. (Loveland, Colorado); LaMotte Co. (Chestertown, Maryland); CHEMetrics, Inc. (Calverton, Virginia); and others. Using a spectrophotometer set at 458 nm, it is possible to determine levels as low as ~6 ppb. A high speed continuous-flow monitor based on this method has been developed (148). An amperometric sensor is the basis of a continuous hydrazine-in-water analyzer offered by Ametek (Paoli, Pennsylvania), especially for use in boiler water. The detection of hydrazine has been described down to 20 ppm in aqueous and alcoholic solutions via thin-layer chromatography (qv) of the *p*-dimethylaminobenzalazine [41463-93-8] (149). The basic ASTM D1385-88 procedure is adaptable to the determination of MMH and UDMH as these also form colored hydrazones. For mixtures of the three hydrazines mentioned, the sample can be derivatized using salicylaldehyde and separated by high pressure liquid chromatography, using uv for detection; for hydrazine, the uv detector should be set at 209 nm (150). Using an electrochemical detector, it is not necessary to derivatize first (151). Polarographic procedures sensitive to levels of 0.25–1.0 ppm (152) and 0–20 ppb (153) have been described. Gas chromatographic techniques for the propellant hydrazines, ie, hydrazine, MMH, and UDMH, have been developed for high concentrations as well as for dilute aqueous solutions (154).

Air monitoring of the workplace is important because of the inherent inhalation toxicity of hydrazine and its volatile derivatives. Hydrazine levels can be determined by passing a known volume of air through dilute sulfuric acid to absorb the hydrazine and measuring the concentration by the colorimetric ASTM D1385–88 method. An alternative is to trap the hydrazines on H_2SO_4-coated silica gel, eluting with water and derivatizing with 2-furaldehyde; the derivatives can then be measured by gas chromatography (155). Continuous air monitors are commercially available from MDA Scientific Inc. (Park Ridge, Illinois), Scott-Bacharach (Exton, Pennsylvania) and others. Some are based on the reduction by hydrazine of a phosphomolybdate-impregnated tape; the resulting blue spot is read photometrically. Models having a 0–0.5 ppm full scale are available. Methyl- and dimethylhydrazines can also be determined with this instrument, but not quantitatively in the presence of each other. An electrochemical gas sensor has been patented (156) and an electrochemical monitor has been developed (157). The feasibility of laser remote sensing of hydrazine, MMH, and UDMH in the gas phase has been studied (158).

9. Health and Safety Factors

The acute and chronic toxicity of hydrazine, the methylhydrazines, phenylhydrazine, and other hydrazine derivatives has received extensive study, and is comprehensively covered in several reviews (159–164).

Hydrazine is toxic and readily absorbed by oral, dermal, or inhalation routes of exposure. Contact with hydrazine irritates the skin, eyes, and respiratory tract. Liquid splashed into the eyes may cause permanent damage to the cornea. At high doses it can cause convulsions, but even low doses may result in central nervous system depression. Death from acute exposure results from convulsions, respiratory arrest, and cardiovascular collapse. Repeated exposure may affect the lungs, liver, and kidneys. Of the hydrazine derivatives studied, UDMH appears to be the least hepatotoxic; MMH seems to be more toxic to the kidneys. Evidence is limited as to the effect of hydrazine on reproduction and/or development; however, animal studies demonstrate that only doses that produce toxicity in pregnant rats result in embryotoxicity (165).

As of 2003, the TLV recommended by the ACGIH is set at 0.01 ppm (hydrazine) TWA; 0.2 ppm (MMH); and 0.5 ppm (UDMH). The TLV is well below the olfactory limit of 3–5 ppm (hydrazine). The latter does not provide adequate warning when exposure exceeds the TLV; therefore, monitoring the working environment by suitable means and providing adequate ventilation is necessary. Because of the same reasoning, there are no approved cartidge respirators approved for hydrazine, supplied air systems must be employed. The recommended exposure level (REL) assigned by NIOSH is 0.03 ppm (0.04 mg/m^3).

Table 11 summarizes values for the median lethal dose (LD$_{50}$) for several species. In case of massive exposure, convulsions must be controlled, and glucose, fluid balance, and urinary output must be maintained. Medical surveillance requires checking for damage to the liver, the organ that apparently sustains initial damage, and monitoring for changes in the blood profile.

The International Agency for Research on Cancer (IARC) classifies hydrazine as a 2B or possible human carcinogen. The American Conference of Governmental Industrial Hygienists (ACGIH) classifies hydrazine as an A3 or confirmed animal carcinogen with unknown relevance to humans. Several animal studies have demonstrated that chronic oral and inhalation exposure to hydrazine can produce tumors. Nasal tumors were observed in long-term inhalation studies

Table 11. **Acute Toxicity of Hydrazine, MMH, and UDMH**

		LD$_{50}$, mg/kg		
Species	Administration route	Hydrazine	MMH	UDMH
mouse	intraperitoneal	62	15	113
	intravenous	57	33	250
	oral	59	29	265
rat	intraperitoneal	59	21	102
	intravenous	55	17	119
	oral	60	32	122
rabbit	percutaneous	91	95	1060
	intravenous	20	12	70
dog	intravenous	25	12	60
monkey	intraperitoneal	20		60–100

in rats, mice, hamsters, and dogs exposed to hydrazine vapors (166). These tumors were often associated with repeated tissue insult (chronic irritation). Long-term exposure of mice to hydrazine via oral administration resulted in the observation of tumors in multiple tissues, including lung, liver, and lymphatic system (167). In studies where hydrazine was administered to rats in their drinking water until the spontaneous death of all the rats (168), only under the toxicity of the highest concentrations could a weak carcinogenic effect of the hydrazine be detected. In a similar study, mice were exposed for their lifetime and no tumors were reported (169).

Hydrazine has not been shown to have carcinogenic potential in humans. An epidemiological study of 427 men occupationally exposed to hydrazine for varying times showed no obvious hazards associated with hydrazine exposure (170). In another, ongoing epidemiological study of a smaller group of occupationally exposed workers, no statistical differences in the incidence of cancers have been observed when compared to the control population (171). These results must be viewed with caution owing to the small number of individuals in both studies; also, the second study is yet in progress as of this writing.

Assays have shown that hydrazine can interact with DNA to elicit mutagenic effects. The mutagenicity of hydrazine has been reviewed (172). Among toxic pollutants that may enter the environment, hydrazine is one of the less persistent because it reacts with oxygen and ozone, particularly in the presence of catalytic surfaces such as metals, oxides, etc. The final products of these reactions are innocuous: nitrogen and water.

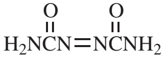
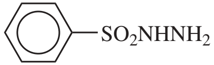
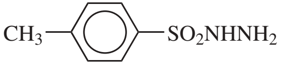
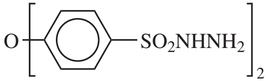
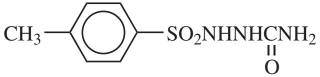
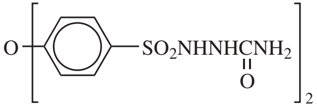
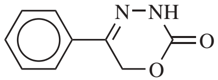
10. Uses

The principal applications of hydrazine solutions include chemical blowing agents, 28%; agricultural pesticides, 25%; water treatment, 31% and pharmaceutical 10%. The remaining 6% finds use in a variety of fields including explosives, polymers and polymer additives, antioxidants, metal reductants, hydrogenation of organic groups, photography, xerography, and dyes.

10.1. Chemical Blowing Agents. Chemical blowing agents are gas-generating compositions used to produce flexible or rigid cellular polymeric or elastomeric foams by a controlled release of gases, generally by thermal decomposition or by reaction with a component of the polymer formulation. To accommodate a wide range of plastics, a series of products is needed, varying in decomposition temperatures, polymer compatibility, etc. The most important commercial products are hydrazine derivatives, which release nitrogen as the principal gaseous product. Some of the more important are listed in Table 12.

By far the largest (~85% of the total) volume chemical blowing agent is azodicarbonamide (**44**), made by the oxidation of hydrazodicarboxamide [110-21-4] (**51**) using chlorine or sodium chlorate. The hydrazo precursor is made by refluxing an aqueous solution of urea and hydrazine (173). In recent years, the use of hydrazine for the production of azodicarbonamide has been severely impacted by the direct oxidation of urea to hydrazodicarbonamide,

Table 12. **Common Hydrazine-Based Blowing Agents**

Compound	CAS Registry number	Molecular formula	Structure	Structure number
azodicarbonamide	[123-77-3]	$C_2H_4N_4O_2$	 $H_2N\overset{O}{\overset{\|}{C}}N{=}N\overset{O}{\overset{\|}{C}}NH_2$	**44**
benzenesulfonylhydrazide	[80-17-1]	$C_6H_8N_2O_2S$		**45**
p-toluenesulfonylhydrazide	[1576-35-8]	$C_7H_{10}N_2O_2S$		**46**
4,4′-oxybis(benzenesulfonylhydrazide)	[80-51-3]	$C_{12}H_{14}N_4O_5S_2$		**47**
p-toluenesulfonylsemicarbazide	[10396-10-8]	$C_8H_{11}N_3O_3S$		**48**
4,4′-oxybis(benzenesulfonylsemicarbazide)	[10195-67-2]	$C_{14}H_{16}N_6O_7S_2$		**49**
5-phenyl-3,6-dihydro-1,3,4-oxadiazin-2-one	[62501-39-7]	$C_9H_8N_2O_2$		**50**

eliminating the use of hydrazine. This has been mostly seen in the southeast Asia markets.

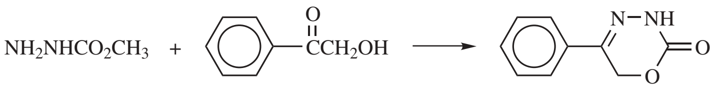
$$2\,H_2N\overset{O}{\overset{\|}{C}}NH_2 + N_2H_4 \xrightarrow{-2\,NH_3} H_2N\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{Cl_2} H_2N\overset{O}{\overset{\|}{C}}N{=}N\overset{O}{\overset{\|}{C}}NH_2 \qquad (37)$$

(**51**) (**44**)

All the sulfonic acid hydrazides are made from hydrazine or semicarbazide and the appropriate sulfonyl chloride in the presence of an HCl acceptor such as ammonia.

p-Toluenesulfonylhydrazide (46) has a higher decomposition temperature than the benzene derivative (45). Decomposing still higher is (47), which is also prepared from the corresponding bis(sulfonylchloride) (174). The sulfonylsemicarbazides (48) and (49) have relatively high gas yields. Decomposition temperatures are also high but if necessary can be lowered using activators, making these compounds useful in the foaming of rubber (see RUBBER CHEMICALS). These are made from the sulfonyl chlorides and semicarbazide or from the sulfonyl hydrazides and isocyanic acid (sodium cyanate/acid) (175).

5-Phenyl-3,6-dihydro-1,3,4-oxadiazin-2-one (**50**) is a high temperature blowing agent used primarily for polycarbonates (qv). It is prepared by the reaction of α-hydroxyacetophenone and methyl carbazate (**52**), made from hydrazine and dimethyl carbonate (176):



(38)

(**52**) (**50**)

The primary domestic producer of these chemical blowing agents is Uniroyal (now Crompton). European producers include Bayer (Germany) and Atofina (France). In Japan and the Pacific Rim the producers include Dong Jin, Otsuka Chemical, Eiwa Chemical Ind. amd Kum Yang. There are a number of small producers in the People's Republic of China. There are several excellent reviews covering the technology of chemical blowing agents (177–179). A tabulation of producers, trade names, and application data can be found in Ref. 180.

10.2. Agricultural Uses. Pesticides represent the second largest commercial market for hydrazine. Hundreds of hydrazine derivatives have been patented for a wide range of agricultural applications. Table 13 presents a sampling of the 50–60 that are commercially available or developmental products. These compounds are made from hydrazine, MMH, and UDMH and are for the most part heterocyclic nitrogen compounds (see INSECTICIDES).

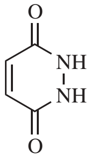
The earliest hydrazine derivative (1948), having extensive agricultural application, was maleic hydrazide (**53**), a plant growth regulator that retards the sprouting of onions and potatoes in storage and prevents sucker growth on tobacco plants. It is prepared from hydrazine and either maleic acid or maleic anhydride (181,182). Additional activity in this area seems to have

Table 13. **Hydrazine-Based Pesticides**

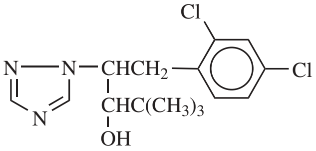
Generic name	CAS Registry number	Compound class	Molecular formula	Trade name	Producer	Use[a]
amitrole	[61-82-5]	triazole	$C_2H_4N_4$	Ustilan	Bayer	H
bitertanol	[55179-31-2]	triazole	$C_{20}H_{23}N_3O_2$	Baycor	Miles	F
clofentezine	[74115-24-5]	tetrazine	$C_{14}H_8Cl_2N_4$	Apollo	Schering AG	I
cyproconazole	[94361-06-5]	triazole	$C_{15}H_{18}ClN_3O$	Alto	Sandoz	F
daminozide	[1596-84-5]	UDMH-hydrazide	$C_6H_{12}N_2O_3$	Dazide, B9	Fine Agrochemical, Uniroyal	PGR
diclobutrazol	[75736-33-3]	triazole	$C_{15}H_{19}Cl_2N_3O$	Vigil	ICI	F
difenzoquat	[49866-87-7]	pyrazole	$C_{17}H_{17}N_2$	Avenge	American Cyanamid	H
flutriafol	[76674-21-0]	triazole	$C_{16}H_{13}F_2N_3O$	Impact	ICI	F
flusilazol	[85509-19-9]	triazole	$C_{16}H_{15}F_2N_3Si$	Punch	Du Pont	F
hexaconazole	[79983-71-4]	triazole	$C_{14}H_{17}Cl_2N_3O$	Anvil	ICI Americas	F
hydramethylnon	[67485-29-4]	azine	$C_{25}H_{24}F_6N_4$	Amdro	American Cyanamid	I
maleic hydrazide	[123-33-1]	dihydroxypyridazine	$C_4H_4N_2O_2$	Drexel MH, Royal MH-30	Drexel Chemical, Uniroyal	PGR–PGR
metamitron	[41394-05-2]	triazine	$C_{10}H_{10}N_4O$	Goltix	Bayer AG	H
metribuzin	[21087-64-9]	triazine	$C_8H_{14}N_4OS$	Sencor	Bayer AG	H
myclobutanil	[88671-89-0]	triazole	$C_{15}H_{17}ClN_4$	Rally	Rohm & Haas	F
paclobutrazol	[76738-62-0]	triazole	$C_{15}H_{20}ClN_3O$	Clipper	ICI Americas	PGR
propiconazole	[60207-90-1]	triazole	$C_{15}H_{17}Cl_2N_3O_2$	Tilt	Ciba-Geigy	F
pyridate	[55512-33-9]	pyridazine	$C_{14}H_{14}AsNO_2$	Tough	Agrolinz	H
tebuthiuron	[34014-18-1]	thiadiazole	$C_9H_{16}N_4OS$	Spike	Eli Lilly	H
triadimefon	[43121-43-3]	triazole	$C_{14}H_{16}ClN_3O_2$	Bayleton	Bayer	F
triadimenol	[55219-65-3]	triazole	$C_{14}H_{18}ClN_3O_2$	Baytan	Miles	F
tricyclazole	[41814-78-2]	triazole	$C_9H_7N_3S$	Beam	Eli Lilly	F
uniconazole	[76714-83-5]	triazole	$C_{15}H_{18}ClN_3O$	Prunit	Chevron	PGR
distinct	[109293-98-3]	hydrazone	$C_{15}H_{12}F_2N_4O_3$	Distinct	BASF	H

[a] F = fungicide; H = herbicide; I = insecticide; PGR = plant growth regulator.

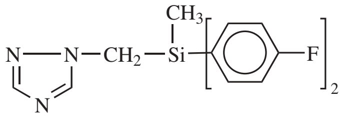
centered on triazole-based fungicides such as typified by diclobutrazol (**54**) and flusilazol (**55**).



(**53**)

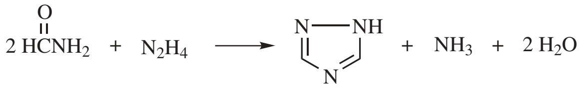


(**54**)



(**55**)

The triazole [288-88-0] (**56**) required for these products can be made from formamide and hydrazine (183,184):



(**56**)

(39)

This class of fungicides has been reviewed (185). Standard compilations of pesticides provide information on names, structures, and uses of these compounds (186,187).

10.3. Water Treatment. Water treatment for corrosion protection represents the third largest market for hydrazine. It is used in boilers and hot-water heating systems to scavenge dissolved oxygen, a primary cause of corrosion. The application of hydrazine in boilers also includes wet lay-up for protection during idle periods (188). Hydrazine has been patented as a corrosion inhibitor for closed circulation cooling systems of internal combustion engines, especially for diesel engines in ships (189). The reaction removes oxygen down to essentially nondetectable levels (Indigo-Carmine Analytical Method, ASTM D888-87). The products of this reaction, nitrogen and water, are innocuous. Minor amounts of ammonia may form by thermal decomposition and this serves to raise the pH of the condensate and feedwater. For water treating, hydrazine is generally sold as a dilute aqueous solution, 35 wt% or less, because such solutions have no flash point and a relatively low partial pressure of hydrazine, minimizing the danger of inhalation by operating personnel.

Oxygen scavengers other than hydrazine are also used, especially catalyzed sodium sulfite, which reacts rapidly with oxygen even at room temperatures to form sodium sulfate. Catalyzed hydrazine formulations are now commercially available that react with oxygen at ambient temperatures at rates comparable to catalyzed sulfite (190). At elevated temperatures, the reaction rates are all similar. Table 14 lists the standard hydrazine solution products offered by Arch Chemicals for sale to the water-treatment market. Other concentrations are available and other companies offer similar products.

Hydrazine has the advantage over sodium sulfite of not contributing dissolved solids to the boiler system, thereby reducing the need for purging. At the high temperatures encountered in utility boilers, hydrazine must be used because sulfite decomposes to corrosive sulfur dioxide and sodium sulfide (191,192).

Table 14. **Composition of Oxygen Scav-Ox Solutions**

Parameter	Scav-Ox	Scav-Ox II
N_2H_4 conc, wt%	35.0	35.0
catalyst		
type		organic
wt%		0.2
color	colorless	light pink/orange

Hydrazine also reacts with iron, probably in a sequence of steps involving oxidation of iron by water (193), to form an adherent magnetite coating on the metal surface that protects against further attack (eq. 40). In addition, hydrazine reduces red iron oxide, Fe_2O_3 (rust) to magnetite (eq. 41); loose magnetite is dense and settles to the bottom of the system for easy removal. This helps avoid deposits on the boiler heat-transfer surfaces that would otherwise impede heat transfer and cause boiler tubes to rupture. Boilers treated for longer periods of time with hydrazine do not develop much rust, thus requiring less clean out. A very low hydrazine residual concentration in the boiler system, generally <0.1 ppm, provides full corrosion protection.

$$3\,Fe + 4\,N_2H_4 + 4\,H_2O \longrightarrow Fe_3O_4 + 8\,NH_3 \tag{40}$$

$$N_2H_4 + 6\,Fe_2O_3 \longrightarrow 4\,Fe_3O_4 + 2\,H_2O + N_2 \tag{41}$$

Concern for personnel exposure to hydrazine has led to several innovations in packaging to minimize direct contact with hydrazine, such as various closed handling systems including drums and tote bins. Carbohydrazide was introduced into this market for the same reason: It is a solid derivative of hydrazine, considered safer to handle because of its low vapor pressure. It hydrolyzes to release free hydrazine at elevated temperatures in the boiler. It is, however, fairly expensive and contributes to dissolved solids (carbonates) in the water (194). In field tests, catalyzed hydrazine outperformed both hydrazine and carbohydrazide when the feedwater oxygen and iron levels were critical (195). A published comparison is available (196) of these and other proposed oxygen scavengers, eg, diethylhydroxylamine, hydroquinone, methyethylketoxime, and isoascorbic acid.

10.4. Propellants and Explosives. Hydrazine fuels include anhydrous hydrazine (AH), MMH, and unsymmetrical UDMH for military and space programs. These compounds are used mainly as bipropellant fuels, ie, with oxidizers, in rockets such as the Titan, MX missile, and the Ariane ($UDMH/N_2O_4$). Using oxygen or fluorine as the oxidizer, hydrazine is exceeded only by hydrogen in specific impulse, ie, Newtons of thrust developed for each kilogram of fuel consumed per second (197).

Hydrazine is also used as a monopropellant, without any oxidant, by decomposing it over a catalyst to form propulsive gases (198) used for auxiliary power units and in thruster engines for attitude and in-orbit control of satellites and spacecraft. A significant advance was the development of catalysts that function at low temperatures without prior heating, such as the Shell 405 iridium on alumina (199). Iridium on alumina appears to be the preferred catalyst (200,201).

The kinetics of this system have been studied (202). Various mixtures of iridium, ruthenium, cobalt, and molybdenum on Al_2O_3 as carrier are also reported as effective catalysts (203). Noncatalytic monopropellant thrusters having integral electric heaters have also been developed (204).

Aerozine-50, an equal mixture of AH and UDMH, was used to power the Titan II launch vehicle for the *Gemini* spacecraft. The Delta II vehicles likewise use Aerozine-50/N_2O_4 in the second stage. UDMH and fuming nitric acid were used in the second stage of the Vanguard. The U.S. Space Shuttle is maneuvered in orbit with MMH/N_2O_4. Space vehicles propelled by hydrazine include the Viking landers on Mars, the Pioneer, Voyager and Cassini interplanetary probes, and the Giotto spaceprobe to Halley's comet.

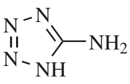
Solid hydrazine derivatives such as the nitrate, monoperchlorate, and diperchlorate salts as well as aluminum perchlorate trihydrazinate [85962-45-4], $Al(ClO_4)_3 \cdot 3N_2H_4$, have also been studied as propellants (205). A review of solid hydrazines as hybrid rocket fuels has been published (206). An excellent reference source for declassified documents covering rocket, missile, space, and gun technology is available from the Chemical Propulsion Information Agency (CPIA) (207), subject to some security restrictions. The most complete bibliography of references in the field of hydrazine propellants is Ref. 9.

Numerous explosives are based on hydrazine and its derivatives, including the simple azide, nitrate, perchlorate, and diperchlorate salts. These are sometimes dissolved in anhydrous hydrazine for propellant applications or in mixtures with other explosives (208). Hydrazine transition-metal complexes of nitrates, azides, and perchlorates are primary explosives (209).

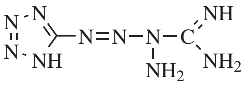
Sodium azide [26628-22-8], NaN_3, was once the compound most often used for gas generation in automobile safety air bags. It can be made from hydrazine by refluxing ethyl or *tert*-butyl nitrite with hydrazine hydrate and sodium hydroxide in alcohol (210,211). It is now being replaced with less hazardous alternatives, several of which are also hydrazine based.

$$N_2H_4 + t\text{-}C_4H_9ONO + NaOH \longrightarrow NaN_3 + t\text{-}C_4H_9OH + 2\,H_2O \qquad (42)$$

An alternative for air bags is 5-aminotetrazole [4418-61-5] (**57**), prepared by nitrosation of aminoguanidine (212). Other compounds under study as gas generators for air bags and fire extinguishers are the guanidinium (213) and triaminoguanidinium (214) salts of 5,5′-azobistetrazole [28623-02-1]. Tetrazene [31330-63-9] (**58**), an explosive primer (215), is made from aminoguanidine. Aminoguanidine, as well as di- and triaminoguanidine are prepared by the reaction of hydrazine with guanidine or cyanamide (216,217). Triaminoguanidinium nitrate is a useful ingredient in gun propellants (218).



(57)



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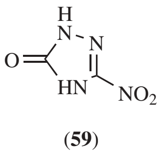
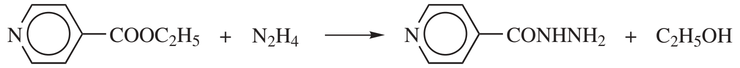


(59)

There is a drive to develop insensitive or less sensitive munitions, ie, those less likely to undergo accidental or sympathetic detonation. A leading candidate is

3-nitro-1,2,4-triazolin-5-one [930-33-6] (**59**), made by the reaction of semicarbazide and formic acid to give 1,2,4-triazolin-5-one [932-64-9] followed by nitration of the triazolone (219).

10.5. Pharmaceuticals. The tuberculostatic drug isoniazid [54-85-3] (**60**), the hydrazide of 4-pyridinecarboxylic acid, was one of the earliest hydrazine-based drugs introduced in the United States. It is made by the reaction of hydrazine and an isonicotinic acid ester (220).



(**60**)

(43)

Chemical structures for established drugs in the United States may be found in Ref. 221.

Table 15 gives a sampling of other pharmaceuticals derived from hydrazine. Cefazolin, a thiadiazole tetrazole derivative, is one of the most widely used antibacterial drugs in U.S. hospitals. Procarbazine, an antineoplastic, is a monomethylhydrazine derivative (222). Fluconazole has shown some promise in the treatment of AIDS-related fungal infections. Carbidopa is employed in the treatment of Parkinson's disease. Furazolidone is a veterinarian antibacterial.

Hydrazine based pharmaceuticals continue to be among some of the most important new drugs in recent years. Among these are alprazolam for anxiety, zaleplon for sleep disorders, celecoxihib for pain relief and sidenafil and vardenafil for erectile disfunction.

Table 15. **Pharmaceutical Chemicals Based on Hydrazine**

Generic name	CAS Registry Number	Chemical type	Trade name	Producers	Use
carbidopa	[28860-95-9]	alkylhydrazine	Lodosyn	Merck	decarboxylase inhibitor
cefazolin	[25953-19-9]	tetrazole	Ancef, Kefzol	Smith Kline, Eli Lilly	antibacterial
fluconazole	[86386-73-4]	triazole	Diflucan	Pfizer	meningitis, antifungal
furazolidone	[67-45-8]	hydrazone		Teva (Israel)	antibacterial (vet)
hydralazine	[304-20-1]	phthalazine	Apresoline	Ciba-Geigy	antihypertensive
isoniazid	[54-85-3]	hydrazide	Cotinazin, Nydrazid	Pfizer, Squibb	tuberculostat
procarbazine	[366-70-1]	alkylhydrazine	Matulane	Hoffmann-LaRoche	antineoplastic
terconazole	[67915-31-5]	triazole		Janssen	antifungal
triazolam	[28911-01-5]	triazole	Halcion	Upjohn	sedative
celecoxihib	[169590-42-5]	pyrazole	Celebrix	Searle	pain relief
zaleplon	[151319-34-5]	pyrazole	Sonata	Wyeth-Ayerst	sleep disorder
alprazolam	[28981-97-7]	triazole	Xanax	Pfizer	anxiety
sidenafil	[139755-83-2]	pyrazole	Viagara	Pfizer	erctile dysfunction
vardenafil	[224785-90-4]	pyrazole	Levitra	Bayer	erectile dysfunction

Hydrazine sulfate [10034-93-2], $N_2H_4 \cdot H_2SO_4$, originally advanced by the Syracuse Cancer Research Institute for treatment of cancerous cachexia and tumor inhibition (223), now has Investigational New Drug (IND) status in the United States. Clinical evaluations are under way at various institutions such as Harbor-UCLA Medical Center (224) and the Mayo Clinic. After extensive trials, hydrazine sulfate has been approved as an anticancer drug in Russia (225).

10.6. Polymers. Polymers based on hydrazine include polyureylenes, polyacylsemicarbazides, polyhydrazides, polyoxadiazoles, and polyaminotriazoles. Aromatic polyhydrazides show excellent dyeability. As films, these materials exhibit a high degree of semipermeability to water, suggesting application as reverse osmosis (qv) membranes for the desalinization of seawater (227). Polyoxadiazoles fibers have been made from hydrazine–terephthalic acid copolymer [27027-96-9] and hydrazine–isophthalic acid–terephthalic acid copolymer [27924-75-0]. Dihydrazides have been patented as epoxy curing agents and chain extenders for polyurea polymers (228). Diacyl hydrazines are stabilizers for polyesters against thermal degradation (229) and similar compounds act as uv absorbers and heat stabilizers (qv) for plastics (230).

10.7. Other Uses. Fuel cells (qv) based on the reaction of hydrazine and oxygen or hydrogen peroxide have been studied for several decades (231). Reactions in this cell involve the anodic oxidation of hydrazine and cathodic reduction of the oxidizing agent in a potassium hydroxide electrolyte, generally on proprietary electrodes. The oxygen-based cell has a theoretical standard potential of 1.56 V. These cells operate quietly, at moderate (40–55°C) temperatures, and contain fairly dilute aqueous solutions of hydrazine. The products of reaction, nitrogen, and water, are innocuous. All of these factors have made such cells interesting for military applications, but civilian use has been hampered by the high cost of hydrazine.

Many hydrazine derivatives find application in photography and other reprographic techniques. Heterocyclics such as triazoles, tetrazoles, tetrazolium salts, and 2,5-dimercapto-1,3,4-thiadiazole are used as stabilizers, fog-inhibitors, and spectral sensitizers. Pyrazoles and pyrazolones are coupling agents. Metal complexes based on formazans are used for textile dyeing, color photography (qv), and inks (qv) (231). Judging from the patent literature, a great deal of work is being done with hydrazine derivatives in these areas. The vast majority of this effort is in Japan.

Many hydrazones and azines are colored and useful as dyestuffs. Examples are 2-hydroxynaphthazine, a yellow fluorescent dye (Lumogen LT Bright Yellow), and the pyridon–azino–quinone class of red-violet dyes. Numerous hydrazine derivatives are antioxidants and stabilizers by virtue of their reducing and chelating powers.

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