

CAPROLACTAM

Caprolactam [105-60-2] (2-oxohexamethylenimine, hexahydro-2*H*-azepin-2-one) is one of the most widely used chemical intermediates. However, almost all of the annual production of 3.0×10^6 t is consumed as the monomer for nylon-6 fibers and plastics (see Fibers survey; Polyamides, plastics). Cyclohexanone, which is the most common organic precursor of caprolactam, is made from benzene by either phenol hydrogenation or cyclohexane oxidation (see Cyclohexanol and cyclohexanone). Reaction with ammonia-derived hydroxylamine forms cyclohexanone oxime, which undergoes molecular rearrangement to the seven-membered ring ϵ -caprolactam.

Caprolactam was first successfully polymerized to Perlon in 1938 by I. G. Farben and the associated technology was acquired as a part of postwar reparations by the Western Allies and the former USSR (1). By 1965 other countries, eg, Italy and Japan, had developed their own caprolactam processes, each involving nitrosation of an aliphatic ring.

In the United States in 1992, annual caprolactam production was about 0.6×10^6 t: 45% by Allied-Signal, Inc.; 30%, BASF; 25%, DSM.

1. Physical Properties

Caprolactam, mol wt 113.16, is a white, hygroscopic, crystalline solid at ambient temperature, with a characteristic odor. It is very soluble in water and in most common organic solvents and is sparingly soluble in high molecular weight aliphatic hydrocarbons. Molten caprolactam is a powerful solvent for polar and nonpolar organic chemicals. Selected physical properties and solubilities of caprolactam are listed in Tables 1 and 2, respectively.

The vapor pressure values have been calculated at the indicated temperatures using the relationship derived from experimental data at Pennsylvania State University, and a critical review of literature references (5). This study is a part of the effort by the American Institute of Chemical Engineers (AIChE) to obtain accurate data through their Design Institute for Physical Property Data (DIPPR).

The vapor pressure for the solid at 25°C has been calculated from the value for the liquid at 70°C and the heats of vaporization and fusion using the Clausius-Clapeyron relationship.

The low melting point of caprolactam and its stability and low viscosity form the basis for commercial transportation practice: caprolactam is handled as a liquid in insulated tank cars or trucks.

The infrared spectrum of caprolactam has been given (3). Melting point data for the caprolactam–water system, as shown in Figure 1, are indicative of successful purification of caprolactam by crystallization from aqueous solution; such purification is very effective for separating and rejecting polar impurities.

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Table 1. Physical Properties of Caprolactam $\text{CH}_2(\text{CH}_2)_4\text{CONH}$

Properties	Values	References
melting point, °C	69.3	2
density (at 77°C), g/cm ³	1.02	3
bulk density, kg/m ³	600–700	(3, 4)
vapor pressure, kPa ^a		
at 270°C	100.6	5
at 180°C	8.13	5
at 150°C	2.62	5
at 130°C	1.10	5
at 115°C	0.53	5
at 70°C	0.032	5
at 25°C (solid)	0.0004	5
refractive index		
at 40°C	1.4935	(3, 6)
at 31°C	1.4965	
viscosity, mPa·s, (=cP)		
at 70°C	12.3	4
at 78°C	9	3
at 80°C	8.5	4
at 90°C	6.1	4
specific heat, J/(kg·K) ^b		
solid		
at 25°C	1380	3
at 28.5°C	1340	4
at 35°C	1420	3
liquid		
at 70°C	2117	3
at 80°C	2269	4
at 110°C	2412	4
at 140°C	2504	4
at 178°C	2608	4
vapor		
at 100°C	1640	7
thermal conductivity, W/(m·K)	0.169	7
heat of fusion, J/g ^c	135.9	8
heat of vaporization at 80°C, J/g ^c	580	5
heat of combustion (liquid at 25°C), J/g ^c	–31,900	(2, 7)
heat of formation (liquid at 25°C), J/g ^c	–2,840	(2, 7)
flash point (closed cup), °C	125	(7, 9)
fire point, °C	140	(7, 9)

^aTo convert kPa to mm Hg, multiply by 7.5.

^bTo convert J/(kg·K) to cal/(g·°C), divide by 4184.

^cTo convert J to cal, divide by 4.184.

2. Reactions

Caprolactam is an amide and, therefore, undergoes the reactions of this class of compounds. It can be hydrolyzed, *N*-alkylated, *O*-alkylated, nitrosated, halogenated, and subjected to many other reactions (3). Caprolactam is readily converted to high molecular weight, linear nylon-6 polymers. Through a complex series of reactions, caprolactam can be converted to the biologically and nutritionally essential amino acid L-lysine (10) (see Amino acids).

Table 2. Solubility of Caprolactam^a

Solvent	Temperature, °C	Solubility, g/100 g solvent
water	25	525
1,2,3-trichloropropane	18	95
1,2-dichloroethane	18	95
1,4-dichlorobutane	10	85
1,3-dichloropropane	18	90
cyclohexane	20	2
	30	2.4
	40	7.3
	50	22.7
toluene	20	35
	30	58
	40	104
	50	198
cyclohexanol	20	82
	30	111
	40	154
	50	223
cyclohexanone	20	53
	30	73
	40	120
	50	214
methyl ethyl ketone	20	53
	30	84
	40	145
	50	280
ethyl acetate	20	32
	30	50
	40	94
	50	195
<i>p</i> -xylene	20	16
	30	37
	40	75
	50	163

^aRefs. 3 and 7.

3. Manufacture

All commercial processes for the manufacture of caprolactam are based on either toluene or benzene, each of which occurs in refinery BTX-extract streams (see BTX processing). Alkylation of benzene with propylene yields cumene (qv), which is a source of phenol and acetone; ca 10% of U.S. phenol is converted to caprolactam. Purified benzene can be hydrogenated over platinum catalyst to cyclohexane; nearly all of the latter is used in the manufacture of nylon-6 and nylon-6,6 chemical intermediates. A block diagram of the five main process routes to caprolactam from basic raw materials, eg, hydrogen (which is usually prepared from natural gas) and sulfur, is given in Figure 2.

3.1. Allied-Signal Process

Cyclohexanone [108-94-1] is produced in 98% yield at 95% conversion by liquid-phase catalytic hydrogenation of phenol. Hydroxylamine sulfate is produced in aqueous solution by the conventional Raschig process, wherein

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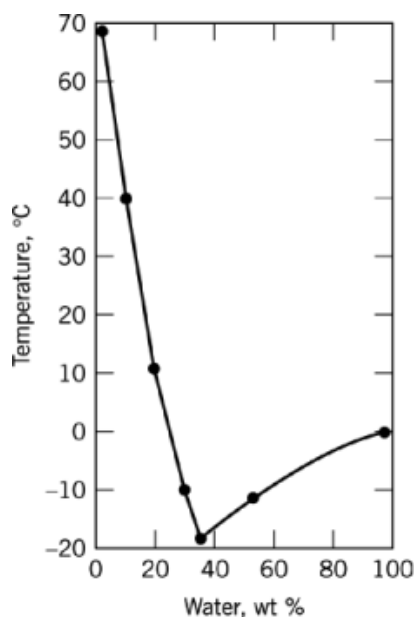
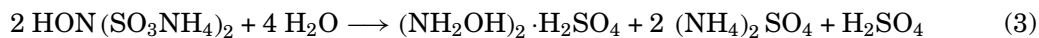
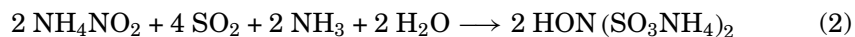
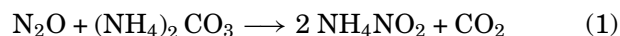
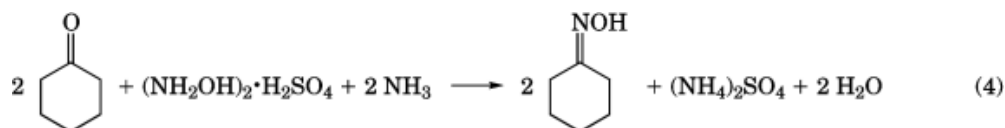


Fig. 1. Melting point data for the caprolactam–water system.

NO_x from the catalytic air oxidation of ammonia is absorbed in ammonium carbonate solution as ammonium nitrite (eq. 1). The latter is reduced with sulfur dioxide to hydroxylamine disulfonate (eq. 2), which is hydrolyzed to acidic hydroxylamine sulfate solution (eq. 3).



Simultaneous neutralization and reaction produce cyclohexanone oxime [100-64-1] (eq. 4).



Concentrations are controlled to yield a molten oxime product layer and a saturated (ca 40 wt %) ammonium sulfate solution; ca 125% (theoretical) ammonium sulfate or 2.9 kg/kg caprolactam is produced as a result of side reactions in the hydroxylamine synthesis.

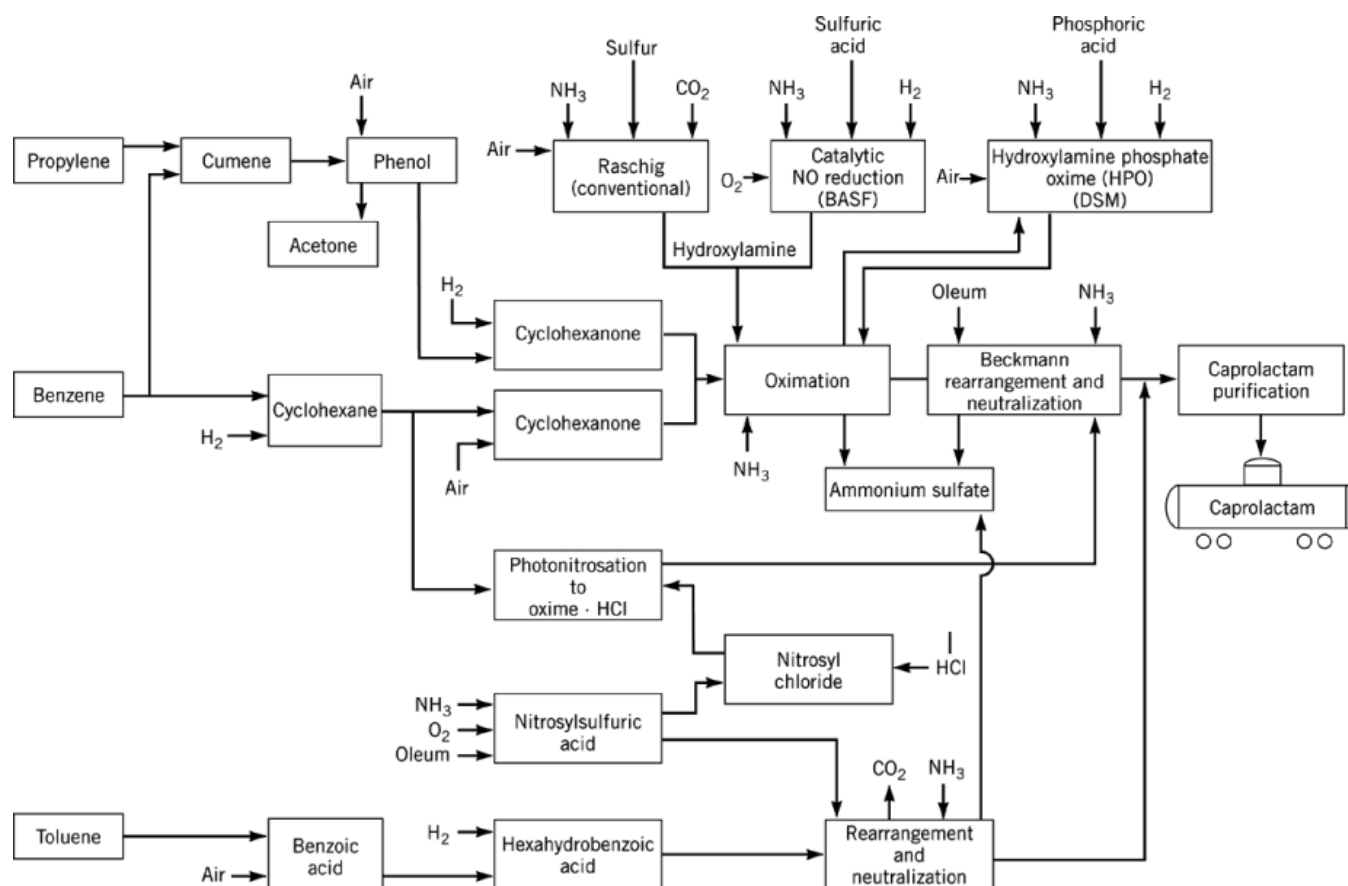
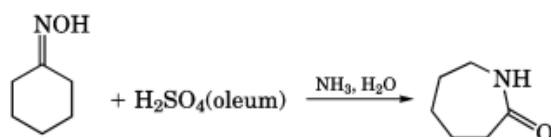


Fig. 2. Caprolactam processes.

Cyclohexanone oxime is converted quantitatively to caprolactam by Beckmann rearrangement in the presence of oleum, which is of sufficient strength to consume the several percent water in the molten oxime. The reaction mass is neutralized with aqueous ammonia to a crude caprolactam layer and a saturated solution of ammonium sulfate. Approximately 1.5 kg of the total 4.4 kg ammonium sulfate per kilogram of caprolactam is produced in this step. Purification is by multistage vacuum crystallization from aqueous solution in nearly quantitative yield.



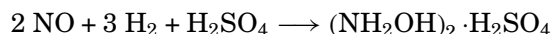
3.2. BASF

In the Badische process, cyclohexanone is produced by liquid-phase catalytic air oxidation of cyclohexane to KA oil, which is a mixture of cyclohexanone and cyclohexanol, and is followed by vapor-phase catalytic

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dehydrogenation of the cyclohexanol in the mixture. Overall yields range from 75% at 10% cyclohexane conversion to 80% at 5% cyclohexane conversion.

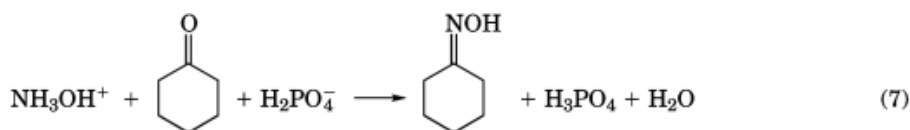
Hydroxylamine sulfate is produced by direct hydrogen reduction of nitric oxide over platinum catalyst in the presence of sulfuric acid. Only 0.9 kg ammonium sulfate is produced per kilogram of caprolactam, but at the expense of hydrogen consumption (11). A concentrated nitric oxide stream is obtained by catalytic oxidation of ammonia with oxygen. Steam is used as a diluent in order to avoid operating within the explosive limits for the system. The oxidation is followed by condensation of the steam. The net reaction is



The formation of oxime and rearrangement to caprolactam are conventional. The rearrangement produces 1.5 kg of the total 2.4 kg by-product ammonium sulfate per kilogram of caprolactam. Purification is accomplished by vacuum distillation. A similar caprolactam process is offered by Inventa (11).

3.3. Dutch State Mines (Stamicarbon)

Vapor-phase, catalytic hydrogenation of phenol to cyclohexanone over palladium on alumina, licensed by Stamicarbon, the engineering subsidiary of DSM, gives a 95% yield at high conversion plus an additional 3% by dehydrogenation of coproduct cyclohexanol over a copper catalyst. Cyclohexane oxidation, an alternative route to cyclohexanone, is used in the United States and in Asia by DSM. A cyclohexane vapor-cloud explosion occurred in 1975 at a co-owned DSM plant in Flixborough, UK (12); the plant was rebuilt but later closed. In addition to the conventional Raschig process for hydroxylamine, DSM has developed a hydroxylamine phosphate-oxime (HPO) process for cyclohexanone oxime; no by-product ammonium sulfate is produced. Catalytic ammonia oxidation is followed by absorption of NO_x in a buffered aqueous phosphoric acid solution (eq. 5), hydrogen reduction over palladium catalyst (eq. 6), and two-phase reaction with cyclohexanone in toluene solvent to an oxime-toluene phase and a recycled aqueous phase (eq. 7) (13).

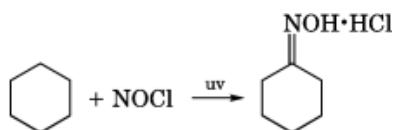


The oxime is converted to caprolactam by Beckmann rearrangement; neutralization with ammonia gives ca 1.8 kg ammonium sulfate per kilogram of caprolactam. Purification is by vacuum distillation. A no-sulfate, extraction process has been described, but incineration of the ammonium bisulfate recovers only sulfur values and it is not practiced commercially (14).

3.4. Toray

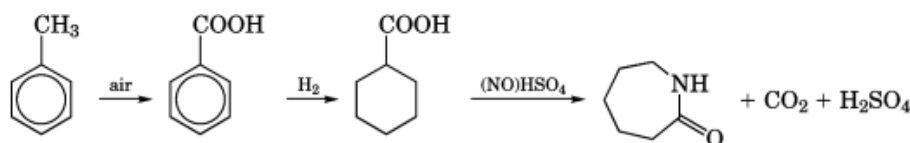
The photonitrosation of cyclohexane or PNC process results in the direct conversion of cyclohexane to cyclohexanone oxime hydrochloride by reaction with nitrosyl chloride in the presence of uv light (15) (see Photochemical technology). Beckmann rearrangement of the cyclohexanone oxime hydrochloride in oleum results in the

evolution of HCl, which is recycled to form NOCl by reaction with nitrosylsulfuric acid. The latter is produced by conventional absorption of NO_x from ammonia oxidation in oleum. Neutralization of the rearrangement mass with ammonia yields 1.7 kg ammonium sulfate per kilogram of caprolactam. Purification is by vacuum distillation. The novel chemistry is as follows:



3.5. Snia Viscosa

Catalytic air oxidation of toluene gives benzoic acid (qv) in ca 90% yield. The benzoic acid is hydrogenated over a palladium catalyst to cyclohexanecarboxylic acid [98-89-5]. This is converted directly to crude caprolactam by nitrosation with nitrosylsulfuric acid, which is produced by conventional absorption of NO_x in oleum. Normally, the reaction mass is neutralized with ammonia to form 4 kg ammonium sulfate per kilogram of caprolactam (16). In a no-sulfate version of the process, the reaction mass is diluted with water and is extracted with an alkylphenol solvent. The aqueous phase is decomposed by thermal means for recovery of sulfur dioxide, which is recycled (17). The basic process chemistry is as follows:



Purification involves chemical treatment and vacuum distillation.

4. Economic Aspects

Estimated worldwide annual caprolactam production capacities are shown in Table 3. New plant construction is planned in Korea, Taiwan, India, China, and Indonesia. Total new capacity over the next 10 years could exceed 500,000 tons per year.

Worldwide caprolactam demand increased about 2% per year during the 1980s, and similar growth is expected into the 1990s. Because of the new capacity coming on-stream in the Far East, production will stay basically flat in the United States and in Europe.

The caprolactam prices shown in Table 4 are for large contracts of molten material. Flaked material is sold in bags, either in small lots or for export, and costs ca \$0.10/kg more than the molten product. Exports normally have risen during periods of recession in the United States, eg, 1970, 1975, 1980, and 1990.

DSM America produces caprolactam only for merchant sales, both domestic and foreign. BASF is a customer, following acquisition of Enka's United States fiber and plastics plants, and also a captive producer of caprolactam. Allied-Signal's production is primarily captive for nylon-6 fibers and plastics, but substantial amounts are supplied to the export market.

Table 3. Estimated Worldwide Annual Production Capacity of Caprolactam^a

Producer	Location	Annual capacity, 10 ³ t			
		1980	1985	1990	1995
United States					
Allied-Signal	Hopewell, Va.	220	250	300	320
BASF	Freeport, Tex.	160	160	180	225
DSM	Augusta, Ga.	170	180	160	160
Subtotal		550	590	640	705
Western Europe					
BASF	Antwerp, Belgium	140	140	140	140
	Ludwigshafen, Germany	140	140	140	140
Bayer	Antwerp, Belgium	90	90	110	110
	Uerdingen, Germany	60	60		
DSM	Geleen, The Netherlands	200	200	230	230
	Flixborough, UK	65			
Nypro	Torviscosa, Italy	15	15	15	15
	Manfredonia, Italy	80	80	100	100
SNIA/Montedipe	Porto Marghera, Italy	75	75	80	80
	Spain, Switzerland	35	35	45	45
other		35	35	45	45
Subtotal		900	835	860	860
Eastern Europe					
Polimex	Poland	110	110	110	110
Techmashimport	Russia	550	550	550	550
Chemopetrol	Czechoslovakia	45	70	70	70
VEB Leunawerke	Germany	60	60	75	75
other	Romania, Bulgaria, Hungary, Yugoslavia	80	90	90	90
Subtotal		845	880	895	895
Japan					
Japan Lactam (Sumitomo)	Nihama, Japan	60	60	75	75
Mitsubishi Chem.	Kurosaki, Japan	80	80	100	100
Toray Ind.	Nagoya, Japan	130	130	145	145
Ube Ind.	Ube/Sakai, Japan	160	160	180	180
Subtotal		430	430	500	500
Latin America					
Univex	Salamanca, Mexico	45	45	70	70
Nitrocarbano	Camacari, Brazil	35	55	55	55
Monomeros	Colombia	25	25	25	25
Subtotal		105	125	150	150
Asia					
Hanook Caprolactam	Ulsan, Korea	40	80	80	80
Hanhua Caprolactam	Korea				80
Chung Tai	Taipei, Taiwan	90	100	110	110
FCFC	Taiwan				120
other	China, India, Turkey, Indonesia, Thailand	55	55	100	300
Subtotal		185	235	290	690
Total		3015	3095	3335	3800

^aRef. 18.

Table 4. U.S. Caprolactam Production, Price, and Exports^a

Year	Production, 10 ³ t	Price (molten), \$/kg	Exports	
			10 ³ t	\$/kg
1963	85	1.01		
1965	131	0.91		
1967	149	0.73	7.0	0.48
1969	218	0.54	18	0.40
1971	261	0.54	18	0.42
1973	298	0.54	8.6	0.48
1975	324	1.07	17	0.87
1977	393	1.11	9.5	0.88
1979	429	1.42	16	1.22
1980	412	1.69	30	1.65
1981	422	1.85	24	1.43
1982	360	1.78	28	1.32
1983	440	1.74	12	1.32
1984	467	1.83	29	1.34
1985	495	1.96	28	1.30
1986	504	1.96	13	1.23
1987	526	2.01	34	1.43
1988	573	2.13	68	1.61
1989	596	2.22	66	1.56
1990 ^b	610	2.10	75	1.90

^aRefs. (19, 20).^b1990 data, estimated.

5. Specifications and Analysis

The main contaminant and its concentration in commercial caprolactam usually is water at <0.1 wt%. Anhydrous caprolactam is produced in small quantity for use in anionic polymerization processes. Commercial product of very high purity is required by the users, ie, the fibers and plastics producers, most of whom utilize technologically advanced processes that are sensitive to monomer quality.

Commercial specifications are listed in Table 5. There are differences in the methods used by producers to measure color and oxidizable impurities. Color is measured from aqueous solutions either as transmission of light of a certain wavelength or by visual comparison with standard solutions. Permanganate oxidizable impurities are determined by spectrophotometric measurement of manganese dioxide, which forms upon addition of potassium permanganate (21), or according to the time taken by a sample containing permanganate to match the color of a reference solution visually. Values of 10,000 s or greater are common. Generally, moisture is measured by Karl Fischer titration; bases or acids by titration; water insolubles, visually; and iron, spectrophotometrically as the *o*-phenanthroline complex. Residual cyclohexanone oxime is measured colorimetrically after undergoing hydrolysis to hydroxylamine, oxidation by iodine to nitrous acid, diazotization of added sulfanilic acid, and formation of a colored compound by a coupling reaction of the diazonium salt with *N*-(1-naphthyl)ethylenediamine [537-09-7] (22). Chromatographic techniques have been used more recently. More details on methods of analysis, assay, and determination of impurities have been given (4, 7).

Flaked caprolactam has been shipped in multiwall, laminated paper bags with separable polyethylene liner, but single-ply polyethylene bags are becoming required for automatic equipment. The bags should be stored in a dry environment. Because molten caprolactam reacts readily with oxygen it is stored at ca 75°C, ie, just above the melting point, in insulated vessels and blanketed with nitrogen containing less than 5 ppm oxygen. Usually it is transported in aluminum or stainless-steel tank trailers or railroad cars.

Table 5. Caprolactam Specifications^a

Property	Value
solidifying point (dry basis), °C	69.0 min
color, APHA	5 max
permanganate number, s	10,000 min
moisture, %	0.10 max
iron (as Fe), ppm	0.5 max
volatile bases (as NH ₃), ppm	10 max
cyclohexanone oxime, ppm	10 max
free alkalinity, meq/kg	0 (neutral) min, 0.04 max

^aTypical.**Table 6. Biological Effects of Caprolactam**

Lethal-dose data ^a	Value
LD ₅₀ (oral, rat), mg/kg	2140
LD _{Lo} (skin, rabbit), mg/kg	1410
LD _{Lo} (intraperitoneal, rat), mg/kg	900
LD _{Lo} (inhalation, human), ppm	100 ^b
LD _{Lo} (subcutaneous, mouse), mg/kg	750
LD _{Lo} (subcutaneous, frog), mg/kg	2800

^aRef. 23.^bIrritant; olfactory threshold is 0.3 mg/m³ (2).

6. Health and Safety Factors

Caprolactam has a low order of toxicity, as shown by the results of numerous and various toxicological tests in Table 6, and it presents no appreciable health hazard if it is handled properly. Prolonged exposure to dust or vapors causes irritation of eyes, mucous membranes, and skin; inhalation may cause irritation of the respiratory tissues. Skin contact, if prolonged, can lead to dermatosis causing a reddening and tightening of the skin, the appearance and sensation of which is similar to sunburn (24). A thorough wash with water, in which caprolactam is very soluble, or with soap and water, normally is sufficient to remove caprolactam from contaminated parts of the body.

Threshold limit values for caprolactam dust and vapor are 1 mg/m³ and 4.3 ppm (20 mg/m³), respectively, although the American Conference of Governmental Industrial Hygienists (ACGIH) has a notice of intended change (1991–1992) of 1 mg/m³ for dust and 5 ppm (23 mg/m³) for vapor with short-term exposure limits (STELs) of 3 mg/m³ and 10 ppm for dust and vapor, respectively (time-weighted averages) (25). Caprolactam has been extensively tested for its mutagenic potential (26). Based on the overall weight of evidence, caprolactam would be considered nonmutagenic. It was also found to be noncarcinogenic in a National Cancer Institute bioassay using F344 rats and B6C3F1 mice (27). Caprolactam is not teratogenic (F344 rats and rabbits) (28). In a three-generation reproduction study conducted in rats, the only effects noted were slight body weight reductions in pups and dams at a high maternally toxic dose (10,000 ppm or 500 mg/kg/day in the diet). All pregnancy and fertility indexes were unaffected by treatment. Based on these results, caprolactam should not pose a hazard to reproduction and fertility and would not be considered a developmental toxicant (29).

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WILLIAM B. FISHER L. CRESCENTINI
Allied-Signal, Inc.

Related Articles

Polyamides, fibers; Polyamides, plastics; Cyclohexanone and cyclohexanone; BTX processing