ACRYLONITRILE

1. Introduction

Prior to 1960, acrylonitrile [107-13-1] (also called acrylic acid nitrile, propylene nitrile, vinyl cyanide, propenoic acid nitrile) was produced commercially by processes based on either ethylene oxide and hydrogen cyanide or acetylene and hydrogen cyanide. The growth in demand for acrylic fibers, starting with the introduction of Orlon by Du Pont around 1950, spurred efforts to develop improved process technology for acrylonitrile manufacture to meet the growing market (see FIBERS, ACRYLIC). This resulted in the discovery in the late 1950s by Sohio (1) and also by Distillers (2) of a heterogeneous vapor-phase catalytic process for acrylonitrile by selective oxidation of propylene and ammonia, commonly referred to as the propylene ammoxidation process. Commercial introduction of this lower cost process by Sohio in 1960 resulted in the eventual displacement of all other acrylonitrile manufacturing processes. Today over 90% of the more than 4,000,000 metric tons produced worldwide each year are made using the Sohio-developed ammoxidation process. Acrylonitrile is among the top 50 chemicals produced in the United States as a result of the tremendous growth in its use as a starting material for a wide range of chemical and polymer products. Acrylic fibers remain the largest use of acrylonitrile; other significant uses are in resins and nitrile elastomers and as an intermediate in the production of adiponitrile and acrylamide.

2. Physical Properties

Acrylonitrile (C_3H_3N, mol wt = 53.064) is an unsaturated molecule having a carbon–carbon double bond conjugated with a nitrile group. It is a polar molecule because of the presence of the nitrogen heteroatom. There is a partial shift in the bonding electrons toward the more electronegative nitrogen atom, as represented by the following heterovalent resonance structures.

$$CH_2{=}CH{-}C{\equiv}N\!: \longleftrightarrow CH_2{=}CH{-}\overset{+}{C}{=}\underset{\cdot\cdot}{\overset{-}{N}}\!: \longleftrightarrow \overset{+}{C}H_2{-}CH{=}C{=}\underset{\cdot\cdot}{\overset{-}{N}}\!:$$

Tables 1 and 2 list some physical properties and thermodynamic information, respectively, for acrylonitrile (3–5).

Table 1. **Physical Properties of Acrylonitrile**

Property	Value
appearance/odor	clear, colorless liquid with faintly pungent odor
boiling point, °C	77.3
freezing point, °C	−83.5
density, 20°C, g/cm^3	0.806
volatility, 78°C, %	>99
vapor pressure, 20°C, kPa[a]	11.5
vapor density (air = 1)	1.8
solubility in water, 20°C, wt%	7.3
pH (5% aqueous solution)	6.0–7.5
critical values	
temperature, °C	246
pressure, MPa[b]	3.54
volume, cm^3/g	3.798
refractive index, $n^{25}{}_{\mathrm{D}}$	1.3888
dielectric constant, 33.5 MHz	38
ionization potential, eV	10.75
molar refractivity (D line)	15.67
surface tension, 25°C, mN/m (=dyn/cm)	26.6
dipole moment, C·m[c]	
liquid	1.171×10^{-29}
vapor	1.294×10^{-29}
viscosity, 25°C, mPa·s (=cP)	0.34

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

[b] To convert MPa to psi multiply by 145.

[c] To convert C·m to debye, divide by 3.336×10^{-30}

Table 2. **Thermodynamic Data**[a]

Property	Value
flash point, °C	0
autoignition temperature, °C	481
flammability limits in air, 25°C, vol %	
lower	3.0
upper	17.0
free energy of formation, ΔG°_g, 25°C, kJ/mol	195
enthalpy of formation, 25°C, kJ/mol	
$\Delta H^\circ_{\mathrm{g}}$	180
$\Delta H^\circ_{\mathrm{l}}$	147
heat of combustion, liquid, 25°C, kJ/mol	1761.5
heat of vaporization, 25°C, kJ/mol	32.65
molar heat capacity, kJ/(kg·K)	
liquid	2.09
gas at 50°C, 101.3 kPa[b]	1.204
molar heat of fusion, kJ/mol	6.61
entropy, S, gas at 25°C, 101.3 kPa[b], kJ/(mol·K)	274

[a] To convert kJ to kcal divide by 4.184.

[b] 101.3 kPa = 1 atm.

Table 3. **Azeotropes of Acrylonitrile**

Azeotrope	Boiling point, °C	Acrylonitrile concentration, wt %
water	71.0	88
isopropyl alcohol	71.6	56
benzene	73.3	47
methanol	61.4	39
carbon tetrachloride	66.2	21
tetrachlorosilane	51.2	11
chlorotrimethylsilane	57.0	7

Table 4. **Solubilities of Acrylonitrile in Water**

Temperature, °C	Acrylonitrile in water, wt %	Water in acrylonitrile, wt %
−50		0.4
−30		1.0
0	7.1	2.1
10	7.2	2.6
20	7.3	3.1
30	7.5	3.9
40	7.9	4.8
50	8.4	6.3
60	9.1	7.7
70	9.9	9.2
80	11.1	10.9

Acrylonitrile is miscible in a wide range of organic solvents, including acetone, benzene, carbon tetrachloride, diethyl ether, ethyl acetate, ethylene cyanohydrin, petroleum ether, toluene, some kerosenes, and methanol. Compositions of some common azeotropes of acrylonitrile are given in Table 3. Table 4 presents the solubility of acrylonitrile in water as a function of temperature (6). Vapor–liquid equilibria for acrylonitrile in combination with acetonitrile, acrolein, HCN, and water have been published (6–9). Table 5 gives the vapor pressure of acrylonitrile over aqueous solutions.

Table 5. **Acrylonitrile Vapor Pressure over Aqueous Solutions at 25°C**

Acrylonitrile, wt %	Vapor pressure, kPa[a]
1	1.3
2	2.9
3	5.3
4	6.9
5	8.4
6	10.0
7	10.9

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

Acrylonitrile has been characterized using infrared, Raman, and ultraviolet spectroscopies, electron diffraction, and mass spectroscopy (10–18).

3. Chemical Properties

Acrylonitrile undergoes a wide range of reactions at its two chemically active sites, the nitrile group and the carbon–carbon double bond. Detailed descriptions of specific reactions have been given (19, 20). Acrylonitrile polymerizes readily in the absence of a hydroquinone inhibitor, especially when exposed to light. Polymerization is initiated by free radicals, redox catalysts, or bases and can be carried out in the liquid, solid, or gas phase. Homopolymers and copolymers are most easily produced using liquid-phase polymerization (see ACRYLONITRILE POLYMERS). Acrylonitrile undergoes the reactions typical of nitriles, including hydration with sulfuric acid to form acrylamide sulfate ($C_3H_5NO{\cdot}H_2SO_4$ [15497-99-1]), which can be converted to acrylamide (C_3H_5NO [79-06-1]) by neutralization with a base; and complete hydrolysis to give acrylic acid ($C_3H_4O_2$ [79-10-7]). Acrylamide (qv) is also formed directly from acrylonitrile by partial hydrolysis using copper-based catalysts (21–24); this has become the preferred commercial route for acrylamide production. Industrially important acrylic esters can be formed by reaction of acrylamide sulfate with organic alcohols. Methyl acrylate ($C_4H_6O_2$ [96-33-3]) has been produced commercially by the alcoholysis of acrylamide sulfate with methanol. Reactions at the activated double bond of acrylonitrile include Diels-Alder addition to dienes, forming cyclic products; hydrogenation over metal catalysts to give propionitrile (C_3H_5N [107-12-0]) and propylamine (C_3H_9N [107-10-8]); and the industrially important hydrodimerization to produce adiponitrile ($C_6H_8N_2$ [111-69-3]) (25–27). Other reactions include addition of halogens across the double bond to produce dihalopropionitriles, and cyanoethylation by acrylonitrile of alcohols, aldehydes, esters, amides, nitriles, amines, sulfides, sulfones, and halides.

4. Manufacturing and Processing

Acrylonitrile is produced in commercial quantities almost exclusively by the vapor-phase catalytic propylene ammoxidation process developed by Sohio (28).

$$C_3H_6 + NH_3 + {}^3/_2\,O_2 \xrightarrow{\text{catalyst}} C_3H_3N + 3\,H_2O$$

A schematic diagram of the commercial process is shown in Figure 1. The commercial process uses a fluid-bed reactor in which propylene, ammonia, and air contact a solid catalyst at 400–510°C and 49–196 kPa (0.5–2.0 kg/cm^2) gauge. It is a single-pass process with about 98% conversion of propylene, and uses about 1.1 kg propylene per kg of acrylonitrile produced. Useful by-products from the process are HCN (about 0.1 kg per kg of acrylonitrile), which is used primarily in the manufacture of methyl methacrylate, and acetonitrile (about 0.03 kg per kg of acrylonitrile), a common industrial solvent. In the commercial operation the hot reactor effluent is quenched with water in a countercurrent

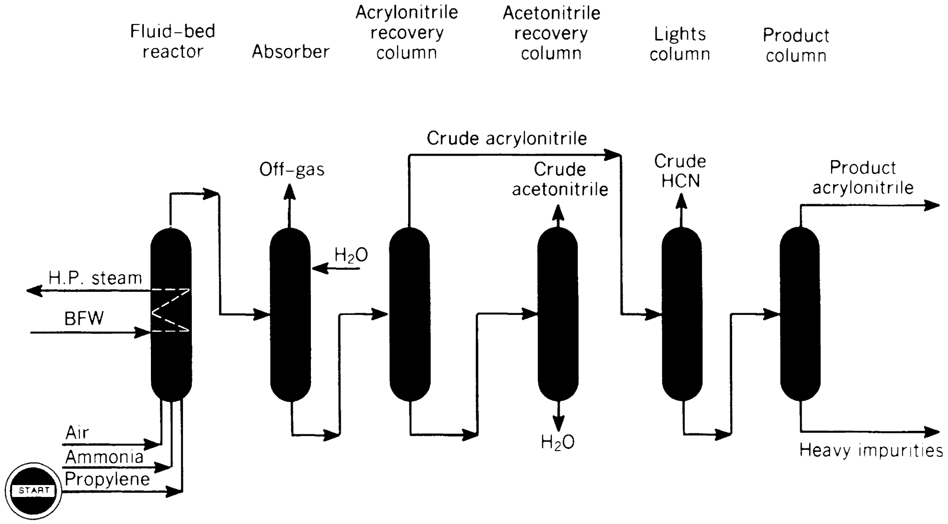

Fig. 1. Process flow diagram of the commercial propylene ammoxidation process for acrylonitrile. *BFW*, boiler feed water.

absorber and any unreacted ammonia is neutralized with sulfuric acid. The resulting ammonium sulfate can be recovered and used as a fertilizer. The absorber off-gas containing primarily N_2, CO, CO_2, and unreacted hydrocarbon is either vented directly or first passed through an incinerator to combust the hydrocarbons and CO. The acrylonitrile-containing solution from the absorber is passed to a recovery column that produces a crude acrylonitrile stream overhead that also contains HCN. The column bottoms are passed to a second recovery column to remove water and produce a crude acetonitrile mixture. The crude acetonitrile is either incinerated or further treated to produce solvent quality acetonitrile. Acrylic fiber quality (99.2% minimum) acrylonitrile is obtained by fractionation of the crude acrylonitrile mixture to remove HCN, water, light ends, and high boiling impurities. Disposal of the process impurities has become an increasingly important aspect of the overall process, with significant attention being given to developing cost-effective and environmentally acceptable methods for treatment of the process waste streams. Current methods include deep-well disposal, wet air oxidation, ammonium sulfate separation, biological treatment, and incineration (29).

Although acrylonitrile manufacture from propylene and ammonia was first patented in 1949 (30), it was not until 1959, when Sohio developed a catalyst capable of producing acrylonitrile with high selectivity, that commercial manufacture from propylene became economically viable (1). Production improvements over the past 30 years have stemmed largely from development of several generations of increasingly more efficient catalysts. These catalysts are multicomponent mixed metal oxides mostly based on bismuth–molybdenum oxide. Other types of catalysts that have been used commercially are based on iron–antimony oxide, uranium–antimony oxide, and tellurium–molybdenum oxide.

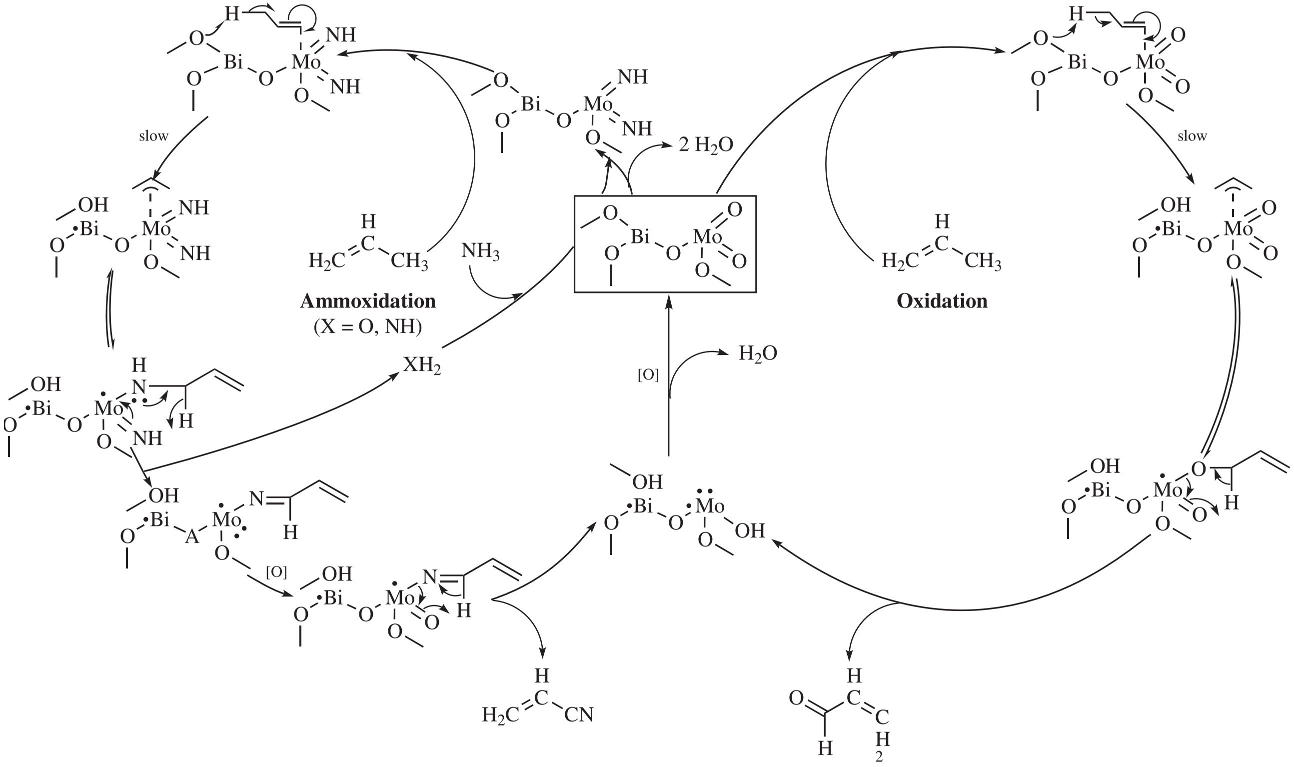

Fig. 2. Mechanism of selective ammoxidation and oxidation of propylene over bismuth molybdate catalysts (31).

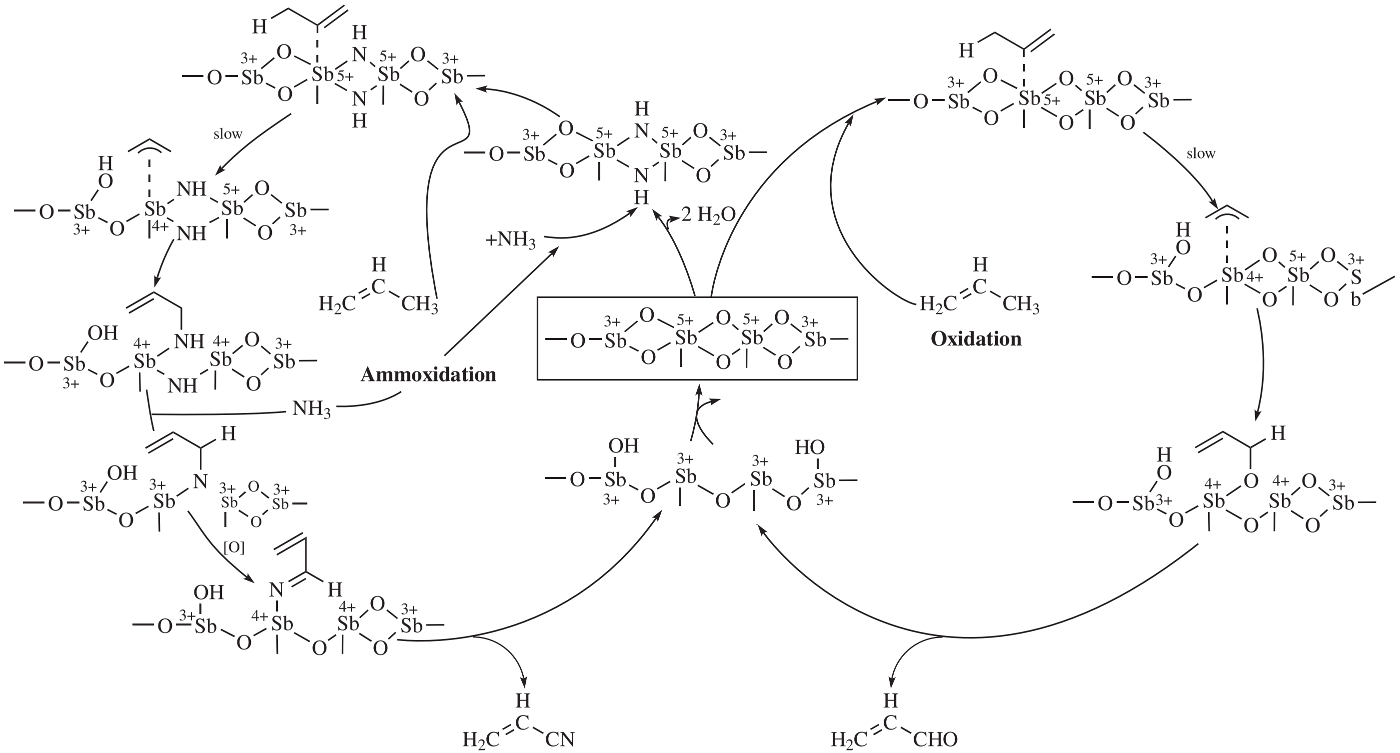

Fig. 3. Mechanism of selective ammoxidation and oxidation of propylene over antimonate catalysts (31).

Fundamental understanding of these complex catalysts and the surface-reaction mechanism of propylene ammoxidation has advanced substantially since the first commercial plant began operation. Mechanisms for selective ammoxidation of propylene over bismuth molybdate and antimonate catalysts are shown in Figures 2 and 3. The rate-determining step is abstraction of an α-hydrogen of propylene by an oxygen in the catalyst to form a π-allyl complex on the surface (31–33). Lattice oxygens from the catalyst participate in further hydrogen abstraction, followed by oxygen insertion to produce acrolein in the absence of ammonia, or nitrogen insertion to form acrylonitrile when ammonia is present (34–36). The oxygens removed from the catalyst in these steps are replenished by gas-phase oxygen, which is incorporated into the catalyst structure at a surface site separate from the site of propylene reaction. In the ammoxidation reaction, ammonia is activated by an exchange with O^{2-} ions to form isoelectronic NH^{2-} moieties according to the following:

$$NH_3 + O^{2-} \longrightarrow NH^{2-} + H_2O$$

These are the species inserted into the allyl intermediate to produce acrylonitrile.

The active site on the surface of selective propylene ammoxidation catalyst contains three critical functionalities associated with the specific metal components of the catalyst (37–39): an α-H abstraction component such as Bi^{3+}, Sb^{3+}, or Te^{4+}; an olefin chemisorption and oxygen or nitrogen insertion component such as Mo^{6+} or Sb^{5+}; and a redox couple such as Fe^{2+}/Fe^{3+} or Ce^{3+}/Ce^{4+} to enhance transfer of lattice oxygen between the bulk and surface of the catalyst. The surface and solid-state mechanisms of propylene ammoxidation catalysis have been determined using Raman spectroscopy (40, 41), neutron diffraction (42–44), x-ray absorption spectroscopy (45, 46), x-ray diffraction (47–49), pulse kinetic studies (36), and probe molecule investigations (50).

5. Obsolete Acrylonitrile Processes

Processes rendered obsolete by the propylene ammoxidation process (51) include the ethylene cyanohydrin process (52–54) practiced commercially by American Cyanamid and Union Carbide in the United States and by I. G. Farben in Germany. The process involved the production of ethylene cyanohydrin by the base-catalyzed addition of HCN to ethylene oxide in the liquid phase at about 60°C. A typical base catalyst used in this step was diethylamine. This was followed by liquid-phase or vapor-phase dehydration of the cyanohydrin. The liquid-phase dehydration was performed at about 200°C using alkali metal or alkaline earth metal salts of organic acids, primarily formates and magnesium carbonate. Vapor-phase dehydration was accomplished over alumina at about 250°C.

$$C_2H_4O + HCN \xrightarrow[\text{catalyst}]{\text{base}} HOC_2H_4CN \xrightarrow[-H_2O]{\text{catalyst}} C_3H_3N$$

A second commercial route to acrylonitrile used by Du Pont, American Cyanamid, and Monsanto was the catalytic addition of HCN to acetylene (55).

$$C_2H_2 + HCN \xrightarrow{\text{catalyst}} C_3H_3N$$

The reaction occurs by passing HCN and a 10:1 excess of acetylene into dilute hydrochloric acid at 80°C in the presence of cuprous chloride as the catalyst.

These processes use expensive C_2 hydrocarbons as feedstocks and thus have higher overall acrylonitrile production costs compared to the propylene-based process technology. The last commercial plants using these process technologies were shut down by 1970.

Other routes to acrylonitrile, none of which achieved large-scale commercial application, are acetaldehyde and HCN (56), propionitrile dehydrogenation (57, 58), and propylene and nitric oxide (59, 60):

$$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \xrightarrow{-H_2O} C_3H_3N$$

$$CH_3CH_2CN \longrightarrow C_3H_3N + H_2$$

$$4\,C_3H_6 + 6\,NO \longrightarrow 4\,C_3H_3N + 6\,H_2O + N_2$$

Numerous patents have been issued disclosing catalysts and process schemes for manufacture of acrylonitrile from propane. These include the direct heterogeneously catalyzed ammoxidation of propane to acrylonitrile using mixed metal oxide catalysts (61–64).

$$C_3H_8 + NH_3 + 2\,O_2 \xrightarrow{\text{catalyst}} C_3H_3N + 4\,H_2O$$

A two-step process involving conventional nonoxidative dehydrogenation of propane to propylene in the presence of steam, followed by the catalytic ammoxidation to acrylonitrile of the propylene in the effluent stream without separation, is also disclosed (65).

$$C_3H_8 \xrightarrow{\text{catalyst}} C_3H_6 + H_2 \xrightarrow[+NH_3]{+\frac{3}{2}\,O_2} C_3H_3N + 3\,H_2O + H_2$$

Because of the large price differential between propane and propylene, which has ranged from \$155/t to \$355/t between 1987 and 1989, a propane-based process may have the economic potential to displace propylene ammoxidation technology eventually. Methane, ethane, and butane, which are also less expensive than propylene, and acetonitrile have been disclosed as starting materials for acrylonitrile synthesis in several catalytic process schemes (66, 67).

6. Economic Aspects

The propylene-based process developed by Sohio was able to displace all other commercial production technologies because of its substantial advantage in

Table 6. **Worldwide Acrylonitrile Production[a], 10^3 t**

Region	1998 (Estimated)	1997
Western Europe	1,112	1,073
Eastern Europe	182	189
United States	1,324	1,493
Japan	730	729
Far East/Asia	841	779
Africa/Middle East	152	147
Latin America/Mexico	246	232
Total	*4,587*	*4,642*

[a] Ref. 71.

overall production costs, primarily due to lower raw material costs. Raw material costs less by-product credits account for about 60% of the total acrylonitrile production cost for a world-scale plant. The process has remained economically advantaged over other process technologies since the first commercial plant in 1960 because of the higher acrylonitrile yields resulting from the introduction of improved commercial catalysts. Reported per-pass conversions of propylene to acrylonitrile have increased from about 65% to over 80% (28, 68–70).

More than half of the worldwide acrylonitrile production is situated in Western Europe and the United States (Table 6). In the United States, production is dominated by BP Amoco Chemicals, with more than a third of the domes-

Table 7. **U.S. Acrylonitrile Producers[a]**

Company	Approximate capacity[b], 10^3 t/y
BP Amoco Chemicals	640
Solutia, Inc.	260
Sterling Chemicals	360
E. I. du Pont de Nemours & Co., Inc.	185
Cytec Industries	220
Total	*1665*

[a] Ref. 71.
[b] As of 1997.

Table 8. **U.S. Acrylonitrile Exports[a], 10^3 t**

Destination	1997	1996
Far East/Asia	334	378
Japan	92	107
Western Europe	91	57
Canada	7	6
Latin America/Mexico	82	50
Middle East/Africa	91	57
Total export	*697*	*655*

[a] Ref. 71.

Table 9. **Worldwide Acrylonitrile Demand, 10^3 t/yr**

Region	1998 (Estimated)	1997	1995	1990	1986
Western Europe	1109	1116	1045	1136	1187
Eastern Europe	141	150	171	311	261
Japan	726	723	674	664	640
North America	781	800	756	641	638
Far East	1297	1264	1025	646	462
Africa/Middle East	261	257	223	135	142
Latin America/Mexico	302	281	244	206	213
Total	*4617*	*4591*	*4138*	*3739*	*3543*

tic capacity (Table 7). Nearly one-half of the U.S. production was exported in 1997 (Table 8), with most going to Far East Asia. The percentage of U.S. production exported grew from around 10% in the mid-1970s to about 42% in 1997 since Far East Asian producers, especially in the People's Republic of China (PRC), have not been able to satisfy the increasing domestic demand in recent years. In addition, the higher propylene costs relative to the United States generally makes it more economical to import acrylonitrile from the United States than to install new domestic production. Nevertheless, additions to Far East Asian acrylonitrile production capacity have been made in the 1990's, notably in South Korea. Table 9 provides a breakdown of worldwide demand between 1986 and 1998. Growth in demand has averaged about 3.6% per year.

7. Analytical Methods and Specifications

Standard test methods for chemical analysis have been developed and published (72). Included is the determination of commonly found chemicals associated with acrylonitrile and physical properties of acrylonitrile that are critical to the

Table 10. **Commercial Specifications for Acrylonitrile**

Parameter	Specification
acetone, ppm, max	300
acetonitrile, ppm, max	500
aldehydes, ppm, max	50
color, APHA, max	15
distillation range, °C, min, ibp	74.2
°C, max, 97%	78.8
HCN, ppm, max	5
inhibitor, hydroquinone monomethyl ether, ppm	35–45
iron, ppm, max	0.10
nonvolatile matter, ppm, max	100
peroxides, ppm, max	0.2
pH, 5% aqueous	6.0–7.5
refractive index, $n^{25}{}_{\mathrm{D}}$	1.3891
water, wt %, max	0.2–0.5
purity, wt %, min	99.0

quality of the product (73–75). These include determination of color and chemical analyses for HCN, quinone inhibitor, and water. Specifications appear in Table 10.

8. Storage and Transport

Acrylonitrile must be stored in tightly closed containers in cool, dry, well-ventilated areas away from heat, sources of ignition, and incompatible chemicals. Storage vessels, such as steel drums, must be protected against physical damage, with outside detached storage preferred. Storage tanks and equipment used for transferring acrylonitrile should be electrically grounded to reduce the possibility of static spark-initiated fire or explosion. Acrylonitrile is regulated in the workplace by OSHA (29 CFR 1910).

Acrylonitrile is transported by rail car, barge, and pipeline. Department of Transportation (DOT) regulations require labeling acrylonitrile as a flammable liquid and poison. Transport is regulated under DOT 49 CFR 172.101. Bill of lading description is: Acrylonitrile, Inhibited, 3, 6.1, UN 1093, PGI, RQ.

9. Health and Safety Factors

Acrylonitrile is absorbed rapidly and distributed widely throughout the body following exposure by inhalation, skin contact or ingestion. However, there is little potential for significant accumulation in any organ with most of the compound being excreted primarily as metabolites in urine. Acrylonitrile is metabolized primarily by two pathways: conjugation with glutathione and oxidation. Oxidative metabolism leads to the formation of an epoxide, 2-cyanoethylene oxide, that is either conjugated with glutathione or directly hydrolyzed by epoxide hydrolase.

The acute toxicity of acrylonitrile is relatively high, with four-hour LC50s in laboratory animals ranging from 300 to 900 mg/m^3 and LD50s from 25 to 186 mg/kg (76, 77). Signs of acute toxicity observed in animals include respiratory tract irritation and two phases of neurotoxicity, the first characterized by signs consistent with cholinergic over-stimulation and the second being CNS dysfunction, resembling cyanide poisoning. In cases of acute human intoxication, effects on the central nervous system characteristic of cyanide poisoning and effects on the liver, manifested as increased enzyme levels in the blood, have been observed.

Acrylonitrile is a severe irritant to the skin, eyes, respiratory tract and mucous membranes. It is also a skin sensitizer.

Acrylonitrile is a potent tumorigen in the rat. Tumors of the central nervous system, ear canal, and gastrointestinal tract have been observed in several studies following oral or inhalation exposure. The mechanism of acrylonitrile's tumorigenesis in the rat and the relevance of these findings to humans is not clear. Available data are insufficient to support a consensus view on a plausible mode of action. There is evidence for weak genotoxic potential, but no evidence of DNA-adduct formation in target tissues. Recent work has provided indications that oxidative stress and resulting oxidative DNA damage may play a role.

There is extensive occupational epidemiology data on acrylonitrile workers. These investigations have not produced consistent, convincing evidence of an increase in cancer risk, although questions remain about the power of the database to detect small excesses of rare tumors. In 1998, The International Agency for Research on Cancer re-evaluated the cancer data for acrylonitrile and made a rare decision to downgrade the cancer risk classification (from probably carcinogen to humans to possibly carcinogenic to humans) based primarily on the growing epidemiology database (78).

Experimental evaluations of acrylonitrile have not produced any clear evidence of adverse effects on reproductive function or development of offspring at doses below those producing paternal toxicity.

The results of genotoxicity evaluations of acrylonitrile have been mixed. Positive findings *in vitro* have occurred mainly at exposures associated with cellular toxicity, and the most reliable *in vivo* tests have been negative.

Acrylonitrile will polymerize violently in the absence of oxygen if initiated by heat, light, pressure, peroxide, or strong acids and bases. It is unstable in the presence of bromine, ammonia, amines, and copper or copper alloys. Neat acrylonitrile is generally stabilized against polymerization with trace levels of hydroquinone monomethyl ether and water.

Acrylonitrile is combustible and ignites readily, producing toxic combustion products such as hydrogen cyanide, nitrogen oxides, and carbon monoxide. It forms explosive mixtures with air and must be handled in well-ventilated areas and kept away from any source of ignition, since the vapor can spread to distant ignition sources and flash back.

Federal regulations (40 CFR 261) classify acrylonitrile as a hazardous waste and it is listed as Hazardous Waste Number U009. Disposal must be in accordance with federal (40 CFR 262, 263, 264, 268, 270), state, and local regulations only at properly permitted facilities. It is listed as a toxic pollutant (40 CFR 122.21) and introduction into process streams, storm water, or waste water systems is in violation of federal law. Strict guidelines exist for clean-up and notification of leaks and spills. Federal notification regulations require that spills or leaks in excess of 100 lb (45.5 kg) be reported to the National Response Center. Substantial criminal and civil penalties can result from failure to report such discharges into the environment.

10. Uses

Worldwide consumption of acrylonitrile increased from 2.5×10^6 in 1976 to $\sim 4.6 \times 10^6$ t/yr in 1998. The trend in consumption over this time period is shown in Table 11 for the principal uses of acrylonitrile: acrylic fiber, acrylonitrile–butadiene–styrene (ABS) resins, adiponitrile, nitrile rubbers, elastomers, and styrene–acrylonitrile resins (SAN). Since the 1960s acrylic fibers have remained the major outlet for acrylonitrile production in the United States and especially in Japan and the Far East. Acrylic fibers always contain a comonomer. Fibers containing 85 wt % or more acrylonitrile are usually referred to as acrylics whereas fibers containing 35 to 85 wt% acrylonitrile are termed modacrylics (see FIBERS, ACRYLIC). Acrylic fibers are used primarily for the manufacture of apparel, including sweaters, fleece wear, and sportswear, as well as for home furnishings, including carpets, upholstery, and draperies. Acrylic fibers

Table 11. **Worldwide Acrylonitrile Uses and Consumption, 10^3 t**

Use	1998 (Estimated)	1997	1995	1990	1986
acrylic fibers	2615	2628	2313	2242	2350
ABS resins/SAN	1095	1079	996	781	598
adiponitrile	494	477	446	330	281
NB copolymers	144	143	134	143	125
misc.	269	264	249	243	189
Total	*4617*	*4591*	*4138*	*3739*	*3543*

consume about 57% of the acrylonitrile produced worldwide. Growth in demand for acrylic fibers in the 1990s is expected to be modest, between 2 and 3% per year, primarily from overseas markets. Domestic demand is expected to be flat.

ABS resins and adiponitrile are the fastest growing uses for acrylonitrile (see ACRYLAMIDE POLYMERS). ABS resins are second to acrylic fibers as an outlet for acrylonitrile. These resins normally contain about 25% acrylonitrile and are characterized by their chemical resistance, mechanical strength, and ease of manufacture. Consumption of ABS resins increased significantly in the 1980s and 1990s with its growing application as a specialty performance polymer in construction, automotive, machine, and appliance applications. Opportunities still exist for ABS resins to continue to replace more traditional materials for packaging, building, and automotive components. SAN resins typically contain between 25 and 30% acrylonitrile. Because of their high clarity, they are used primarily as a substitute for glass in drinking cups and tumblers, automobile instrument panels, and instrument lenses. The largest increase among the end uses for acrylonitrile has come from adiponitrile, which has grown to become the third largest outlet for acrylonitrile. It is used by Solutia as a precursor for hexamethylenediamine (HMDA, $C_6H_{16}N_2$ [124-09-4]) and is made by a proprietary acrylonitrile electrohydrodimerization process (25). HMDA is used exclusively for the manufacture of nylon-6,6. The growth of this acrylonitrile outlet in recent years stems largely from replacement of adipic acid ($C_6H_{10}O_4$ [124-04-9]) with acrylonitrile in HDMA production rather than from a significant increase in nylon-6,6 demand. The use of acrylonitrile for HMDA production should continue to grow at a faster rate than the other outlets for acrylonitrile, but it will not likely approach the size of the acrylic fiber market for acrylonitrile consumption.

Acrylamide (qv) is produced commercially by heterogeneous copper-catalyzed hydration of acrylonitrile (21–24). Acrylamide is used primarily in the form of a polymer, polyacrylamide, in the paper and pulp industry and in waste water treatment as a flocculant to separate solid material from waste water streams (see ACRYLONITRILE POLYMERS). Other applications include mineral processing, coal processing, and enhanced oil recovery in which polyacrylamide solutions were found effective for displacing oil from rock.

Nitrile rubber finds broad application in industry because of its excellent resistance to oil and chemicals, its good flexibility at low temperatures, high abrasion and heat resistance (up to 120°C), and good mechanical properties. Nitrile rubber consists of butadiene–acrylonitrile copolymers with an acrylonitrile content ranging from 15 to 45% (see ELASTOMERS, SYNTHETIC, NITRILE RUBBER). In addition to the traditional applications of nitrile rubber for hoses, gaskets, seals, and oil well equipment, new applications have emerged with the development of nitrile rubber blends with poly(vinyl chloride) (PVC). These blends combine the chemical resistance and low temperature flexibility characteristics of nitrile rubber with the stability and ozone resistance of PVC. This has greatly expanded the use of nitrile rubber in outdoor applications for hoses, belts, and cable jackets, where ozone resistance is necessary.

Other acrylonitrile copolymers have found specialty applications where good gas-barrier properties are required along with strength and high impact resistance. An example is BP Amoco Chemicals' Barex 210 acrylonitrile–methyl acrylate–butadiene copolymer and Monsanto's Lopac styrene-containing nitrile copolymer. These barrier resins compete directly in the alcoholic and other beverage bottle market with traditional glass and metal containers as well as with poly(ethylene terephthalate) (PET) and PVC in the beverage bottle market (see BARRIER POLYMERS). Other applications include food, agricultural chemicals, and medical packaging. Total acrylonitrile consumption for barrier resin applications is small, consuming less than about 1% of the total U.S. acrylonitrile production. Projections of a significant growth in demand for nitrile barrier resins remain unfulfilled because of an FDA ban in 1977 on the use of acrylonitrile-based copolymers in beverage bottles. Although the ban was lifted in 1982 and limits were set on acrylonitrile exposure in beverage and food packaging applications, it is uncertain that acrylonitrile copolymers can penetrate the current plastic bottle market dominated by PET.

A growing specialty application for acrylonitrile is in the manufacture of carbon fibers. They are produced by pyrolysis of oriented polyacrylonitrile fibers and are used to reinforce composites (qv) for high performance applications in the aircraft, defense, and aerospace industries. These applications include rocket engine nozzles, rocket nose cones, and structural components for aircraft and orbital vehicles where light weight and high strength are needed. Other small specialty applications of acrylonitrile are in the production of fatty amines, ion-exchange resins, and fatty amine amides used in cosmetics, adhesives, corrosion inhibitors, and water treatment resins. Examples of these specialty amines include 2-acrylamido-2-methylpropanesulfonic acid ($C_7H_{13}NSO_4$ [15214-89-8]), 3-methoxypropionitrile (C_4H_7NO [110-67-8]), and 3-methoxypropylamine ($C_4H_{11}NO$ [5332-73-0]).

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