United States
Environmental Protection
Agency

AIR

Office of Air Quality
Planning And Standards
Research Triangle Park, NC 27711

EPA-450/4-84-007a
March 1984

EPA

LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF ACRYLONITRILE

EPA-450/4-84-007a
March 1984

LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF ACRYLONITRILE

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRYLONITRILE

SECTION 1

PURPOSE OF DOCUMENT

EPA, States, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. This document specifically deals with acrylonitrile. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of acrylonitrile and making gross estimates of air emissions therefrom.

Because of the limited amounts of data available on acrylonitrile emissions, and since the configuration of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about (1) the types of sources that may emit acrylonitrile, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for acrylonitrile to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions for any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment and operating practices. Thus, in situations where an accurate assessment of acrylonitrile emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State, and local air pollution agencies and others who are interested in locating potential air emitters of acrylonitrile and making gross estimates of air emissions therefrom. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of acrylonitrile, its commonly occurring forms and an overview of its production and uses. A table summarizes the quantities of acrylonitrile consumed in various end uses in the United States. This background section may be useful to someone who needs to develop a general perspective on the nature of the substance and where it is manufactured and consumed.

The fourth and fifth sections of this document focus on major industrial source categories that may discharge acrylonitrile air emissions. Section 4 discusses the production of acrylonitrile and Section 5 discusses the use of acrylonitrile as an industrial feedstock in the production of acrylic fibers, SAN/ABS resins, nitrile elastomers, acrylamide, and adiponitrile. For each major industrial source category described in Section 4 and Section 5, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor estimates are presented that show the potential for acrylonitrile emissions before and after controls employed by industry. Individual companies are named that are reported to be involved with either the production and/or use of acrylonitrile, based on industry contacts and available trade publications.

The final section of this document (Section 6) summarizes available procedures for source sampling and analysis of acrylonitrile. Details are not prescribed nor is any EPA endorsement given or implied to any of these sampling and analysis procedures. At this time, EPA has generally not evaluated these methods. Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

This document does not contain any discussion of health or other environmental effects of acrylonitrile, nor does it include any discussion of ambient air levels or ambient air monitoring techniques.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Source Analysis Section (MD-14)
Air Management Technology Branch
U. S. Environmental Protection Agency
Research Triangle Park, N. C. 27711

SECTION 3

BACKGROUND

NATURE OF POLLUTANT

Acrylonitrile is a colorless liquid at normal temperatures and pressure and has a faint characteristic odor. The chemical formula for acrylonitrile is CH2=CH-C=N. Acrylonitrile has several synonyms and tradenames including propenenitrile, vinyl cyanide, cyanoethylene, Acrylon®, Carbacryl®, Fumigrain®, and Ventox®. Selected physical and chemical properties of acrylonitrile are presented in Table 1.1

Acrylonitrile is relatively volatile with a vapor pressure of 13.3 kPa (1.9 psi) at 25°C (77°F) and a boiling point of 77.3°C (171.1°F). It readily ignites and can form explosive mixtures with air. In addition, acrylonitrile polymerizes explosively in the presence of strong alkalinity. Acrylonitrile is photochemically reactive and has an estimated atmospheric residence time 5.6 days. Atmospheric residence time represents the time required for a quantity of an individual chemical to be reduced to 1/e (37 percent) of its original value.[2]

OVERVIEW OF PRODUCTION AND USE

Acrylonitrile monomer is currently produced by four companies at six manufacturing sites. Table 2 lists acrylonitrile producers and their manufacturing locations.[3] In 1982, 914 Gg (2,016 x 10^6 lbs) of acrylonitrile monomer were actually produced.[4]

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF ACRYLONITRILE[a,b,c]

Property	Value
Molecular weight	53.06
Boiling point, °C	77.3
Freezing point, °C	-83.55 + 0.05
Critical pressure, kPa	3536
Critical temperature,°C	246
Density at 20°C, g/cm3	.806
Viscosity, mPa-s (or cP)	0.34
Vapor density (theoretical)	1.83 (air = 1.0)
Dielectric constant, at 33.5 MHz	38
Dipole moment, cm (liquid phase)	1.171 x 10-29
(vapor phase)	1.294 x 10-29
Vapor pressure, kPa	
8.7°C	6.7
23.6°C	13.3
45.5°C	33.3
64.7°C	66.7
77.3°C	101.3
Flash point, °C, tag open cup	-5
Ignition temperature, °C	481
Explosive limits in air, vol 96	3.05-17.0 + 0.5
Entropy of vapor, kJ/mol	274.06
Heat of formation of vapor, kJ/mol	185.02
Heat of combustion of liquid, 25°C, kJ/mol	1761.47
Latent heat of vaporization, kJ/mol	32.65
Latent heat of fusion, kJ/mol	6635
Molar heat capacity of liquid, kJ/(kg-K)	2.09
Molar heat capacity of vapor of 50°C (kJ/(kg-K)	1.204
Solubility in water at 20°C, g/100g H_2O	7.35

(a) Reference 1.1

(b) Synonyms: Propenenitrile, vinyl cyanide, cyanoethylene. CAS Registry No. 107-13-1.

(c) properties at 25°C and 101.3 kPa unless otherwise indicated.

TABLE 2. ACRYLONITRILE MONOMER PRODUCTION SITES[3]

Company	Location (a)
American Cyanamid Company	Avondale, Louisiana
E.I. duPont de Nemours & Company, Inc.	Beaumont, Texas
Monsanto Company	Chocolate Bayou, Texas Texas City, Texas
The Standard Oil Company	Green Lake, Texas
(Ohio) Vistron Corp. (subsid.)	Lima, Ohio

(a) The locations given in the literature for some of these plants vary even though the plant is the same. Alternate locations for those given above are as follows.

American Cyanamid: Avondale or Westwego, LA
Monsanto: Chocolate Bayou or Alvin, TX
Standard Oil: Green Lake or Victoria, TX

NOTE: This listing is subject to change as market conditions change, acility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of acrylonitrile emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

A single process, the Sohio process of propylene ammoxidation, is used by all domestic producers of acrylonitrile. In this process, near stoichiometric ratios of propylene, ammonia, and air are reacted in a fluidized bed at a temperature of about 450°C (850°F) and a pressure of 200 kPa (2 atm) in the presence of a catalyst. Acrylonitrile is the major product of this reaction, but byproducts acetonitrile and hydrogen cyanide together account for about 25 percent of the total yield.[5] The reactor product stream is quenched and neutralized to remove unreacted ammonia. Wastewater and light gases are then removed in separate operations. Finally, acrylonitrile, acetonitrile, and hydrogen cyanide are separated by a series of distillations.

The major end use of acrylonitrile is in the production of acrylic fibers. It is also used in the production of plastics such as acrylonitrile-butadiene-styrene (ABS) and styrene acrylonitrile (SAN). ABS is used primarily in pipes and fittings, automotive parts and appliances. SAN is used most widely in appliances and other household items such as coat hangers, ice buckets, jars, and disposable utensils. Another use of acrylonitrile is in the production of nitrile rubbers and nitrile barrier resins. Nitrile rubbers are used extensively in the engineering and process industries due to their good dielectric properties and their resistance to chemicals, oil, solvents, heat, aging, and abrasion. Nitrile barrier resins have the potential for rapid future growth in the food, cosmetic, beverage, and chemical packaging industries. Acrylonitrile is also used in the production of adiponitrile, an intermediate in the manufacture of nylon, and in the production of acrylamide, which is used in a variety of chemical products. Miscellaneous uses of acrylonitrile include cyanoethylation of alcohols and other amines, production of fatty amines, organic synthesis of glutamic acid, use as an absorbent, and use in fumigant formulations. Figure 1 shows how the market for acrylonitrile is distributed and Table 3 presents an approximate breakdown of acrylonitrile consumption by product type.6,7,8,9 Table 4 lists the major consumers of acrylonitrile by product type.[10] The manufacturers and consumers of acrylonitrile and acrylonitrile products may change over time due to changes in market

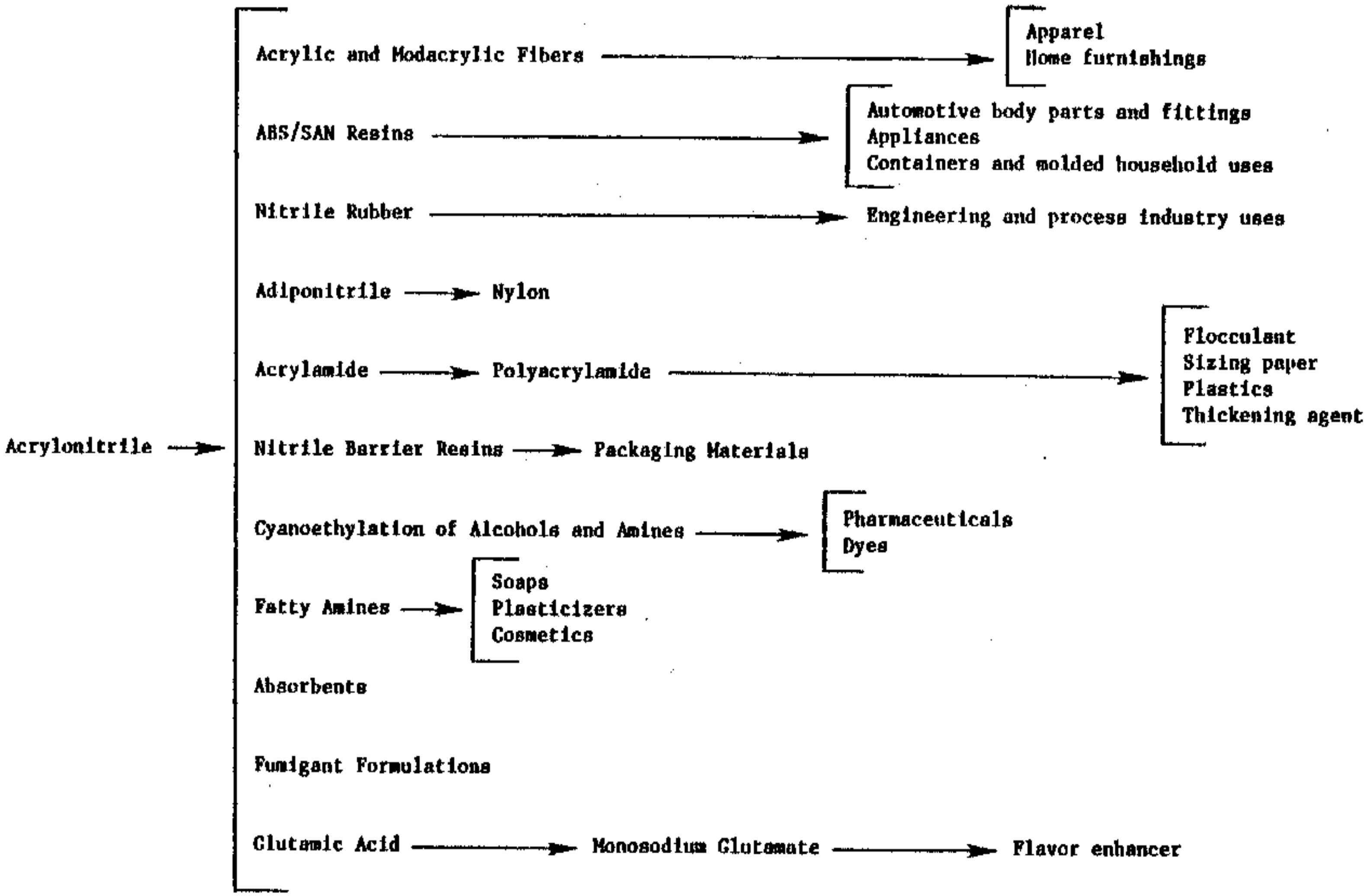


Figure 1. End use distribution of acrylonitrile.[6-9]

TABLE 3. ESTIMATED CONSUMPTION OF ACRYLONITRILE BY PRODUCT TYPE IN 1979[6-9]

MARKET	% TOTAL ACRYLONITRILE CONSUMPTION
Fibers	37.7
Exports	21.3
ABS/SAN Resins	17.1
Adiponitrile	9.5
Acrylamide	3.1
Nitrile Elastomers	2.9
Barrier Resins	1.2
Miscellaneous	4.0[a]
Unaccounted for	3.2[b]

(a) Includes fumigants for tobacco, super absorbents, fatty amine production,and cyanoethylation of alcohols and amines.

(b) Includes accumulated inventory.

TABLE 4. MAJOR ACRYLONITRILE CONSUMERS

Producer	Location(a)	Acrylonitrile Products						
		Acrylic Fibers	Modacrylic Fibers	ABS Resin	SAN Resin	Nitrile Elastomer and Latex	Adiponi-trile	Acryl-amide
American Cyanamid	Linden, NJ							x
	Milton, FL	x						
	Avondale, LA							x
Badische	Williamsburg, VA	x						
Borg-Warner	Washington, WV			x				
	Ottawa, IL			x				
	Port Bienville, MS			x				
Copolymer Rubber	Baton Rouge, LA					x		
Dow Chemical	Gales Ferry, CT			x				
	Ironton, OH			x				
	Midland, MI			x	x			x
	Pevely, MO				x			
	Torrance, CA			x				
DuPont	Camden, SC	x	x					
	Waynesboro, VA	x						
Tennessee Eastman	Kingsport, TN		x					
B.F. Goodrich	Akron, OH					x		
	Louisville, KY					x		
Goodyear	Akron, OH					x		
	Houston, TX					x		
Monsanto	Decatur, AL	x	x				x	
	Addyston, OH			x	x			
	Muscatine, IO			x				

TABLE 4. MAJOR ACRYLONITRILE CONSUMERS

Nalco	Garyville, LA				x
Reichhold Chemical	Cheswold, DE			x	
Uniroyal	Painesville, OH			x	

(a)The locations given in the literature for some of these plants vary even though the plant is the same. Alternate locations for those given above are as follows:
American Cyanamid: Avondale or Westwego, LA
Dow Chemical: Gales Ferry or Allyns Point, CT

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of acrylonitrile emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

conditions. Publications such as the Stanford Research Institute (SRI) Directory of Chemical Producers and the Chemical Marketing Reporter (Schnell Publishing, New York) are good sources of up-to-date information on chemical producers. Chemical trade associations such as the Chemical Manufacturers Association, the Acrylonitrile Group, and the Synthetic Organic Chemical Manufacturers Association would also be good contacts to determine the status of the acrylonitrile industry.

Some potential exists for volatile substances, including acrylonitrile, to be emitted from waste treatment, storage and handling facilities. Reference 11 provides general theoretical models for estimating volatile substance emissions from a number of generic kinds of waste handling operations, including surface impoundments, landfills, landfarming (land treatment) operations, wastewater treatment systems, and drum storage/handling processes.11 Since no test data were available on acrylonitrile emissions from any of these operations at the time of publication, no further discussion is presented in this document. If such a facility is known to handle acrylonitrile, the potential should be considered for some air emissions to occur.

REFERENCES FOR SECTION 3

1. Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Volume 1. Acrylonitrile. John Wiley and Sons, New York, NY, 1980. pp. 414-426.

2. Cupitt, L. T. (U. S. EPA). Fate of Toxic and Hazardous Materials in the Air Environment. EPA-600/3-80-084. August 1980. pp. 20-22.

3. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. pp. 410-411.

4. Chemical Engineering News. May 2, 1983. p. 11.

5. Blackford, J. L., et al. Chemical Conversion Factors and Yields, Commercial and Theoretical. Second Edition. Stanford Research Institute, Menlo Park, California. 1977. p. 6.

6. Textile Economics Bureau, Inc. Textile Organon. New York. February 1981.

7. Stanford Research Institute. 1978 Chemical Economics Handbook. Menlo Park, California. 1978. p. 607.5032J.

8. United States International Trade Commission. Synthetic Organic Chemicals, United States Productions and Sales. 1979.

9. 1980 Facts and Figures of the Plastics Industry. Society of the Plastics Industry. New York. 1980.

10. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. pp. 300, 409, 412, 569, 593, 814, and 831.

11. Evaluation and Selection of Models for Estimating Air Emissions from Hazardous Waste Treatment, Storage, and Disposal Facilities. Revised Draft Final Report. Prepared for the U. S. Environmental Protection Agency under Contract Number 68-02-3168, Assignment No. 77 by GCA Corporation, Bedford, Mass. May 1983.

SECTION 4

EMISSIONS FROM ACRYLONITRILE PRODUCTION

The potential for acrylonitrile emissions occurs both during the production of the monomer and during its consumption as a raw material in other manufacturing processes: This section includes a detailed description of the acrylonitrile production process along with possible emitting operations. Emission factors relating acrylonitrile emissions to acrylonitrile production rates are also presented. Manufacturing processes that use acrylonitrile monomer as a raw material are similarly discussed in Section 5.

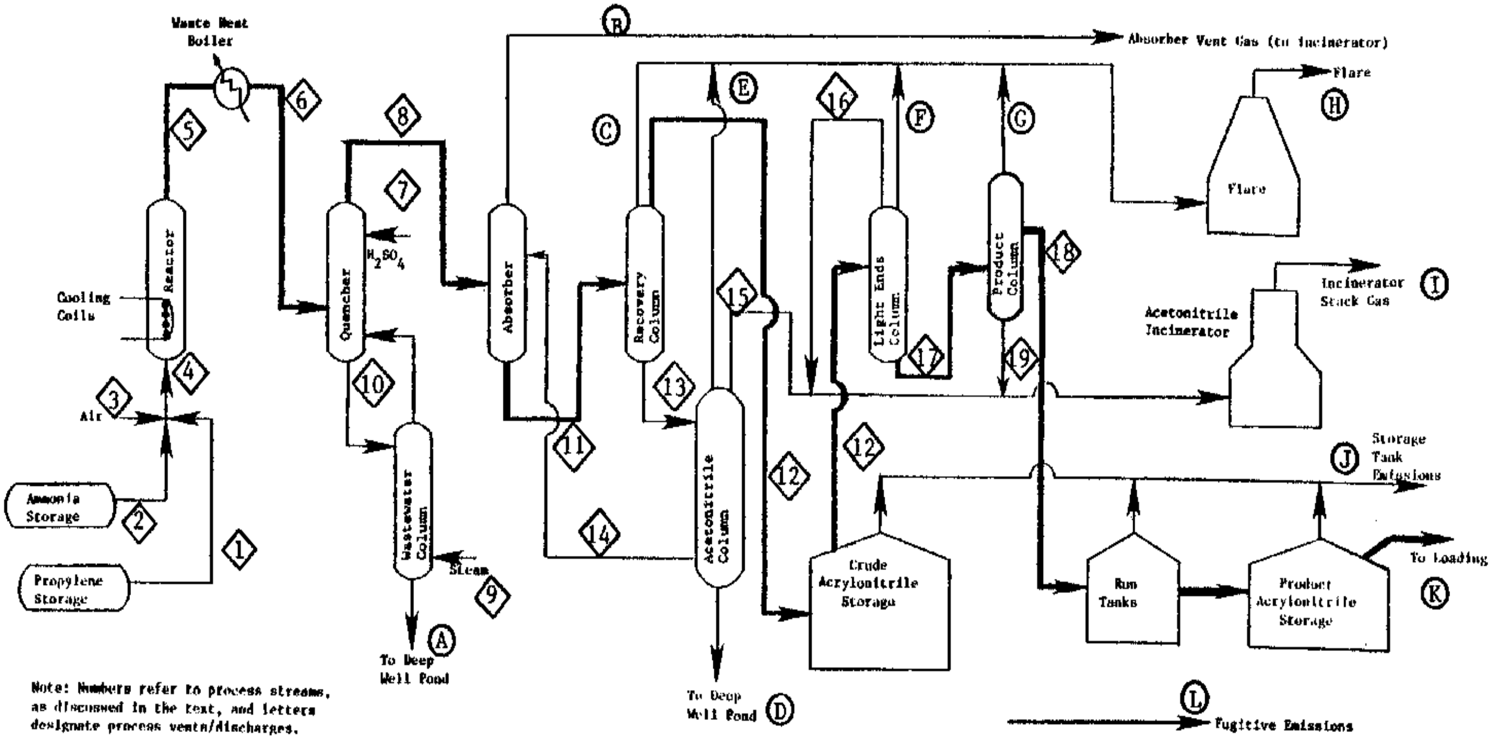
ACRYLONITRILE PRODUCTION

Process Description [1-3]

Acrylonitrile is produced domestically by a single process - the Sohio process of propylene ammoxidation. Four companies at six locations currently use this process.[4] A simplified flow diagram of the basic Sohio process is presented in Figure 2 and explanations of the stream codes in Figure 2 are given in Table 5. The reaction governing the production of acrylonitrile is:

$$2CH_2{=}\ CH\text{-}CH_3 + 2NH_3 + 30_2 \ \text{-->}\ 2CH_2{=}\ CH\text{-}CN + 6H_2O.$$

Propylene, ammonia (NH_3), and air are fed to the reactor (Stream 4) in near stoichiometric ratios. The molar ratio of propylene/ammonia/air fed to the reactor is typically 1/1.06/8.4. A slight excess of ammonia forces the reaction closer to completion and a slight excess of air continually regenerates the catalyst used in the reaction.[1] Raw material specifications call for the use of refinery-grade propylene (90+ percent purity) and fertilizer or refrigerant-grade ammonia (99.5+ percent purity). The vapor-phase reaction takes place in a fluidized



Note: Numbers refer to process streams, as discussed in the text, and letters designate process vents/discharges. Darkened lines indicate product stream flow.

Figure 2. Basic operations and controls that may be used in acrylonitrile production plants.

TABLE 5. STREAM, VENT, AND DISCHARGE CODES FOR FIGURE 2 [1,2]

Stream/Vent/Discharge	Description
Stream	
1	Propylene feed
2	Ammonia feed
3	Process air
4	Reactor feed
5	Reactor product
6	Cooled reactor product
7	Sulfuric acid
8	Quenched reactor product
9	Stripping steam
10	Wastewater column volatiles
11	Absorber bottoms
12	Crude acrylonitrile
13	Crude acetonitrile
14	Water recycle
15	Acetonitrile
16	Hydrogen cyanide
17	Light ends column bottoms
18	Product acrylonitrile
19	Heavy ends
Vent/Discharge	
A	Wastewater column bottoms
B	Absorber vent gas
C	Recovery column purge vent
D	Acetonitrile column bottoms
E	Acetonitrile column purge vent
F	Light ends column purge vent
G	Product column purge vent
H	Flare
I	Acetonitrile incinerator stack gas
J	Storage tank emissions
K	Product transport loading facility vent
L	Fugitive losses from pumps, compressors, and valves

bed reactor at approximately 200 kPa (2 atm) and 400-510°C (750-950°F) in the presence of Catalyst 41, a Sohio-developed product. The composition of this catalyst is described in the patent literature as 70 percent by weight P_2O_5:Bi_2O_3:MoO_3 in a molar ratio of 1:9:24.[5] The conversion of propylene in the reactor is essentially complete. The yield of acrylonitrile monomer from this reaction is typically 73 weight percent with approximately 12 weight percent yields of each of the byproducts acetonitrile and hydrogen cyanide (HCN).[6] The stream exiting the reactor (Stream 5) contains not only acrylonitrile and byproducts but also unreacted oxygen, propylene, carbon monoxide, carbon dioxide, and nitrogen.

The propylene ammoxidation reaction generates substantial quantities of heat which must be removed. Heat removal from the product stream (Stream 5) is generally accomplished by utilizing excess heat to generate steam in a waste heat boiler. The cooled product stream leaving the waste heat boiler (Stream 6) passes to a water quench tower where sulfuric acid (Stream 7) is added to neutralize unreacted ammonia. Wastewater containing the ammonium salts and spent catalyst fines is passed through a steam stripping column where volatiles are separated out and recycled to the quench tower (Stream 10). Wastewater containing ammonium sulfate and heavy hydrocarbons is discharged to a deep well pond for disposal (Discharge A).

Meanwhile, the quenched product stream (Stream 8) is passed to a counter-current absorber which removes inert gases and vents them to the atmosphere (Vent B). In some cases the absorber vent gas is incinerated prior to release to the atmosphere. The stream containing acrylonitrile, acetonitrile, HCN, and some water (Stream 11) then undergoes a series of atmospheric distillations to obtain products and byproducts of the desired purity, as described below.

In the first recovery column, acrylonitrile and HCN (Stream 12) are separated from acetonitrile and water (Stream 13). Water is then removed from the acetonitrile in the acetonitrile column and recycledto the absorber (Stream 14). The heavy bottoms from the acetonitrile column are discharged to the deep well pond (Discharge D). The acetonitrile byproduct (Stream 15) may be recovered to 99+ percent purity for commercial sales but, due to lack of demand, the stream is usually incinerated. [2,7]

The crude acrylonitrile exiting the first recovery column (Stream 12) is passed to storage facilities and then to a light-ends column where HCN is recovered. The HCN byproduct (Stream 16) may be further purified to 99+ percent for sales. All acrylonitrile producers currently market a small percentage of HCN, but the majority of the byproduct is incinerated.7 In the final product column, heavy ends are removed (Stream 19) and incinerated. The heavy ends stream from the product column contains essentially no acrylonitrile. The acrylonitrile product (Stream 18) obtained from the Sohio process has a purity of 99+ percent.

Emissions

Emissions of acrylonitrile produced via the Sohio process may occur from several sources including the absorber vent, column purge vents, storage tanks, transport and loading facilities, and deep well ponds. Fugitive emissions may also occur from leaks in pumps, compressors, and valves. These emission sources are depicted in Figure 2. Acrylonitrile emissions represent only a small fraction of the total VOC emitted from these sources, accounting for approximately 6 weight percent of the total uncontrolled VOC emissions and 15 weight percent of the total VOC emissions after typical controls.[8]

Process Emissions--

Acrylonitrile process emissions from the Sohio process occur from the absorber vent (Vent B) during normal operation, the absorber vent (Vent B) during startup, and the distillation column purge vents (Vents C, E, F and G) during normal operation. During normal operation, the absorber vent gas contains only about 0.001 weight percent acrylonitrile and 1.25 weight percent total VOC.[8] The absorber gases are usually incinerated at removal efficiencies of 98 percent or higher. The majority of the acrylonitrile production facilities utilize thermal incineration, although one facility has employed catalytic incineration on the absorber vent.[2] Because of the large percentage (97+ percent) of nitrogen and other noncombustibles normally present in the absorber vent gas stream, supplemental fuel must be added to ensure proper combustion.[8]

Emissions of acrylonitrile during startup are substantially higher than during normal operation, even when averaged over an entire year on a mass per unit time basis. During startup the reactor is heated to operating temperature before the reactants (propylene and ammonia) are introduced. Thus, the reactor product stream is initially oxygen-rich. As the startup progresses and the reactants are introduced, the acrylonitrile and VOC content of the reactor effluent increases until the acrylonitrile-rich composition indicative of normal operation is reached. During part of this startup process, the composition of the reactor product stream is within its explosive limits and must, therefore, be vented to the atmosphere to prevent explosions in the lines to the absorber.[1] Emissions of acrylonitrile from a single reactor during startup may be as high as 4500 kg/hr (10,000 lbs/hr).[8] However, emissions associated with startup occur rather infrequently, with each reactor having about four startups of 1-hour duration per year. Even so, acrylonitrile emissions during startup totalled over an entire year are higher than emissions from the absorber vent during normal operation. Incineration may be an acceptable method of control for startup emissions but is not generally used due to the potentially high NO_x emissions which could result from the combustion of a stream containing a large percentage of acrylonitrile, hydrogen cyanide, and acetonitrile.

The acrylonitrile content of the combined column purge vent gases (Vents C, E, F, and G) is high, about 50 weight percent of the total VOC emitted from the columns.[8] The vent gases from the recovery, acetonitrile, light-ends, and product columns are typically controlled by a single flare. No acrylonitrile emissions are expected from the incineration of byproduct acetonitrile (Vent I).

Other Emissions--

Acrylonitrile is emitted from crude acrylonitrile storage tanks (Vent J), acrylonitrile run tanks (Vent J), product storage tanks (Vent J), and during loading into railroad tank cars and barges (Vent K). These emissions are generally uncontrolled but in some cases safety considerations dictate the use of recovery systems.[7] Water scrubbers used for this purpose in acrylonitrile production facilities have demonstrated removal efficiencies up to 99 percent.[8] Floating roof tanks may also be used in place of fixed roof tanks to reduce acrylonitrile emissions up to 95 percent.[8]

Emissions of acrylonitrile may also occur from fugitive sources (Vent L) and from deep well ponds. Fugitive sources, such as leaks from pumps, compressors, and valves, are normally uncontrolled but can be minimized if fugitive leaks are detected and corrected. Fugitive emissions and various control measures used to minimize them are described in Reference 9.9 Emissions of acrylonitrile from deep well ponds are usually very small because the wastewater discharged to the deep well pond contains less than 0.02 percent acrylonitrile and the surface is covered with high molecular weight oil to prevent the escape of most VOC vapors.[2,8,10]

Emission Factors--

Table 6 gives acrylonitrile emission factors before and after the application of possible controls for a hypothetical plant using the Sohio process.[8] The hypothetical plant is assumed to use thermal incineration for the control of absorber vent gases, flares for the control of column purge vents, and water scrubbers for the control of storage tank and loading emissions. The values presented for controlled fugitive emissions are based on the assumption that leaks from valves and pumps, resulting in concen trations greater than 10,000 ppm acrylonitrile on a volume basis, are detected and that appropriate measures are taken to correct the leaks. Only the startup emissions are uncontrolled. Uncontrolled emission factors are based on the

TABLE 6. UNCONTROLLED AND CONTROLLED ACRYLONITRILE EMISSION FACTORS FOR A HYPOTHETICAL ACRYLONITRILE PRODUCTION PLANT[a,b]

		Uncontrolled	Controlled		
Vent[c]	Source	Emission Factor g/Kg	Control Device or Technique	Assumed Emission Reduction (%)	Emission Factor g/Kg
B	Absorber vent				
	(normal)	0.10	Thermal incinerator	98[n]	0.002
	(startup)(e)	0.187	No control		0.187
C,E,F,G	Column vents	5.00	Flare (vent H)	98[o]	0.10
J	Storage vents				
	Crude acrylonitrile	0.048[g]	Water scrubber[h]	99[a]	0.00048
	Acrylonitirle run tanks	0.128[g]	Water scrubber[h]	99[a]	0.00128
	Acrylonitirle storage	0.531[g]	Water scrubber[h]	99[a]	0.00531
K	Handling[i,j]				
	Tank car loading[k]	0.167	Water scrubber	99[a]	0.0017
	Barge loading[l]	0.150	Water scrubber	99[a]	0.0011
L	Fugitive[m]	0.806	Detection and correction of major leaks	71	0.238
	TOTAL	7.07			0.537

(a) Reference 8

(b) Hypothetical plant produces 180,000 Mg (198,000 tons) per year of acrylonitrile monomer. It also produces 21,600 Mg (23,800 tons) of hydrogen cyanide and 5000 Mg (5500 tons) of acetonitrile per year as byproducts. Values in Table are based on 8760 hours/year of operation. Values are based on the assumption that 40 percent of the hydrogen cyanide and all of the acetonitrile produced are incinerated. Note that any given acrylontrile production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

(c) See Figure 2

(d) g of acrylonitrile emitted per kg acrylonitrile produced.

(e) Startup emissions are vented to the atmosphere to prevent possible explosion in absorber lines. This factor represents average rates for entire year, based on 8 startups (two reactors, each with four startups) per year lasting 1 hour. Thus, during startup each reactor emits 4250 kg (1930 lb)acrylonitrile.

(f) Storage tanks were assumed to be fixed-roof types, half full, with diurnal temperature variation of 11°C (20°F), and a bulk liquid temperature of 27°C (81°F). Assumes the following tank sizes and turnover rates:

Tank	Volume (m3)	Turnovers per year per tank
Crude Acrylonitrile	2500	6
Acrylontrile run tanks (two tanks)	380	294
Acrylonitrile storage (two tanks)	5680	20

(g) Reference 11. Section 4.3. Supplement 12.

(h) Floating-roof tanks are also used in some cases to control storage emissions, with reported reductions of uncontrolled emission of greater than 95 percent.

(i) Reference 11. Section 4.4. Supplement 9.

(j) Assumes 55% of acrylonitrile loaded into tank cars and 45% onto barges.

(k) Assumes submerged loading and dedicated normal service.

(l) Assumes submerged loading.

(m) Process pumps and valves are potential sources of fugitive emissions of acrylonitrile. The assumedequipment list (reference 8) and emission factors (reference 12) are as follows:

	Emission factor (kg\hr), each pump/valve	
Equipment	Uncontrolled	Controlled
25 pumps in light-liquid service	0.12	0.03
100 pipeline valves in gas/vapor service	0.021	0.002
500 pipeline valves in light-liquid service	0.010	0.003
40 safety/relief valves in gas/vapor service	0.16	0.061

Controlled emission factors are based on the assumption that leaks encountered during monthly inspections having VOC concentrations of at least 10,000 ppmv are corrected within 15 days.

(n) Reference 14 and 15.

(o) Reference 16.

assumptions given in footnotes to Table 6. An annual average emission rate of acrylonitrile from the hypothetical controlled facility shown in Table 6 is slightly greater than 0.5 g/kg of acrylonitrile produced, including startup emissions. However, some facilities in the acrylonitrile production industry may have controlled emission factors two to three times higher than the hypothetical plant described here due to differences in operating conditions or control methods.[2,13]

REFERENCES FOR SECTION 4

1. Anguin, M. T. and S. Anderson (Acurex Corporation). Acrylonitrile Plant Air Pollution Control. EPA-600/2-79-048. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. February 1979.

2. Tierney, D. R., T. R. Blackwood, and G. E. Wilkins. Status Assessment of Toxic Chemicals: Acrylonitrile. EPA-600/2-79-210a. U.S. Environmental Protection Agency. Cincinnati, Ohio. December 1977.

3. Industrial Process Profiles for Environmental Use: Chapter 6: The Industrial Organic Chemicals Industry. EPA-600/2-77-023f. U.S. Environmental Protection Agency. Cincinnati, Ohio. February 1977.

4. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. pp. 410-411.

5. Lowenbach, W. and J. Schleslinger. Acrylonitrile Manufacture: Pollutant Prediction and Abatement. (Prepared for U. S. Environmental Protection Agency, EPA Contract No. 68-01-3188). The MITRE Corporation. McLean, Virginia. February 1978.

6. Blackford, J. L, et al. Chemical Conversion Factors and Yields, Commercial and Theoretical. Second Edition. Stanford Research Institute. Menlo Park, California. 1977. p. 6.

7. Control Techniques for Volatile Organic Emissions from Stationary Sources. EPA-450/2-78-022. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. May 1978.

8. Key, J. A. and F. T. Hobbs (IT Enviroscience). Acrylonitrile. Organic Chemical Manufacturing Volume 10: Selected Processes. EPA-450-3/80-028e. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. December 1980.

9. V0C Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry--Background Information for Proposed Standards. EPA-450/3-80-033a. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. November 1980.

10. Hughes, T. W. and D. A. Hour (Monsanto Research Corp.). Source Assessment: Acrylonitrile Manufacture (Air Emissions). EPA Contract No. 68-02-1874. September 1977. pp. 21-22.

11. Compilation of Air Pollutant Emission Factors. 3rd Edition. AP-42. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. August 1977.

12. Dubose, D. A. et al (Radian Corporation). Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units. EPA-600/2-79-044. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. February 1979.

13. Suta, Benjamin (SRI International). Assessment of Human Exposures to Atmospheric Acrylonitrile. Human Exposure to Atmospheric Concentrations of Selected Chemicals. EPA Contract No. 68-02-2835. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. August 1979.

14. Memo from Mascone, D. C., U. S. EPA to Farmer, J. R., U. S. EPA. June 11, 1980. Thermal Incinerator Performance for NSPS.

15. Memo from Mascone, D. C., U. S. EPA to Farmer, J. R., U. S. EPA. July 22, 1980. Thermal Incinerator Performance for NSPS, Addendum.

16. McDaniel, M. D. A Report on a Flare Efficiency Study, Volume 1 (Draft). Engineering-Science. Austin, Texas. 1983.

SECTION 5

EMISSIONS FROM INDUSTRIES USING ACRYLONITRILE AS A FEEDSTOCK

This section describes various production processes using acrylonitrile monomer as a feedstock and discusses the emissions resulting from these processes. The processes included are acrylic and modacrylic fiber production, production of ABS/SAN resins, production of nitrile rubbers, and the production of acrylamide and adiponitrile. The process descriptions included in this section are for hypothetical plants generally achieving a high degree of monomer recovery and emission control through the use of flashing, stripping, and scrubbing. The reader should note, however, that all facilities may not be as adequately equipped for monomer recovery and emissions control as these hypothetical plants.

Acrylonitrile is also used as a feedstock in the production of nitrile barrier resins, in the production of fatty amines, in the cyanoethylation of alcohols and amines, in fumigant formulations, and as an absorbent. However, the percentage of acrylonitrile consumed in these miscellaneous processes is small and very limited information is available concerning process descrip tions and emissions. Consequently, no discussion of these miscellaneous processes is included in this report.

ACRYLIC AND MODACRYLIC FIBER PRODUCTION[1-9]

The major use of the acrylonitrile monomer is as a feedstock for acrylic and modacrylic fiber production. Acrylic fibers are classified as having greater than 85 weight percent acrylonitrile while modacrylic fibers have less than 85 percent but greater than 35 percent acrylonitrile. Comonomers used in the production of acrylic fibers include methyl acrylate, methyl methacrylate, and vinyl acetate. Vinylidene chloride and vinyl chloride are the most often used comonomers in the production of modacrylic fibers. In the remainder of this section, acrylic and modacrylic fibers will both be referred to as acrylic.

Process Descriptions

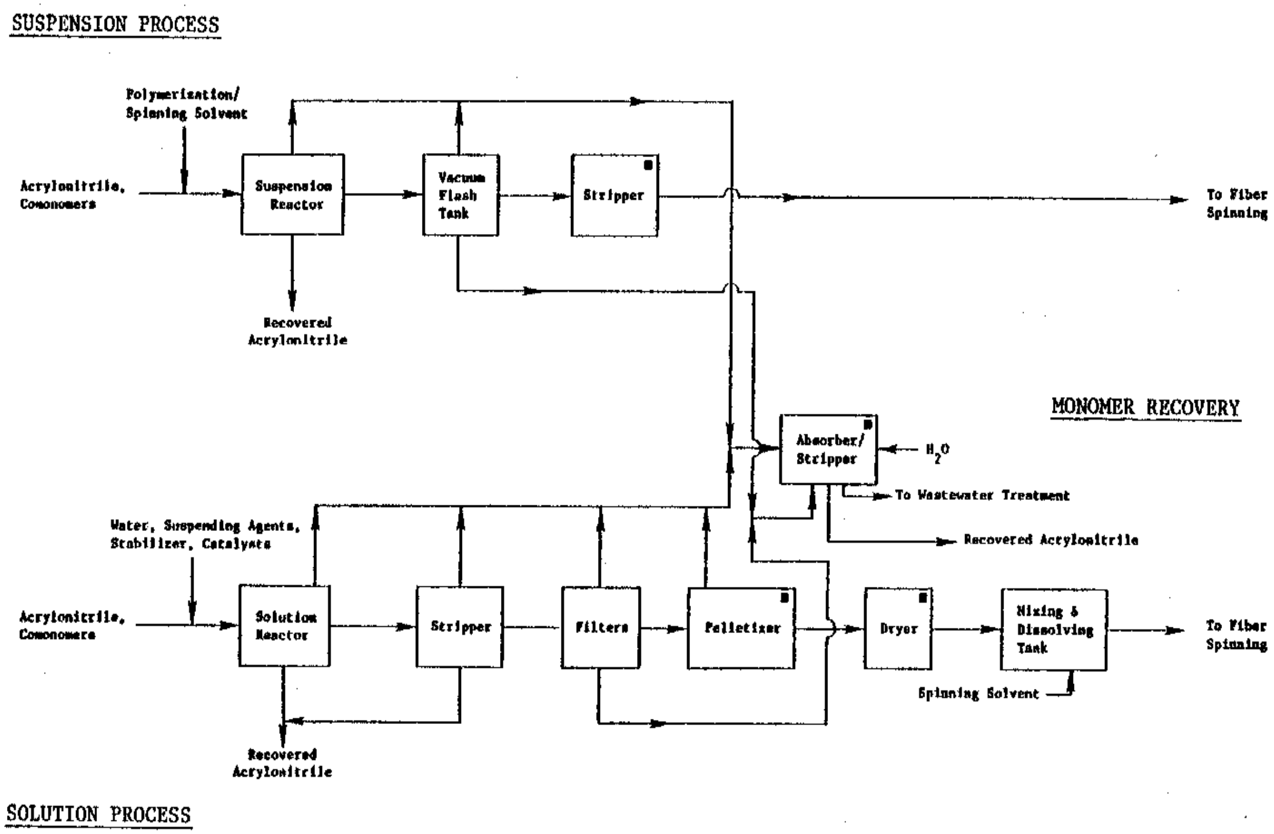
In the production of acrylic fibers, the acrylonitrile and comonomers are first polymerized using either a suspension or a solution polymerization process. The resulting polymer is then spun into fibers using either wet spinning or dry spinning techniques. Finally, the spun fibers must be treated to remove excess solvent and to improve fiber characteristics. The fiber treating process has a negligible contribution to acrylonitrile emissions and is not discussed in this section. Each of the polymerization and spinning processes is discussed below.

Polymerization--

In 1977-78 the suspension polymerization process accounted for 87 percent of the total acrylic fiber production, while the solution process accounted for 13 percent. Each of these processes may be carried out in either a batch or a continuous mode. A general block flow diagram is shown in Figure 3 indicating the process operations involved in the suspension and solution polymerization processes. In the suspension process, insoluble beads of polymer are formed in a suspension reactor. Unreacted monomer is removed from the polymer by flashing/stripping and the polymer is filtered, dried, and then dissolved in solvent in preparation for spinning. In the solution process, polymer formed in the reactor is soluble in the spinning solvent present. Reactor effluent, after monomer recovery, is therefore ready for spinning. Several steps, including filtration and drying, are thus avoided using the solution process.

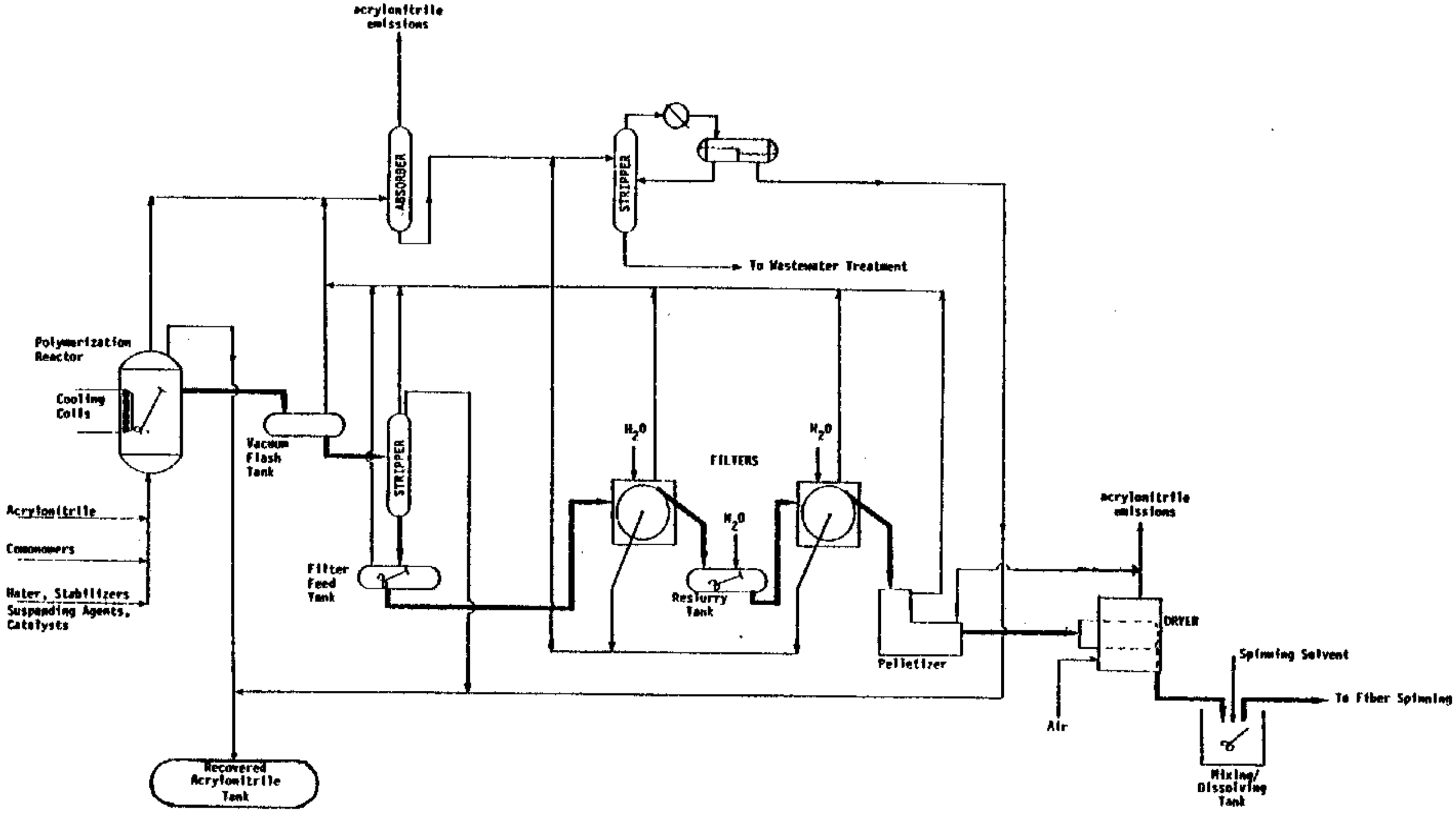
Suspension Polymerization--

A more detailed schematic flow diagram of a hypothetical suspension polymerization process is shown in Figure 4. Slight variations in this process may occur from plant to plant, however.



■ Indicates an uncontrolled acrylonitrile emission point.

Figure 3. Basic suspension and solution polymerization processes used in the production of acrylic fibers.



Note: Darkened lines indicate product stream flow.

Figure 4. Acrylic fiber production via the suspension polymerization process.

In this process acrylonitrile and comonomers are mixed and then passed to the polymerization reactors along with water, suspending agents, stabilizers, and catalysts. The reactor is equipped for heat removal and is agitated to maintain the monomers in suspension in the water. The reaction of acrylonitrile monomers in the suspension reactor is typically carried out to about 65 to 85 percent completion, and results in the formation of insoluble beads of polymer. Essentially all of the comonomers are consumed in this process.

Unreacted acrylonitrile monomer is removed from the polymer product by flashing and stripping. Approximately 80 percent of the unreacted monomer is released overhead from the vacuum flash tank and nearly all of the remaining acrylonitrile is released overhead by countercurrent contact with steam in the slurry stripper. The acrylonitrile-containing streams from the vacuum flash tank and slurry stripper are passed to the acrylonitrile recovery unit. Some acrylonitrile is also recovered from the reactor and slurry stripper overhead condensers and decanters (not shown in Figure 4).

The stripper bottoms, containing stripped polymer and water, are pumped via a filter feed tank to the filtration unit, typically consisting of two rotary vacuum filters. These filters serve to concentrate the polymer in a cake to reduce the load in the dryers and to remove most of the residual acrylonitrile from the polymer. Filter cake from the first filter is reslurried with water and transferred to the second filter. Filter cake from the second filter is pelletized and filtrate is transferred to the acrylonitrile recovery system. The pelletized polymer is then dried with steam heated air and stored in bins or silos. In preparation for spinning into fiber, the dry polymer is mixed with solvent and dissolved to form spinning dope which is then filtered, deaerated, and pumped to the spinneret which is a metal plate perforated with 200-30,000 holes of approximately 0.008 cm (0.003 in) diameter.

Acrylonitrile recovery is accomplished by the use of an absorber/stripper system. Acrylonitrile-containing gases from the reactor, vacuum flash tank, slurry stripper, filter feed tank, filters, pelletizer, and recovered acrylonitrile tank are scrubbed with water in the acrylonitrile absorber. Absorber overhead is vented to the atmosphere and absorber bottoms are sent to the acrylonitrile stripper, along with filtrate from the rotary filters. Acrylonitrile monomer is released overhead along with a considerable amount of steam. An overhead condenser followed by a decanter serves to separate the acrylonitrile from the water. The water-rich phase is treated and recycled to the stripper and the acrylonitrile-rich phase is recycled to the recovered acrylonitrile tank.

Solution Polymerization--

The basic process flow diagram for solution polymerization is similar to that for suspension polymerization (shown in Figure 4) except that the filtration, pelletizing, and drying steps are eliminated. In the solution polymerization process, acrylonitrile and comonomers are fed to a monomer mix tank where they are dissolved in a solvent. Typical solvents include organic solvents such as dimethylformamide (DNF), dimethylacetamide (DMAC) or acetone, and concentrated aqueous solutions of zinc chloride, sodium thiocyanate, or nitric acid. The monomer/solvent solution is transferred to the polymerization reactors where addition of an initiator causes the reaction to proceed. Polymer formed by solution polymerization is soluble in the solvent. The polymer solution is flashed to release about 80 percent of the unreacted acrylonitrile monomer, and then pumped to the top of the stripper where virtually all of the remaining acrylonitrile monomer is stripped overhead by countercurrent contact with steam. The stripper overhead stream is vented to the atmosphere. Finally, the stripped polymer solution is heated, filtered, deaerated and pumped to the spinnerets to be spun into fibers.

An absorber/stripper system is used to recover unreacted acrylonitrile from gases generated by storage tanks, the reactor, and the vacuum flash tank. This absorber/stripper system is similar to the one used in the suspension polymerization process. The acrylonitrile-containing gases are scrubbed with water in the acrylonitrile absorber and overhead from the absorber is vented to the atmosphere. Bottoms from the absorber are pumped to the acrylonitrile stripper where acrylonitrile monomer is stripped overhead with steam. Phase separation is accomplished by means of a condenser and decanter, and the water-rich phase is returned to the stripper while the acrylonitrile-rich phase is recycled to the polymerization reactor.

Spinning--

Acrylic and modacrylic fibers may be spun in either a wet spinning or a dry spinning process. Wet spinning may be carried out in a batch or a batch-continuous process whereas dry spinning is always a batch process. Both the wet spinning and dry spinning processes require that the polymer be dissolved in solvent, forming a viscous solution that is then forced through a spinneret. Common spinning solvents are acetone and dimethylformamide.

The main difference between the wet and dry spinning processes is the method used to remove solvent from the fiber upon extrusion from the spinneret. In the dry spinning process, the solvent is evaporated by hot gases, while in the wet spinning process the solvent is removed by leaching or washing.[2] The wet fibers produced by wet spinning must then be dried in an air dryer. The resulting fibers from both processes are then stretched, crimped, and thermally stabilized.

Vaporized solvent from the dry spinning process is condensed and recycled to the dissolving step of the polymerization process. Wash water from the wet spinning process, containing solvent and some residual acrylonitrile monomer, is directed to a solvent recovery unit and an acrylonitrile recovery unit. In some cases, the exhaust from the fiber dryer is also sent to the solvent recovery unit.

Emissions

Acrylonitrile emissions from the combination of suspension polymerization followed by wet spinning occur at the pelletizer and polymer dryer. Potential emissions of acrylonitrile from the polymerization reactor, flash tank, slurry stripper, filter feed tank and filters, and pelletizer are reduced by passing the vent gases through an absorber/stripping system for acrylonitrile recovery. Acrylonitrile emissions from this absorber/stripping system are very low. Emissions from the combination of solution polymerization followed by wet spinning may occur at the stripper and in the spinning and washing steps. Potential acrylonitrile emissions from the polymerization reactor and flash tank are reduced by passing the vent gases through the acrylonitrile recovery unit. Some of the emissions associated with spinning and washing may also be reduced in this manner. Monomer storage tank vents for both processes are generally controlled by flares. Fugitive emissions from pumps, valves, and seals may also occur during the production of acrylic fibers. Information concerning acrylonitrile emissions from the dry spinning process is not available. Also, no information concerning reactor startup emissions is available.

Many of the controls typically employed at acrylic fiber production facilities are integral parts of the process design. Most of the controls are actually recovery systems which reduce downstream emissions in addition to recovering monomer for reuse in the process. Strippers, scrubbers, condensers, and flash systems are used for recovery purposes. In the suspension process, unreacted monomer is also removed from the polymer in the washing and filtration steps. Most of these controls remove unreacted monomer from the polymer thereby reducing the amount of monomer that would otherwise be released in the drying ovens. The drying ovens are generally uncontrolled due to the high cost of treating large air flows with dilute VOC concentrations.

Sufficient information is not available to develop emission factors for the various process operations given above. The reader is encouraged to contact State and local air pollution control agencies where these types of plants are located and the specific plants of interest to determine the extent of potential acrylonitrile emissions from fiber production.

Source Locations

Five companies at six locations produce acrylic fibers. A list of these companies and their locations is given in Table 7.[10] Acrylonitrile monomer is not produced at any of these facilities.

The manufacturers of acrylonitrile products such as acrylic and modacrylic fibers may change over time due to changes in market conditions. Publications such as the SRI Directory of Chemical Producers and the Chemical Marketing Reporter are good sources of up-to-date information on chemical producers. Chemical trade associations such as the Chemical Manufacturers Association, the Acrylonitrile Group, and the Synthetic Organic Chemical Manufacturers Association would also be good contacts to determine the status of the acrylonitrile products industry.

PRODUCTION OF SAN AND ABS RESINS[1-9,11]

Acrylonitrile monomer is used extensively in the production of styrene-acrylonitrile (SAN) resins and acrylonitrile-butadiene-styrene (ABS) resins. SAN resins may contain up to about 35 weight percent acrylonitrile. ABS resins are two-phase systems formed by grafting SAN onto a rubber phase and then blending the grafted rubber with SAN. The amount of rubber in ABS varies from 5 to 30 percent. Most SAN produced is used captively in the production of ABS although some is marketed separately. Only one producer manufactures SAN exclusively for sale on the merchant market.

TABLE 7. DOMESTIC ACRYLIC FIBER PRODUCERS IN 1983[10]

Company	Location
American Cyanamid Co.	Milton, Florida
Badische Corporation	Williamsburg, Virginia
E. I. duPont de Nemours and Co., Inc.	
	Camden, South Carolina
	Waynesboro, Virginia
Tennessee Eastman Co.	Kingsport, Tennessee
Monsanto Co.	Decatur, Alabama

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of acrylonitrile emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

Process Descriptions And Emissions

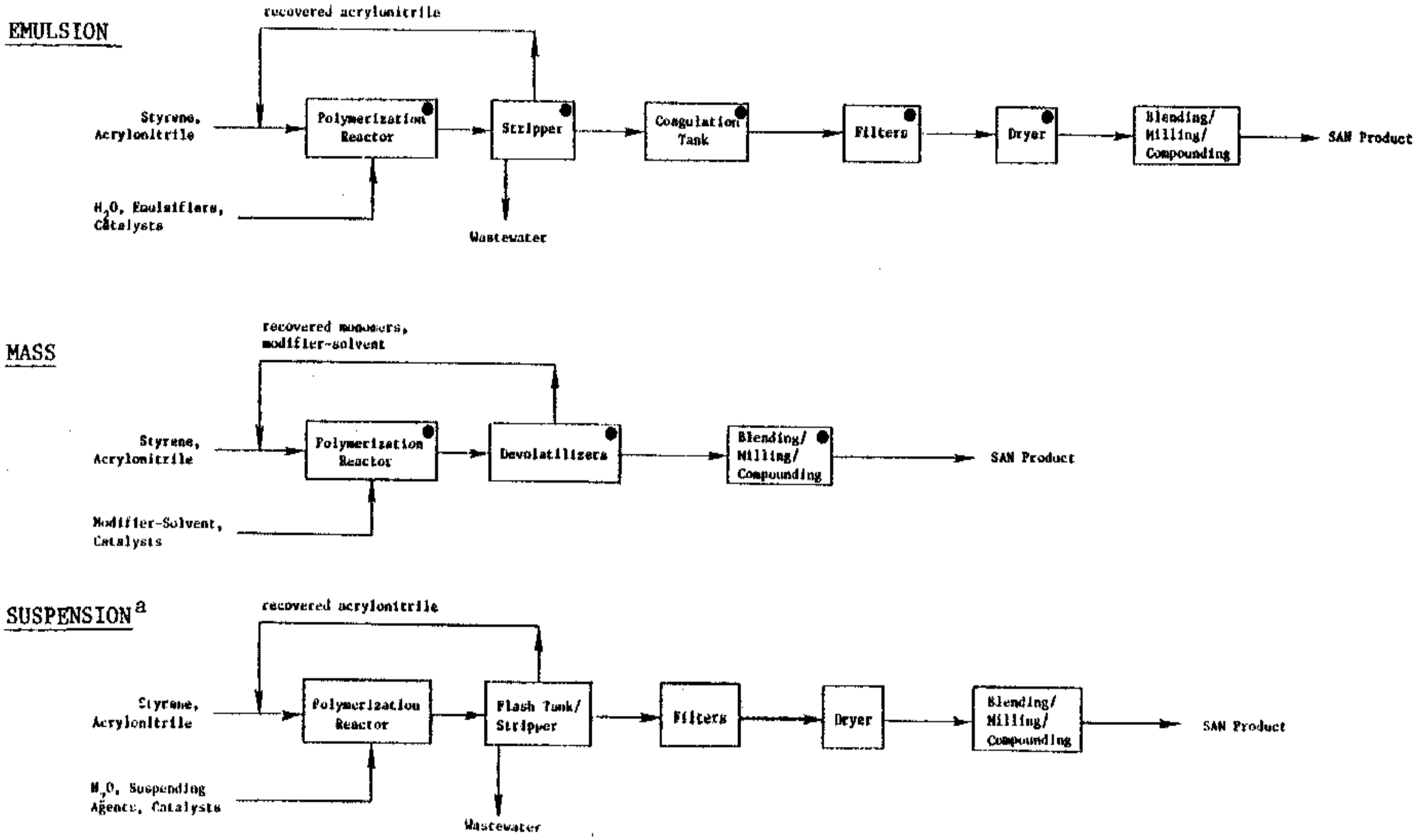
ABS and SAN resins are produced by emulsion, suspension, and mass polymerization processes. Currently most ABS and most SAN for captive use are produced using the emulsion polymerization process. Mass polymerization is the method most often used to produce SAN for sale in the marketplace.

Process and operating conditions used to produce SAN and ABS may vary considerably from plant to plant depending on the composition of the finished product. Likewise, emissions and methods of emission control and monomer recovery may vary from plant to plant. For this reason, it is difficult to give precise process descriptions for each of the various polymerization processes. The process descriptions and flow diagrams presented in this section are, therefore, very general in nature. Brief discussions of each of the processes used to produce SAN are included in the section followed by a discussion of methods used to produce ABS.

San Production Processes--

The three polymerization processes used to produce SAN are emulsion, mass, and suspension polymerization. Simplified block diagrams of these three processes are shown in Figure 5.

SAN produced via the emulsion polymerization process may be formed by either a batch or a continuous process. In either process, styrene and acrylonitrile monomers are fed to the reactor along with an emulsifier, deionized water, and catalysts. The polymerization reaction takes place at about 70-100°C (160-212°F) and proceeds to 90-98 percent conversion. Unreacted monomers are recovered from the resulting SAN latex by steam stripping. The SAN latex is then subjected to coagulation, filtration, and drying before the solid SAN product is produced. Potential acrylonitrile emission points include storage tanks, polymerization reactors, the latex stripper, the coagulation



[a] Information concerning acrylonitrile emissions from this process is unavailable.

● Indicates an acrylonitrile emissions point. These emissions are typically controlled by an incinerator/flare or by water scrubbing.

Figure 5. SAN production processes: emulsion, mass, and suspension polymerization.

tank, filters, and the dryer. However, acrylonitrile emissions from these points are generally reduced by incinerating/flaring the vent gas streams and/or passing them through a water scrubber.

The mass polymerization process used to produce SAN is generally a continuous process with inherently low acrylonitrile emissions. The styrene and acrylonitrile monomer mixture is heated together with an appropriate modifier-solvent and pumped to the polymerizaton reactor. Polymerization takes place in the presence of a catalyst in an agitated reactor maintained at about 275 kPa (40 psia) and 100-200°C (212-390°F). The reaction proceeds only to about 20 percent conversion. The conversion is limited in order to control viscosity. The reaction products are discharged to a series of devolatilizers that separate the SAN polymer from unreacted monomers and the modifier-solvent. Devolatilization is carried out under vacuum at temperatures of 120 to 260°C (250 to 500°F). Inerts, unreacted monomers, and the modifier-solvent are removed overhead from the devolatilizers. Overheads are condensed and passed through a refrigerated styrene scrubber to recover monomers and modifier-solvent which are then recycled to the feed tank. The refrigerated scrubber vent gas contains a negligible amount of acrylonitrile.

The bottoms from the final devolatilizer are almost pure polymer melt. This polymer is extruded and chopped into pellets. The pellets are then blended, milled and compounded. Acrylonitrile and other volatile organic compounds that are released from the milling operation are passed through a scrubber prior to being vented to the atmosphere. Acrylonitrile emissions from the feed tank, reactor, and devolatilizers are vented to an incinerator/flare.

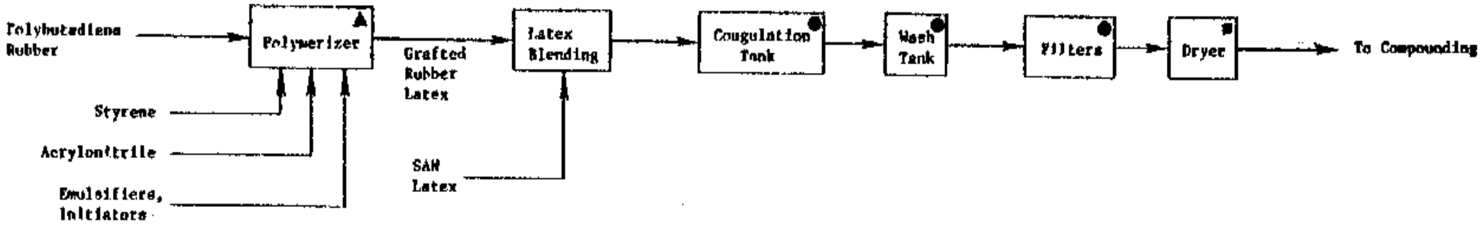
SAN produced via the suspension polymerization process may be produced in either a batch or a continuous mode, although batch processes are predominant. In this process, styrene and acrylonitrile monomers are dispersed mechanically in water containing catalysts and suspending agents. The monomer droplets are polymerized while suspended by agitation, and insoluble beads of polymer are formed. The temperature of the polymerization reactor ranges from 60-150°C (140-300°F) and a monomer conversion of 95 percent is normally achieved. Unreacted monomer is recovered by flashing and steam or vacuum stripping. The solid and liquid phases of the polymer slurry are separated by centrifugation and/or filtration. The solid phase is then dried in a rotary dryer and the dried polymer is finished by mechanically blending in dyes, antioxidants and other additives using extruders and rolling mills. The polymer sheets from these operations are then pelletized and packaged. Although emissions of acrylonitrile from the various process operations described above would be expected, information detailing these emissions and methods of control is unavailable.

ABS Production Processes--

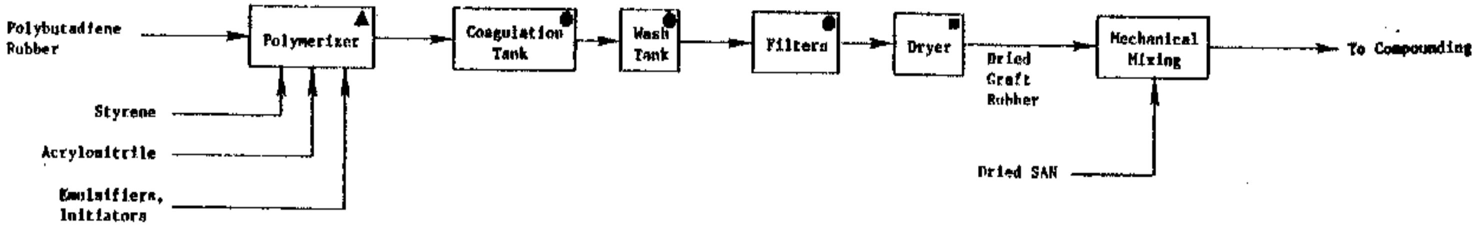
As mentioned previously, ABS is a two-phase system consisting of an SAN-grafted rubber blended with SAN. Polybutadiene is normally used as the backbone or substrate rubber but nitrile rubbers and styrene-butadiene rubbers may also be used. The backbone rubber may be produced at the ABS facility for captive use or it may be purchased from other sources. Like SAN, ABS may be produced by the emulsion, mass, and suspension polymerization processes.

ABS by Emulsion Polymerization-- There are three different routes by which ABS may be produced using the emulsion polymerization process. Block diagrams for each of these routes are depicted in Figure 6. In the first route pictured in Figure 6, styrene and acrylonitrile monomers are grafted onto the backbone rubber, usually polybutadiene rubber. The SAN-grafted rubber latex is then blended with SAN resin latex (produced by emulsion polymerization) followed by coagulation, washing, filtration, and drying.

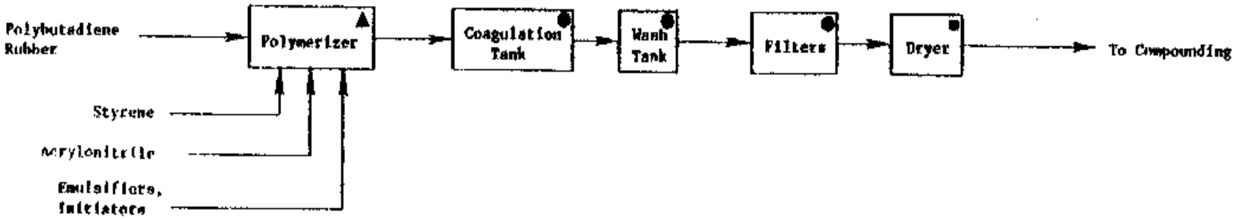
In the second route shown in Figure 6, the SAN-grafted rubber is coagulated, washed, filtered and dried. Then the dry grafted-rubber is mechanically blended with dry SAN solid. Solid SAN copolymer produced by the emulsion, suspension or mass polymerization processes may be utilized in the mechanical blending step. In the third route shown in



a. SAN latex blended with graft rubber latex.



b. Dry SAN mechanically blended with dry graft rubber.



c. SAN-graft and styrene-acrylonitrile copolymerization occurring in one step.

▲ Unreacted acrylonitrile monomer is passed through a water scrubber for monomer recovery. Acrylonitrile emissions from the scrubber are then incinerated or flared.

● Indicates an acrylonitrile emissions point. These emissions are typically controlled by an incinerator or flare.

■ Indicates an uncontrolled acrylonitrile emissions point.

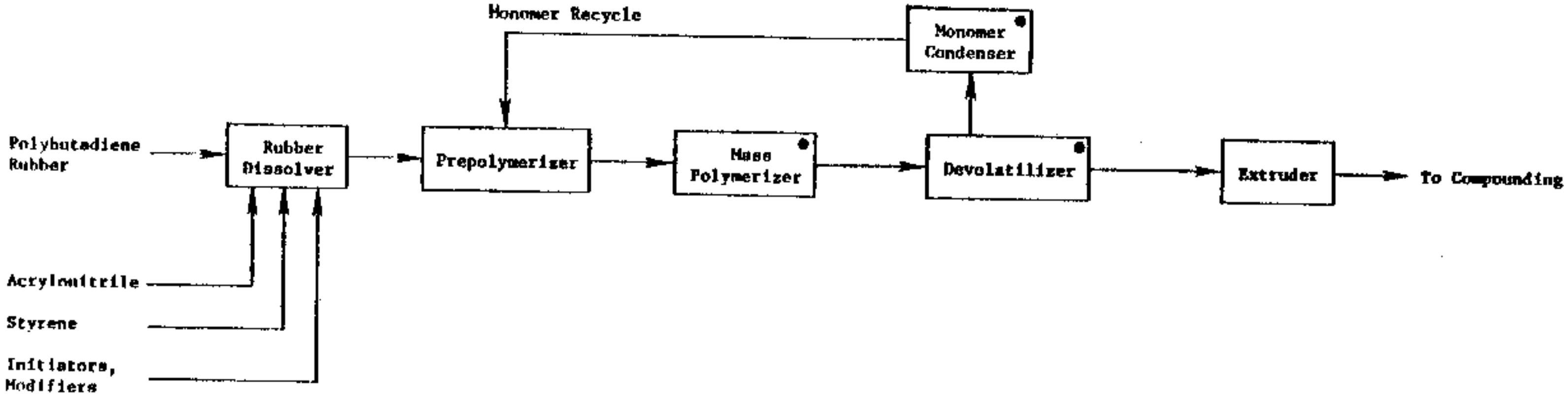
Figure 6. ABS emulsion polymerization processes.

Figure 6, the SAN-graft and styrene-acrylonitrile copolymerization occur in the same reaction vessel. The resulting ABS latex is then coagulated, washed, filtered and dried.

Each of these routes uses a water scrubber to recover unreacted acrylonitrile monomer from the emulsion polymerization reactor vent gas. Acrylonitrile emissions from the water scrubber, coagulation tank, wash tanks, and filters are incinerated/flared before being released to the atmosphere. Generally, emissions from the polymer dryer are uncontrolled.

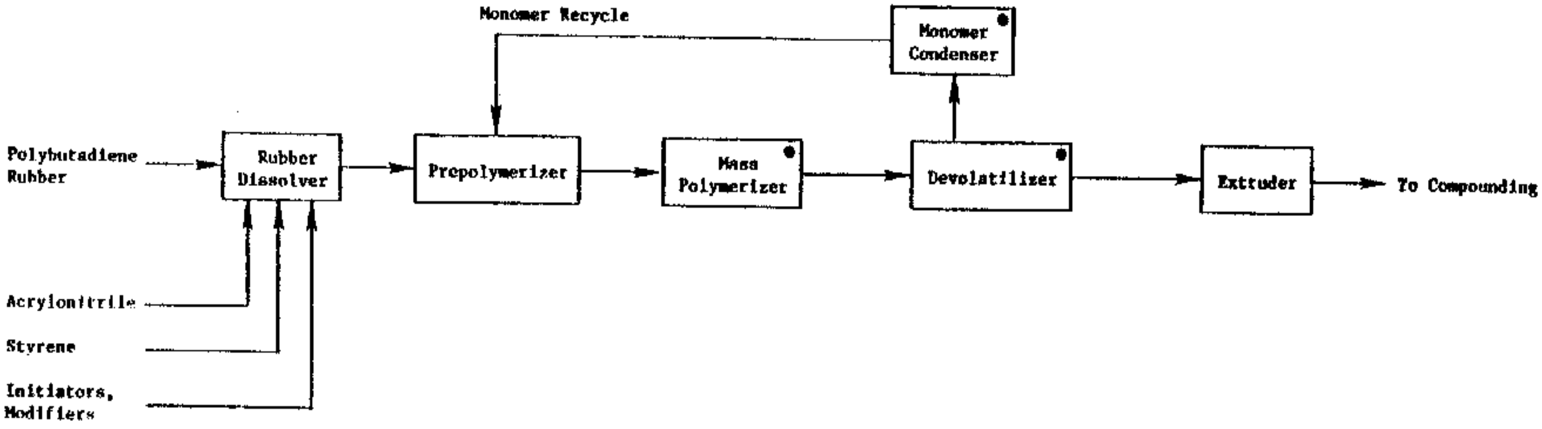
ABS by Mass Polymerization-- A block flow diagram for ABS produced via the mass polymerization process is shown in Figure 7. The rubber used in this process must be soluble in the styrene and acrylonitrile monomers. The rubber is dissolved in the monomers along with initiators and modifiers and then passed to the prepolymerizer, an agitated vessel where a 20 to 30 percent conversion of the monomers occurs. The resulting monomer-polymer mixture is pumped directly to the mass polymerization reactor where an overall conversion of 50 to 80 percent is achieved. Unreacted monomers are removed from the polymer in a series of devolatilizers, and are then condensed and recycled to a prepolymerizer. To produce the product resin, ABS polymer is extruded and chopped into pellets. Acrylonitrile emission points include the polymerization reactor, devolatilizers, and monomer vapor condenser. Vent incineration is typically used to reduce acrylonitrile emissions from this process.

ABS by Suspension Polymerization-- The suspension polymerization process used to produce ABS is shown by a block flow diagram in Figure 8. This process is sometimes called a mass-suspension process because the dissolving and prepolymerizations steps are identical to those of the mass polymerization process. The monomer/polymer mixture from the prepolymerizer is passed to the suspension reactor to which is added water and suspending agents. When the desired conversion is reached, the reaction products are cooled, dewatered by filtration or centrifugation, and dried. Possible acrylonitrile emission sources from



● Indicates an acrylonitrile emissions point. These emissions are typically controlled by an incinerator or flare.

Figure 7. ABS produced via mass polymerization.



● Indicates an acrylonitrile emissions point. These emissions are typically controlled by an incinerator or flare.

Figure 8. ABS produced via suspension polymerization.

this process include the prepolymerizer, polymerization reactor, dewatering system, and the dryer. Emissions from these sources are often reduced by incineration.

Emissions Summary

Acrylonitrile emission sources vary depending upon the type of polymerization process used: emulsion, mass, or suspension. Possible emission sources and typical methods of control were previously discussed for each of the various polymerization processes used to produce SAN and ABS. In addition to acrylonitrile emissions from the various process operations, fugitive emissions of acrylonitrile from pumps, valves, and flanges may also occur. Sufficient information was unavailable to develop emission factors for specific facilities, process operations, or fugitive emission sources. Also, no information concerning reactor startup emissions is available in the literature for ABS/SAN production processes. The reader is encouraged to contact State and local air pollution control agencies where these types of plants are located and the specific plants of interest to determine the extent of potential acrylonitrile emissions from ABS/SAN production.

Source Locations

ABS/SAN resins are produced by three companies at 10 locations. A list of these producers and their locations is given in Table 8.12 Although all ABS manufacturers have SAN production capabilities, essentially all of this SAN is used captively in the production of ABS.

The manufacturers of acrylonitrile products such as ABS and SAN resins may change over time due to changes in market conditions. Publications such as the SRI Directory of Chemical Producers and the Chemical Marketing Reporter are good sources of up-to-date information on chemical producers. Chemical trade associations such as the Chemical

TABLE 8. DOMESTIC ABS/SAN RESIN PRODUCERS IN 1983[12]

Company	Location	Products	
		SAN	ABS
Borg-Warner Corp.	Ottawa, Illinois		yes
	Washington, West Virginia	-	yes
	Port Bienville, Mississippi	-	yes
Dow Chemical	Gales Ferry, Connecticut (b)	-	yes
	Ironton, Ohio		yes
	Midland, Michigan (a)	yes	yes
	Pevely, Missouri	yes	
	Torrance, California		yes
Monsanto Co. (c)	Addyston, Ohio (a)	yes	yes
	Muscatine, Iowa		yes

(a) Produce some SAN for the merchant market. Most SAN is used captively in ABS production.

(b) This plant is also referred to as the Allyns Point plant.

(c) Reference 12 indicates that Monsanto has an ABS resin plant in Springfield, Massachusetts; however, information obtained from Reference 13 and Reference 14 has more recently indicated that this facility no longer produces ABS resins.[12-14]

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of acrylonitrile emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

Manufacturers Association, the Acrylonitrile Group, and the Synthetic Organic Chemical Manufacturers Association would also be good contacts to determine the status of the acrylonitrile products industry.

NITRILE RUBBER AND LATEX PRODUCTION[1-9]

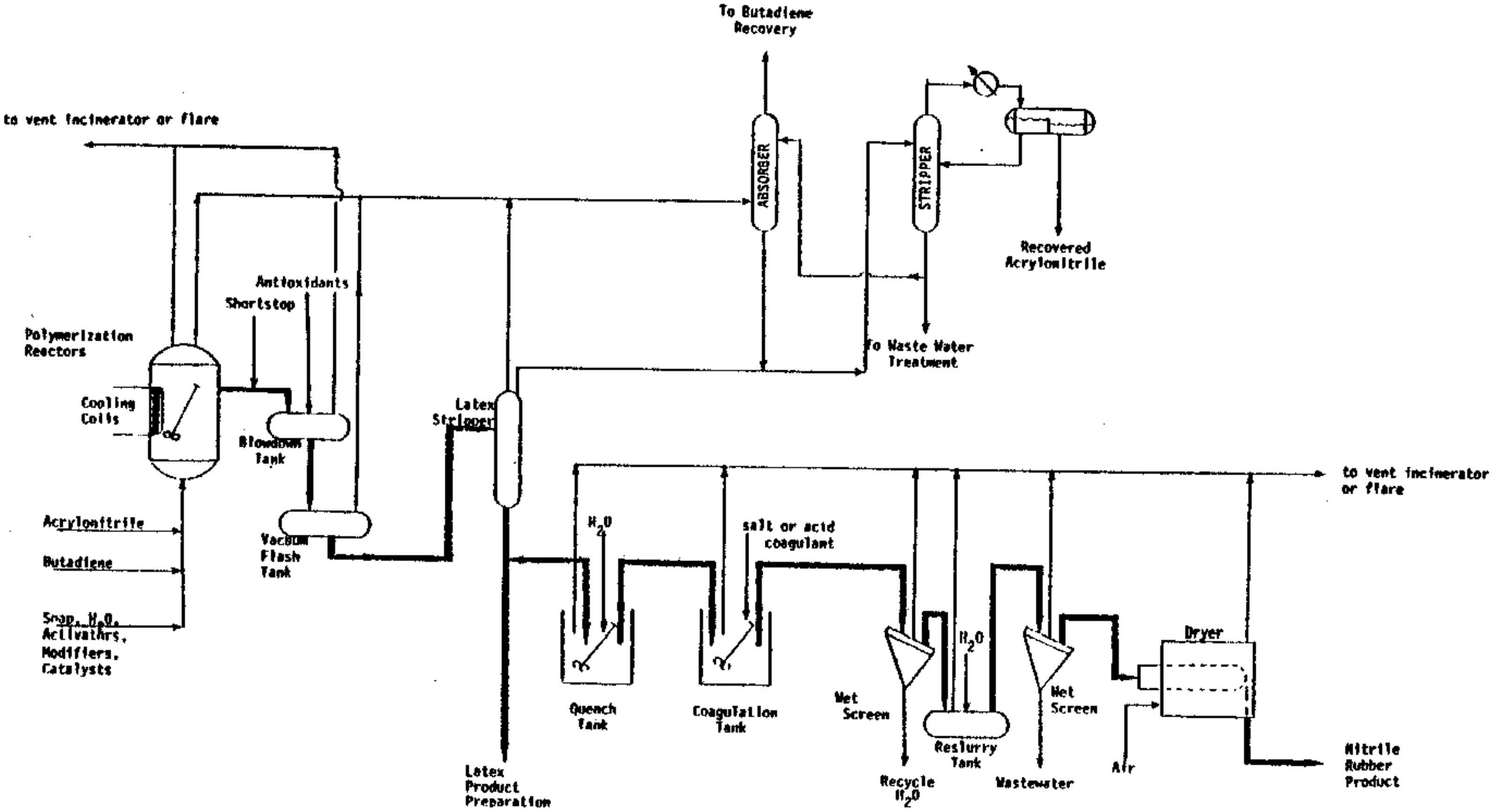
Another use for acrylonitrile monomer is in the production of nitrile elastomers, in both crumb rubber and latex form. The rubbers and latexes are manufactured using the emulsion copolymerization of acrylonitrile and butadiene. Acrylonitrile content in these nitrile products may range from 20 to 50 weight percent but is typically in the 30 to 40 percent range. The acrylonitrile content of a particular product is dictated by the end use of the product. The oil resistance of the product increases with increasing acrylonitrile content, but the low temperature flexibility decreases.

Process Descriptions

Nitrile rubbers and latexes are produced by emulsion polymerization in batch or continuous reactors. This process involves polymerization of acrylonitrile and butadiene monomers, recovery of unreacted monomers, and coagulation, washing and drying. A schematic flow diagram of the process is shown in Figure 9.

Polymerization--

Acrylonitrile and butadiene monomers are fed to the agitated polymerization reactors along with a soap solution and additives. Additives include catalysts and activators, which initiate and promote the polymerization reaction, and modifiers which control polymer properties such as viscosity and molecular weight (chain length). Early in the reaction the soap provides the microscopic bubbles called micelles in which the reaction takes place. Later, the soap covers the rubber particles formed and keeps the mixture in liquid form. The soap solution is used to produce an emulsion of monomers in an aqueous medium.



Note: Darkened lines indicate product stream flow.

Figure 9. Hypothetical nitrile elastomer production process.

The polymerization process is carried out under either cold conditions [4-7°C and 101 to 205 kPa (40-45°F and 0 to 15 psig)] using ammonia refrigeration to remove heat of reaction, or under hot conditions [35-49°C and 377 to 515 kPa (95-120°F and 40 to 60 psig)] using cooling water. Reaction times may vary considerably (from an hour to several days) depending on the ingredients used. When the desired level of conversion has been attained, the reaction is stopped by destroying the catalyst and adding a shortstop solution. Two common shortstop ingredients are sodium dimethyl dithiocarbamate and hydroquinone. Monomer conversion for rubber products is typically 60 to 90 percent while 95 percent conversion is typical for latex products. The resulting reaction mixture, a milky white emulsion called latex, is sent to blowdown tanks where antioxidants are normally added to maintain product quality.

Unreacted Monomer Recovery--

Unreacted monomers must be removed from the latex, requiring a series of flashing and stripping operations. First, the latex is subjected to several vacuum flash steps where most of the unreacted butadiene and some acrylonitrile are released. Then the latex is usually stripped with steam under vacuum to remove residual butadiene and most of the unreacted acrylonitrile. A thorough flash/stripping operation will remove better than 99 percent of the unreacted monomers from the latex. Stripped latex at about 43 to 55°C (110 to 130°F) is pumped to blend tanks.

Butadiene and acrylonitrile monomers released from the latex flashing/stripping operation are passed through a water absorber along with reactor process vent gases, effecting separation of the two monomers. Butadiene is passed to a separate recovery unit and the monomer is then recycled to the process. Acrylonitrile monomer recovery is normally accomplished by combining the acrylonitrile-containing streams from the absorber and latex stripper and passing the combined stream through a steam stripper. Acrylonitrile released overhead from the stripper is condensed and recycled to the process.

Coagulation, Washing And Drying--

The coagulation, washing, and drying steps are omitted if the desired end product is latex. These steps are necessary, however, for the production of rubber. In the production of rubber, latex is first coagulated into a slurry of fine crumbs by the addition of various salts or acids which destroy the protective soap cover. Coagulated crumb rubber is quenched and then separated from the coagulation liquor in a shaker screen and the liquor is recycled to the coagulation tank along with fresh acid or brine. The screened crumb is washed with water in a reslurry tank to remove residual coagulation liquor from the rubber. The crumb rubber slurry is again dewatered on a second screen. Although not depicted in Figure 9, a vacuum filter or press may be used further to dewater the crumb which typically has a moisture content of 10 to 50 percent. The crumb rubber is then dried in a gas-fired or steam-heated dryer where it is contacted with hot air. Finally, the nitrile rubber product is weighed and pressed into bales in preparation for shipment.

Emissions

Essentially all of the process operations shown in Figure 9 are potential sources of acrylonitrile emissions. However, emissions from these sources are generally reduced through a combination of monomer recovery by absorption and stripping, and vent incineration or flaring. Unreacted acrylonitrile and butadiene, released from the polymerization reactor as well as from the latex during flashing/stripping, are recovered and recycled to the process. Acrylonitrile emissions from the acrylonitrile absorber and stripper are negligible. Acrylonitrile emissions from polymerization reactors, the blowdown tank, the quench tank, the coagulation tank, wet screens, the reslurry tank, and the dryer are typically vented to an incinerator or flare. Fugitive emission sources include storage tanks, pumps, valves, flanges and drains. Sufficient information is not available to develop emission factors for various facilities, process operations, or fugitive emission sources. Also, no information is available in the literature to accurately quantify reactor startup emissions. The reader is encouraged to contact State and local air pollution control agencies where these types of plants are located and the specific plants of interest to determine the extent of potential acrylonitrile emissions from nitrile rubber and latex production.

Source Locations

Nitrile rubber is produced by five companies at seven locations. These companies and their locations are listed in Table 9.15,16 The manufacturers of acrylonitrile products such as nitrile rubber and latex may change over time due to changes in market conditions. Publications such as the SRI Directory of Chemical Producers and the Chemical Marketing Reporter are good sources of up-to-date information on chemical producers. Chemical trade associations such as the Chemical Manufacturers Association, the Acrylonitrile Group, and the Synthetic Organic Chemical Manufacturers Association would also be good contacts to determine the status of the acrylonitrile products industry.

PRODUCTION OF ADIPONITRILE[17]

Adiponitrile may be produced by as many as four processes; however, only one of these processes involves the use of acrylonitrile. Adiponitrile from acrylonitrile involves the hydrodimerization of acrylonitrile in an electrochemical process. This process is used only by Monsanto Company, who is also the original process developer.

The Monsanto electro-hydrodimerization (EHD) process is represented by the following equation:

$$2H_2C{=}CHCN \;+\; 2e^- \;+\; 2H^+ \;+\; NC(CH_2)_4CN.$$

This reaction takes place in an electrolytic cell, using electrical energy to provide the impetus for the chemical reaction. Either graphite and magnetite or cadmium and iron may be employed as

TABLE 9. DOMESTIC NITRILE ELASTOMER PRODUCERS IN 1983[15,16]

Company	Location
Copolymer Rubber and Chemical Corp.	Baton Rouge, Louisiana
BF Goodrich Co.	Akron, Ohio Louisville, Kentucky
Goodyear Tire and Rubber Co.	Akron, Ohio Houston, Texas
Reichhold Chemical	Cheswold, Delaware
Uniroyal, Inc.	Painesville, Ohio

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of acrylonitrile emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

cathodes and anodes, respectively. A tetraalkylammonium salt is used to increase conductivity and to reduce the formation of byproduct propionitrile by hydrogenation of acrylonitrile.

The reaction itself is carried out by rapidly pumping a two-phase emulsion through the cathode-anode system. This two-phase emulsion consists of an aqueous phase containing the conducting salt and small amounts of acrylonitrile, and an organic phase containing acrylonitrile and adiponitrile. After passing through the electrolytic cell, the organic and aqueous phases are separated by distillation. The aqueous phase containing the conducting salt is recycled, and adiponitrile is recovered from byproducts, propionitrile, and biscyanoethyl ether. The adiponitrile selectivity in this reaction is approximately 90 percent.

No process information is available to formulate acrylonitrile emission factors for the Monsanto EHD adiponitrile process. The reader is encouraged to contact State and local air pollution control agencies where these types of plants are located and the specific plants of interest to determine the extent of potential acrylonitrile emissions from adiponitrile production.

The Monsanto plant where adiponitrile is produced by the EHD process is located in Decatur, Alabama.[18]

PRODUCTION OF ACRYLAMIDE[19]

Acrylamide is produced on the industrial scale by the hydration of acrylonitrile. As shown in Table 10, three companies at four locations are currently producing acrylamide.[20] Two hydration methods are currently used in the United States: acid hydrolysis (partial hydrolysis) and catalytic hydrolysis (direct hydrolysis).

In the acid hydrolysis process, acrylonitrile is reacted with stoichiometric amounts of sulfuric acid (H_2SO_4) to form acrylamide

TABLE 10. DOMESTIC ACRYLAMIDE PRODUCERS IN 1983[20]

Company	Location
American Cyanamid	Linden, New Jersey Avondale, Louisiana[a]
Dow Chemical	Midland, Michigan
Nalco Chemical	Garyville, Louisiana

(a) This plant is also referred to in the literature as being located in Westwego, Louisiana.

NOTE: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of acrylonitrile emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

sulfate. The acrylamide sulfate intermediate is then reacted with ammonia (NH_3) forming acrylamide and ammonium sulfate. The equation governing the acid hydrolysis reaction is:

$$CH_2{=}CHCN + H_2SO_4 \bullet H_2O \text{--->} CH_2{=}CHCONH_2 \bullet H_2SO_4$$

$$\xrightarrow{2NH_3} CH_2{=}CHCONH_2 + (NH_4)_2SO_4$$

Ammonium sulfate and acrylamide are then separated by several involved crystallization steps.

In the catalytic hydrolysis process, acrylamide is produced by the direct hydrolysis of acrylonitrile over copper catalysts in an aqueous solution. The advantage of this method is that, after filtering off the catalyst and distilling to remove unreacted acrylonitrile, an essentially pure aqueous acrylamide solution is obtained. This solution can then be used directly or further concentrated depending upon its end use.

Information concerning emissions of acrylonitrile from the production of acrylamide is unavailable. The reader is encouraged to contact State and local air pollution control agencies where these types of plants are located and the specific plants of interest to determine the extent of potential acrylonitrile emissions from acrylamide production.

REFERENCES FOR SECTION 5

1. Click, C.N. and D.O. Moore. Emission, Process and Control Technology Study of the ABS/SAN, Acrylic Fiber, and NBR Industries (prepared for U.S. Environmental Protection Agency. Contract No. 68-02-2619, Task 6). Pullman Kellogg. Houston, Texas. April 1979.

2. Considine, D. Chemical and Process Technology Encyclopedia. McGraw-Hill, New York, New York. 1974. pp. 27-28.

3. Encyclopedia of Polymer Science and Technology. Volume 1: Acrylic Fibers. p. 352.

4. 1980 Kline Guide to the Chemical Industry. pp. 343-344.

5. Work, R. W. Man-Made Textile Fibers. In: Riegel's Handbook of Industrial Chemistry. Kent, J. (ed). Van Nostrand Reinhold. New York. 1974. p. 332.

6. Development Document for Proposed Effluent Limitations Guideline and New Source Performance Standards for the Synthetic Resins Segment of the Plastics and Synthetic Materials Manufacturing Point Source Category.U.S. Environmental Protection Agency. EPA-940/1-73-01O. September 1973. p. 71.

7. Click, C.N. and D.O. Moore. Emission, Process and Control Technology Study of the ABS/SAN, Acrylic Fiber, and NBR Industries (prepared for U.S. Environmental Protection Agency. Contract No. 68-02-2619, Task 6). Pullman Kellogg. Houston, Texas. April 1979. pp. 80-85.

8. Work, R. W. Man-Made Textile Fibers. In: Riegel's Handbook of Industrial Chemistry. Kent, J. (ed). Van Nostrand Reinhold. New York. 1974. pp. 348-351.

9. U. S. International Trade Commission. Synthetic Organic Chemicals, U. S. Productions and Sales. 1979.

10. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. p. 593.

11. Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Volume 1. Acrylonitrile Polymers. John Wiley and Sons, New York, New York. 1980. pp. 427-456.

12. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. pp. 814 and 831.

13. Letter and attachments from Romano, R. R., Chemical Manufacturers Association to Lahre T., U. S. EPA. August 11, 1983. Comments on emission factor reports.

14. Telecon. Lahre, T. F., U. S. EPA with Massachusetts Department of Environmental Quality Engineering. December 6, 1983. Status of the Monsanto-Springfield ABS resin plant.

15. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. p. 569.

16. Letter and attachments from Blower, K. E., Standard Oil to Lahre, T. F., U. S. EPA. June 13, 1983. Comments on the draft acrylonitrile emission factor report.

17. Weissermel, K. and H. Arpe. Industrial Organic Chemistry: Important Raw Materials and Intermediates. Verlag Chemie, New York, New York. 1978. pp. 216-219.

18. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. p. 412.

19. Weissermel, K. and H. Arpe. Industrial Organic Chemistry: Important Raw Materials and Intermediates. Verlag Chemie, New York, New York. 1978. pp. 270-272.

20. Stanford Research Institute International. 1983 Directory of Chemical Producers. Menlo Park, California. 1983. p. 409.

SECTION 6

SOURCE TEST PROCEDURES

The results of a literature survey and review of References 2 through 25 indicate that gas chromatography is the analytical method generally preferred for acrylonitrile.[1] Table 11 lists several sampling and analytical techniques evaluated, along with their advantages and disadvantages. The major differences among the various methods are in sample collection and preconcentration, and the choice of detector used for quantification.

The need to concentrate samples is determined by the level of the acrylonitrile in the sample and by the detection limit of the particular instrumentation chosen for quantification. When acrylonitrile levels are low, provisions must be built into the method for the determination of these low levels.

LITERATURE REVIEW OF SAMPLING METHODS

Although several researchers have used aqueous or aqueous/organic solvent mixtures in bubblers or impingers for sampling acrylonitrile, the most widely reported trapping methods are those employing solid adsorbent tubes of charcoal, Tenax®, or other porous polymers such as those used for gas chromatographic supports. Of these solid adsorbents, the one which has received the most attention and is used most often is Tenax-GC®. However, the data presented in the various publications surveyed in this review indicate that the retention characteristics of acrylonitrile on Tenax® are such that the safe sampling volumes would be quite small. The safe sampling volume is approximately 3 liters of air per gram (48 ft^3 per pound) of Tenax® for a flow rate of 5 to 200 ml/min at 25°C (77°F). Because of the small sample, the concentration factor would also be very small.

TABLE 11. ADVANTAGES AND DISADVANTAGES OF ACRYLONITRILE SAMPLING AND ANALYSIS PROCEDURES[1]

Method	Advantages	Disadvantages
SAMPLING		
aqueous/organic solvent bubblers	simple, inexpensive	not much information available on recoveries
Tenax or other GC adsorbent or porous polymer	thermally desorbed	very low sampling volumes
charcoal	high capacity	poor recovery for low levels of analyte
ANALYSIS		
gas chromatography with flame ionization detection (GC/FID)	simple, inexpensive	not very specific, sensitive to low quantities, many interferences expected
gas chromatography with nitrogen specific phos phorus detection (GC/NPD)	high, sensitivity, eliminates some interference	not completely specific
gas chromatography with mass spectroscopy (GC/MS)	highly specific, intermediate sensitivity	expensive

For Poropak N, a porous polymer often used for GC supports, the breakthrough volume was reported and found to be 3 to 5 liters of air at 100 ml/min at 25°C. The maximum recommended sampling volume for this sorbent was estimated to be 50 to 75 percent of the breakthrough volume, or 1.5 to 2.5 liters. With such small concentrations, the sensitivity of the measurement technique becomes very important.

Most sampling of air and exhaust samples for acrylonitrile is done using charcoal. The adsorptive capacity of charcoal for acrylonitrile is on the order of 4 percent by weight according to one report (NIOSH method), but this can vary depending upon the characteristics of the adsorbent. The main problem with charcoal adsorption tubes is the possibility of losses of small amounts of acrylonitrile upon desorption with organic solvents.

A recent investigation of recoveries of acrylonitrile from charcoal concluded that acrylonitrile could be recovered (>90 percent) with good precision from charcoal at a level of 16 µg per 100 mg charcoal using a mixture of acetone and carbon disulfide instead of methanol for desorption.13 This correspondends to vapor levels of 0.5 ppm for a 15 liter air sample. Below the 16 µg/100 mg charcoal level, recoveries were generally less than 90 percent for vapor phase application of acrylonitrile.

Because of possible low recoveries of acrylonitrile on charcoal, large sampling volumes might be required to achieve lower detection limits, but, at the same time, backup sections of charcoal adsorbent would be required should the levels be higher than expected.

LITERATURE REVIEW OF ANALYTICAL PROCEDURES

The three possible choices of detectors for GC separation of acrylonitrile are flame ionization detection, nitrogen specific detection, and low or high resolution mass spectrometry, with or without selected ion monitoring.

Flame ionization detection (FID) can only be used with relatively high levels of acrylonitrile. The use of high resolution mass spectrometry with selected ion monitoring (SEM) is the preferred detection technique, but the increased cost associated with SEM is prohibitive in some cases. Therefore, the most logical choice for a detection method, based upon cost and ease of use, is nitrogen specific detection with either a alkali flame detector (AFD), a thermionic specific detector (TSD), or nitrogen specific phosphorus detection (NPD). The use of nitrogen specific detection should reduce background interferences encountered with the FID and increase sensitivity. One source estimated the detection limit of the nitrogen specific detector at 10 pg.[10]

REFERENCES FOR SECTION 6

1. Cooke, M. et al. (Battelle); J.C. Harris and V. Grady (Arthur D. Little). Candidate Techniques for Sampling and Analysis for Twenty-One Suspect Carcinogens. Draft Report. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. September 28, 1982.

2. Kogaczewska, T. Acrylonitrile Determination in Air. Med. Pr.. 27(2) 115-126, 1976. (In Polish).

3. Nagarova, V.I. and L.K. Nakrop. Determination of Acrybutrile in Air. M. Anal. K. Kach. Prod. Khum. Prom., 5:28-29, 1978. (In Russian).

4. Knodo, M. Sampling and Measurement of Organic Cyanogen Compounds. Kankyo Hoken Reporti Environ. Health Rept., 30:83-88, 1974. (In Japanese).

5. Fasitta, V. and G. Ticciardello. Determination of Acetonitrile and Acrylonitrile in Air by Gas Chromatography. Ann. Inst. Super. Sanita., 13(1-2):245-248, 1977. (In Italian).

6. Schultzl, O., J.J. Prater, and S.R. Ruddell. Sampling and Analysis of Emissions for Stationary Sources. I. Odor and Total Hydrocarbons. JAPCA, 25(9):925-932, 1975.

7. Penton, S. Measurement of Acrylonitrile in Industrial Air by Gas Chromatography. Varian Instrument Appl., 13(2):4-5, 1979.

8. Sawicki, E. Organic Solvent Vapors in Air. Analytical Method. Health Lab. Sci., 12(4):394-402, 1975.

9. Gomez, C.R. and B.G. Linder. Quantitative Determination of Acrylonitrile in Work Areas. Traub. Simp. Hyg. Ind., 3:495-506, 1979. (In Spanish).

10. Marano, R.S., S.D. Levine and T.M. Harvey. Trace Determination of Subnanogram Amounts of Acrylonitrile in Complex Matrices by Gas Chromatography with a Nitrogen Selective Detector. Anal. Chem., 50:(13), 1948-1950, 1978.

11. Oomens, A.C. Experience With a Dual Detector Headspace Gas Chromatograph for Acrylonitrile Analysis. Appl. Headspace Gas Chromatography., 1980, pp. 111-116.

12. Taylor, D.G., coord. NIOSH Manual of Analytical Methods, Vol. 3, 2nd ed., 1977. pp. 5156-1 to 5156-8.

13. Gagnum, Y.T., and J.C. Posner. Recovery of Acrylonitrile from Charcoal Tubes at Low Levels. Am. Ind. H . Assoc. J., 40(10):923-925, 1979. 14. Russell, J.W. Analysis of Air Pollutants Using Sampling Tubes and Gas Chromatography. Environ. Sci. Technol., 9(13):1175-1178, 1975.

14. Russell, J.W. Analysis of Air Pollutants Using Sampling Tubes and Gas Chromatography. Environ. Sci. Technol., 9(13):1175-1178, 1975.

15. Parsons, J.S., and S. Mitzner. Gas Chromatographic Method for Concentration and Analysis of Traces of Industrial Organic Pollutants in Environmental Air and Stacks. Environ. Sci. Technol., 9(12):1053-1058, 1975.

16. Brown, R.H., and C.J. Purnell. Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres. The Performance of Tenax-GC Adsorbent Tube. J. Chromatogr., 178(1):79-90, 1979.

17. Campbell, D.N., and R.H. Moore. The Quantitative Determination of Acrylonitrile, Acrolein, Acetonitrile and Acetone in Workplace Air. Am. Ind. Hyg. Assoc. J., 40(10) 904-909, 1979.

18. Schabel, X.H., and R. Casper. Headspace Gas Chromatography in Industrial Hygiene. Appl. Headspace Gas Chromatogr., 1980, pp. 32-40.

19. Casper, R.H. Special Analytical Methods with Respect to Industrial Hygiene. Annu. Meet. Proc.-Int. Inst. Symp. Rubber Prod., 18, Paper No. 6, 1977, pp. 15.

20. Jacobs, H., and R. Syrjola. The Use of Infrared Analyzers for Monitoring Acrylonitrile. J. Am. Ind. Hyg. Assoc., 39(2) 161-165, 1978.

21. Syyrjola, R.J. Quantitative Analysis of Atmospheric Pollutants Using a Microcomputer Controlled Single Beam Infrared Spectrometer. Envir. Anal., 1977, pp. 111-125.

22. Satoh, S. Gas Chromatography-Mass Spectrometric Identification of Organic Compounds and Determination of Acrylonitrile in the Air of the Kawasaki Industrial Area. Koenshu-Iyo Masu Kenkywkui., 4:113-120, 1979.

23. Koosker, A.A.M. Measurement of Organic Gases in the Atmosphere. PT-Procestech., 34(7):409-415, 1979.

24. Harris, J.C., M.J. Hayes, P.L. Levins, and D.B. Lindsay, EPA/IERL-RTP Procedures for Level 2 Sampling and Analysis of Organic Materials EPA-6O0/7-79-033, U.S. Environmental Protection Agency, 1979. pp. 165.

25. Thrun, K.E., J.C. Harris, C.E. Rechsteiner, D.J. Sorling. Methods for Level 2 Analysis by Organic Compound Category, EPA-600/7-81-029, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1981. pp. 123-131.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-450/4-84-007a

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF ACRYLONITRILE

5. REPORT DATE
March 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Radian Corporation
3024 Pickett Road, Durham, NC 27705

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
U. S. Environmental Protection Agency
Office Of Air Quality Planning And Standards
MD 14
Research Triangle, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

EPA Project Officer: Thomas F. Lahre

16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with acrylonitrile. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of acrylonitrile and in making gross estimates of air emissions therefrom.

This document presents information on 1) the types of sources that may emit acrylonitrile, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for acrylonitrile release into the air from each operation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Acrylonitrile Sources Locating Sources of Emissions Toxic Substances		

18. DISTRIBUTION STATEMENT	**19. SECURITY CLASS** *(This Report)*	**21. NO. OF PAGES** 68
	20. SECURITY CLASS *(This page)*	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE