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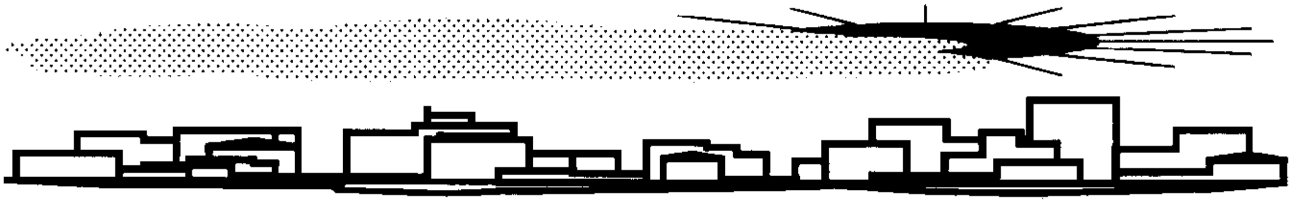
PRELIMINARY DATA SEARCH REPORT FOR LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF CYANIDE COMPOUNDS



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PRELIMINARY DATA SEARCH REPORT FOR

LOCATING AND ESTIMATING AIR TOXIC EMISSIONS FROM SOURCES OF CYANIDE COMPOUNDS

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This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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SECTION 1
PURPOSE OF DOCUMENT

The U. S. Environmental Protection Agency (EPA), State, 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, little information exists on the ambient air concentration of these substances or about 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. Prior documents in the series are listed below:

Substance	EPA Publication Number
Acrylonitrile	EPA-450/4-84-007a
Carbon Tetrachloride	EPA-450/4-84-007b
Chloroform	EPA-450/4-84-007c
Ethylene Dichloride	EPA-450/4-84-007d
Formaldehyde	EPA-450/4-91-012
Nickel	EPA-450/4-84-007f
Chromium	EPA-450/4-84-007g
Manganese	EPA-450/4-84-007h
Phosgene	EPA-450/4-84-007i
Epichlorohydrin	EPA-450/4-84-007j
Vinylidene Chloride	EPA-450/4-84-007k
Ethylene Oxide	EPA-450/4-84-007l

Chlorobenzene	EPA-450/4-84-007m
Polychlorinated Biphenyls(PCB's)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM)	EPA-450/4-84-007p
Benzene	EPA-450/4-84-007q
Perchloroethylene and Trichloroethylene	EPA-450/2-89-013
Municipal Waste Combustion	EPA-450/2-89-006
Coal and Oil Combustion	EPA-450/2-89-001
1,3-Butadiene	EPA-450/2-89-021
Chromium (Supplement)	EPA-450/2-89-002
Sewage Sludge	EPA-450/2-90-009
Styrene	EPA-454/R-93-011
Cadmium	EPA-454/R-93-040
Mercury	EPA-454/R-93-023
Methylene Chloride	EPA-454/R-93-006
Medical Waste	Number to be Assigned
TCDD/TCDF	Number to be Assigned
Toluene	Number to be Assigned
Xylenes	Number to be Assigned
Methyl Ethyl Ketone	Number to be Assigned
Methyl Chloroform	Number to be Assigned
Chlorobenzene (Update)	Number to be Assigned
Chloroform (Update)	Number to be Assigned

This document differs from the previous locating and estimating documents listed above because of the lack of published test data. It is being published to solicit additional data to allow the document to be finalized. The document deals specifically with cyanide compounds (e.g., hydrogen cyanide, sodium cyanide, potassium cyanide). Sources of cyanide compound emissions evaluated in this document include: (1) cyanide compound production; (2) emissions resulting from major uses of cyanide compounds; and (3) emissions from miscellaneous sources. Data presented in this document are total cyanide compound emissions.

In addition to the information presented in this document, another potential source of emissions data for cyanide compounds is the Toxic Chemical Release Inventory (TRI) form required by Section 313 of Title III of the 1986 Superfund Amendments and Reauthorization Act (SARA 313).[1] SARA 313 requires owners and operators of facilities in certain Standard Industrial Classification Codes (SIC) that manufacture, import, process or otherwise use toxic chemicals (as listed in Section 313) to report annually their releases of these chemicals to all environmental media. As part of SARA 313, EPA provides public access to the annual emissions data. The TRI data include general facility information, chemical information, and emissions data. Air emissions data are reported as total facility release estimates for fugitive emissions and point source emissions. No individual process or stack data are provided to EPA under the program. The TRI requires sources to use stack monitoring data for reporting, if available, but the rule does not require stack monitoring or other measurement of emissions if it is unavailable. If monitoring data are unavailable, emissions are to be quantified based on best estimates of releases to the environment.

The reader is cautioned that the TRI will not likely provide facility, emissions, and chemical release data sufficient for conducting detailed exposure modeling and risk assessment. In many cases, the TRI data are based on annual estimates of emissions (i.e., on emission factors, material balance calculations, and engineering judgment). We recommend the use of TRI data in conjunction with the information provided in this document to locate potential emitters of cyanide compounds and to make preliminary estimates of air emissions from these facilities.

Cyanide compounds are of particular importance as a result of the Clean Air Act Amendments of 1990. Cyanide compounds are included in the Title III list of hazardous air pollutants and will be subject to standards established under Section

112, including maximum achievable control technology (MACT). These standards are to be promulgated no later than 10 years following the date of enactment.

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 cyanide compounds and estimating air emissions from these sources. 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 document.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of hydrogen cyanide and other cyanide compounds and an overview of their production and uses. This background section may be useful to someone who wants to develop a general perspective on the nature of the substance and where it is manufactured and consumed and reported TRI emissions.

Sections 4 through 6 of this document focus on the major industrial source categories that may discharge air emissions containing cyanide compounds. Section 4 discusses the production of major cyanide compounds. Section 5 discusses the different major uses of cyanide compounds as an industrial feedstock. Section 6 discusses emissions from miscellaneous sources. For each major industrial source category described, process descriptions and flow diagrams are given wherever possible; potential emission points are identified, and available emission factor estimates are presented that show the potential for cyanide compound emissions before and after controls are employed by industry. Individual companies are identified that are reported to be involved with the production and/or use of cyanide compounds based on industry contacts, the Toxic Release Inventory (TRI), and available trade publications.

Section 7 summarizes available procedures for source sampling and analysis of cyanide compounds. Details are not prescribed nor is any EPA endorsement given or implied for any of these sampling and analysis procedures. Section 8 presents the references. Appendix A presents calculations used to derive the estimated 1990 nationwide cyanide compound emissions presented in Section 3. Appendix B presents a list of iron and steel production facilities that use electric arc furnaces and the crude oil distillation capacity at U.S. refineries.

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

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

Chief, Emission Factor and Methodology Section (MD-14)
Emission Inventory Branch
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

SECTION 3
BACKGROUND

This section provides a brief summary of the physical and chemical characteristics of hydrogen cyanide and other cyanide compounds. This section also gives an overview of the production, use, and emissions of hydrogen cyanide and other cyanide compounds.

3.1 NATURE OF THE POLLUTANT

3.1.1 Hydrogen Cyanide

Hydrogen cyanide (CAS 74-90-8), HCN, is a colorless, poisonous liquid with the characteristic odor of bitter almonds. It is a low viscosity liquid at 25°C and has a boiling point of 25.70°C. Hydrogen cyanide is miscible in all portions in water and alcohol, and is soluble in ether. Hydrogen cyanide polymerizes spontaneously when not absolutely pure or stabilized. The stabilizer used is sulfur dioxide and sulfuric acid. Table 3-1 summarizes the physical and chemical properties of HCN. Hydrogen cyanide is primarily used as a basic building block for other chemical products such as adiponitrile, methyl methacrylate, cyanuric chloride, sodium cyanide, potassium cyanide, and a variety of chelating agents.[2-4]

Hydrogen cyanide is a very weak acid, having an ionization constant of the same magnitude as natural amino acids. As the nitrile of formic acid, HCN undergoes many typical nitrile reactions. For example, HCN can be hydrolyzed to formic acid by aqueous sulfuric acid, converted to phenylformamidine with

TABLE 3-1. PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN CYANIDE

Property	Value
Structural formula: HCN	
Synonyms: hydrocyanic acid, prussic acid, formonitrile	
CAS Registry No.: 74-90-8	
Molecular weight	27.03
Melting point, °C	-13.24
Boiling point, °C	25.70
Triple point, °C	-13.32
Density, liquid, g/ml	
0°C	0.7150
10°C	0.7017
20°C	0.6884
Specific gravity, aqueous solution, d^{18}_{18}	
10.04% HCN	0.9838
20.29% HCN	0.9578
60.23%	0.829
Vapor pressure, kPa[a]	
-29.5°C	6.697
0°C	35.24
27.5°C	107.6
Vapor density, at 31°C (air = 1)	0.947
Heat of formation, kJ/molb	
Gas	-128.6
Liquid at 18°C, 100 kPa[a]	-10.1
Heat of combustion, kJ/mol[b]	667

Source: Reference 2-5.

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

[b] To convert J to cal, divide by 4.184.V

aniline and hydrogen chloride, or hydrogenated to methylamine.[2,5] It also reacts with the carbonyl group of aldehydes and ketones to form cyanohydrins. The most important uses of this type of reaction are in the manufacture of acetone cyanohydrin (an intermediate in the production of methyl methacrylate) and in the production of adiponitrile from HCN and butadiene.[5]

3.1.2 Sodium Cyanide[6]

Sodium cyanide (CAS 143-33-9), NaCN, is a white, cubic crystalline solid and is very soluble in liquid ammonia. It is odorless when dry but emits an odor of bitter almonds when damp. Today, NaCN is produced by the neutralization or wet process, in which liquid HCN and sodium hydroxide solution react and water is evaporated. Table 3-2 summarizes the physical and chemical properties of NaCN.

3.1.3 Potassium Cyanide[6]

Potassium cyanide (CAS 151-50-8), KCN, is a white crystalline solid that dissolves to liquid by absorbing moisture from the air. Commercial KCN is currently produced by the neutralization or wet process, which reacts as aqueous solution of potassium hydroxide with hydrogen cyanide to produce KCN at 99 percent purity. Potassium cyanide of 99.5+ percent purity can be prepared by using high-quality HCN and potassium hydroxide (KOH). Potassium cyanide does not form a dihydrate. Table 3-3 gives physical and chemical properties of KCN.

3.1.4 Other Cyanide Compounds[6]

Other cyanide compounds include lithium cyanide, rubidium cyanide, cesium cyanide, ammonium cyanide, strontium cyanide, magnesium cyanide, barium cyanide, and calcium cyanide. Of these compounds, only calcium cyanide is commercially

TABLE 3-2. PHYSICAL AND CHEMICAL PROPERTIES OF SODIUM CYANIDE

Property	Value
Structural formula: NaCN	
Synonyms: White cyanide, cyanogran, cyanide of sodium, sodium salt, cymag, M-44 cyanide capsules	
CAS Registry No.: 74-90-8	
Molecular weight	49.02
Melting point, °C (100%)	563.7 (±1)
(98%)	560
Boiling point (extrapolated), °C	1500
Density, g/cm3	
Cubic	1.6
Orthorhombic	1.62-1.624
Molten, at 700°C	1.22 (approx.)
Vapor pressure, kPa[a]	
800°C	0.103
900°C	0.4452
1000°C	1.652
1100°C	4.799
1200°C	11.9
1300°C	27.2
1360°C	41.8
Heat capacity[b], 25-72°C, J/g[c]	1.38
Heat of vaporization, J/g[c]	3,190
Heat of fusion, J/g[c]	314
Heat of formation, ΔHf °, NaCN(c), J/mol[c]	-89.9×10^3
Heat of solution[d], $\Delta Hsoln$, J/mol[c]	1,510
Hydrolysis constant, K_h, 25°C	2.51×10^{-5}
Viscosity, 26 wt% NaCN-H2 O, 30°C, mPa•s(=cP)	4

Source: References 6-8.

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] The heat capacity of sodium cyanide has been measured between 100° and 345° K.
[c] To convert J to cal, divide by 4.184.
[d] In 200 mol H2 O.3

TABLE 3-3. PHYSICAL AND CHEMICAL PROPERTIES OF POTASSIUM CYANIDE

Property	Value
Structural formula: KCN	
Synonyms: Cyanide of potassium, potassium salt	
CAS Registry No.: 151-50-8	
Molecular weight	65.11
Melting point, °C	
100%	634.5
96.05%	622
Density, g/cm^3	
Cubic at 20°C	1.553
Cubic at 25°C	1.56
Orthorhombic at -60°C	1.62
Specific heat, 25° to 72°C, J/g[a]	1.01
Heat of fusion, J/mol[a]	14.7 x 103
Heat of formation, ΔH_f °, J/mol[a]	-113 x 103
Heat of soln, ΔH_{soln} ° , J/mol[a]	+11.7 x 103
Hydrolysis constant, 25°C	2.54 x 10-5
Solubility in water at 25°C, g/100 g H_2O	71.6
Resistivity, Ω•cm	
0.25 normal soln	70
0.5 normal soln	15
1.0 normal soln	10
2.0 normal soln	5

Source: References 6-8.

[a] To convert J to cal, divide by 4.184.

important, although manufacture has been greatly reduced in recent years. It is marketed in flake form, as a powder, or as cast blocks by American Cyanamid Company and is manufactured in Canada and South Africa.

3.2 OVERVIEW OF PRODUCTION, USE, AND EMISSIONS OF CYANIDES

3.2.1 Production

Hydrogen cyanide--

Hydrogen cyanide production in the United States is primarily accomplished through either the Andrussow process or the Blausaure Methane Anlage (BMA) Process by Degussa.[2] The Andrussow process involves the reaction of ammonia, methane (natural gas), and air over platinum metals as catalysts and is the dominant commercial process. The BMA process involves the reaction of ammonia with methane and is not as widely used as the Andrussow process. The Andrussow process accounts for 74 percent of the total U.S. HCN production. The BMA process is used at only one facility, which accounts for only 3 percent of U.S. HCN production.[4] Hydrogen cyanide is also produced as a byproduct in the manufacture of acrylonitrile by the ammoxidation of propylene (Sohio technology).[2] The Sohio process accounts for the remaining 23 percent of HCN production in the U.S.[4] Since storage and shipment of HCN is difficult, producers are primarily the end users.[3]

Sodium cyanide--

Sodium cyanide can be prepared by heating sodium amide with carbon or by melting sodium chloride and calcium cyanamide in an electric furnace.[7] However, almost all of the NaCN currently manufactured is produced by the neutralization or so-called wet process, in which liquid hydrogen cyanide reacts with sodium hydroxide solution.[6]

Potassium cyanide--6

Potassium cyanide is made commercially by the neutralization or wet process, which reacts aqueous solution of potassium hydroxide with hydrogen cyanide.

3.2.2 Uses

Hydrogen cyanide--

Forty-three percent of the HCN produced in the United States is used in the manufacture of adiponitrile (a starting material of Nylon 6,6). Another 33 percent is used in the production of acetone cyanohydrin, an intermediate in the production of methyl methacrylate (MMA), and an additional 9 percent is used in sodium cyanide production. Cyanuric chloride production and chelating agents production use 6 and 5 percent of HCN, respectively. The remaining HCN (4 percent) is used in miscellaneous processes such as methionine and nitrilotriacetic acid productions. Figure 3-1 illustrates these uses.[9]

Historically, the growth in demand for HCN has been 4.8 percent per year from 1980 to 1989. Future demand is expected to be about 3 percent per year from 1989 through 1994.[8] Growth in MMA production and the start-up of at least three sodium cyanide plants in the United States will require an increase in HCN capacity.[9]

Sodium cyanide--

The principal use of sodium cyanide is for the extraction and recovery of minerals and metals from ores, specifically in the cyanidation recovery of gold and silver, the froth flotation beneficiation of sulfide ores, and the refinement of metal concentrates. Gold recovery by cyanidation is the single largest mining use for NaCN. Electroplating, especially for zinc, copper, brass, and cadmium, was the largest single market for NaCN, but a substantial decline in use has occurred in recent years due to tighter restrictions

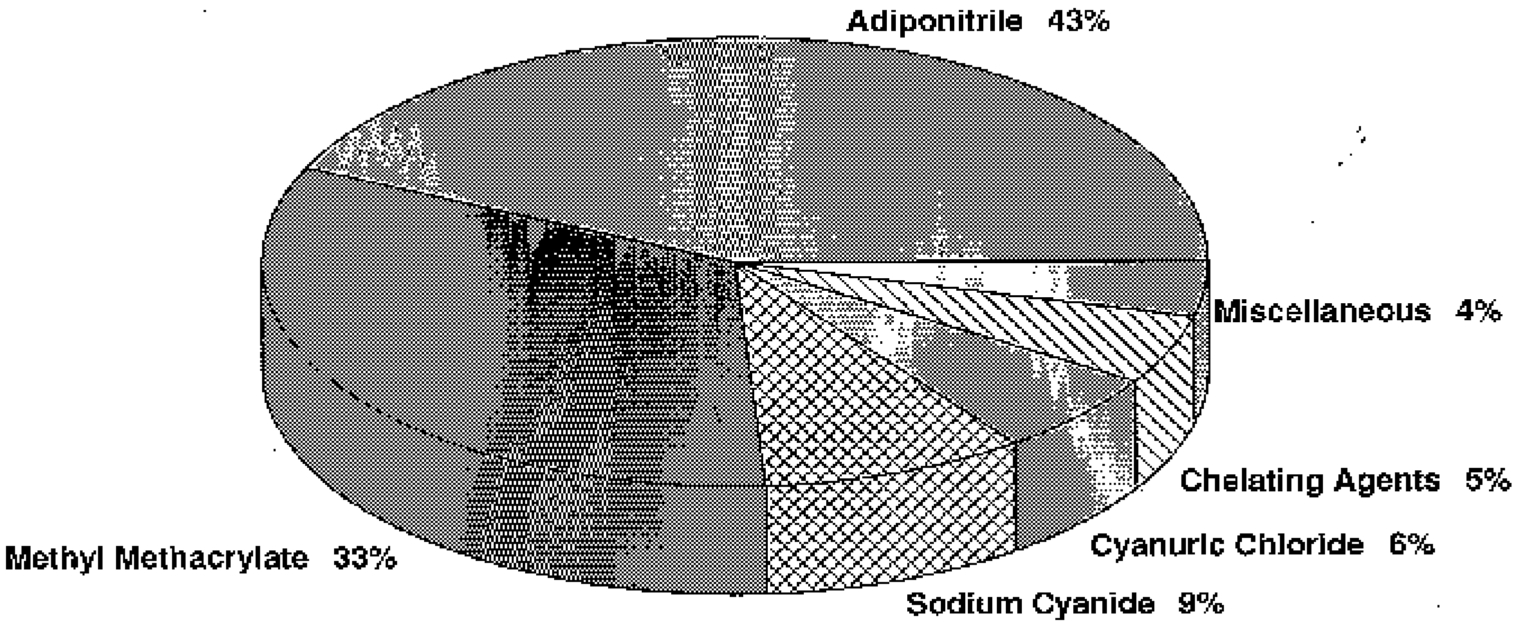


Figure 3-1. End uses of hydrogen cyanide.[9]

on cyanide discharge and conservation of plating and rinse solutions. Sodium cyanide is also used for five general categories of chemical uses (dryers, agricultural chemicals, pharmaceuticals, chelating or sequestering agents, and specialty chemicals). Miscellaneous uses of NaCN include metal stripping, heat-treating, and compounds used for cleaning smut (sooty matter). No specific emissions data exist for NaCN.[10]

Potassium cyanide--

Potassium cyanide is used primarily for fine silver plating but is also used for dyes and specialty products. There are no emissions data specific for KCN.

Other cyanide compounds--[6]

Of the remaining cyanide compounds, only Ca(CN)2 has any industrial uses. It is made commercially by heating crude calcium cyanamide in an electric furnace above 1000°C (1832°F) in the presence of sodium chloride, and then cooling the result rapidly to prevent reversion back to calcium cyanamide. Calcium cyanide is marketed in the form of dark gray flakes and is used primarily for the extraction or cyanidation of precious metal ores. It is also used in the froth flotation of minerals, as a depressant or inhibitor of the flotation of certain minerals, as a fumigant and rodenticide, and in limited quantities in the production of prussiates or ferrocyanides.

3.2.3 Emissions

Two distinct methods were used to develop nationwide emission estimates for specific source categories. The first method involved developing source-specific emission factors and applying those emission factors to estimates of nationwide source activity to calculate nationwide HCN emission estimates. The second method relied on extrapolating emission estimates from the Toxic Chemicals Release Inventory (TRI).[11]

Hydrogen cyanide is emitted from a number of industrial processes such as HCN/NaCN/KCN production, adiponitrile production, acetone cyanohydrin production, cyanuric chloride production, and production of chelating agents. Other indirect sources include petroleum refineries and mobile sources.

Primary sources of information for HCN emission data or emission factors included ongoing EPA regulatory development activities, information being collected by EPA to develop toxic air pollutant emission factors in AP-42, and an EPA data base on toxic air pollutant emission factors.[12,13] With the exception of mobile sources, no HCN emission factor data were available. For mobile sources, an emission factor was used to estimate emissions. For all other potential sources of HCN emissions, use of emission estimates from the TRI[11] and the EPA study[4] were used for estimation of nationwide cyanide emissions.

Cyanide compounds are emitted from a number of industrial processes such as NaCN/KCN production, adiponitrile production, acetone cyanohydrin production, cyanuric chloride production, and production of chelating agents. Cyanide compounds are formed as by-products during these processes. Other operations that emit cyanide compounds include iron and steel production, carbon black production and electroplating. For those processes, no HCN emission factor data were available. For source categories that involve the use of cyanide compounds, the source of emissions information was TRI data.[11]

Table 3-4 presents a compilation of SIC codes that have been associated with cyanide compound emissions.[11,12] This table lists the SIC codes that were identified as a potential

TABLE 3-4. SIC CODES ASSOCIATED WITH HYDROGEN CYANIDE AND OTHER CYANIDE COMPOUND EMISSIONS

SIC Code	Description
2819[a]	Industrial inorganic chemicals
2824[b]	Organic fibers, noncellulosic
2833	Medicinals and botanicals
2834	Pharmaceuticals
2865[a]	Cyclic crudes and intermediates
2869	Industrial organic chemicals
2879	Agricultural chemicals
2891	Adhesives and sealants
2895	Carbon black
2899a	Chemical preparations
2911[b]	Petroleum refining
3079 & 3089[a]	Miscellaneous plastic products
3312[a]	Blast furnaces and steel mills
3313	Electrometallurgical products
3315	Steel wire and related products
3316	Cold finishing of steel
3334	Primary aluminum
3339	Primary nonferrous metals
3341	Secondary nonferrous metals
3351	Copper rolling and drawing
3355	Aluminum rolling and drawing
3357	Nonferrous wire drawing/insulating
3398	Metal heat treating
3429	Hardware
3432	Plumbing fixtures
3452	Bolts/nuts/rivets/washers
3471	Plating and polishing
3482	Small arms ammunition

TABLE 3.4 (CONTINUED)

SIC	Description
3492	Valves and hose fittings
3494	Valves/pipe fittings
3496	Miscellaneous fabricated wire products
3497	Metal foil and leaf
3519	Internal combustion engines
3562	Ball and roller bearings
3566	Speed changers/drives/gears
3610	Electrical distributors
3624[b]	Carbon and graphite products
3621	Motors/generators
3625	Relays and industrial controls
3643	Wiring devices
3644	Noncurrent carrying wire devices
3678	Electronic connectors
3714	Motor vehicle parts and accessories
3721	Aircraft
3724	Aircraft engines and parts
3728	Aircraft parts
3743	Railroad equipment
3825	Instruments/transformers
3914	Silverware and plated ware
3949	Sporting and athletic goods
3963	Buttons
3964	Needles/pins/hooks/buttons/etc.
3965	Fasteners/buttons/needles/pins
4925	Gas production/distribution
NA	Mobile sources

[a] The HCN emissions reported by facilities belonging to SIC Codes 2879, 2865, 2899, 3079 & 3089, and 3312 in the 1991 TRI collectively constituted approximately 0.3 percent of total HCN emissions reported in the 1991 TRI.

[b] The HCN emissions reported by facilities belonging to SIC Codes 2824, 2869, 2911, and 3624 collectively constituted approximately 99.7 percent of total HCN emissions reported in the 1991 TRI.

source of cyanide emissions, provides a description of the SIC code, and identifies other emission sources that do not have an assigned SIC code.[11-13]

It should be noted that the companies reporting to TRI specify the type of compound emitted, either HCN or cyanide compounds in general. Unfortunately, there is not consistent reporting (e.g., some companies reported their HCN emissions as HCN emissions, and some companies reported their HCN emissions as cyanide compound emissions). This primarily occurs for companies with SIC code 3312, which includes coke ovens and blast furnaces. Sources indicate that the emissions from coke ovens/blast furnaces (which are reported in TRI as cyanide compound emissions) are primarily HCN emissions (see Section 6).

In selected cases, facilities reported to TRI under multiple SIC codes. As a result, it was difficult to assign emissions to a specific SIC code. In those cases, efforts were made to determine the appropriate SIC codes associated with the emissions. If appropriate SIC codes could not be explicitly identified, the data were not used in the analysis.

Table 3-5 provides a summary of the estimated 1991 nationwide cyanide compound emissions for those point source categories where adequate information was available (i.e., emission factors and production data). Appendix A presents the data used for each of these estimates, assumptions, and emission calculations for each of these point source categories. The estimated emissions were based on emission factors provided in this document or calculated from source test data and appropriate process information, if available.

From the data shown in Table 3-5 for point source categories, cyanide emissions from carbon black production contributed 412 Mg or approximately 47 percent of the total emissions. Of the remaining point source categories, the next

TABLE 3-5. ESTIMATED 1991 NATIONWIDE CYANIDE COMPOUND EMISSIONS FOR SELECTED POINT SOURCE CATEGORIES

	Cyanide compound emissions		
Point source category	Mg	Tons	Basis[a]
Hydrogen cyanide production	154	170	TRI + EPA
Sodium cyanide production[b]	-	-	TRI + EPA
Adiponitrile production[b]	0.013	0.014	TRI
Acetone cyanohydrin production[b,c]	3.0	3.3	TRI
Cyanuric chloride[b]	-	-	TRI
Chelating agents[d]	1.3	1.4	TRI
Electroplating	10	11	TRI
Iron and steel production	180	198	TRI
Carbon black production[e]	412	454	TRI
Carbon fiber production[f]	74	82	TRI
Petroleum refineries[g]	49	54	TRI
Total	883	974	

[a] TRI = Reference 11; EPA = Reference 4.

[b] HCN emissions reported under HCN production include HCN emissions for the other production processes because most facilities that produce HCN also produce the other products that use HCN.

[c] These are cyanide compound emission estimates for two of four facilities. There is no basis to estimate HCN emissions from the other two facilities. Hydrogen cyanide emission estimates are included in hydrogen cyanide production figures.

[d] These are emission estimates for only 3 of 22 facilities. Hydrogen cyanide emissions from 3 other facilities are included in hydrogen cyanide production. There is no basis to estimate HCN emissions from all other facilities producing chelating agents.

[e] These emission estimates are for 6 of 24 facilities. There is no basis to estimate cyanide emissions from the other facilities.

[f] These emission estimates are for five of eight facilities. There is no basis to estimate cyanide emissions from the other facilities.

[g] These emission estimates are for 3 of the 104 petroleum refineries listed in Appendix B. There is no basis to estimate cyanide emissions from the other facilities.

four categories having the highest emissions are iron and steel production (20 percent), hydrogen cyanide production (17 percent), carbon fiber production (8 percent), and petroleum refineries (6 percent). These five categories constitute about 98 percent of the total emissions shown in Table 3-5. All other categories contribute insignificant quantities compared to the total amount.

SECTION 4
EMISSIONS FROM PRODUCTION OF MAJOR CYANIDE COMPOUNDS

This section discusses potential emission sources from production of major cyanide products, hydrogen cyanide (HCN), sodium cyanide (NaCN), and potassium cyanide (KCN). Process descriptions, emission control measures, and potential emissions are provided below for each of the production processes.

4.1 HYDROGEN CYANIDE PRODUCTION

Table 4-1 presents a list of domestic HCN manufacturing facilities.14 The 1990 annual HCN production capacity was 533 million kilograms (kg) (1,175 million pounds [lb]) and the estimated demand for 1994 is 590 million kg (1,300 million lb), respectively.[9]

Hydrogen cyanide is produced by three different processes: (1) direct synthesis using methane, ammonia, and oxygen, based on the Andrussow process, (2) synthesis using methane and ammonia based on Blausaure Methane Anlage (BMA) process, and (3) the Sohio process where HCN is obtained as a byproduct of the reaction between propylene, ammonia, and oxygen. The Andrussow process accounts for 74 percent of the HCN produced in the United States. The BMA process is used at one facility, which accounts for only 3 percent of U.S. HCN production. The remaining 23 percent is produced by the Sohio process. A description of each of these production processes is given below.[4]

TABLE 4-1. DOMESTIC PRODUCERS OF HYDROGEN CYANIDE

Facility	Location	1991 Production capacity, Mg (tons)
American Cyanamid[c]	Avondale, LA	29,510 (32,500)
BP Chemicals[c]	Green Lake, TX	27,240 (30,000)
BP Chemicals[c]	Lima, OH	15,890 (17,500)
CIBA-Geigy[a]	St. Gabriel, LA	45,400 (50,000)
Cyanco Co.[a]	Winnemucca, NV	7,264 (8,000)
Degussa Corp.[b]	Theodore, AL	24,970 (27,500)
Dow Chemical[a]	Freeport, TX	9,080 (10,000)
DuPont[c]	Beaumont, TX	27,240 (30,000)
DuPont[a]	Memphis, TN	90,800 (100,000)
DuPont[a]	Orange, TX	145,280 (160,000)
DuPont[a]	Victoria, TX	136,200 (150,000)
FMC Corp.[d]	Green River, WY	14,982 (16,500)
Monsanto[c]	Alvin, TX	22,700 (25,000)
Rohm & Haas[a]	Deer Park, TX	90,800 (100,000)
Sterling Chemicals[c]	Texas City, TX	38,590 (42,500)
TOTAL		725,946 (799,500)

Source: Reference 14.

[a] Hydrogen cyanide is manufactured based on the Andrussow process at these facilities (Reference 4).

[b] Hydrogen cyanide is manufactured using the BMA process at these facilities (Reference 4).

[c] Hydrogen cyanide is manufactured using the Sohio process at these facilities (Reference 4).

[d] FMC Corp. manufactures HCN using the Androssow process for captive use within the facility to produce cyanide.

4.1.1 Process Descriptions

Andrussow process [4]--

A simplified process flow diagram for the Andrussow process with ammonia recycle is shown in Figure 4-1. The same process without ammonia recycle is shown in Figure 4-2. In this process, air and anhydrous ammonia react in the presence of a platinum/rhodium catalyst at a reaction temperature of 1100°C (2012°F). The reaction heat is supplied by simultaneous combustion of methane supplied in the form of natural gas. This reaction is as follows:

$$\underset{\text{Ammonia}}{2NH3} + \underset{\text{Methane}}{2CH4} + 302 \rightarrow \underset{\substack{\text{Hydrogen}\\ \text{Cyanide}}}{2HCN} + 6H_{2}0$$

As shown in Figure 4-1, ammonia, air, and natural gas (CH4)are fed to the reactor. The reactor off-gas, containing HCN, excess ammonia, water, and excess air, is routed to a waste-heat-boiler to cool the gas to below 400°C (752°F). This cooling minimizes decomposition of HCN and ammonia and also produces steam for energy efficiency. The gas steam then passes through an ammonia absorber to remove the remaining ammonia.

If ammonia recycle is used, a monoammonium phosphate solution can be used to absorb the ammonia and form diammonium phosphate. The diammonium phosphate solution then passes through two stripper columns. The ammonia stripper removes any absorbed NH3 . The NH3 removed from the absorber is recycled back to the reactor. The second column strips the HCN stream with steam. The overheads are then fractionated under pressure to yield ammonia gas for recycle. If ammonia recycle is not used (Figure 4-2), the ammonia is absorbed using a sulfuric acid solution to produce ammonium sulfate.

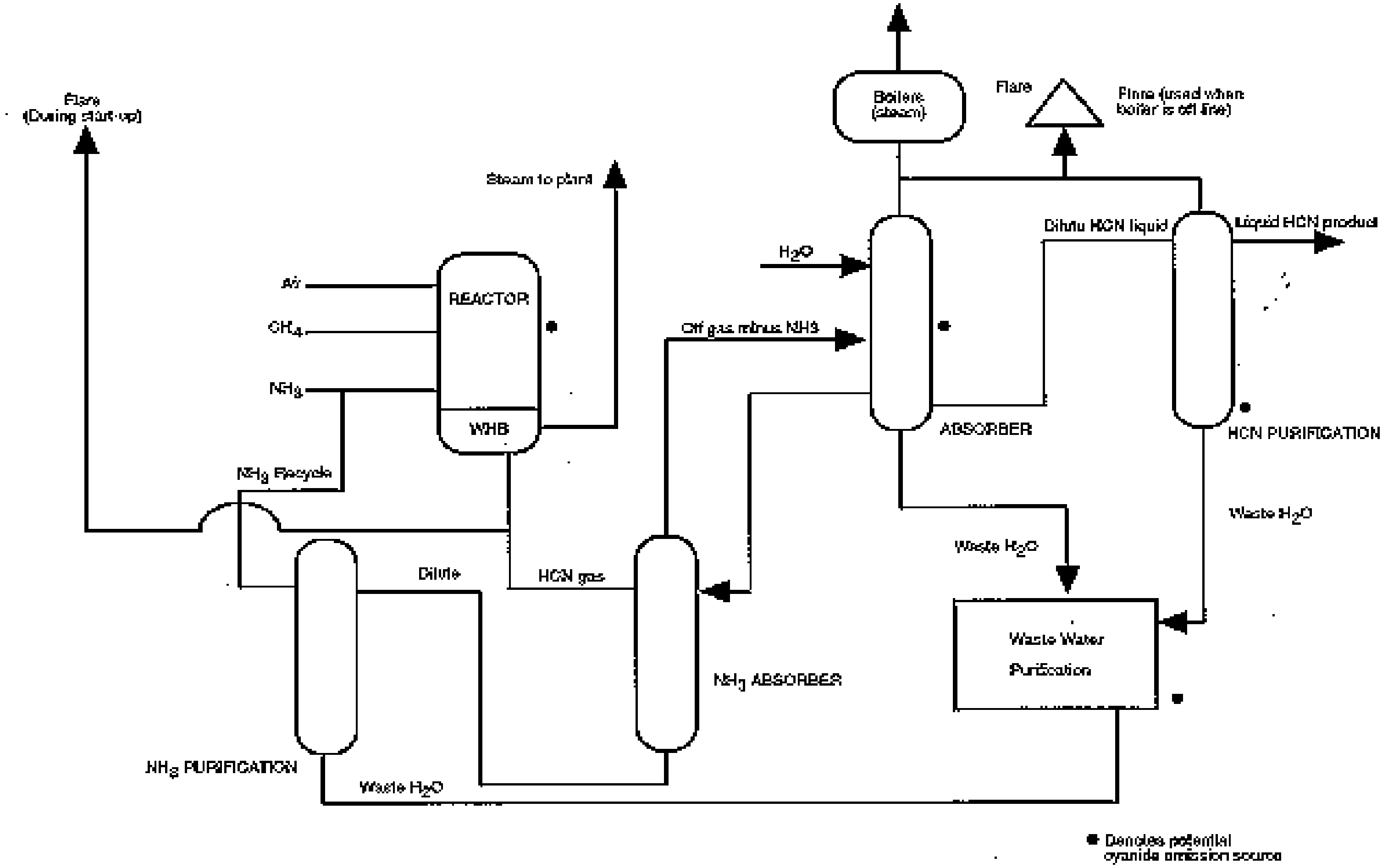


Figure 4-1. Andrussow HCN production process with ammonia recycle.[4]

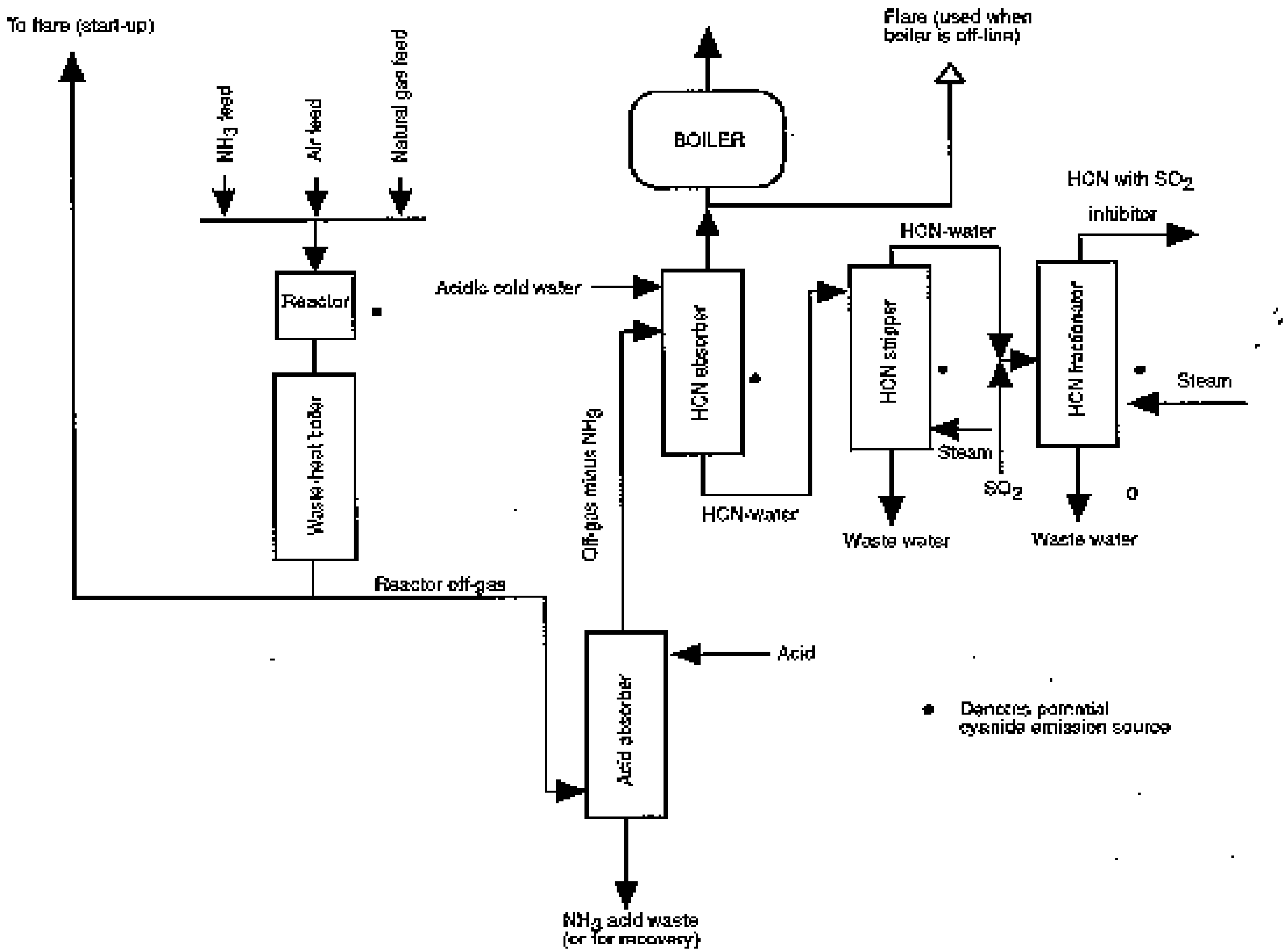


Figure 4-2. Andrussow HCN production process without ammonia recycle.[4]

After ammonia absorption, the product gas stream passes through an HCN absorber where HCN is recovered as a dilute solution in water. The HCN solution is then purified to over 99-percent purity using conventional stripping and distillation columns. The off-gas from the HCN absorber, which contains some HCN, is usually routed to a boiler for energy recovery. Wastewater resulting from the absorber, HCN purification, and the ammonia purification process is collected and treated. Details pertaining to the methods used for collection, treatment, and ultimate disposal are not available.

The major emission sources for this process are the reactor, HCN absorber, and HCN distillation column. The off-gases from the HCN absorber and the distillation column are routed to boilers or flares and are shown by solid circles in Figures 4-1 and 4-2. In addition, the reactor off-gas is routed to a flare during startup until the reactor reaches its desired operating range. Depending on the concentration of HCN in the wastewater resulting from the absorber, HCN purification and ammonia purification steps, the wastewater treatment operation may also result in HCN emissions.

Other sources of HCN emissions include fugitive emission sources such as storage, valves, joints, and other fittings. Data from the 1991 TRI show nonpoint emissions to be about 10 percent of the total reported emissions.

Blausaure Methane Anlage (BMA) production process [4]--

In the BMA process, only methane (as natural gas) and ammonia are supplied to the reactor. The process reaction is as follows:

$$CH_4 + NH_3 \rightarrow HCN + 3H_2$$

The heat of reaction is supplied to the reactor by external heating of the ceramic or alumina tubes coated with a thin layer of platinum.

Figure 4-3 presents a simplified flow diagram for this process. The effluent gas exiting the reactor is cooled and then routed to an absorber where the ammonia is removed using a sulfuric acid solution to produce ammonium sulfate. Details pertaining to the reactor design and the cooling system are not available. After ammonia absorption, the product gas passes through the HCN absorber where HCN is absorbed as a dilute solution in water. The dilute solution is then enriched in the same fashion as the Andrussow process.

The off-gas from the HCN absorber is mainly hydrogen. This gas stream is used in other processes. This process also routes the reactor off-gas to a flare during startup. Wastewater may be generated as a result of absorption and HCN distillation. Details pertaining to collection, treatment, and ultimate disposal of wastewater are not available.

The major advantages of the BMA process compared to the Andrussow process are higher feedstock yields of HCN and a relatively pure hydrogen byproduct stream. Higher yields reduce the size and the cost of the recovery equipment, while byproduct hydrogen can be used as a fuel for other processes or used in other processes. However, the BMA process requires a more complex reactor system.

The major emission sources (shown in Figure 4-3 by solid circles) are the reactor and HCN distillation column. During startup, the reactor off-gases are routed through a flare. Depending on the concentration of HCN in the wastewater produced from the various process steps, the wastewater treatment operation may also result in HCN emissions. Other

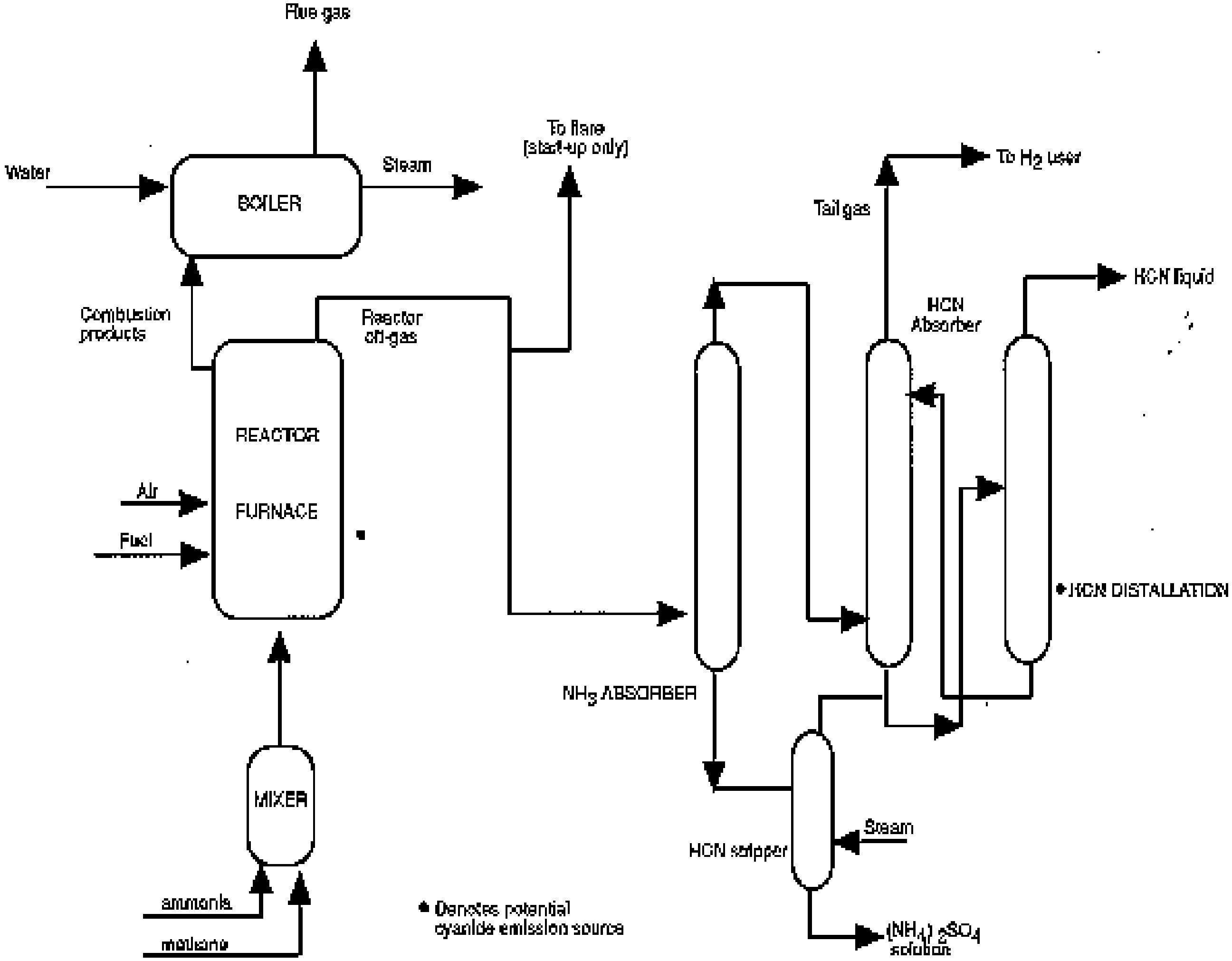


Figure 4-3. Blausaure Methane Anlage HCN production process.[4]

sources of HCN emissions include fugitive emission sources such as valves, joints, and other fittings. However, information pertaining to these sources is not available.

Sohio production process [4]--

All six of the U.S. plants producing acrylonitrile use the Sohio process. In this process, propylene, anhydrous ammonia, and air are combined to produce acrylonitrile and byproducts of HCN and acetonitrile. The reactions which occur in this process are as follows:

Primary Reaction:

$$\underset{\text{Propylene}}{2C_3H_6} + \underset{\text{Ammonia}}{2NH_3} + 3O_2 \rightarrow \underset{\text{Acrylonitrile}}{2CH_2=CHCN} + 6H_2O$$

Secondary Reactions:

$$C_3H_6 + 3NH_3 + 3O_2 \rightarrow \underset{\text{Hydrogen Cyanide}}{3HCN} + 6H_2O$$

$$2C_3H_6 + 3NH_3 + 3O_2 \rightarrow \underset{\text{Acetonitrile}}{3CH_3CN} + 6H_2O$$

Figure 4-4 presents a simplified flow diagram for the Sohio process. Propylene, ammonia, and air are introduced into a fluid bed catalytic reactor operating at 35 to 207 kPa (5 to 30 psig) and 400° to 510°C (750° to 950°F). The reactor off-gas containing the reaction products passes through a quencher to lower the temperature. Sulfuric acid may be added in the quencher to neutralize any excess ammonia. The gas stream then goes to an absorber where the HCN and other products are absorbed into a dilute solution. The gas stream from the absorber is then routed to a waste heat boiler for energy recovery.

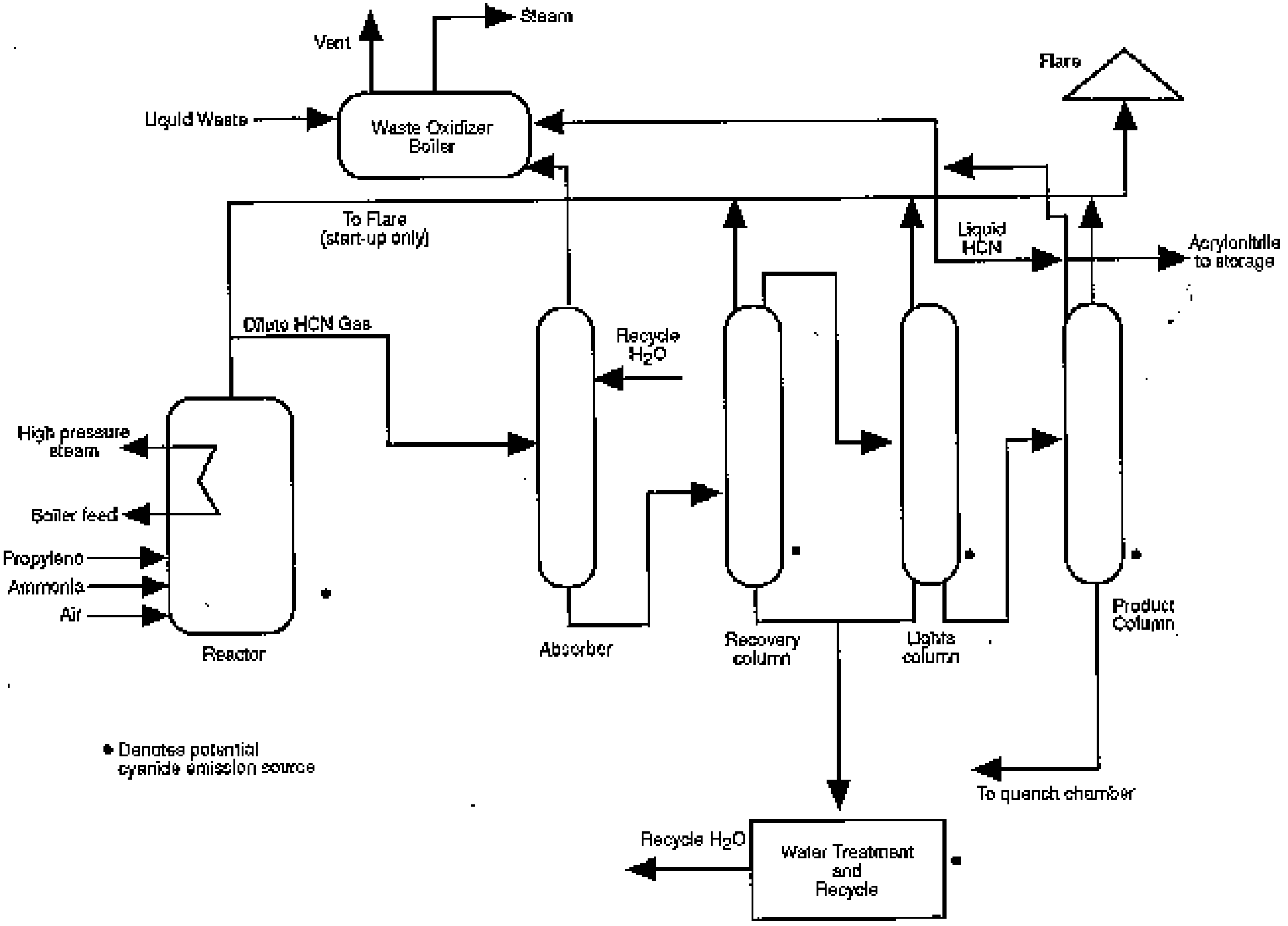


Figure 4-4. Sohio production process for acrylonitrile/HCN production.[4]

The solution containing acrylonitrile and HCN from the absorber goes to a series of distillation columns where the acrylonitrile and HCN are separated and purified. The gaseous streams from the distillation columns, which contain acetonitrile along with trace amounts of HCN, are routed through a flare. The Sohio process allows yields of 0.9 pounds of acrylonitrile and 0.1 pounds of HCN per pound of propylene feed.

The major emission points for this process as denoted on Figure 4-4 are reactor and distillation column off-gas streams, which are routed to the flare during startup, and the absorber off-gas, which is typically routed to a boiler for energy recovery.

Wastewater resulting from the absorber and distillation columns is collected, heated, and recycled. Information pertaining to the treatment methods used is not available. Depending on the concentration of HCN in the wastewater, the wastewater treatment system may also potentially emit HCN.

Other sources of HCN emissions include fugitive emission sources such as valves, joints, and other fittings. No information is available pertaining to these sources.

4.1.2 Emission Control Measures[4]

In the Andrussow process, the reactor off-gases are destroyed in a flare only during startup, until the desired operating conditions are reached. The emissions from the absorber are burned in a boiler onsite. Emissions from the HCN distillation column are routed to a flare. Details pertaining to the operating conditions of the control systems and destruction efficiencies of HCN are not available. Additionally, information pertaining to control of HCN emissions resulting from wastewater treatment is not available.

In the BMA process, the reactor off-gases are also destroyed in a flare during startup. Information pertaining to control of HCN emissions from other sources, such as HCN distillation column and wastewater treatment, is not available.

In the Sohio process, the reactor off-gases are destroyed in a flare during startup only. Emission streams containing trace amounts acetonitrile and HCN from the absorber and distillation columns are destroyed in a flare. Details pertaining to destruction efficiency are not available.

4.1.3 Emissions

Test data are not available for HCN emissions occurring during the different steps of HCN production. However, 12 of the 15 HCN manufacturing facilities have reported facilitywide HCN emissions in the 1991 Toxic Chemical Release Inventory (TRI). The TRI data are presented in Table 4-2.[11]

Hydrogen cyanide emission data for the remaining three facilities were not contained in the 1991 TRI. The U. S. Environmental Protection Agency has estimated annual HCN emissions for all 15 of the domestic HCN producing facilities.4 Table 4-2 also presents HCN emission data estimated by EPA for the three remaining facilities for which 1991 TRI data were not available.[4]

4.2 SODIUM CYANIDE PRODUCTION

Sodium cyanide accounts for 9 percent of HCN use.[14] Table 4-3 presents a list of domestic NaCN manufacturers.[4,14] This section presents a description of the NaCN production

TABLE 4-2. HYDROGEN CYANIDE PRODUCERS REPORTING HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY

	Emissions, kg (lb)			
Facility	Nonpoint	Point	Total	Source
BP Chemicals Lima, OH	998 (2,200)	4,308 (9,500)	5,306 (11,700)	TRI
Ciba-Geigy St. Gabriel, LA	29 (63)	93 (204)	122 (267)	TRI
Degussa Corp. Theodore, AL	345 (760)	771 (1,700)	1,116 (2,460)	TRI
Dow Chemical Freeport, TX	2 (4)	0 (0)	2 (4)	TRI
DuPont Beaumont, TX	1,360 (3,000)	1,496 (3,300)	2,856 (6,300)	TRI
DuPont Memphis, TN	459 (1,012)	13,224 (29,159)	13,683 (30,171)	TRI
DuPont Orange, TX	1,002 (2,210)	30,970 (68,288)	31,972 (70,498)	TRI
DuPont Victoria, TX	1,038 (2,290)	2,531 (5,580)	3,569 (7,870)	TRI
FMC Corp. Green River, WY	0 (0)	36 (79)	36 (79)	TRI
Monsanto Alvin, TX	680 (1,500)	635 (1,400)	1,315 (2,900)	TRI
Rohm & Haas Deer Park, TX	254 (560)	49,887 (110,000)	50,141 (110,560)	TRI
Sterling Chemicals Texas City, TX	3,936 (8,680)	17,451 (38,480)	21,387 (47,160)	TRI
American Cyanamid[a] Avondale, LA	727 (1,600)	909 (2,000)	1,636 (3,600)	EPA
BP Chemicals[b] Green Lake, TX	5,909 (13,000)	15,000 (33,000)	20,909 (46,000)	EPA
Cyanco Winnemucca, NY	N/E	N/E	N/E	EPA
TOTAL	16,739 (36,879)	137,311 (302,690)	154,050 (339,569)	

Source: References 4 and 11.

[a] The emission data for American Cyanamid are based on data reported to TRI. However, the year is unknown.

[b] The basis of estimation of emissions from BP Chemicals is not known.

N/E = Not estimated.

process, emission control measures, along with a discussion on emissions resulting from the production process.

TABLE 4-3. DOMESTIC PRODUCERS OF SODIUM CYANIDE

Facility	Location	1991 Production capacity, Mg (ton)
Cyanco Co.	Winnemucca, NV	12,712 (14,000)
Dow Chemical	Freeport, TX	N/A
DuPont	Memphis, TN	113,500 (125,000)
DuPont	Texas City, TX	N/A
FMC Corp.	Green River, WY	N/A
Sterling Chemicals	Texas City, TX	45,400 (50,000)
Degussa Corp.	Theodore, AL	27,240 (30,000)

Source: References 4 and 14.
N/A = not available.

4.2.1 Process Description[4]

The process description given below is based on very limited information and references available at this time. All the facilities listed in Table 4-3 produce NaCN using the neutralization or wet process. The reaction for this process is as follows:

$$NaOH + HCN \rightarrow NaCN + H_2O$$

A flow diagram for this process is shown in Figure 4-5. Hydrogen cyanide and sodium hydroxide are mixed in a reactor vessel to produce NaCN and water. Excess sodium hydroxide is used to maintain an alkaline condition. This prevents reformation of HCN. Once past the reactor, there is no HCN remaining in any of the process streams.

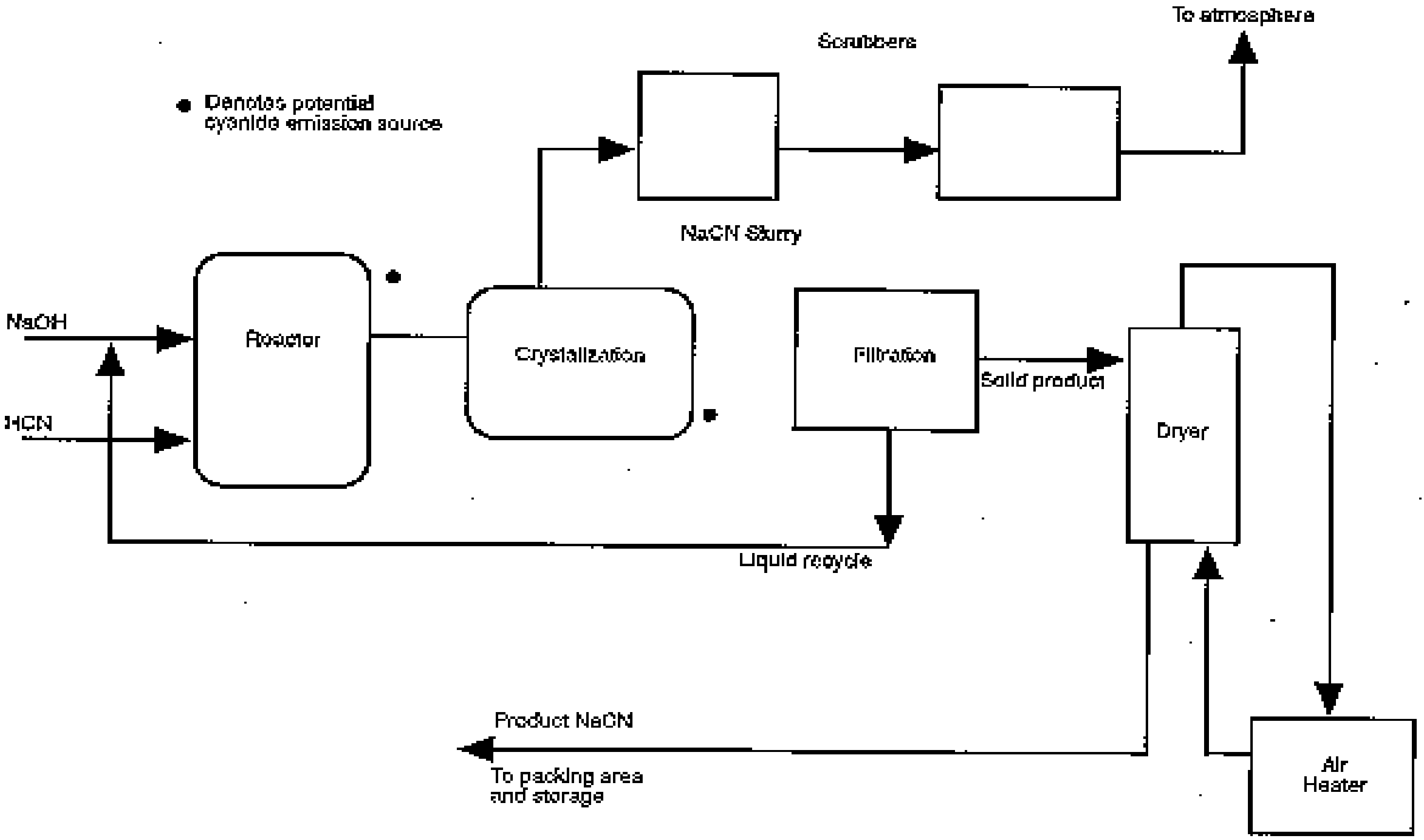


Figure 4-5. Sodium cyanide neutralization production process.[4]

The slurry produced by the reaction is typically routed to a crystallizer and then to a drum filter where the NaCN solids are separated from the water. The solids are dried and conveyed pneumatically to a briquetter; then, they are packed in drums or plastic-lined crates for bulk shipment.

The major cyanide emissions source for this process is the vent from the crystallizer. This vent typically passes through water and then a caustic scrubber to recover any traces of residual HCN. Based on the limited available information, some facilities vent the reactor to a flare. The hot air used for drying is recycled so there is no emission potential. If air is used to convey the NaCN, then the air exhaust stream becomes a potential emission point of NaCN. Typically, a cyclone is used to remove NaCN from the airstream when this is the case.

4.2.2 Emission Control Measures

The main source of NaCN emissions is the crystallizer. The gases from the crystallizer are vented through a caustic scrubber to remove the NaCN. In cases where the reactor is equipped with a vent, the off-gases are routed through a flare. Information pertaining to cyanide compound reduction achievable in the caustic scrubber and the flare is not available. Also, information pertaining to NaCN emissions resulting from pneumatic conveying and its control are not available.

4.2.3 Emissions

Test data are not available for cyanide compound emissions occurring during the different steps of NaCN production. However, five of the seven NaCN manufacturing facilities shown in Table 4-4 have reported facilitywide HCN emissions in the 1991 TRI; these five facilities also manufacture HCN. The TRI data are presented in Table 4-2.[11] It is not clear as to what

TABLE 4-4. HYDROGEN CYANIDE AND SODIUM CYANIDE EMISSIONS FROM NaCN PRODUCTION FACILITIES

	Emissions, kg (lb)		
Facility	Process vent emissions	Fugitive emissions	Total
Cyanco Co. Winnemucca, NV	40 (88)a	NAb	40 (88)a
DuPont Memphis, TN	NA	NA	HCN 4,536 (10,000) NaCN 1,361 (3,000)
FMC Corp. Green River, WY	NA	NA	NA
Sterling Chemicals Texas City, TX	HCN 9 (20) NaCN 18 (39)	HCN 49 (108) NaCN 32 (70)	HCN 58 (128) NaCN 50 (109)
Degussa Corp. Theodore, AL	HCN 125 (276) NaCN NA	NA	HCN 125 (276) NaCN NA

Source: Reference 4.

[a] Hydrogen cyanide and sodium cyanide emissions combined.

[b] NA = Not available.

fraction of the HCN emissions result due to the manufacture of HCN itself, as opposed to the manufacture of NaCN. The EPA study presented a summary of emissions from NaCN production for four of the seven producers in 1991.[4] These data are presented in Table 4-4 and, where available, show values for both HCN and NaCN. No breakdown between process vents and fugitive emissions were available for the DuPont Memphis plant.

4.3 POTASSIUM CYANIDE

Two facilities, DuPont, Memphis, TN, and W. R. Grace, Nashua, NH, manufacture KCN.[14] Production capacity data for these two facilities are not available.

The process used in the manufacture of KCN is similar to that used in the manufacture of NaCN.[15] The only difference is that instead of NaOH, KOH is used as the raw material which is reacted with HCN. The process description for the manufacture of NaCN is presented in the previous section.

Emission control measures for the control of HCN and KCN emissions are assumed to be the same as that used during the manufacture of NaCN. Test data pertaining to emissions of HCN and KCN resulting from the different steps in the manufacture of KCN are not available. Table 4-2 presents facilitywide HCN emissions reported by DuPont in the 1991 TRI. DuPont has also reported a facilitywide cyanide compound emissions of 1,385 kg (3,053 lb) in the 1991 TRI. Details pertaining to the nature of cyanide compounds are not available. DuPont manufactures several cyanide compounds at the Memphis, TN, location. W.R. Grace has reported a facilitywide HCN emission of 1,028 kg (2,267 lb) in the 1991 TRI. W.R. Grace also manufactures other cyanide compounds, in addition of KCN. Therefore, it is difficult to determine how much of the HCN emissions reported in the 1991 TRI resulted due to KCN production alone.

SECTION 5
EMISSIONS FROM MAJOR USES OF CYANIDE COMPOUNDS

Hydrogen cyanide (HCN) is used as a feedstock for manufacturing adiponitrile, acetone cyanohydrin which is used in the production of methyl methacrylate, cyanuric chloride, and chelating agents. In the manufacture of all of these substances, hydrogen cyanide is used as a raw material which participates in chemical reactions. In these reactions, hydrogen cyanide emissions (and emissions of other cyanide compounds) can be expected to occur during the raw material preparation steps and product purification steps.

This section presents process information, air pollution control measures, and estimates of hydrogen cyanide (and other cyanide compounds) emissions from these sources.

5.1 ADIPONITRILE PRODUCTION

Adiponitrile, which is derived from adipic acid, accounts for 43 percent of HCN use.[9] Adiponitrile is used as an intermediate for the manufacture of hexamethylenediamine, a principal component of Nylon 6,6. Three facilities currently manufacture adiponitrile in the United States (U.S.), as indicated in Table 5-1.[14] DuPont manufactures adiponitrile by hydrocyanation of butadiene where butadiene is reacted with HCN. In the DuPont process, unreacted HCN may potentially be emitted as an air pollutant. Monsanto produces adiponitrile from electrohydrodimerization of acrylonitrile and does not involve the use of HCN.

TABLE 5-1. DOMESTIC ADIPONITRILE PRODUCERS

Facility	Location	1991 Production capacity, Mg (tons)
DuPont	Orange, TX	220,450 (242,500)
DuPont	Victoria, TX	215,910 (237,500)
Monsanto[a]	Decatur, AL	188,640 (207,500)

Source: Reference 14.

[a] Process does not use HCN.

A process description of the hydrocyanation of butadiene used to manufacture adiponitrile and a discussion of the emissions resulting from the various operations are presented below.

5.1.1 Process Description[17]

Hydrocyanation of Butadiene--

Figure 5-1 presents a process flow diagram for manufacturing adiponitrile by hydrocyanation of butadiene. In this process, butadiene is fed to a separator where it is dried by separating the impurities through molecular sieves. The dried butadiene is fed into a reactor along with HCN and a catalyst. As a result of the catalytic reaction, intermediates consisting of pentenenitriles are formed.

The pentenenitriles stream, consisting of unreacted raw materials and the catalyst (carried over from the reactor), is fed into an absorption column where butadiene is used as the absorbent to recover unreacted butadiene. The pentenenitrile stream now containing predominantly the catalyst is sent to a catalyst removal system to recover the catalyst. The purified pentenenitrile stream continues to a distillation column where

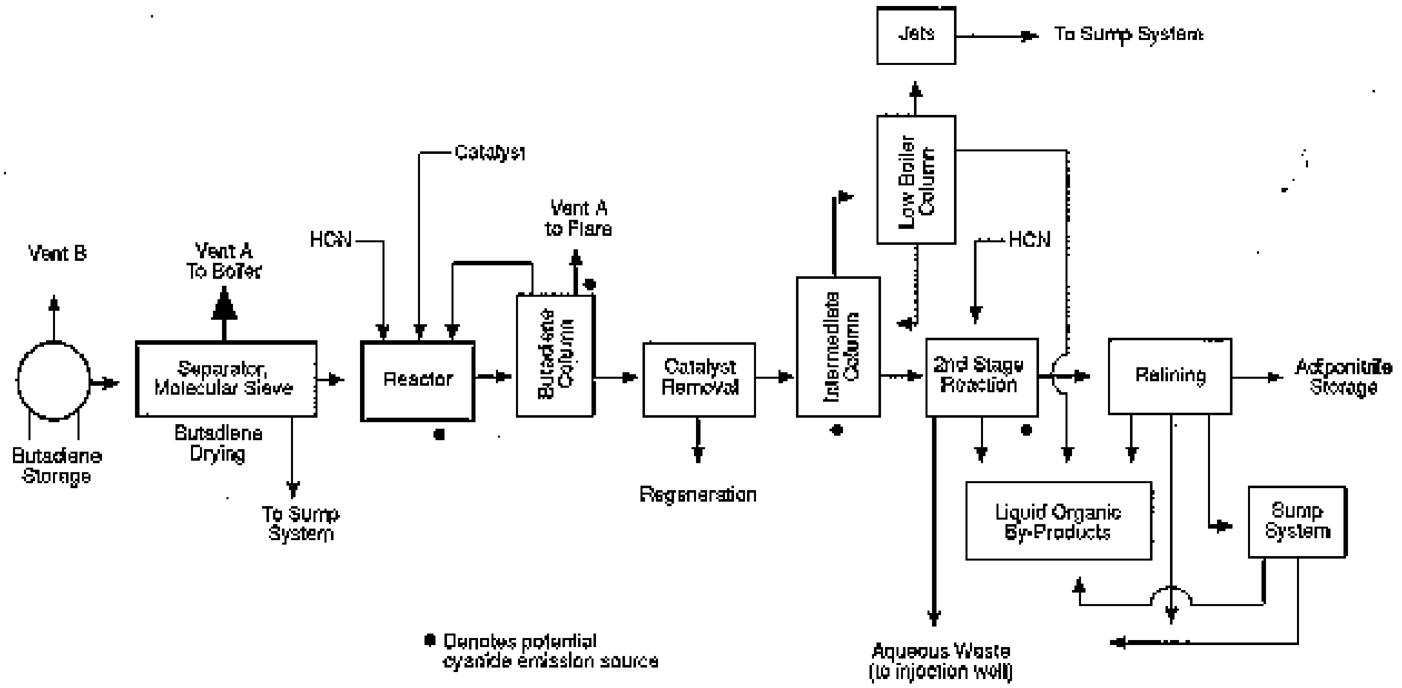


Figure 5-1. Process flow diagram for production of adiponitrile by hydrocyanation of butadiene.[16]

low boiling fractions are removed. The bottoms from the distillation column, containing mononitriles, are passed to a second-stage reactor where additional HCN is added to convert the mononitriles to dinitriles. The dinitrile stream is purified in an additional refining step to separate adiponitrile.

5.1.2 Emission Control Measures[16]

Emissions resulting from the butadiene absorption column may contain HCN and are destroyed in a flare. The gas streams from the distillation column and the second-stage reactor may also contain HCN. However, information pertaining to HCN destruction efficiencies obtained during combustion in the boiler or flare is not available.

5.1.3 Emissions

Sources of HCN emissions are shown in Figure 5-1 by solid circles. Hydrogen cyanide emissions can potentially result from the primary and second stage reactors. Other sources may include the butadiene absorption column and the pentenenitrile distillation column. Emissions of HCN may also result from sources of fugitive emissions such as joints, valves, and other fittings. However, details pertaining to fugitive emissions are not available. Hydrogen cyanide may be present in the aqueous waste from the second stage reaction, which is sent to an injection well.

Test data pertaining to cyanide emissions from individual sources at adiponitrile manufacturing facilities are not available. However, two facilities manufacturing adiponitrile have reported cyanide compound emissions in the Toxic Release Inventory (TRI) for the year 1991. The TRI data are presented in Table 5-2.[11] Both facilities produce multiple derivatives of HCN. Therefore, it is not clear which specific sources emit cyanide compounds and/or HCN.

TABLE 5-2. ADIPONITRILE PRODUCERS REPORTING CYANIDE COMPOUND OR HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY[a]

	Cyanide compound emissions, kg (lb)			Hydrogen cyanide emissions, kg (lb)		
Facility	Nonpoint	Point	Total	Nonpoint	Point	Total
Dupont	12	1.4	13.4	1,002	30,970	31,972
Orange, TX	(26)	(3)	(29)	(2,210)	(68,288)	(70,498)
Dupont	0	0	0	1,038	2,531	3,569
Victoria, TX	(0)	(0)	(0)	(2,290)	(5,580)	(7,870)
Total	12	1.4	3.4	2,040	33,501	35,541
	(26)	(3)	(29)	(4,500)	(73,868)	(78,368)

Source: Reference 11.

[a] These facilities produce multiple derivatives of HCN. Therefore, it is not clear as to what the specific sources are that emit cyanide compounds and/or HCN.

5.2 ACETONE CYANOHYDRIN

Acetone cyanohydrin is an intermediate in the manufacture of methyl methacrylate. Most of the acetone cyanohydrin produced is used to produce methyl methacrylate, and it accounts for 6 percent of HCN use.[9] Acetone cyanohydrin is produced by directly reacting acetone with HCN. The four facilities which produce acetone cyanohydrin in the U.S. are presented in Table 5-3.[18] Three of these facilities use the acetone cyanohydrin in a captive process to produce methyl methocrylate. The production capacity of the fourth producer, BP America, Inc., is not available. A description of the process used to manufacture acetone cyanohydrin and a discussion of the emissions resulting from the various operations are presented below.

TABLE 5-3. DOMESTIC ACETONE CYANOHYDRIN PRODUCERS

Facility	Location	1991 Production capacity, Mg (tons)
BP American, Inc.	Green Lake, TX	N/A
CYRO Industries	New Orleans, LA	N/A
DuPont	Memphis, TN	N/A
Rohm & Haas Company	Deer Park, TX	N/A

Source: Reference 14.
N/A = Not available

5.2.1 Process Description[18]

Figure 5-2 presents a process flow diagram for the process of manufacturing acetone cyanohydrin by the catalytic reaction of acetone with HCN. Acetone and HCN are fed continuously along with sodium hydroxide catalyst into the reactor where the following reaction takes place:

$$\underset{\text{Acetone}}{(CH_3)_2\ CO} + HCN \rightarrow \underset{\substack{\text{Acetone}\\ \text{Cyanohydrin}}}{(CH_3)_2C(OH)CN} + \text{heat}$$

Because the reaction is exothermic, the reaction mixture is chilled. The crude product stream is transferred to an intermediate holding tank to force the equilibrium towards acetone cyanohydrin production. The mixture is then sent to a neutralization tank where it is neutralized with sulfuric acid to a pH between 1 and 2 to prevent decomposition of the cyanohydrin. As a result of the neutralization, the sodium catalyst that is carried over precipitates as sodium sulfate. The neutralized product stream is routed through a filter where the sodium sulfate is separated. The crude acetone cyanohydrin mixture is fed to a distillation column where the

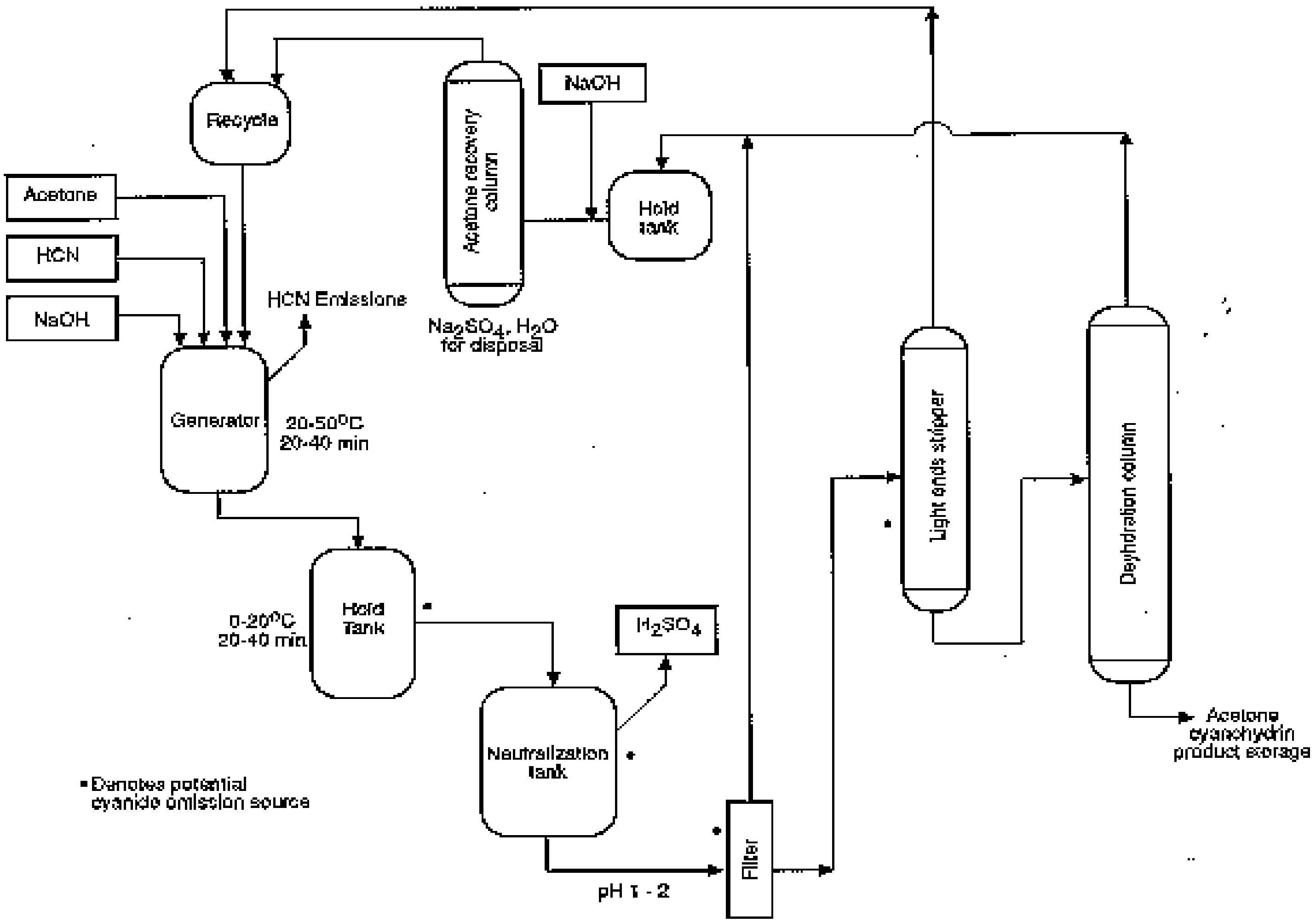


Figure 5-2. Process flow diagram for production of acetone cyanohydrin.[18]

light ends are separated. The bottoms from the distillation column, containing concentrated acetone cyanohydrin and water, is then fed to a dehydration column where water is removed and anhydrous acetone cyanohydrin is recovered.

Three facilities--CYRO Industries, (New Orleans, Louisiana) DuPont (Memphis, Tennessee), and Rohm & Haas Company (Deer Park, Texas)--use the acetone cyanohydrin directly for the production of methyl methacrylate.[14] The production of methyl methacrylate does not involve the use of HCN.[19] Therefore, it is believed that the process steps starting with acetone cyanohydrin, leading to the production of methyl methacrylate, do not result in HCN emissions.

5.2.2 Emission Control Measures

Information pertaining to HCN emission control during the production of acetone cyanohydrin is not available.

5.2.3 Emissions

Sources of HCN emissions are shown in Figure 5-3 by solid circles. Emissions of HCN can potentially result from the reactor, holding tank, neutralization tank, filter, and light ends distillation column. However, approximately 99 percent or more of the HCN fed to the reactor is converted to acetone cyanohydrin. Therefore, very little HCN is present in the process streams. Emissions of HCN may also result from sources of fugitive emissions such as storage, wastewater treatment operations, joints, valves and other fittings. Data reported in the TRI show that the nonpoint emissions are only about one percent of the total emissions.

Test data pertaining to cyanide emissions from individual sources at acetone cyanohydrin manufacturing facilities are not available. However, three of the four facilities manufacturing acetone cyanohydrin have reported cyanide compound emissions in the TRI for the year 1991. The TRI data are presented in Table 5-4.[11] All of these facilities produce multiple derivatives of HCN. Therefore, it is not clear which specific sources emit cyanide compounds and/or HCN.

TABLE 5-4. ACETONE CYANOHYDRIN PRODUCERS REPORTING CYANIDE COMPOUNDS OR HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY[a]

	Cyanide compound emissions, kg (lb)			Hydrogen cyanide emissions, kg (lb)		
Facility	Nonpoint	Point	Total	Nonpoint	Point	Total
Dupont	205	1,180	1,385	459	13,224	3,683
Memphis, TN	(451)	(2,602)	(3,053)	(1,012)	(29,159)	(30,171)
Rohm & Haas	1,224	426	1,650	254	49,887	50,141
Deer Park, TX	(2,700)	(940)	(3,640)	(560)	(110,000)	(110,560)
BP Chemicals, Inc.	0	0	0	3,810	11,791	15,601
Green Lake, TX	(0)	(0)	(0)	(8,400)	(26,000)	(34,400)
Total	1,429	1,606	3,035	4,523	74,902	79,425
	(3,151)	(3,542)	(6,693)	(9,972)	(165,159)	(175,131)

Source: Reference 11.

[a] These facilities produce multiple derivatives of HCN. Therefore, it is not clear as to what the specific sources are that emit cyanide compounds and/or HCN.

5.3 CYANURIC CHLORIDE

Cyanuric chloride, which is used to produce pesticides, accounts for 6 percent of HCN used in the United States. Cyanuric chloride is produced in two steps. In the first step, chlorine is reacted with HCN to produce cyanogen chloride. In the second step, cyanogen chloride is trimerized to form cyanuric chloride. Two facilities, Degussa Corp. in Theodore, Alabama, and Ciba-Giegy in St. Gabriel, Louisiana, are reported to produce cyanuric chloride.[4] Information pertaining to cyanide chloride production capacity at both plants is not available. A description of the process used to manufacture cyanuric chloride and a discussion of the emissions resulting from the various operations are presented below.

5.3.1 Process Description[4,20]

Figure 5-3 presents a process flow diagram for the manufacture of cyanuric chloride by the reaction of chlorine with HCN. Chlorine and HCN are added to the reactor (chlorinator) where the reaction to form cyanogen chloride (CNCl) takes place at a temperature between 20° and 40°C (68° and 104°F). The cyanogen chloride formed in the chlorinator is washed with water in a scrubber. The wash water dissolves the excess HCN and HCl from the reactor. The water containing HCN and HCl goes to a stripper that recycles any dissolved cyanogen chloride and HCN and releases HCl. Cyanogen chloride, which is devoid of HCl, is passed through a drying unit to remove traces of water. After exiting the dryer, chlorine is added to the cyanogen chloride and the mixture sent to the trimerizer where the CNCl is trimerized on activated charcoal at temperatures above 300°C (572°F) to form cyanuric chloride. Cyanuric chloride vapors from the trimerizer are condensed to molten or solid product, which is dissolved in a solvent for captive use or filled from a hopper into containers. Tail gases (containing CNCl and Cl_2) are scrubbed. The CNCl yield in this process exceeds 95 percent and the $(CNCl)_3$ yield exceeds 90 percent.

5.3.2 Emission Control Measures[4,20]

As described above, HCN, cyanogen chloride and cyanuric chloride emissions may occur as a result of the manufacture of cyanuric chloride. The HCN and cyanogen chloride emissions from the reactor are controlled by a water scrubber. Emissions of cyanogen chloride resulting from the cyanuric chloride condenser (following the trimerizer) are controlled by a water scrubber followed by a caustic scrubber. The control efficiency of these scrubbers for cyanogen chloride are unknown but it could be anticipated to be an efficient method because of the solubility of the compound in water. However, the ultimate control depends upon the specific

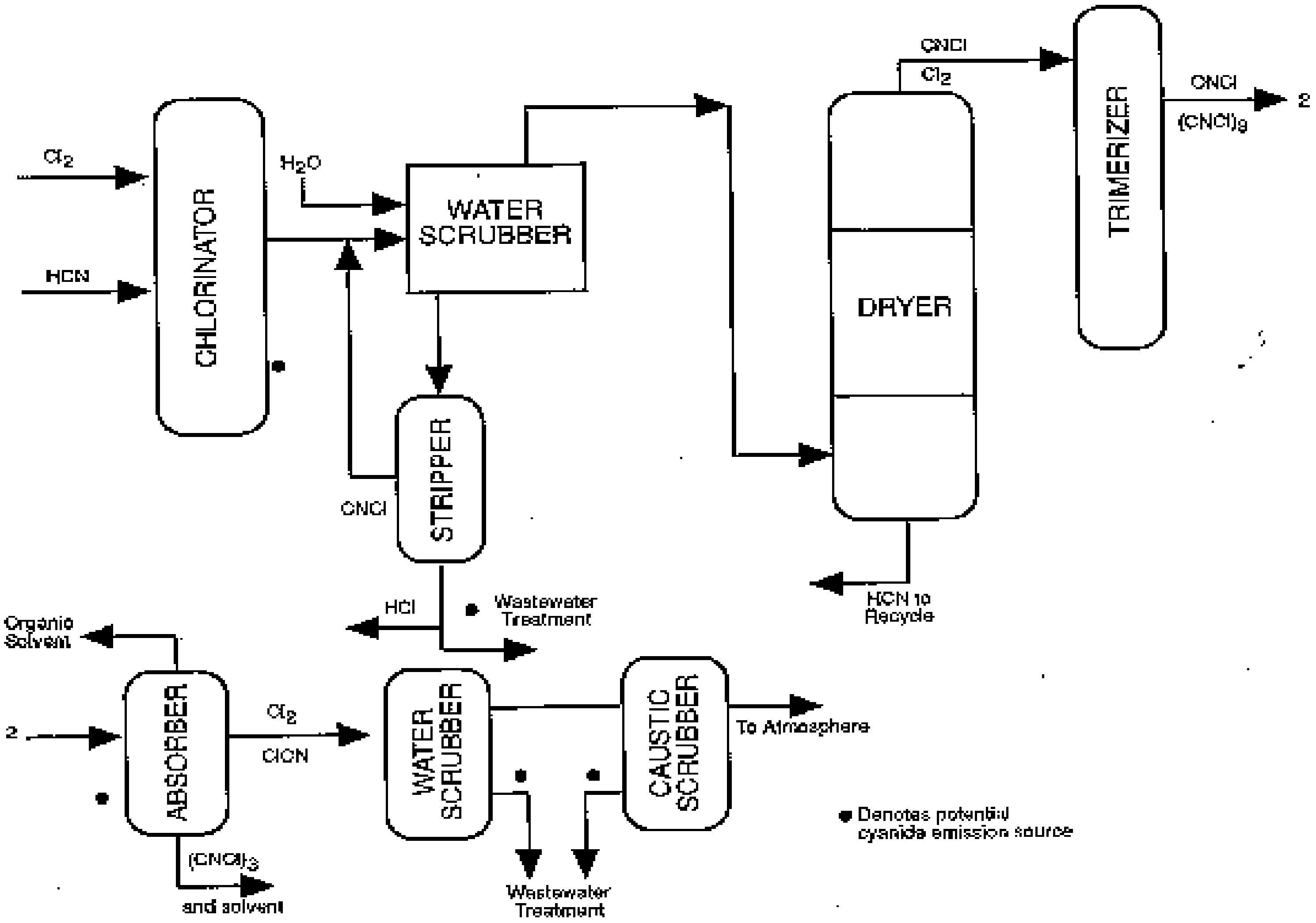


Figure 5-3. Process flow diagram for production of cyanuric chloride.[4]

wastewater treatment practices, which are unknown.

5.3.3 Emissions

Sources of HCN, cyanogen chloride, and cyanuric chloride emissions are shown in Figure 5-3 by solid circles. Test data pertaining to cyanide emissions from individual sources during the manufacture of cyanuric chloride are not available. Degussa Corp. and Ciba-Geigy have reported hydrogen cyanide emissions of 1,116 kg (2,460 lb) and 121 kg (267 lb), respectively, to the TRI, for the year 1991.[11] Of the total emissions from the Degussa facility, 31 percent were from nonpoint sources; for the Ciba-Geigy facility, 24 percent were from nonpoint sources.

5.4 CHELATING AGENTS PRODUCTION

Chelating agents are a minor use of HCN, consuming 5 percent of the HCN produced in the United States.[9] The primary chelating agents using HCN as a raw material are ethylenediaminetetraacetic acids (EDTA), aliphatic hydroxycarboxylic acids, and nitrilotriacetic acids (NTA). Table 5-5 lists the U.S. producers of these agents.[14]

5.4.1 Process Descriptions

Ethylenediaminetetraacetic acids--[21]

The two-step Singer synthesis is the only commercial process currently used to manufacture EDTA that uses HCN as a raw material. The Singer synthesis has two separate steps, the cyanomethylation step and hydrolysis. In cyanomethylation, hydrogen cyanide and formaldehyde react with ethylenediamine to form insoluble (ethylenedinitrilo)tetra-acetonitrile (EDTN). The intermediate nitrile is then

TABLE 5-5. U.S. PRODUCERS OF HCN-USING CHELATING AGENTS

Chelating agent	Company	Location
Ethylenediaminetetraacetic acids[a]		
	CIBA-GEIGY Corp.	McIntosh, AL
	Dow Chemical	Freeport, TX
	Eastman Kodak Co.	Rochester, NY
	Emkay Chemical Co.	Elizabeth, NJ
	GFS Chemicals, Inc.	Columbus, OH
	Hart Products Corp.	Jersey City, NJ
	Hickson DanChem Corp.	Danville, VA
	Mayo Chemical Co.	Dalton, GA
	Vinings Industries, Inc.	Marietta, GA
	Vinings Industries, Inc.	Washougal, WA
	W.R. Grace & Co.	Nashua, NH
Hydroxycarboxylic acids		
-Butyrolactone	BASF Corp.	Geismar, LA
	GAF Corp.	Calvert City, KY
	GAF Corp.	Texas City, TX
-Citric acid[b]	Archer Daniels Midland Co.	Southport, NC
	Bayer USA, Inc.	Dayton, OH
	Bayer USA, Inc.	Elkhart, IN
	Cargill, Inc.	Eddyville, IA
	Pfizer, Inc.	Groton, CT
-Lactic acid	Sterling Chemicals, Inc.	Texas City, TX
	Pfanstiehl Laboratories, Inc.	Waukegan, IL
Nitrilotriacetic acids		
	Dow Chemical, Inc.	Freeport, TX
	W.R. Grace & Co.	Nashua, NH
	Mayo Chemical Co.	Dalton, GA
	Monsanto Co.	Alvin, TX

Source: Reference 14.

[a] It could not be verified whether all U.S. producers of EDTA use the Singer process.

[b] Production capacity data are available only for citric acid, as below:

Archer Daniels Midland Co., Southport, NC	110 million pounds
Bayer USA, Inc., Dayton, OH	65 million pounds
Bayer USA, Inc., Elkhart, IN	86 million pounds
Cargill, Inc., Eddyville, IA	55 million pounds
Pfizer, Inc., Groton, CT	70 million pounds

separated, washed, and hydrolyzed with sodium hydroxide to tetrasodium EDTA. Ammonia is liberated as a byproduct.

Aliphatic Hydroxycarboxylic Acids [22]--

Aliphatic hydroxycarboxylic acids are manufactured in many different ways. Two processes utilize HCN in their syntheses. a-Hydroxycarboxylic acids (e.g., (R,S)-lactic acid) are produced by cyanohydrin synthesis. ß-Hydroxcarboxylic acids can be prepared by treating epoxides with HCN and then hydrolyzing the intermediate nitriles. No information is available regarding what percentage of hydroxycarboxylic acids are prepared by either of these two methods. It is not known which of the plants listed in Table 5-5 uses the HCN-based process for the manufacture of aliphatic hydroxycarborylic acids.

Nitrilotriacetic Acids [23]--

Nitrilotriacetic acids (Na3 NTA) are produced by two processes. The older process, the alkaline process, utilizes NaCN, not HCN, and is not discussed here. A newer, two-stage process (the acid process) uses HCN as a raw material and was developed due to the significant yield of byproducts produced by the alkaline process. In the first stage of the acid process, ammonia reacts with formaldehyde to produce hexamethylene-tetramine, which then reacts with HCN in sulfuric acid solution to yield triscyanomethylamine. The solid triscyanomethylamine is filtered off, washed, and saponified with NaOH to produce Na3 NTA. It is not known which of the two nitrilotriacetic acid manufacturing processes is used predominantly in the United States.

5.4.2 Emission Control Measures

Information pertaining to controlling cyanide emissions resulting from the production of chelating agents is not available.

5.4.3 Emissions

Test data pertaining to cyanide emissions from individual sources at chelating agent manufacturing facilities are not available. Additionally, based on the limited process data available, it is not possible to identify the potential emission sources of HCN or cyanide compounds during the manufacture of chelating agents. However, seven facilities manufacturing chelating agents have reported facilitywide cyanide compounds or HCN emissions to the TRI for the year 1991. The TRI data are presented in Table 5-6.[11]

TABLE 5-6. PRODUCERS OF CHELATING AGENTS REPORTING CYANIDE COMPOUND OR HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY[a]

	Cyanide compound emissions, kg (lb)			Hydrogen cyanide emissions, kg (lb)		
Facility	Nonpoint	Point	Total	Nonpoint	Point	Total
Ciba-Geigy McIntosh, AL	N/R	N/R	N/R	113 (250)	113 (250)	226 (500
Dow Chemical Freeport, TX	0 (0)	0 (0)	0 (0)	2 (4)	0 (0)	2 (4)
W.R. Grace Nashua, NH	0 (0)	0 (0)	0 (0)	812 (1,790)	216 (477)	1,028 (2,267)
Pfizer, Inc. Groton, CT	0 (0)	2.3 (5)	2.3 (5)	N/R	N/R	N/R
Sterling Chemicals Texas City, TX	0 (0)	0 (0)	0 (0)	3,936 (8,680)	17,451 (38,480)	21,387 (47,160)
Pfanstiehl Labs Waukegan, IL	0 (0)	0 (0)	0 (0)	N/R	N/R	N/R
Monsanto Alvin, TX	N/R	N/R	N/R	680 (1,500)	635 (1,400)	1,315 (2,900)
Total	0 (0)	2.3 (5)	2.3 (5)	5,543 (12,224)	18,415 (40,607)	23,958 (52,831)

Source: Reference 11.

N/R = not reported in 1991 TRI.

[a] These facilities produce multiple derivatives of HCN. Therefore, it is not clear as to what the specific sources are that emit cyanide compounds and/or HCN.

5.5 CYANIDE ELECTROPLATING

Cyanide compounds are used in a number of electroplating solutions. Cyanide compounds are used in copper, brass, cadmium, gold, indium, silver, and zinc plating baths. The primary cyanide compounds used in electroplating solutions are sodium or potassium cyanide and the metal cyanide, such as gold and silver cyanide. In some cases, cyanide plating baths are being replaced with baths composed of less toxic compounds. However, there are specific applications and plating operations that require the use of cyanide-based plating solutions.

Table 5-7 presents the number of metal finishing job shops that perform the types of plating operations listed above.[24] Some duplication of shops will be presented because most metal finishing operations perform more than one type of electroplating operation. Copper and zinc plating baths are the most common plating solutions that use cyanide compounds. The demand for precious metal deposits is not as high as that for functional deposits, such as copper and zinc. In addition, not all of the job shops accounted for in Table 5-7 will use the cyanide version of the plating bath. Some operations may use substitute baths that have been developed to replace the cyanide plating baths, such as acid copper plating baths.

Metal finishing shops are typically located at or near industries they serve. Therefore, the geographical distribution of the metal finishing shops closely follows that of the U.S. manufacturing base.

5.5.1 Process Description

A flow diagram for a typical cyanide electroplating process is presented in Figure 5-4. Prior to plating, the parts undergo a series of pretreatment steps to smooth the

TABLE 5-7. ESTIMATED NUMBER OF METAL FINISHING JOB SHOPS PERFORMING SELECTED PLATING OPERATIONS

Type of plating operation	Percent of total job shops, %	Estimated number of job shops
Copper plating	41	1,649
Zinc plating	35	1,408
Cadmium plating	29	1,166
Silver plating	22	885
Gold plating	18	724
Brass plating	17	684

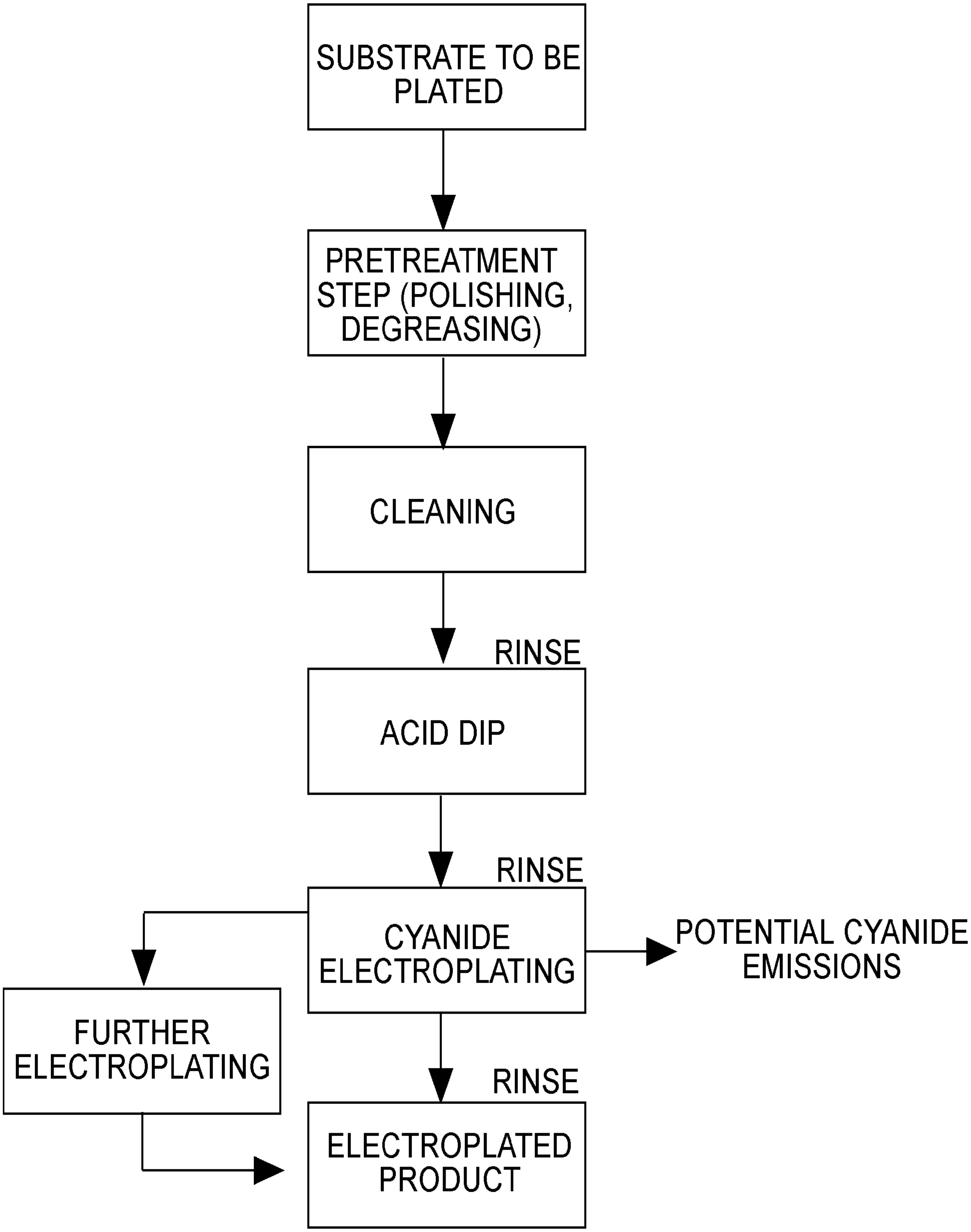
Source: Reference 24.

surface of the part and to remove any surface soil, grease, or oil. Pretreatment steps include polishing, grinding, and/or degreasing of the part to prepare for plating. The part being plated is rinsed after each process step to prevent carry-over of solution that may contaminate the baths used in successive process steps.

Polishing and grinding are performed to smooth the surface of the part. Degreasing is performed either by dipping the part in organic solvents or by vapor degreasing the part using organic solvents. Vapor degreasing is typically used when the surface loading of oil or grease is excessive. The two organic solvents most commonly used for cleaning applications are trichloroethylene and perchloroethylene.

Alkaline cleaning is sometimes used to dislodge surface soil and prevent it from settling back onto the metal. These cleaning solutions are typically made up of compounds, such as sodium carbonate, sodium phosphate, and sodium hydroxide; they usually contain a surfactant. Alkaline cleaning techniques include soaking and cathodic and anodic cleaning.

Acid dips may be used to remove any tarnish or oxide films formed in the alkaline cleaning step and to neutralize the


SUBSTRATE TO BE PLATED
PRETREATMENT STEP (POLISHING, DEGREASING)
CLEANING
RINSE
ACID DIP
RINSE
CYANIDE ELECTROPLATING
POTENTIAL CYANIDE EMISSIONS
FURTHER ELECTROPLATING
RINSE
ELECTROPLATED PRODUCT

alkaline film. Acid dip solutions typically contain from 10 to 30 percent by volume hydrochloric or sulfuric acid in water.

The exact pretreatment steps depend upon the amount of soil, grease, or oil on the parts and the type of plate being used. Following pretreatment, the parts are transferred to the plating tank.

Tables 5-8 through 5-14 present the plating bath formulations that use cyanide compounds as a integral part of the plating bath.[25] In these plating operations, the part(s) is placed in a tank and connected into the electrical circuit as the cathode. If small parts are to be plated, the parts are first placed in a plating barrel or on a plating rack. The barrel or plating rack is then placed in the tank and connected to the electrical circuit. The efficiency of the plating bath is based on the amount of current that is consumed in the deposition reaction versus the amount of current that is consumed by other side reactions. Cyanide plating baths range from very efficient baths (90 to 99 percent) to less efficient baths (50 to 75 percent). For the less efficient baths, the temperature of the plating bath plays an important role in determining how efficient the bath will operate.

Following cyanide plating, the parts can be sent to another series of plating tanks to add further layers of metal or may be rinsed and sold as final end products. Some of the cyanide plating baths, such as copper, are used as an underplate for other metals. For example, a plate of copper, nickel, and chromium is used in the decorative chromium plating process for parts, such as automotive trim. Other plates, such as gold or silver, may not undergo any further treatment other than rinsing prior to their use as a final end product.

TABLE 5-8. COMPOSITION AND OPERATING PARAMETERS OF A TYPICAL COPPER CYANIDE PLATING BATH

Component	Operating range
Composition of bath, g/L (oz/gal)	
Copper cyanide	60 to 75 (8 to 10)
Potassium or sodium cyanide	102 or 97.5 (13.6 or 13.0)
Potassium carbonate or sodium carbonate	15 (2)
Potassium hydroxide or sodium hydroxide	15 (2)
Rochelle salt (if potassium bath is used)	45 (6)
Operating Parameters	
Temperature, °C (°F)	60 to 71 (140 to 160)
Current density, A/m^2 (A/ft^2)	up to 860 (up to 80)
Cathode efficiency, %	90 to 99

Source: Reference 25.

TABLE 5-9. COMPOSITION AND OPERATING PARAMETERS OF A TYPICAL ZINC CYANIDE PLATING BATH

Component	Operating range		
Composition of bath, g/L (oz/gal)			
	Low cyanide	Mid cyanide	High cyanide
Zinc oxide or zinc cyanide	7.5 - 11.2	13.5 - 18.7	26 - 34
	(1.0-1.5)	(1.8-2.5)	(3.5-4.5)
Sodium hydroxide	75 to 90	75 to 90	75 to 90
	(10-12)	(10-12)	(10-12)
Sodium cyanide	11.2 - 18.7	26 - 45	82 - 105
	(1.5-2.5)	(3.5-6.0)	(11-14)
Operating Parameters			
Temperature, °C (°F)		15 to 38 (60 to 100)	
Bath efficiency, %		65 to 80	

Source: Reference 25.

TABLE 5-10. COMPOSITION AND OPERATING PARAMETERS OF A TYPICAL CADMIUM CYANIDE PLATING BATH

Component	Operating range
Composition of bath, g/L (oz/gal)	
Cadmium	20 (2.7)
Cadmium oxide	22 (3.0)
Sodium carbonate	30-60 (4.0-8.0)
Sodium cyanide	101 (13.5)
Sodium hydroxide	14 (1.9)
Operating Parameters	
Temperature, °C (°F)	15 to 38 (60 to 100)
Current density, A/m^2 (A/ft^2)	54 to 970 (5-90)
Cathode efficiency, %	90 to 95

Source: Reference 25.

TABLE 5-11. COMPOSITION AND OPERATING PARAMETERS OF A TYPICAL SILVER CYANIDE PLATING BATH

Component	Operating range
Composition of bath, g/L (oz/gal)	
Silver as KAg(CN2)	5 to 40 (0.7 to 6)
Potassium cyanide	12 to 120 (1.6 to 16)
Potassium carbonate	15 (2)
Operating Parameters	
Temperature, °C (°F)	20 to 30 (70 to 85)
Current density, A/m2 (A/ft2)	10 - 430 (1 - 40)

Source: Reference 25.

TABLE 5-12. COMPOSITION AND OPERATING PARAMETERS OF A TYPICAL GOLD ALKALINE CYANIDE PLATING BATH

Component	Operating range
Composition of bath, g/L (oz/gal)	
Gold as potassium gold cyanide	8-20 (1.1-2.7)
Dipotassium phosphate	22-45 (2.9-6.0)
Potassium cyanide	15-30 (2.0-4.0)
Operating Parameters	
Temperature, °C (°F)	49 to 70 (120 to 160)
Current density, A/m2 (A/ft2)	33 to 54 (3 to 5)
Cathode efficiency, %	90 to 95

Source: Reference 25.

TABLE 5-13. COMPOSITION AND OPERATING PARAMETERS OF A TYPICAL BRASS CYANIDE PLATING BATH

Component	Operating range
Composition of bath, g/L (oz/gal)	
Copper cyanide	32 (4.2)
Zinc cyanide	10 (1.3)
Sodium cyanide	50 (6.5)
Sodium carbonate	7.5 (1)
Ammonia	2.5 to 5 ml/L (1 to 2 qts/gal)
Sodium bicarbonate	10 (1.5)
Operating Parameters	
Temperature, °C (°F)	25 to 35 (75 to 95)

Source: Reference 25.

TABLE 5-14. COMPOSITION AND OPERATING PARAMETERS OF A TYPICAL INDIUM CYANIDE PLATING BATH

Component	Operating range
Composition of bath, g/L (oz/gal)	
Indium as metal	33 (4)
Dextrose	33 (4)
Potassium cyanide	96 (12.8)
Potassium hydroxide	64 (8.5)
Operating Parameters	
Temperature, °C (°F)	room temperature
Cathode efficiency, %	50 to 75
Current Density, A/m^2 (A/ft^2)	162-216 (15-20)

Source: Reference 25.

5.5.2 Emission Control Measures

No data were available on the use of air pollution control measures on cyanide plating tanks. However, most cyanide plating tanks are ventilated as a precautionary measure against worker exposure.

5.5.3 Emissions

No emission test data were available for the cyanide plating operations listed above. Based on emission estimates reported in the 1991 TRI, a total of 123 facilities reported cyanide emissions under SIC 3471, Plating and Polishing. Cyanide emission estimates for these facilities totaled 10,117 kg (22,309 lb).

SECTION 6
CYANIDE COMPOUND EMISSIONS FROM MISCELLANEOUS SOURCES

Cyanide emissions have been reported from miscellaneous sources, including production of iron and steel, carbon black, carbon fiber, and mobile sources. It is not known whether cyanide emissions occur as a result of the chemical changes that take place during the different manufacturing steps or as a result of volatilization of cyanide compounds present in the raw materials processed during the production process. This section presents process information, air pollution control measures, and estimates of cyanide emissions from these sources.

6.1 IRON AND STEEL PRODUCTION [26-28]

Two types of iron and steel plants will be discussed in this section: integrated and nonintegrated. Integrated iron and steel plants are those iron and steelmaking facilities that are capable of starting with iron ore as a raw material feed and producing finished steel products. At a minimum, these facilities have blast furnace facilities for pig iron production; steelmaking furnaces (generally one or more basic oxygen furnaces), and steel finishing operations. Many facilities also have coke making operations, sinter plants, and electric arc furnace shops for melting scrap. In its simplest form, the integrated iron and steel process begins with pig iron production from iron ore or pellets in the blast furnace. The molten iron is transferred from the blast furnace to the basic oxygen furnace, where the hot pig iron and scrap metal are heated and transformed metallurgically to carbon steel. This carbon steel is then cast and rolled into a final project.

Nonintegrated plants consist of "minimills" or specialty mills that produce carbon steel, stainless steel and other steel alloys from scrap. Typical operations at these facilities include electric arc furnaces for steelmaking and steel casting and finishing operations, as well as alloying operations. Table B-1 lists those facilities that use electric arc furnaces. Total steel (carbon and alloy) production for 1991 was 79.7 x 10^6 Megagrams (Mg)(87.8 x 10^6 tons).

The principal components of the process are iron production, steelmaking, and steel finishing. However, two important ancillary components are coke making and sinter production. The process steps discussed below apply to an integrated plant. Process differences will be noted for nonintegrated plants.

Frequently, the first step in the process for an integrated plant is to produce metallurgical coke (elemental carbon) for the blast furnace. Coke is used to: (1) provide a substrate for raw materials in the blast furnace, (2) function as fuel for the hot blast air, and (3) remove iron ore oxides. Nonintegrated plants do not use blast furnaces and, therefore, do not need coke. The coke is made from coal that is pulverized and then heated in a coke oven without oxygen at 1050°C (1925°F) for 12 to 20 hours. Volatiles are driven off, and elemental carbon (coke) and ash are formed. No information is available for cyanide emissions from coke production.

A second ancillary process found at many integrated plants is the sintering operation. The sintering process is a materials-recovery process, which converts fine-sized raw materials, including iron ore, coke breeze (undersized coke), limestone, mill scale, and flue dust, into an agglomerated product called "sinter."

The initial process common to all integrated plants is the blast furnace, which is used to produce molten iron ("pig iron"). Iron ore, coke, limestone flux and sinter are introduced ("charged") into the top of the furnace. Heated air is injected through the bottom of the furnace. This blast air combusts the coke contained in the breeze to melt the sinter, and flux with the iron oxides in the ore and form molten iron, slag, and carbon monoxide (CO). The molten iron and the slag collect in the hearth at the base of the furnace and are periodically tapped. The molten iron from the blast furnace undergoes desulfurization, after which it is introduced to a basic oxygen furnace (BOF) or open hearth furnace to make steel. There are two types of BOF's: conventional BOF's and the newer Quelle Basic Oxygen process (Q-BOP) furnaces. The open-hearth furnace (OHF) is a shallow, refractory-lined basin in which scrap and molten iron are melted together and then refined into steel. Nonintegrated plants use electrical arc furnaces (EAF's) to produce carbon and alloy steels. The raw material for an EAF is typically 100 percent scrap.

Molten steel from the furnace is cast into molds or is continuously cast to form a finished product. This final product consists of shapes called blooms, slags, and billets.

If steel parts are produced at the iron and steel production facilities, the parts thus produced are subjected to a "carburizing" step to provide wear resistance. Two processes are used for carburizing. In the first process, steel parts are immersed in a molten-salt bath containing about 30 percent sodium cyanide (NaCN) at an approximate temperature of 870°C (1600°F) for a period range between 1/2 to 1-hour to obtain a light (shallow) (0.01 inch) hard case for wear resistance. In the second process, carburizing is carried out in activated baths which employ a floating slag of calcium cyanide as the active agent and which produce deeper cases which are lower in nitrogen and higher in carbon than those obtained with just the NaCN bath. A typical composition of an activated bath used in the second process is as given below:

Calcium cyanamide (CaCN2)	2-5%
Calcium cyanide (Ca(CN)2)	43-48%
Sodium chloride (NaCl)	30-35%
Calcium oxide (CaO)	14-16%
Carbon (C)	4-5%

It is not known which carburizing process is more popularly used.

Based on the limited information available, it is assumed that the carburizing step is the only source of emissions of cyanide compounds. The cyanide compounds emitted as a result of carburizing may include NaCN, $CaCN_2$, and $Ca(CN_2$, depending on which of the two carburizing processes is used.

6.1.1 Emission Control Measures

No information is available pertaining to control of cyanide compound emissions resulting from the carburizing step in iron and steel production facilities.

6.1.2 Emissions

No test data are available pertaining to cyanide emissions resulting from carburizing step during iron and steel production. However, 21 facilities have reported emissions of cyanide compounds in the 1991 Toxic Release Inventory (TRI). The TRI data are presented in Table 6-1.[11]

6.2 CARBON BLACK PRODUCTION

Carbon black is produced by partial combustion of hydrocarbons. The most predominantly used process (which

TABLE 6-1. IRON/STEEL AND COKE PRODUCTION FACILITIES REPORTING CYANIDE COMPOUND EMISSIONS IN THE 1991 TOXIC RELEASE INVENTORY

	Emission, kg (lb)		
Facility	Nonpoint	Point	Total
New Boston Coke Corp. New Boston, OH	0.5 (1)	2,132 (4,700)	2,132 (4,701)
Acme Steel Co. Chicago, IL	190 (420)	63,492 (140,000)	63,682 (140,420)
ARMCO Steel Co. Middletown, OH	45 (100)	45 (100)	90 (200)
ARMCO Steel Co. Ashland, KY	100 (220)	116 (255)	216 (475)
Bethlehem Steel Chesterton, IN	0 (0)	0 (0)	0 (0)
Bethlehem Steel Sparrows Point, MD	50 (110)	45,351 (100,000)	45,401 (100,110)
Carpenter Technology Reading, PA	26 (58)	0 (0)	26 (58)
Detroit Coke Corp. Detroit, MI	0 (0)	23 (51)	23 (51)
Granite City Steel Granite City, IL	2.3 (5)	2,086 (4,600)	2,088 (4,605)
Gulf States Steel Gadsden, AL	0 (0)	0 (0)	0 (0)
Inland Steel Co. East Chicago, IN	2,222 (4,900)	0 (0)	2,222 (4,900)
LTV Steel Co. East Chicago, IN	0 (0)	363 (800)	363 (800)
LTV Steel Co. Aliquippa, PA	0 (0)	363 (800)	363 (800)
Sharon Steel Corp. Monessen, PA	0 (0)	0 (0)	0 (0)
USS Clairton Works Clairton, PA	4,535 (10,000)	17,687 (39,000)	22,222 (49,000)
USS Gary Works Gary, IN	4,989 (11,000)	14,059 (31,000)	19,048 (42,000)
USS Mon Valley Works Braddock, PA	0 (0)	0 (0)	0 (0)
USS Fairfield Works Fairfield, AL	0 (0)	0 (0)	0 (0)
Wheeling-Pittsburgh Steel Follansbee, WV	5,442 (12,000)	16,780 (37,000)	22,222 (49,000)
Wheeling-Pittsburgh Steel Mingo Junction, OH	0 (0)	0 (0)	0 (0)
Wheeling-Pittsburgh Steel Steubenville, OH	0 (0)	0 (0)	0 (0)
TOTAL	17,602 (38,814)	162,497 (358,306)	180,098 (397,120)

Source: Reference 11.

accounts for more than 98 percent of carbon black produced) is based on a feedstock consisting of a highly aromatic petrochemical or carbochemical heavy oil. Cyanide compounds can be expected to be present in the feedstock. However, data pertaining to the content of cyanide compounds in petrochemical or carbochemical heavy oil are not available. A compilation of facilities, locations, type of process, and annual capacity is presented in Table 6-2.[14] A description of the process used to manufacture carbon black and the emissions resulting from the various operations are presented below.

6.2.1 Process Description[29]

Figure 6-1 contains a flow diagram for the carbon black production process. Three primary raw materials used in this process are: preheated feedstock (either the petrochemical oil or carbochemical oil), which is preheated to a temperature between 150° and 250°C (302° and 482°F); preheated air; and an auxiliary fuel, such as natural gas. A turbulent, high-temperature zone is created in the reactor by combusting the auxiliary fuel, and the preheated oil feedstock introduced in this zone as an atomized spray. In this zone of the reactor, most of the oxygen would be used to burn the auxiliary fuel resulting in insufficient oxygen to combust the oil feedstock. Thus, pyrolysis (partial combustion) of the feedstock is achieved, and carbon black is produced. Any cyanide compounds that may be present in the feedstock will be emitted in the hot exhaust gas from the reactor.

The product stream from the reactor is quenched with water, and any residual heat in the product stream is used to preheat the oil feedstock and combustion air before recovering the carbon in a fabric filter. Carbon recovered in the fabric filter is in a fluffy form. The fluffy carbon black may be ground in a grinder, if desired. Depending on the end use,

TABLE 6-2. CARBON BLACK PRODUCTION FACILITIES

Company	Location	Type of process[a]	Annual capacity[b] 10^3 Mg	 10^6 lbs
Cabot Corporation	Franklin, Louisiana	F	141	310
North American Rubber Black Division	Pampa, Texas	F	32	70
	Villa Platte, Louisiana	F	127	280
	Waverly, West Virginia	F	82	180
Chevron Corporation Chevron Chemical Company, subsidiary Olevins and Derivatives Division	Cedar Bayou, Texas	A	9	20
Degussa Corporation	Arkansas Pass, Texas	F	57	125
	Belpre, Ohio	F	59	130
	Louisa, Louisiana	F	91	200
Ebonex Corporation	Melvindale, Michigan	C	4	8
General Carbon Company	Los Angeles, California	C	0.5	1
Hoover Color Corporation	Hiwassee, Virginia	C	0.5	1
J.M. Huber Corporation	Baytown, Texas	F	102	225
	Borger, Texas	F and T	79	175
	Orange, Texas	F	61	135
Phelps Dodge Corporation	El Dorado, Arkansas	F	50	110
Colombian Chemical Company, subsidiary	Moundsville, West Virginia	F	77	170
	North Bend, Louisiana	F	109	240
	Ulysses, Kansas	F	36	80
Sir Richardson Carbon & Gasoline Company	Addis, Louisiana	F	66	145
	Big Spring, Texas	F	52	115
	Borger, Texas	F	98	215
Witco Corporation	Phenix City, Alabama	F	27	60
Continental Carbon Company, subsidiary	Ponca City, Oklahoma	F	66	145
	Sunray, Texas	F	45	100
		TOTAL	1,471	3,240

Source: Reference 14.

[a] A = acetylene decomposition
C = combustion
F = furnace
T = thermal

[b] Capacities are variable and based on SRI estimates as of January 1, 1991

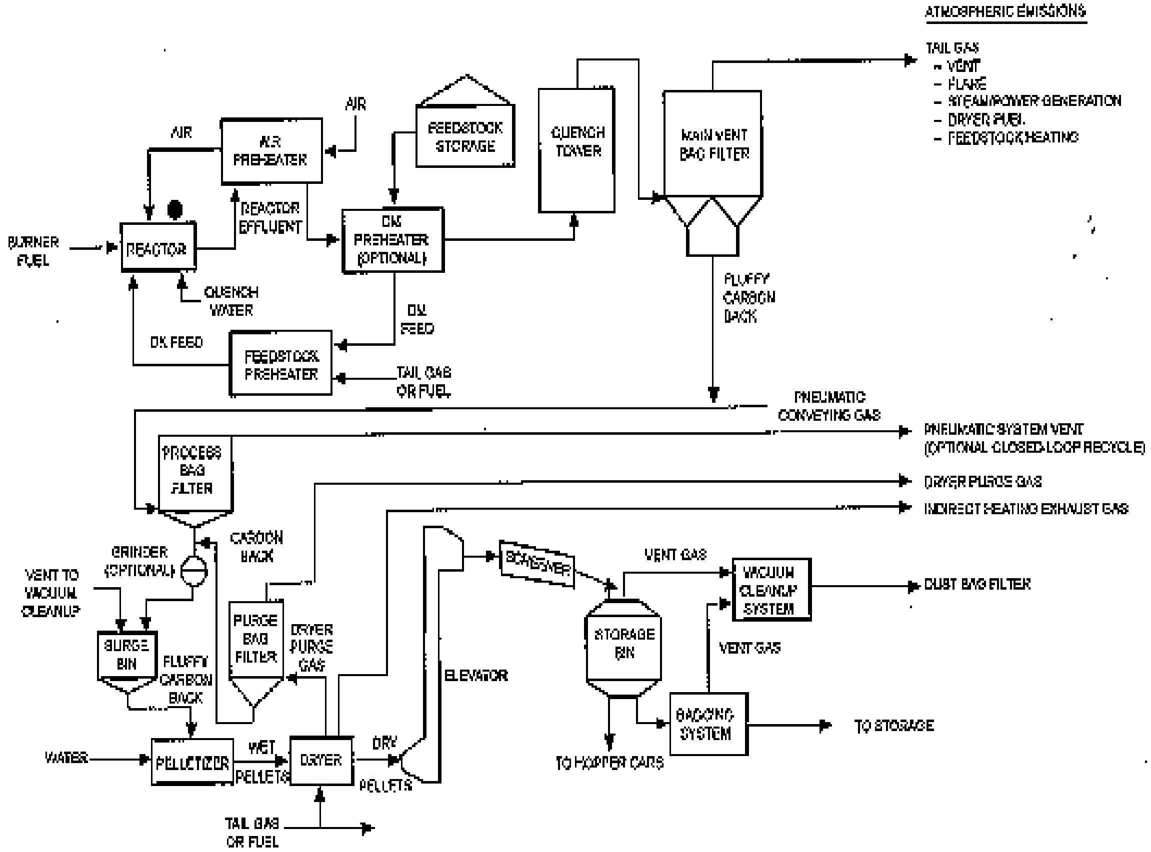


Figure 6-1. Process flow diagram for carbon black manufacturing process.[29]

carbon black may be shipped in a fluffy form or in the form of pellets. Pelletizing is done by a wet process in which carbon black is mixed with water along with a binder and fed into a pelletizer. The pellets are subsequently dried and bagged prior to shipping.

6.2.2 Emission Control Measures[29]

High-performance fabric filters are reported to be used to control PM emissions from main process streams during the manufacture of carbon black. It is reported that the fabric filters can reduce PM emissions to levels as low as 6 mg/m^3 (normal m^3). If the cyanide emissions from the reactor are primarily in the vapor phase (and not as particulate), these emissions will proceed through the main process streams to the fabric filters. If the cyanide remains in the vapor phase, the cyanide control efficiency by the fabric filters is expected to be low. If the product gas stream is cooled to below 170°C (325°F), the fabric filter may capture a significant fraction of the condensed cyanide compounds, thus providing a high degree of emission control.

6.2.3 Emissions

The processing unit with the greatest potential to emit cyanide emissions is the reactor. Cyanide emission sources are indicated in Figure 6-1 by solid circles. Cyanide compounds, which may be present in the oil feedstock, can potentially be emitted during the pyrolysis step. Test data pertaining to cyanide emissions from carbon black production are not available. However, only six of 24 facilities have reported facilitywide emissions of cyanide compounds in the 1991 TRI. The TRI data are presented in Table 6-3.[11]

TABLE 6-3. CARBON BLACK PRODUCERS REPORTING CYANIDE COMPOUND EMISSIONS IN THE 1991 TOXIC RELEASE INVENTORY

	Emissions, kg (lb)		
Facility	Nonpoint	Point	Total
Cabot Corp. Franklin, LA	0 (0)	231,610 (510,700)	231,610 (510,700)
Cabot Corp. Waverly, WV	2.3 (5)	22 (48)	24 (53)
Cabot Corp. Pampa, TX	113 (250)	53,297 (117,520)	53,410 (117,770)
Degussa Corp. Louisa, LA	0 (0)	81,633 (180,000)	81,633 (180,000)
Degussa Corp. Arkansas Pass, TX	0 (0)	15,420 (34,000)	15,420 (34,000)
Degussa Corp. Belpre, OH	0 (0)	30,385 (67,000)	30,385 (67,000)
TOTAL	115 (255)	412,367 (909,268)	412,482 (909,523)

Source: Reference 11.

6.3 CARBON FIBER PRODUCTION

Carbon fibers are black fibers used as yarns, felt, or powderlike short monofilaments with diameters smaller than 10 micrometers (µm). They are primarily applied to reinforce polymers, much like glass fibers are used in fiber glass. Carbon fibers are important because of their superior stiffness, high strength, and low density.30 Table 6-4 presents a list of domestic carbon fiber manufacturing facilities.[14]

This section presents a description of the carbon fiber production process, emission control measures, and emissions occurring as a result of the production process.

TABLE 6-4. DOMESTIC PRODUCERS OF HIGH PERFORMANCE CARBON FIBERS

Company/location	Annual capacity, (thousands of pounds)
Fortafil Fibers, Inc., Rockwood, TN	1,000
Amoco Corporation, Piedmont, SC	2,500
BASF Corporation, Rock HIll, SC	1,000
BP America, Inc., Gardena, CA	50
Grafil, Inc., Sacramento, CA	900
Hercules, Inc., Magna (Bacchus), UT	3,100
Textron, Inc., Lowell, MA	100
Zoltek Corporation, Lowell, MA	250
TOTAL	8,900

Source: References 4 and 14.

The most common carbon fiber production process uses polyacrylonitrile (PAN) as the raw material. Therefore, only the PAN-based process will be described in this section.

6.3.1 Process Description[30]

All commercial production processes for carbon fibers are based on carbonization of polymer fiber precursors. For PAN-based carbon fibers, the simplified process involves spinning the polymer fibers by a wet-spinning process, stretching the precursor before or during stabilization, stabilizing the thermoplastic precursor, and carbonizing the fibers. The most important step in this process in terms of carbon fiber quality and process economy is the stabilization step when oxidation occurs. The carbonization step, which can be carried out much faster than the stabilization step, produce volatile byproducts such as water, HCN, carbon dioxide, and nitrogen.

The quality of the final carbon fiber product is determined by the precursor fiber, the stabilization treatment, oxygen content, and the carbonization schedule.

6.3.2 Emission Control Measures

No information is available pertaining to the control of emissions resulting from carbon fiber production.

6.3.3 Emissions

Test data pertaining to cyanide emissions resulting from the carbonization step during carbon fiber production are not available. However, five of the eight facilities have reported facilitywide emissions of hydrogen cyanide in the 1991 TRI. The TRI data are presented in Table 6-5.[11]

6.4 PETROLEUM REFINING

Petroleum refining involves the conversion of crude petroleum oil into refined products, including liquified petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petroleum industry.

As of January 1992, there were 32 oil companies in the United States with operable atmospheric crude oil distillation capacities in excess of 100,000 barrels per calendar day. These oil companies operated refiners at a total of 110 different locations. In addition, there were 72 companies with distillation capacities of less than 100,000 barrels per calendar day. A listing of all companies, specific refinery locations, and distillation capacities is presented in Table B-2 of Appendix B.[31]

6.4.1 Process Description[12,32]

The operations at petroleum refineries are classified into five general categories, as listed below:

TABLE 6-5. CARBON FIBER PRODUCERS REPORTING HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY

	Emissions, kg (lb)		
Facility	Nonpoint	Point	Total
Fortafil Fibers, Inc. Rockwood, TN	113 (250)	1,950 (4,300)	2,063 (4,550)
Amoco Corp. Piedmont, SC	5,533 (12,200)	1,361 (3,000)	6,894 (15,200)
BASF Corp. Rock Hill, SC	113 (250)	38,549 (85,000)	38,662 (85,250)
Grafil, Inc. Sacramento, CA	1.4 (3)	9,289 (20,482)	9,290 (20,485)
Hercules, Inc. Magnar, UT	0 (0)	17,343 (38,242)	17,343 (38,242)
TOTAL	5,760 (12,703)	68,492 (151,024)	74,252 (163,727)

Source: Reference 11.

1. Separation processes,
2. Petroleum conversion processes,
3. Petroleum treating processes,
4. Feedstock and product handling, and
5. Auxiliary facilities.

Separation processes--

Constituents of crude oil include a large number of paraffinic, naphthenic, and aromatic hydrocarbon compounds, as well as numerous impurities which may include sulfur, nitrogen, and metals. The processes used to separate these constituents include: atmospheric distillation, vacuum distillation, and recovery of light ends (gas processing).

Conversion processes--

Conversion processes include cracking, coking, and visbreaking, which break large molecules into smaller molecules; isomerization and reforming processes to rearrange the structures of molecules; and polymerization and alkylation to combine small molecules into large ones.

Equipment commonly used during conversion includes process heaters and reformers. Process heaters are used to raise the temperature of petroleum feedstocks to a maximum of 510°C (950°F). Fuels burned include refinery gas, natural gas, residual fuel oils, or combinations. Reformers are reactors where the heat for the reaction is supplied by burning fuel.

Treatment processes--

Petroleum treatment processes include hydrodesulfurization, hydrotreating, chemical sweetening, acid gas removal, and deasphalting. These treatment methods are used to stabilize and upgrade petroleum products. Removal of undesirable elements, such as sulfur, nitrogen, and oxygen, is accomplished by hydrodesulfurization, hydrotreating, chemical sweetening, and acid gas removal. Deasphalting is carried out to separate asphaltic and resinous materials from petroleum products. Hydrotreating is a process in which the oil feed is treated by mixing with hydrogen in a fixed-bed catalyst reactor. Removal of acid gas involves controlling emissions of sulfur dioxide (SO2). Elemental sulfur is recovered as a byproduct.

Feedstock and product handling--
This includes storage, blending, loading, and unloading of petroleum crude and products. No cyanide emissions are expected during these steps.

Auxiliary facilities--
Auxiliary facilities include boilers, gas turbines, wastewater treatment facilities, hydrogen plants, cooling towers, and sulfur recovery units. Boilers and gas turbines cogeneration units within petroleum refineries may burn refinery gas.

Two petroleum refineries have reported facilitywide HCN emissions. It is not known which source operations result in HCN emissions because details pertaining to the mechanism of HCN formation are not available. It is assumed that processes in which petroleum fractions come into contact with air at high temperature will result in HCN emissions. Based on this assumption, process heaters and reformers are the potential sources of HCN emissions.

6.4.2 Emission Control Measures

No information is available pertaining to control of HCN emissions at petroleum refineries.

6.4.3 Emissions

Test data pertaining to HCN emissions from individual sources at petroleum refineries are not available. Three facilities, Ultramar, Inc., in Wilmington, CA, Koch Refining Co. in Rosemount, MN, and Murphy Oil, USA in Superior, WI, have reported facilitywide HCN emissions totalling 48,613 kg (107,192 lb) in the 1991 TRI. Because HCN emission factors are not available for petroleum refineries, it is not possible to estimate HCN emissions from other refineries.

6.5 MOBILE SOURCES

Historically, the major emissions measured and regulated under Title II of the Clean Air Act from mobile sources are CO, NOx , and hydrocarbons (HC). Emission factors for these specific pollutants among the different motor vehicle classes are compiled in AP-42, Volume II.[33] Gasoline-powered motor, on-road, light-duty vehicles comprise the most significant mobile emission sources because of their large numbers. According to the 1990 Statistical Abstract, 1988 nationwide registrations were estimated to be 183.5 million cars, trucks, and buses. Of that number, 140.7 million were passenger cars and 42.8 million were trucks and buses.[34] In 1990, the total vehicle miles traveled (VMT) in the United States were 3,457,478 million kilometers (2,147,501 million miles).[35]

Small amounts of HCN (levels around 1.0 mg/mile) have been measured in gasoline-fueled vehicle exhaust under normal operating conditions. In the Federal Test Procedure (FTP) driving schedule, these emission rates can increase to as high as 112 mg/km, or 179 mg/mile, under malfunction conditions (rich idle, misfire, high oil consumption, etc.). (All reported emissions include HCN and cyanogen emissions since attempts to isolate the two separately have been unsuccessful.)

Table 6-6 lists calculated fleet average emission factors. These values are obtained by multiplying each vehicle class VMT fraction by the corresponding emission factor for that class, giving a fraction quantity of pollutant emitted from that particular vehicle category. These are totaled and then averaged to obtain a total fleet average of 11.4 mg/mile for HCN. [36]

TABLE 6-6. FLEET AVERAGE EMISSION FACTORS FOR HYDROGEN CYANIDE

Vehicle class	Fraction, VMT	Emission factor, mg/mile	EF x VMT fraction
Light-duty diesel vehicles	0.015	3.2	0.048
Light-duty diesel trucks	0.002	3.2	0.006
Heavy-duty diesel trucks	0.027	22.4	0.605
Light-duty gasoline vehicles			
Noncatalyst; no air pump	0.147	4.5	0.662
Noncatalyst; air pump	0.098	4.5	0.441
Ox. catalyst; no air pump	0.289	2.4	0.694
Ox. catalyst; air pump	0.261	0.9	0.235
3-way catalyst; no air pump	0.012	16.0	0.192
3-way plus ox. catalyst; air pump	0.008	24.7	0.198
Light-duty gasoline trucks			
Noncatalyst	0.096	4.5	0.432
Catalyst	0.010	2.4	0.024
Heavy-duty gasoline trucks	0.035	224.0	7.840
Total fleet average			11.4 Mg/mile

Source: Reference 36.

SECTION 7
SOURCE TEST PROCEDURES

7.1 INTRODUCTION

A number of sampling methods exist to determine cyanide compound (cyanide) emissions from stationary sources. Several EPA offices and some State agencies, and some other Federal agencies have developed source-specific or dedicated sampling methods for cyanide. Other industry sampling methods do exist, but none of these methods have been validated and are not discussed in this section.

Subsequent parts of this section discuss EPA reference or equivalent sampling methods for cyanide. To be a reference method, a sampling method must undergo a validation process and be published. Sampling methods fall into one of two categories: (1) methods for stationary source emissions or (2) ambient air sampling methods. Methods from both categories will be described in this section; differences among the methods are pointed out, and a citation is provided for additional detailed information about the methods. Table 7-1 presents a summary of cyanide sampling methods. In addition to the methods summarized in the table, other analytical methods for several matrixes are described, and citations are provided. Depending upon the specific source, these methods may be used to augment the sampling methods in Table 7-1.

TABLE 7-1. CYANIDE SAMPLING METHODS

Method	Type	Capture device	Analysis	Method range
CARB 426	Stationary source	Glass fiber filter, sodium hydroxide impinger	Titration with silver nitrate	>1 mg CN- /L 0.02-1 mg CN- /L
NIOSH 7904	Ambient	Cellulose ester filter, potassium hydroxide impinger	Ion-specific electrode	0.05-2 mg CN- /L

7.2 STATIONARY SOURCE SAMPLING METHODS

7.2.1 CARB Method 426, "Determination of Cyanide Emissions from Stationary Sources"[37]

Method 426 is used to determine cyanides in aerosol and gas emissions from stationary sources. In this sampling and analysis method, particulate and gaseous emissions are extracted isokinetically from a stack and passed through an impinger-filter train where the cyanide is collected on a glass-fiber filter and in a solution of sodium hydroxide (NaOH). The combined filter extract and impinger solution are analyzed for cyanide by titration with silver nitrate or a colorimetric procedure (see EMSLC, 335.1 on p. 7-4). A diagram of the Method 426 sampling train is presented in Figure 7-1.

7.3 AMBIENT AIR SAMPLING METHODS

7.3.1 NIOSH Method 7904, "Determination of Cyanide Concentrations in Workplace Atmosphere"[38]

Method 7904 is used to determine cyanide in aerosols and gases in a workplace atmosphere. In this sampling and analysis method, airborne cyanides are collected on a cellulose ester membrane filter and in a potassium hydroxide (KOH) bubbler. Cyanide concentration is determined with an ion-specific electrode. A diagram of the Method 7904 sampling

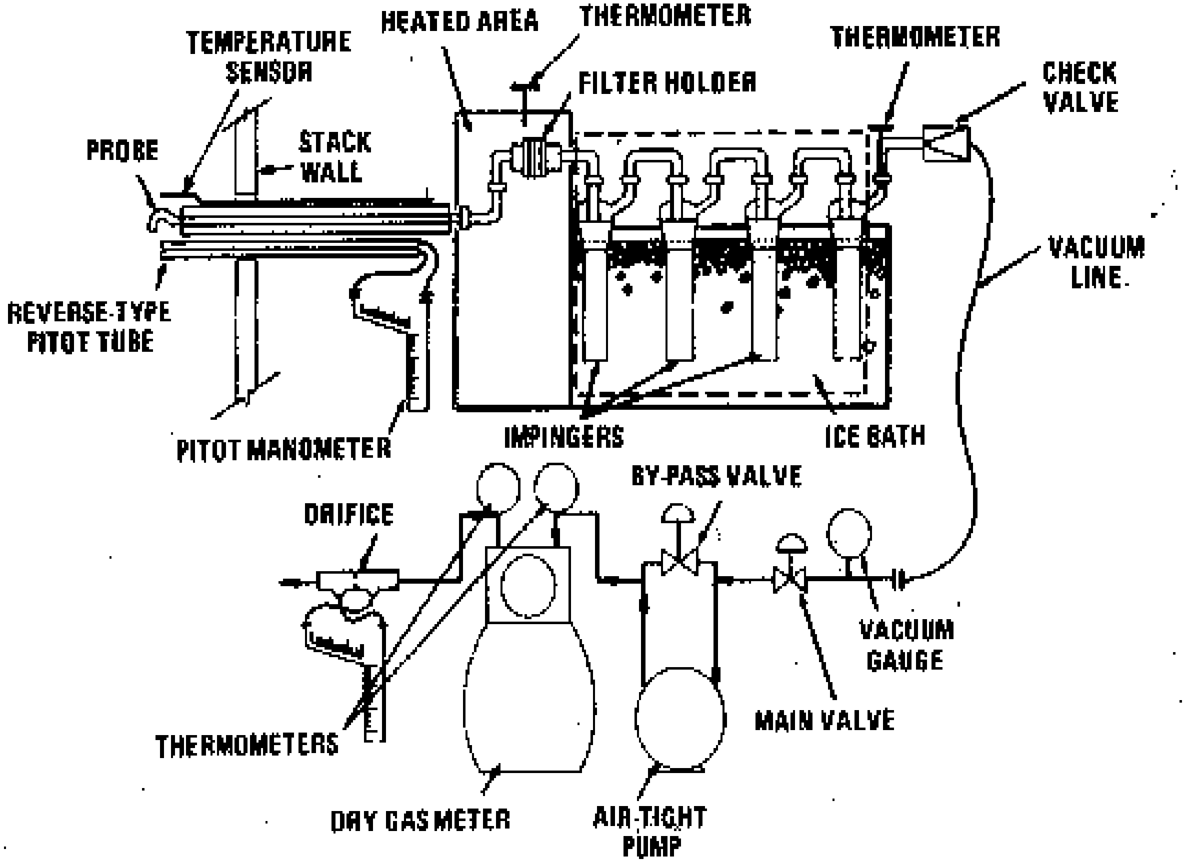


Figure 7-1. Schematic of CARB Method 426 sampling train.

train is presented in Figure 7-2.

7.4 ANALYTICAL METHODS

7.4.1 EMSLC, 335.1, "Cyanides, Amenable to Chlorination (Titrimetric and Spectrophotometric)"

A portion of the sample is chlorinated at a pH greater than 11 to decompose the cyanide. Cyanide levels in chlorinated and unchlorinated aliquots are determined by the method for Cyanide, Total (Method 335.2). Cyanides amenable to chlorination are then calculated by difference.

The titration procedure is used for measuring concentrations of cyanide exceeding 1 milligram per liter (mg/L) after removal of cyanides amenable to chlorination. Below this level, the colorimetric determination is used.

7.4.2 EMSLC, 335.2, "Cyanide, Total (Titrimetric and Spectrophotometric)"

The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of reflux-distillation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbed solution is then determined by volumetric titration or colorimetrically.

In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine- pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nanometers (nm) when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain

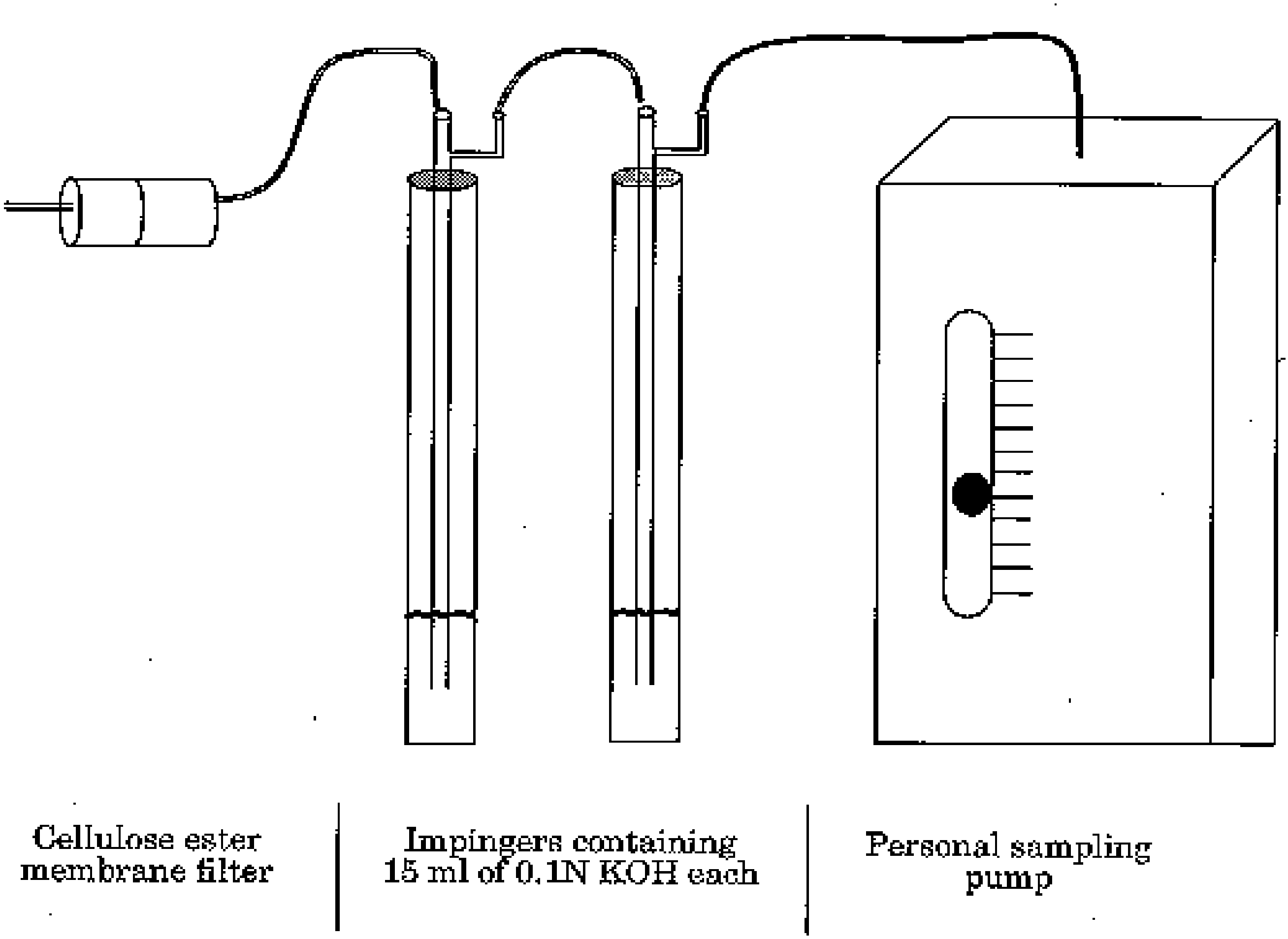


Figure 7-2. Schematic of NIOSH Method 7904 sampling train.

colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

7.4.3 EMSLC, 335.3, "Cyanide, Total (Colorimetric, Automated UV)"

Cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of ultraviolet (UV) digestion and distillation. Cyanides are converted to cyanogen chloride by reactions with chloramine-T, which subsequently reacts with pyridine and barbituric acid to give a red-colored complex. The cyanide is then determined by automated UV colorimetry.

7.4.4 OSW, 9010A, "Method 9010A, Total and Amenable Cyanide"

The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide in the absorbing solution is then determined colorimetrically or titrametrically.

In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

7.4.5 OSW, 9012A, "Method 9012A, Total and Amenable Cyanide (Colorimetric, Automated UV)"

The OSW Method 9012A is identical to the OSW Method 9010A except that an automated ultraviolet spectrophotometer is used for analysis.

7.5 COMBINED SAMPLING/ANALYTICAL METHODS

7.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR is a spectrophotometer that scans and records the infrared (IR) range of absorbance from an IR beam transmitted through a sample. The sample's absorbance record is converted to absorbance plots via fast fourier transform calculations. The resulting plots are then compared to a spectra library of known compounds for identification. The FTIR can be operated as a closed-cell for extractive stationary-source testing or as an open-cell for ambient testing.

No approved method of sampling and analysis for cyanide using FTIR exists. Many problems must be resolved before extractive, stationary-source FTIR testing for cyanide can be performed. The use of FTIR in this application is currently under development by EPA.

7.5.2 ASTM, D4490, "Standard Practice for Measuring the Concentration of Toxic Gasesor Vapors Using Detector Tubes"

Detector tubes may be used for either short-term sampling (grab sampling; 1 to 10 minute) or long-term sampling (dosimeter sampling 1 to 8 hours) of atmospheres containing toxic gases or vapors. A given volume of air is pulled through the tube by a mechanical pump (grab sampling) or is pulled through the detector tube at a slow, constant flow rate by an electrical pump (dosimeter sampling).

If the substance for which the detector tube was designed is present, the indicator chemical in the tube will change color. The concentration of the gas or vapor may be estimated by either (a) the length-of-stain compared to a calibration chart, or (b) the intensity of the color change compared to a set of standards.

7.6 SUMMARY

All of the sampling methods described in this section collect a sample for analysis of cyanide. Significant criteria of each method were presented previously in Table 7-1. The major differences in the methods include: (1) type of impinger solution, (2) volume of sample required, and (3) isokinetic or nonisokinetic sampling.

Two EPA sampling methods are commonly modified and used to perform cyanide sampling. Method 5 is the EPA reference method to determine particulate emissions from stationary sources, and Method 6 is the EPA reference method to determine sulfur dioxide emissions from stationary sources.[39,40] The driving considerations in choosing which of these two sampling methods to use for cyanide sampling are the temperature and moisture content of the emission source. Those sources with moisture-laden (saturated) gas streams must be sampled using isokinetic methods, such as a modified version of EPA Method 5, in order to collect cyanides emitted as aerosols. Drier gas steams in which cyanide exists as a gas can be sampled using a modified version of EPA Method 6. Both Methods 5 and 6 are modified by charging the impingers with solutions of 0.1N potassium hydroxide (KOH) or sodium hydroxide (NaOH) as called for in the analytical method used.

In assessing cyanide emissions from test reports, the age or revision number of the method indicates the level of precision and accuracy of a method. Older methods are sometimes less precise or accurate than those that have undergone more extensive validation. Currently, EPA Method 301 from 40 CFR Part 63, Appendix A can be used to validate or prove the equivalency of new methods.

SECTION 8
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39. EPA Method 5, Determination of Particulate Emissions from Stationary Sources. 40 Code of Federal Regulations, Part 61, Appendix A. Washington, DC. U.S. Government Printing Office. 1992.

40. EPA Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources. 40 Code of Federal Regulations, Part 61, Appendix A. Washington, DC. U.S. Government Printing Office. 1992.

APPENDIX A

NATIONWIDE EMISSION ESTIMATES

EMISSIONS OF HYDROGEN CYANIDE FROM HCN AND NaCN PRODUCTION

Hydrogen Cyanide Production

Basis of estimate: Toxic Release Inventory (TRI) data and EPA data.

A list of domestic HCN producing facilities is given in Section 4, Table 4-1. Fifteen facilities currently produce HCN.

Emission factors for HCN emissions from individual sources are not available. The only emission data available are the HCN emission data reported by 12 facilities in the 1991 TRI and HCN emissions estimated by U.S. Environmental Protection Agency, Industrial Studies Branch (ISB).[1,2] Because the 1991 TRI data for the 12 facilities constitute the most recent data, the EPA estimates were not used for these 12 facilities. However, for two facilities, American Cyanide and BP Chemicals (Green Lake, TX facility), HCN emission estimates reported by EPA were used. The HCN emission data for these fourteen facilities are summarized in Table A-1.

Emission estimates for HCN emissions at Cyanco Co. are not available either in the 1991 TRI or in Reference 2. Therefore, HCN emissions at this facility were extrapolated based on facilitywide HCN emissions reported in Table A-1 and production capacity data given in Section 4, Table 4-1. Based on HCN production capacity data given in Table 4-1 and HCN emission estimates given in Table A-1, the ratio of HCN emissions to individual HCN production capacity (for the fourteen facilities in Table A-1) ranges between 6.6×10^{-4} and 1.5 lb/ton of HCN produced. Based on a conservative assumption that the HCN emission to production ratio at Cyanco is 1.5 lb/ton of HCN produced, HCN emissions at Cyanco for the year 1991 are estimated to be 12,000 kg (26,400 lb).

Thus the nationwide HCN emissions resulting from HCN production is estimated to be 166,050 kg (365,969 lb). This is the sum total of HCN emissions estimated for Cyanco and the HCN emission reported for the other fourteen facilities in Table A-1.

TABLE A-1. HYDROGEN CYANIDE PRODUCERS REPORTING HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY

	Emissions, kg (lb)		
Facility	Nonpoint	Point	Total
BP Chemicals Lima, OH	998 (2,200)	4,308 (9,500)	5,306 (11,700)
Ciba-Geigy St. Gabriel, LA	29 (63)	93 (204)	122 (267)
Degussa Corp. Theodore, AL	345 (760)	771 (1,700)	1,116 (2,460)
Dow Chemical Freeport, TX	2 (4)	0 (0)	2 (4)
DuPont Beaumont, TX	1,360 (3,000)	1,496 (3,300)	2,856 (6,300)
DuPont Memphis, TN	459 (1,012)	13,224 (29,159)	13,683 (30,171)
DuPont Orange, TX	1,002 (2,210)	30,970 (68,288)	31,972 (70,498)
DuPont Victoria, TX	1,038 (2,290)	2,531 (5,580)	3,569 (7,870)
FMC Corp. Green River, WY	0 (0)	36 (79)	36 (79)
Monsanto Alvin, TX	680 (1,500)	635 (1,400)	1,315 (2,900)
Rohm & Haas Deer Park, TX	254 (560)	49,887 (110,000)	50,141 (110,560)
Sterling Chemicals Texas City, TX	3,936 (8,680)	17,451 (38,480)	21,387 (47,160)
American Cyanamid[a] Avondale, LA	727 (1,600)	909 (2,000)	1,636 (3,600)
BP Chemicals[a] Green Lake, TX	5,909 (13,000)	15,000 (33,000)	20,909 (46,000)
TOTAL	16,739 (36,879)	137,311 (302,690)	154,050 (339,569)

Source: References 1 and 2.

[a] The emission estimates in Reference 2 were used for American Cyanamid and BP Chemicals (Green Lake, TX). For all other facilities, emissions reported in Reference 1 were used.

Sodium Cyanide Production

Basis of estimate: Toxic Release Inventory (TRI) data.

A list of domestic NaCN producing facilities is given in Section 4, Table 4-3. Seven facilities currently produce NaCN.

Six of these seven facilities that produce NaCN also produce HCN. Facilitywide emissions of HCN estimated for these facilities are reported in Table A-1. Therefore HCN emissions from these six facilities are not duplicated for this production process. No emission data were available for the Du Pont, TX facility, which was the only facility that produces NaCN but did not report cyanide emissions in the TRI or the EPA report.

EMISSIONS OF HCN AND CYANIDE COMPOUNDS FROM MAJOR USES OF HYDROGEN CYANIDE

Adiponitrile Production

Basis: TRI data

A list of domestic adiponitrile producing facilities is given in Section 5, Table 5-1. Three facilities currently produce adiponitrile.

Emission factors for HCN and cyanide compound emissions from individual sources are not available. The only emission data available are the HCN and cyanide compounds emission data reported by individual facilities in the 1991 TRI. Two facilities have reported HCN and/or cyanide compound emissions in the 1991 TRI. These data are presented in Section 5, Table 5-2, and are once again summarized in Table A-2. Emissions of HCN reported in Table A-2 are already included in Table A-1, therefore, they should not be included in the estimation of nationwide emission estimates. However, emissions of cyanide compounds given in Table A-2 should be included. A total of 13.4 kg (29 lb) of cyanide compound emissions have been reported in the 1991 TRI.

Acetone Cyanohydrin Production

Basis: TRI data

Four facilities produce acetone cyanohydrin. Facility data are presented in Section 5, Table 5-3.

Emission factors for HCN and cyanide compound emissions from individual sources are not available. The only emission data available are the HCN and cyanide compounds emission data reported by individual facilities in the 1991 TRI. Three facilities have reported HCN and/or cyanide compound emissions in the 1991 TRI. These data are presented in Section 5, Table 5-4, and are once again summarized in Table A-3. Emissions of HCN reported in Table A-3 are already included in Table A-1; therefore, they should not be included in the estimation of nationwide emission estimates. However, emissions of cyanide compounds given in Table A-3 should be included. A total of 3,035 kg (6,693 lb) of cyanide compound emissions have been reported in the 1991 TRI. One facility, CYRO Industries, New Orleans, LA, has not reported cyanide compound emissions in the 1991 TRI. The limited data given in Table A-4 for cyanide compounds are not sufficient to extrapolate for the estimation of cyanide compound emissions from the other facility.

TABLE A-2. ADIPONITRILE PRODUCERS REPORTING CYANIDE COMPOUND OR HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY[a]

	Cyanide compound emissions, kg (lb)			Hydrogen cyanide emissions, kg (lb)		
Facility	Nonpoint	Point	Total	Nonpoint	Point	Total
Dupont Orange, TX	12 (26)	1.4 (3)	13.4 (29)	1,002 (2,210)	30,970 (68,288)	31,972 (70,498)
Dupont Victoria, TX	0 (0)	0 (0)	0 (0)	1,038 (2,290)	2,531 (5,580)	3,569 (7,870)
Total	12 (26)	1.4 (3)	13.4 (29)	2,040 (4,500)	33,501 (73,868)	35,541 (78,368)

[a] These facilities produce multiple derivatives of HCN. Therefore, it is not clear as to what the specific sources are that emit cyanide compounds and/or HCN.

Source: Reference 1.

TABLE A-3. ACETONE CYANOHYDRIN PRODUCERS REPORTING CYANIDE COMPOUNDS OR HYDROGEN CYANIDE EMISSIONS IN THE 1991 TOXICS RELEASE INVENTORY[a]

	Cyanide compound emissions, kg (lb)			Hydrogen cyanide emissions, kg (lb)		
Facility	Nonpoint	Point	Total	Nonpoint	Point	Total
Dupont Memphis, TN	205 (451)	1,180 (2,602	1,285 (3,053)	459 (1,012)	13,224 (29,159)	13,683 (30,171)
Rohm & Haas Deer Park, TX	1,224 (2,700)	426 (940)	1,650 (3,640)	254 (560)	49,887 (110,000)	50,141 (110,560)
BP Chemicals, Inc. Green Lake, TX	0 (0)	0 (0)	0 (0)	3,810 (8,400)	11,791 (26,000)	15,601 (34,400)
Total	1,429 (3,151)	1,606 (3,542)	3,035 (6,693)	713 (1,572)	63,111 (139,159)	63,824 (140,731)

[a] These facilities produce multiple derivatives of HCN. Therefore, it is not clear as to what the specific sources are that emit cyanide compounds and/or HCN.

Source: Reference 1.

Cyanuric Chloride Production

Basis: TRI data

Only two facilities, Degussa Corp in Theodore, AL, and Ciba-Geigy in St. Gabriel, LA, produce cyanuric chloride. Both facilities have reported facilitywide HCN emissions in the 1991 RTI. However, it is not clear as to how the facilitywide HCN emissions are distributed, i.e., how much of them occur due to HCN production as opposed to other derivatives of HCN. Therefore, only the HCN emissions reported in Table A-1 should be used to estimate nationwide emissions.

Production of Chelating Agents

Basis: TRI data

Twenty-two facilities produce chelating agents. Facility information is given in Section 5, Table 5-5.

Emission factors for HCN and cyanide compound emissions from individual sources are not available. The only emission data available are the HCN and cyanide compound emission data reported by individual facilities in the 1991 TRI. Seven facilities have reported HCN and/or cyanide compound emissions in the 1991 TRI. These data are presented in Section 5, Table 5-6. Emissions of HCN reported by three facilities in Table 5-6, Dow Chemical, Sterling Chemicals, and Monsanto, are already included in Table A-1; therefore, they should not be included in the estimation of nationwide emission estimates. However, HCN emissions reported by Ciba-Geigy, McIntosh, AL, and W. R. Grace, Nashua, NH, need to be included in the estimation of nationwide HCN emission rates. These two facilities have jointly reported HCN emissions totalling 1,254 kg (2,767 lb).

Emissions of cyanide compounds given in Table 5-6 should also be included. A total of 2.3 kg (5 lb) of cyanide compound emissions was reported in the 1991 TRI by five facilities. The remaining 17 facilities did not report any emissions in the TRI.

Electroplating

Basis: TRI data

A total of 123 facilities have reported emissions of cyanide compounds in the 1991 TRI. Cyanide compound emission estimates for these facilities totaled 10,117 kg (22,309 lb). It is assumed that these also represent nationwide emissions resulting from electroplating.

EMISSIONS FROM MISCELLANEOUS SOURCES

Iron and Steel Production

Basis: TRI data

A list of domestic iron and steel producing facilities (integrated) is given in Section 6, Table 6-1. Twenty-nine facilities currently produce iron and steel.

Emission factors for cyanide emissions from individual sources are not available. The only emission data available are the cyanide compound emission data reported by individual facilities in the 1991 TRI. Twenty-one facilities have reported cyanide compound emissions in the TRI. These data are presented in Section 6, Table 6-3. Cyanide compound emission estimates for the 21 facilities totaled 180,098 kg (397,120 lb).

Carbon Black Production

Basis: TRI data

A list of domestic carbon black producing facilities is given in Section 6, Table 6-4. Twenty-four facilities currently produce carbon black.

Emission factors for cyanide compound emissions from individual sources are not available. The only emission data available are the cyanide compound emission data reported by individual facilities in the 1991 TRI. Six facilities have reported cyanide compound emissions to the TRI. These data are presented in Section 6, Table 6-5. There are no cyanide compound emission factors available to estimate the emission rates from the remaining 18 facilities.

Carbon Fiber Production

Basis: TRI data

A list of domestic carbon fiber producing facilities is given in Section 6, Table 6-6. Eight facilities currently produce carbon fiber.

Emission factors for cyanide compound emissions from individual sources are not available. The only emission data available are the cyanide compound emission data reported by individual facilities in the 1991 TRI. Five facilities have reported cyanide compound emissions to the TRI. These data are presented in Section 6, Table 6-7. There are no cyanide compound emission factors available to estimate the emission rates from the remaining three facilities.

Petroleum Refining

Basis: TRI data

Only three facilities have reported emissions of HCN totalling 48,613 kg (107,192 lb) in the 1991 TRI. Because HCN emission factors are not available for petroleum refineries, it is not possible to estimate HCN emissions at other refineries.

Mobile Sources (Nonpoint source category)

Basis: Cyanide emission factor of 11.4 mg/mile (Section 6, Page 6-21)
Total vehicular miles travelled in 1990 - 2,147,501 million miles (Section 6, Page 6-21).

Nationwide cyanide emissions resulting from automobiles are estimated to be:

$$(11.4 \text{ mg/mile}) \times (2,147,501 \times 10^6 \text{ miles/yr})$$
$$= 24,481,512 \text{ kg } (53,972,430 \text{ lb})$$

REFERENCES FOR APPENDIX A

1. U. S. Environmental Protection Agency. 1991 Toxics Release Inventory. Office of Toxic Substances. Washington, DC. June, 1993.

2. U. S. Environmental Protection Agency. Preliminary Source Assessment for Cyanide Chemical Manufacturing. Draft Report. Office of Air and Radiation. Office of Air Quality Planning and Standards. Industrial Studies Branch. Research Triangle Park, NC. September 1992.

APPENDIX B

ELECTRIC ARC FURNACES IN IRON AND STEEL PRODUCTION CRUDE OIL DISTILLATION CAPACITY

TABLE B-1. COMPANIES USING ELECTRIC ARC FURNACES IN IRON AND STEEL PRODUCTION[a]

Company/location	No. of furnaces	Shell diameter, ft
Allegheny Ludlum Corp.		
Brakenridge Works, Brackenridge, PA	2	18
	2	17
Special Materials Div., Lockport, NY	3	12
AL Tech Specialty Steel		
Waterviet Plant, Waterveit, NY	2	13.6
Arkansas Steel Associates		
Newport AR	1	12
	1	12.5
Armco, Inc.		
Baltimore Specialty Steel Corp., Baltimore, MD	1	15
Butler Works, Butler, PA	3 total (No. 2, 3, and 4)	22 ea
	No. 5 (1)	
Kansas City Works, Kansas City, MO	No. 6 (1)	22
	1 (melting)	22
Northern Automatic Electric Foundry, (NAEF),	1 (holding)	9
Ishpeming, MI	9	
Atlantic Steel		
Cartersville Works, Cartersville, GA	1	22
Auburn Steel		
Auburn, NY	1	16
Bayou Steel		
LaPlace, LA	2	18
Bethlehem Steel		
Bethlehem Plant, Bethlehem, PA	1	15
Johnstown Plant, Johnstown, PA	1	18
Steelton Plant, Steelton, PA	1	18
	3	22
	2	24
Birmingham Steel		
Illinois Steel Div., Birmingham, AL	1	18
Mississippi Steel Div., Jackson, MS	1	14
Salmon Bay Street, Kent, WA[b]	2	12.5
Southern United Steel Div., Birmingham, AL	1	15
Border Steel Mills		
El Paso, TX	1	12
	1	12
Braeburn Alloy Steel		
Div., of CCX, Inc., Lower Burrell, PA	2	11
Calumet Steel		
Chicago Heights, IL	2	12.5
Carpenter Technology		
Reading Plant, Reading, PA	A	11
	B	11
	C	11
	D	11
	E	11
	F	13.5
Cascade Steel Pulling Mills		
McMinville, OR	2	12
	1	19 (egg shaped)
CF&I Steel		
Pueblo, CO	1	22
	1	22
Champion Steel		
Orwell, OH	1	8.5
Chaparral Steel		
Midlothian, TX	1	19
	1	22
Charter Electric Melting		
Chicago, IL	1	13.5

TABLE B-1. (Continued)

Company/Location	No. of furnaces	Shell diameter, ft
Citisteel USA, Inc.		
Claymont, DE	1	22
CMC Steel Group		
SMI Steel, Inc., Birmingham, AL	2	14
SMI-Texas, Seguin, TX	1	18
Columbia Tool Steel		
Chicago Heights, IL	1	11
Copperweld Steel		
Warren, OH	No. 5	18
	No. 6	18
	No. 8	18
	No. 9	18
Crucible Materials Corp.		
Crucibile Specialty Metals Div., Syracuse, NY	1	15
	1	11.5
Cyclops Corp.		
Bridgeville Works, Bridgeville, PA	D	12
	C	12
	G	15
Empire-Detroit Steel Div., Mansfield, OH	No. 8	20
	No. 9	22
Eastern Stainless Steel		
Baltimore Works, Baltimore, MD	1	16
	1	17
Edgerwater Steel, Oakmont, PA	1	15
Electralloy Corp.		
Oil City, PA	1	12.5
Ellwood Uddeholm Steel		
New Castle, PA	1	13.5
A. Finkl & Sons		
Chicago, IL	1	Oval/15x17
	1	15
Florida		
Charlotte Mill, Charlotte, NC	1	17
Jacksonville Mill, Baldwin, FL	1	18
Knoxville Div., Knoxville, TN	1	12
	1	12.5
Tampa Mill, Tampa, FL	1	17
Tennessee Mill, Jackson, TN	1	20
Georgetown Steel		
Georgetown, SC	2EF	18.5
	2LF	--
Hawaiian Western Steel		
Ewa, HI	1	11
Haynes International		
Kokomo Works, Kokomo, IN	1	9
	1	11
Inco Alloys International, Inc.		
Huntington Works, Huntington, WV	2	14
Inland Steel Bar Company		
Indiana Harbor Works, East Chicago, IN	2	22
IRI International		
Specialty Steel Div., Pampa, TX	1	11
Jessop Steel		
Athlone Industries, Inc., Washington, PA	1	11
	1	12
	1	11

TABLE B-1. (Continued)

Company/Location	No. of furnaces	Shell diameter, ft
J&L Specialty Steel Products		
Midland Plant, Midland, PA	4	--
	2	24
Jorgensen Forge		
Seattle, WA	2	24
Keystone Consolidated Industries		
Keystone Steel and Wire Div., Peoria, IL	1	22
	1	22
Laciede Steel		
Alton, IL	2	24
Latrobe Steel		
Latrobe, PA	A	12
	B	13.5
Lone Star Steel		
Texas Specialty Flatroll, Inc., Lone Star, TX	2	16
LTV Steel		
Cleveland Works, Cleveland, OH	2	22
Lukens Steel		
Coatsville, PA	1	22
	1	22
MacSteel		
Jackson, MI	2	14
Ft. Smith, AR	2	15
Marathon LeTourneau		
Longview Div., Longview, TX	D	13
	E	13
Marion Steel		
Marion, OH	A	13.5
	B	13.5
McLouth Steel Products		
Trenton Works, Trenton, MI	2	24.5
National Forge		
Irvine Forge Div., Irvine, PA	1	15
New Jersey Steel		
Sayreville, NJ	1	19
North Star Steel		
Milton Plant, Milton, PA[c]	3	12
Monroe Plant, Monroe, MI	1	19
St. Paul, Div., St. Paul, MN	2	16
Texas Div., Beaumont, TX	2	22
Wilton Plant, Wilton, IA	1	16.5
Youngstown Div., Youngstown, OH	2	18
Northwestern Steel and Wire		
Sterling Works, Sterling, IL	1	38
	1	32
	1	38
NS Group, Inc.		
Kentucky Electric Steel Corp., Ashland, KY	2	15
Koppel Steel Corp., Koppel, PA	1	20
	1	20
	1	20
	1	18
	1	16
	1	19
Newport Steel Corp., Wilder, KY	1	19
	1	19
	1	19

TABLE B-1. (Continued)

Company/Location	No. of furnaces	Shell diameter, ft
Nucor Corp.		
Crawfordsville, IN	2	22
Darlington Mill, Darlington, SC	1	12.5
	1	12.5
	1	12.5
	1	14
	1	14
Jewell Mill, Jewell, TX	1	13.5
	1	13.5
	1	13.5
	1	13.5
	1	13.5
Norfolk Mill, Norfolk, NE	1	13.5
	1	13.5
	1	13.5
	1	13.5
	1	12.5
Plymouth Mill, Plymouth, UT	1	15
	2	15
Nucor-Yamato Steel Company		
Nucor-Yamato Works, Blytheville, AR	2	24
Ocean State Steel, Inc.		114
E. Providence, RI	2	(1,366")
Oregon Steel Mills, Inc.		
Oregon Steel Mills, Portland, OR	1	18
Owen Electric Steel Company of South Carolina, Columbia, SC	1	10
	1	11
	1	12
Raritan River Steel		
Perth Amboy, NJ	1	20
Republic Engineered Stees, Inc.,		
No. 4 Melt Shop, Carlton, OH	3	26
No. 3 Melt Shop, Carlton, OH	2	20
Roanoke Electric Steel		
Roanoke, VA	1	14
	1	18
Rouge Steel		
Rouge Works, Dearborn, MI	2	24
Seattle Steel Inc.[b]		
Seattle, WA	2	20
Sharon Steel		
Steel Div., Farrell, PA	2	20 ea
Sheffield Steel		
Sand Springs, OK	2 ea	18 ea
Slater Steels		
Ft. Wayne Specialty Alloy Div.,	1	11
Ft. Wayne, IN	1	12
Standard Steel		
Burnham Plant, Burnham, PA	1	14
	1	15
	1	17
Latrobe, PA	1	13
Steel of West Virginia		
Huntington, WV	3	15 ea
Tamco		
Etiwanda, CA	1	20

TABLE B-1. (Continued)

Company/Location	No. of furnaces	Shell diameter, ft
Teledyne Vasco		
Latrobe Plant, Latrobe, PA	1	10
Thomas Steel		
Lemont Works, Lemont, IL	2	13'5"
	1	12'5"
Timken Company Steel Business		
Harrison Plant, Canton, OH	1	22
	1	20
	1	22
	1	22
Faircrest Mill, Canton, OH	1	24
Union Electric Steel		
Hamon Creek Plant, Burgettstown, PA	1	14
USS Div. of USX Corp.		
South Works, Chicago, IL	2	24
	1[d]	20
Washington Steel		
Fitch Works, Houston, PA	2	14,16
	1	14
	1	16

[a] Source: Huskonen, W. W. Adding the Final Touches. 33 Metal Producing. 29:28-131. May 1991.

[b] Birmingham Steel is proceeding with a plan to close the Salmon Bay Steel melt shop and will merge the operation with the Seattle Steel, Inc., facilities it is acquiring.

[c] Presently idle.

[d] On standby.

TABLE B-2. REFINER'S OPERABLE ATMOSPHERIC CRUDE OIL DISTILLATION CAPACITY AS OF JANUARY 1, 1992

Refiner	Barrels per Calendar Day
Companies with Capacity Over 100,000 bbl/cd	
Chevron U.S.A. Inc.	1,503,700
Port Authur, Texas	315,900
Pascagoula, Mississippi	295,000
El Segundo, California	254,000
Richmond, California	220,000
Philadelphia, Pennsylvania	175,000
Perth Amboy, New Jersey	80,000
El Paso, Texas	66,000
Honolulu, Hawaii	52,800
Salt Lake City, Utah	45,000
Exxon Co. U.S.A.	1,157,000
Baton Rouge, Louisiana	421,000
Baytown, Texas	396,000
Linden (Bayway), New Jersey	170,000
Benicia, California	128,000
Billings, Montana	42,000
Amoco Oil Co.	982,000
Texas City, Texas	433,000
Whiting, Indiana	370,000
Mandan, North Dakota	58,000
Yorktown, Virginia	53,000
Salt Lake City, Utah	40,000
Savannah, Georgia	28,000
Shell Oil Co.	966,900
Wood River, Illinois	274,000
Deer Park, Texas	215,900
Norco, Louisiana	215,000
Martinez, California	144,100
Anacortes, Washington	89,300
Odessa, Texas	28,600
Mobil Oil Corp.	838,000
Beaumont, Texas	275,000
Joliet, Illinois	180,000
Chalmette, Louisiana	160,000
Torrence, California	123,000
Paulsboro, New Jersey	100,000
BP America Inc.	741,400
BP Oil Corp.	
Belle Chasse (Alliance), Louisiana	218,000
Marcus Hook, Pennsylvania	168,000
Lima, Ohio	145,000
Toledo, Ohio	126,100
Ferndale, Washington	84,300
USX Corp.[a]	620,000
Marathon Oil Co.	
Garyville, Louisiana	255,000
Robinson, Illinois	175,000
Detroit, Michigan	70,000
Texas City, Texas	70,000
Indianapolis, Indiana[b]	50,000
Star Enterprise	615,000
Port Arthur/Neches, Texas	250,000
Convent, Louisiana	225,000
Delaware City, Delaware	140,000
Sun Co. Inc.	515,000
Marcus Hook, Pennsylvania	175,000
Toledo, Ohio	125,000
Tulsa, Oklahoma	85,000
Sun Refining & Marketing	
Philadelphia, Pennsylvania	130,000
Petroleos De Venezuela	479,000
Citgo Petroleum Corp.	
Lake Charles, Louisiana	305,000
Champion Refining & Chemical Inc.	
Corpus Christi, Texas	130,000
Seaview Oil Co.[c]	
Paulsboro, New Jersey	44,400
Atlantic Richfield Co.	424,500
Arco Products Co.	
Los Angeles, California	223,000
Ferndale (Cherry Point), Washington	174,500
Arco Alaska Inc.	
Prudhoe Bay, Alaska	15,000
Anchorage, Alaska	12,000
E.I. DuPont De Nemours & Co.	412,000
Conoco Inc.	
Westlake, Louisiana	165,000
Ponca City, Oklahoma	140,000
Billings, Montana	49,500
Commerce City, Colorado	48,000
Santa Maria, California	9,500
Ashland Oil Inc.	346,500
Catlettsburg, Kentucky	213,400
St. Paul, Minnesota	67,100
Canton, Ohio	66,000
Unocal Corp.	341,100
Wilmington (Los Angeles), California	228,000
Rodeo (San Francisco), California	73,100
Arroyo Grande (Santa Maria), California	40,000
Koch Industries Inc.	325,000
St. Paul (Pine Bend), Minnesota	200,000
Corpus Christi, Texas	125,000
Texaco Refining & Marketing Inc.	324,000
Anacortes (Puget Sound), Washington	132,000
El Dorado, Kansas	80,000
Wilmington (Los Angeles), California	64,000
Bakersfield, California	48,000
Phillips Petroleum Co.	305,000
Phillips 66 Co.	
Sweeny, Texas	175,000
Borger, Texas	105,000
Woods Cross, Utah	25,000
Trans-America Natural Gas Corp.	
Trans-American Refining Co.	
Norco (Good Hope), Louisiana	300,000
Solomon Inc.	290,500
Phibro Refining Inc.[d]	
Texas City, Texas	119,600
Houston, Texas	70,900
Krotz Springs, Louisiana	60,000
Saint Rose, Louisiana	40,000

TABLE B-2. (Continued)

Refiner	Barrels per Calendar Day
Coastal Corp., The	275,300
Coastal Refining & Marketing Inc.	
Corpus Christi, Texas	85,000
El Dorado, Kansase	30,400
Wichita, Kansase	28,800
Coastal Eagle Point Oil Co.	
Westville, New Jersey	104,500
Coastal Mobile Refining Co.	
Chickasaw, Alabama	26,600
Lyondell Petrochemical Co.	
Houston, Texas	265,000
Fina Oil & Chemical Co.	199,000
Port Arthur, Texas	144,000
Big Spring, Texas	55,000
Total Petroleum Inc.	197,600
Ardmore, Oklahoma	68,000
Arkansas City, Kansas	56,000
Alma, Michigan	45,600
Colorado Refining Co.	
Commerce City, Colorado	28,000
Mapco Petroleum Inc.	192,500
North Pole, Alaska	116,500
Memphis, Tennessee	76,000
Diamond Shamrock Refining & Marketing Co.	165,000
Sunray (McKee), Texas	112,000
Three Rivers, Texas	53,000
Kerr-McGee Corp.	156,800
Southwestern Refining Co. Inc.	
Corpus Christi, Texas	104,000
Kerr-McGee Refining Corp.	
Wynnewood, Oklahoma	45,000
Cotton Valley, Louisiana	7,800
Crown Central Petroleum Corp.	155,000
Pasadena, Texas	100,000
La Glona Oil & Gas Co Tyler, Texas	55,000
Uno-Ven Co.	
Lemont (Chicago), Illinois	147,000
Tosco Corp.	
Tosco Refining Co.	
Martinez (Avon), California	131,900
Sinclair Oil Corp.	128,500
Sinclair, Wyoming	54,000
Tulsa, Oklahoma	50,000
Little America Refining Co.	
Evansville (Casper), Wyoming	24,500
Murphy Oil U.S.A. Inc.	128,200
Meraux, Louisiana	95,000
Superior, Wisconsin	33,200
Horsham Corp	121,600
Clark Oil & Refining Corp	
Blue Island, Illinois	64,600
Hartford, Illinois	57,000
Total	**13,750,400**

**Companies with Capacity
30,001 to 100,000 bbl/cd**

Refiner	Barrels per Calendar Day
Pacific Resources Inc.	
Hawaiian Independent Refinery Inc.	
Ewa Beach, Hawaii	93,500
Farmland Industries Inc.	82,900
Coffeyville, Kansas	56,600
Phillipsburg, Kansas	26,400
LL&E Petroleum Marking	
Saraland (Mobile), Alabama	80,000
National Cooperative Refinery Association	
McPherson, Kansas	75,600
Tesoro Petroleum Corp.	
Kenai, Alaska	72,000
Pennzoil Co. Inc.	69,900
Pennzoil Producting Co.	
Shreveport, Louisiana	46,200
Rouseville, Pennsylvania	15,700
Roosevelt, Utah	8,000
American Ultramar Ltd	
Ultramar Refining	
Wilmington, California	68,000
Holly Corp.	63,700
Navajo Refining Co.	
Artesia, New Mexico	57,000
Montana Refining Co.	
Great Falls, Montana	6,700
United Refining Co.	
Warren, Pennsylvania	60,000
Castle Energy Corp.	
Indiana Refining	
Lawrenceville, Illinois	55,000
The Coastal Corp/Sinochem	
Pacific Refining Co.	
Hercules, California	55,000
El Paso Refinery, L.P.	
El Paso, Texas	50,000
Placid Refining Co.	
Port Allen, Louisiana	48,500
Lion Oil Co.	
El Dorado, Arkansas	48,000

TABLE B-2. (Continued)

Refiner	Barrels per Calendar Day
Thrifty Oil Co.	
Golden West Refining Co.	
Santa Fe Springs, California	47,000
Paramount Acquisiton Corp.	
Paramount Petroleum Corp.	
Paramount, California	46,500
Powenne Oil Co.	
Santa Fe Springs, California	45,000
Cirillo Brothers Oil Co.	
Cibro Petroleum Products Inc.	
Albany, New York	41,850
Cenex	
Laurel, Montana	41,450
Frontier Refining Co.	
Cheyenne, Wyoming	38,670
Hunt Consolidated Inc.	
Hunt Refining Co.	
Tuscaloosa, Alabama	33,500
Time Oil Co.	
U.S. Oil & Refining Co.	
Tacoma, Washington	32,400
Total	**1,291,220**

Companies with Capacity
10,001 to 30,000 bbd/cd

Refiner	Barrels per Calendar Day
Amerada Hess Corp.	
Purvis, Mississippi	30,000
Honda Co.	
Fletcher Oil & Refining Co.	
Carson, California	29,675
Gold Line Refining Ltdf	
Lake Charles, Louisiana	27,600
Petroserve Ltd.	
Triffinery	
Corpus Christi, Texas	27,000
Valero Refining Co.	
Corpus Christi, Texas	25,000
Crysen Corp.	24,400
Crysen Refining Inc.	
Woods Cross, Utah	12,500
Sound Refining Inc.	
Tacoma, Washington	11,900
San Joaquin Refining Co. Inc.	
Bakersfield, California	24,300
Huntway Refining Co.	24,100
Benicia, California	8,600
Wilmington, California	5,500
Sunbelt Refining Co.	
Coolidge, Arizona	10,000
Flying J. Petroleum Inc.	
Big West Oil Co.	
North Salt Lake, Utah	24,000
Kern Oil & Refining Co.	
Bakersfield, California	21,400
Countrymark Cooperative Inc.g	
Mount Vernon, Indiana	21,200
United Refining of Phoenix	
Texas United Refining Corp.h	
Nixon, Texas	20,900
Ergon Inc.	
Vicksburg, Mississippi	20,600
Giant Industries of Arizona Inc.	
Giant Refining Co.	
Gallup, New Mexico	20,000
Barrett Refining Corp.	17,500
Thomas (Custer), Okalahoma	10,500
Vicksburg, Mississippii	7,000
Gary Williams Co.	
Bloomfield Refining Co.	
Bloomfield, New Mexico	16,800
VGS Corp.	16,800
Southland Oil Co.	
Sandersville, Mississippi	11,000
Lumberton, Mississippi	5,800
Endevco Inc.	16,000
Dubach Gas Co.	
Dubach, Louisiana	8,500
Lisbon, Louisianaj	7,500
Chemoil Refining Corp.	
Long Beach, California	14,200
CAS Refining Co.	
Jennings (Mementau), Louisiana	13,500
Longview Refining Associates	
Longview, Texas	13,300

TABLE B-2. (Continued)

Refiner	Barrels per Calendar Day
Wyoming Refining Co.	
Newcastle, Wyoming	12,555
Transworld Oil U.S.A. Inc.	
Calcassieu Refining Co.	
Lake Charles, Louisiana	12,000
Sabine Resources Group	
Stonewall, Louisiana*	12,000
World Oil Co.	
Sunland Refining Corp.	
Bakersfield, California	12,000
Bechtel Investment Inc.	11,500
Petra Source Refining Partners	
Eagle Springs, Nevada*	7,000
Tonopah, Nevada	4,500
Quaker State Corp.	
Newell, West Virginia	11,500
Grant Trading Co.	
Eco Asphalt Inc.	
Long Beach, California	10,550
Total	**530,000**
Companies with Capacity 10,000 bbl/cd or Less	
Landmark Petroleum Inc.	
Fruita, Colorado	10,000
Witco Corp.	
Bradford, Pennsylvania	9,915
Asphalt Materials	
Laketon Refining Corp.	
Laketon, Indiana	8,700
Lunday Thagard Co.	
South Gate, California	8,100
Anchor Gasoline Corp.	
Canal Refining Co.	
Church Point, Louisiana	8,000
Three B Oil Co.	
Rattlesnake Refining Corp.	
Wickett, Texas	8,000
Cross Oil & Refining Co. Inc.	
Smackover, Arkansas	7,000
Petro Star Inc.	
North Pole, Alaska	7,000
WSGP Partners L.P.	
Petrowax Pennsylvania, Inc.	
Farmer's Valley (Smethport), Pennsylvania	6,700
Primary Corp.	
Richmond, Virginia	6,100
Calumet Lubricants Co. LP	
Princeton, Louisiana	6,000
Martin Gas Sales Inc.	
Berry Petroleum Co.	
Stephens, Arkansas	5,700
Young Refining Corp.	
Douglasville, Georgia	5,540
Somerset Refinery Inc.	
Somerset, Kentucky	5,500
Phoenix Refining Co.	
Saint Mary's, West Virginia*	4,500
Oil Holdings Inc.	
Tenby Inc.	
Oxnard, California	4,000
Thriftway Co.	
Bloomfield, New Mexico	4,000
Crystal Refining Co.	
Carson City, Michigan	3,000
GNC Energy Corp.	
Greensboro, North Carolina	3,000
Howell Corp.	
Howell Hydrocarbons & Chemical Inc.k	
San Antonio, Texas	1,900
Petrolite Corp.	
Kilgroe, Texas	1,000
Total	**123,655**
U.S. TOTAL	**15,696,155**

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[a] Formerly U.S. Steel Corp.
[b] Formerly Rock Island Refining.
[c] Formerly Seaview Petroleum Co., L.P.
[d] Formerly Hill Petroleum Co.
[e] Formerly Coastal Derby Refining Co.
[f] Formerly American International Refinery Inc.
[g] Formerly Indiana Farm Bureau Coop. Assn.
[h] Formerly Lead Petroluem Corp.
[i] Formerly Petro Source Resources Inc.
[j] Formerly Claborne Gasoline Co.
[k] Formerly Howell Hydrocarbons Corp.
* Refinery was reactivated on January 1, 1992.

bbl/cd = Barrels per calendar day.

Source: United States Refining Capacity, January 1, 1990, National Petroleum Refineries Association, Washington, D.C.