BACKGROUND REPORT

AP-42 SECTION 6.2

ADIPIC ACID PRODUCTION

Prepared for

U.S. Environmental Protection Agency
OAQPS/TSD/EIB
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AP-42 BACKGROUND REPORT

TECHNICAL SUPPORT DIVISION

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

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1.0 INTRODUCTION

The document "Compilation of Air Pollutant Emission Factors" (AP-42) has been published by the U.S. Environmental Protection Agency (the EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by the EPA to respond to new emission factor needs of the EPA, state and local air pollution control agencies, and industry.

Emission factors relate the quantity (weight) of pollutants emitted to the units of activity of a source. They are usually developed using information gathered from several facilities within a source category and may not be representative of emissions from any individual facility. When used in conjunction with activity data, they provide a means of estimating emissions from a source category and therefore, are useful for developing emission inventories.

This report discusses the use of process and emissions information obtained from industry for the development of emission factors. Including the introduction (Chapter 1) this report contains four chapters. Chapter 2 gives a description of the adipic acid manufacturing industry. It includes a characterization of the industry, an overview of the different process types, a description of emissions, and a description of the technology used to control emissions resulting from adipic acid production.

Chapter 3 is a review of emissions data collection and analysis procedures. It describes the literature search, the screening of quantitative emissions information, and the quality rating system for both emission data and emission factors. Chapter 4 details criteria and noncriteria pollutant emission factor development. It includes the review of specific data sets and the results of data analysis. Appendix A presents Section 6.2 from the 5th Edition of AP-42 which was designated Section 5.1 in the 4th Edition.

2.0 INDUSTRY DESCRIPTION

2.1 GENERAL

Adipic acid, $HOOC(CH_2)_4COOH$, is a white crystalline solid used primarily in the manufacture of nylon-6,6 polyamide. It is produced by three companies at four U.S. plants, with nearly two-thirds of the 780,000 Mg (860,000 ton) capacity occurring at duPont's two Texas facilities.

2.2 PROCESS DESCRIPTION

One adipic acid manufacturing facility, representing less than two percent of U.S. production, utilizes phenol as the feedstock for its adipic acid manufacturing process; the other three facilities all use cyclohexane. Adipic acid is manufactured from cyclohexane in two major reactions. The first step, shown in Figure 2.2-A, is the oxidation of cyclohexane to produce cyclohexanone (a ketone) and cyclohexanol (an alcohol). This ketone-alcohol (KA) mixture is then converted to adipic acid by oxidation with nitric acid in the second reaction, as shown in Figure 2.2-B. Following these two reaction stages, the wet adipic acid crystals are separated from water and nitric acid. The product is dried and cooled before packaging and shipping. Dibasic acids (DBA) may be recovered from the nitric acid solution and sold as a coproduct. The remaining nitric acid is then recycled to the second reactor.

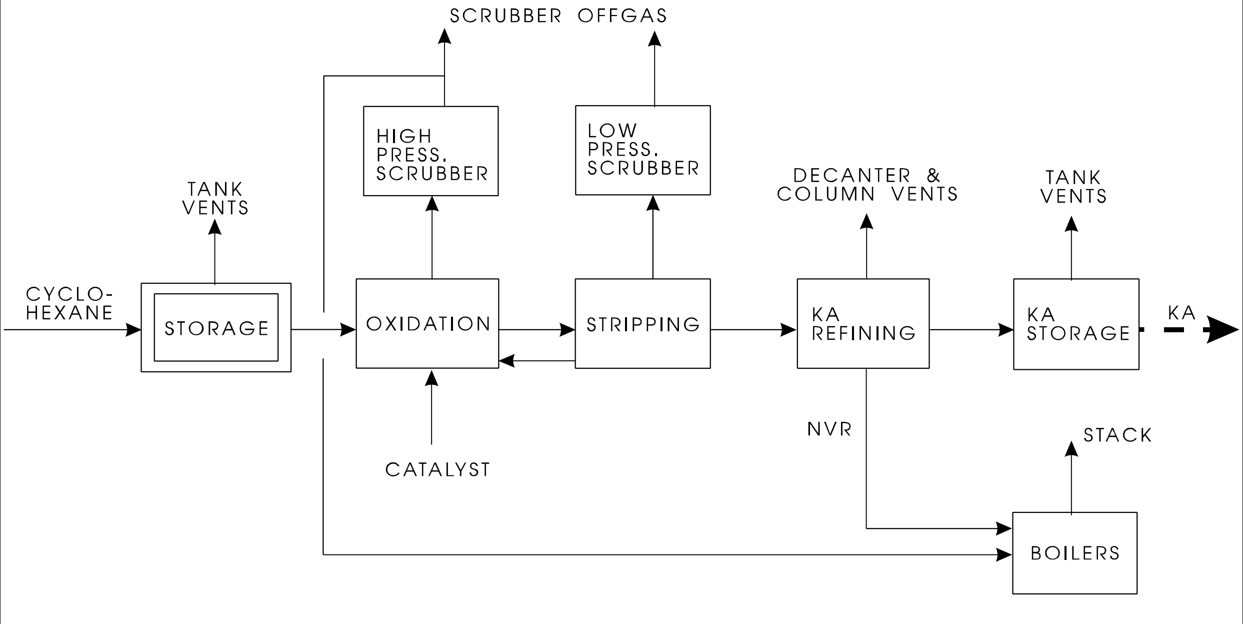

Figure 2.2-A Adipic acid manufacturing: Oxidation of cyclohexane

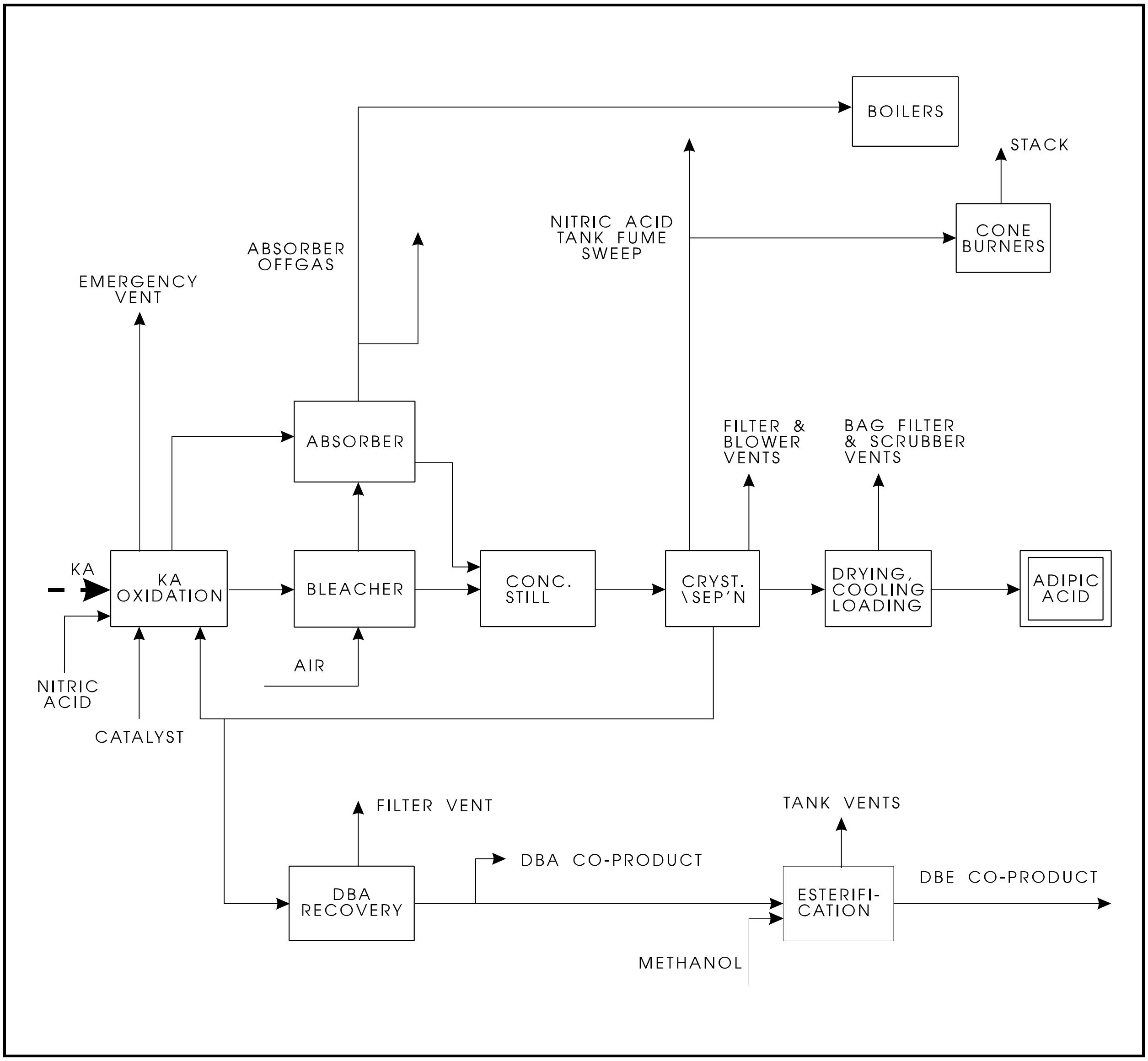

Figure 2.2-B Adipic acid manufacturing: Nitric acid oxidation of KA mixture

The predominant method of cyclohexane oxidation is metal-catalyzed oxidation, which employs a small amount of cobalt, chromium, and/or copper at moderate temperatures and pressures. Air, catalyst, cyclohexane, and in some cases small quantities of benzene are fed into a multiple-stage column reactor or a series of stirred tank reactors, with a low conversion rate from feedstock to oxidized product. This low rate of conversion necessitates effective recovery and recycling of unreacted cyclohexane through distillation of the oxidizer effluent.

The conversion of the intermediates cyclohexanol and cyclohexanone to adipic acid uses the same fundamental technology as that developed and used by duPont since the early 1940s, which entails oxidation with 45 to 55 percent nitric acid in the presence of copper and vanadium catalysts. This results in a very high yield of adipic acid. The reaction is exothermic, and can reach an autocatalytic runaway state if temperatures exceed 150° C (300° F). Process control is achieved with the use of large amounts of nitric acid. Nitrogen oxides are removed by bleaching with air. Water is removed by vacuum distillation, and the adipic acid is separated from the nitric acid by crystallization. Further refining, typically recrystallization from water, is needed to achieve polymer-grade material.

2.3 EMISSIONS AND CONTROLS

Emissions from the manufacture of adipic acid consist primarily of hydrocarbons and carbon monoxide from the first reaction, oxides of nitrogen from the second reaction, and particulate matter from product cooling, drying, storage, and loading. Emissions quantification of products of in-process combustion, evaporation losses associated with fractional distillation, oxidizer effluent streams and storage of volatile raw or intermediate materials, is outside the scope of Section 6.2 but is addressed in other Chapters of AP-42.

The waste gas stream resulting from the oxidation of cyclohexane will, after removal of most of the valuable unreacted cyclohexane by one or more scrubbers, still contain CO, CO_2, and organic compounds. In addition, the most concentrated waste stream, which comes from the final distillation column (sometimes called the "nonvolatile residue") will contain metals, residues from catalysts, and volatile and nonvolatile hydrocarbons. Both the scrubbed gas stream and the nonvolatile residue may be used as fuel in process heating units. If a caustic soda solution is used as a final purification step for the KA, the spent caustic waste can be burned or sold as a recovered byproduct. Analyses of gaseous effluent streams at two plants indicate that compounds containing cobalt and chromium, in addition to normal products of combustion, are emitted from the burning of nonvolatile residue (Ref. 6). These analyses also indicate that caproic, valeric, butyric, and succinic acids are emitted from tanks storing the nonvolatile residue, and that cyclohexanone, cyclohexanol, and hexanol are among the organic compounds emitted from the cyclohexane recovery equipment (such as decanters and distillation columns).

The nitric acid oxidation of the KA results in two main streams, one liquid and one gaseous. The liquid effluent contains primarily water, nitric acid and adipic acid, as well as significant quantities of NO_x, which are considered a part of the process stream with recoverable economic value. The NO_x component is stripped from the stream in a bleaching column using air. The gaseous effluent from oxidation contains NO_x, CO_2, CO, and DBA. The gaseous effluent from both the bleaching column and the oxidation reactor are typically passed through an absorption tower to recover most of the NO_x; this process does not significantly reduce the concentration of nitrous oxide (N_2O) in the stream, however. The absorber offgases and fumes from tanks storing solutions high in nitric acid content are controlled by extended absorption at one of the three plants utilizing cyclohexane oxidation, and thermal reduction at the remaining two. Extended absorption is accomplished by simply increasing the volume of the absorber, extending the residence time of the NO_x-laden gases with the absorbing water, and by providing sufficient cooling to remove the heat released by the absorption process. Thermal reduction involves reacting the NO_x with excess fuel in a reducing atmosphere. Control cost data reported by the three facilities utilizing cyclohexane as the raw material indicates a cost effectiveness of $108 per megagram ($98 per ton) for NO_x reduction by extended absorption, compared with $505 per megagram ($458 per ton) for thermal NO_x reduction.

Scrubbers and bag filters are both commonly used to control adipic acid dust particulate emissions from product drying, cooling, storage, and loading operations. Nitric acid emissions occur from the product blowers and from the centrifuges and/or filters used to recover adipic acid crystals from the effluent stream leaving the second reactor. When chlorine is added to product cooling towers, all of it can typically be assumed to be emitted to the atmosphere; if DBA are recovered from the nitric acid solution and converted to dibasic esters (DBE) using methanol, methanol emissions will also occur.

2.4 REVIEW OF REFERENCES FOR CHAPTER 2

The following sources were contacted to obtain the most up-to-date information on industrial processes, emissions, and control techniques for this industry:

1) Allied-Signal Corporation, Allied Fibers Division, Hopewell, Virginia

2) E.I. duPont de Nemours & Co., duPont Petrochemicals Department, Victoria Plant, Victoria, Texas

3) E.I. duPont de Nemours & Co., duPont Petrochemicals Department, Sabine River Works, Orange, Texas

4) Monsanto Chemical Co., Pensacola, Florida

5) State of Florida, Department of Environmental Regulation, Bureau of Air Quality Management, Tallahassee, Florida

6) Texas Air Control Board, Austin, Texas

7) Texas Air Control Board, Region 10, Beaumont, Texas

8) Virginia State Air Pollution Control Board, Richmond, Virginia

9) Chemical Manufacturers Association, Washington, DC

10) Synthetic Organic Chemical Manufacturers' Association, Washington, DC.

Responses were received from duPont and Allied-Signal (numbers 1 and 2), but Monsanto (number 4) declined to participate in the update process. The Florida Department of Environmental Regulation (number 5) provided information from its Air Pollutant Information System. No responses were received from the remaining agencies, nor from either of the trade associations. The information received from these sources was incorporated into the AP-42 section revision to better reflect current industry practices and emissions.

A brief discussion of each reference used to revise AP-42 Section 6.2 is provided below. With few exceptions, the descriptions of the adipic acid industry and its industrial processes and commonly used control techniques are taken from widely available reference literature. Specific emissions data are taken primarily from information obtained from the adipic acid producers and air pollution control agencies listed above.

Reference #1: *Kirk-Othmer Encyclopedia of Chemical Technology*

This reference provided descriptions of the chemical processes utilized in adipic acid production that were more detailed and more representative of the practices currently used in this industry than that in Section 5.1 (4th Edition of AP-42). This reference also provided information concerning the properties and uses of adipic acid.

Reference #2: *Control Technologies for Hazardous Air Pollutants*

This reference provided much of the information presented concerning control techniques and associated equipment utilized in the adipic acid manufacturing industry.

Reference #3: *1990 Directory of Chemical Producers*

This reference provided the most current profile of the adipic acid manufacturing industry available for this update.

Reference #4: *Alternative CTG -- Nitric and Adipic Acid Manufacturing*

This reference provided information comparing the cost effectiveness of alternative techniques for controlling emissions of oxides of nitrogen. This information appears in the "Emissions and Controls" sections of this report and AP-42 Section 6.2.

Reference #5: *Confidential Letter from Allied-Signal*

This reference provided information concerning the production of adipic acid from phenol. No source test data were included, nor mentioned, but the facility is permitted to emit cyclohexanone and cyclohexanol from the tanks storing these intermediates; NO_x from the centrifuge and acid recovery column; and adipic acid particulate from the cooler, conveying system, and storage bins.

2.5 REFERENCES FOR CHAPTER 2

1. *Kirk-Othmer Encyclopedia of Chemical of Chemical Technology, "Adipic Acid,"* Vol. 1, 4th Ed., New York, Interscience Encyclopedia, Inc., 1991.

2. *Handbook: Control Technologies for Hazardous Air Pollutants*, EPA-625/6-91-014, U.S. Environmental Protection Agency, Cincinnati, OH, June 1991.

3. *1990 Directory of Chemical Producers: United States*, SRI International, Menlo Park, CA.

4. *Alternative Control Techniques Document* -- *Nitric and Adipic Acid Manufacturing Plants*, EPA-450/3-91-026, U.S. Environmental Protection Agency, Research Triangle Park, NC, December 1991.

5. Confidential letter from C.D. Cary, Allied-Signal Inc., Hopewell, VA to D. Beauregard, U.S. Environmental Protection Agency, Research Triangle Park, NC, 9 March 1992.

3.0 GENERAL EMISSION DATA REVIEW AND ANALYSIS PROCEDURES

3.1 LITERATURE SEARCH AND SCREENING

The first step of this investigation involved a search of available literature related to criteria and noncriteria pollutant emissions associated with adipic acid production. This search included, but was not limited to, the following references:

1) AP-42 background files maintained by the Emission Factor and Methodologies Section.

2) "Locating and Estimating" reports (as applicable) published by the Emission Factor and Methodologies Section.

3) Publications generated by and available through the EPA Control Technology Center (CTC).

4) *Handbook of Emission Factors, Part I and II*, Ministry of Health and Environmental Protection, The Netherlands, 1980/1983.

5) The EPA *Clearinghouse for Inventories and Emission Factors* (CHIEF) and *National Air Toxics Information Clearinghouse* (NATICH).

To reduce the large amount of literature collected to a final group of references pertinent to this report, the following general criteria were used:

1. Emissions data must be from a primary reference, i.e. the document must constitute the original source of test data.

2. The referenced study must contain test results based on more than one test run.

3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions (e.g., one-page reports were generally rejected).

A final set of reference materials was compiled after a thorough review of the pertinent reports, documents, and information according to these criteria. The final set of reference materials is given in Chapter 4.

3.2 EMISSION DATA QUALITY RATING SYSTEM

As part of the analysis of the emission data, the quantity and quality of the information contained in the final set of reference documents were evaluated. The following data were excluded from consideration:

1. Test series averages reported in units that could not be converted to the selected reporting units;

2. Test series representing incompatible test methods (i.e., comparison of the EPA Method 5 front-half with the EPA Method 5 front- and back-half);

3. Test series of controlled emissions for which the control device was not specified;

4. Test series in which the source process was not clearly identified and described; and

5. Test series in which it was not clear whether the emissions were measured before or after the control device.

Data sets that were not excluded were assigned a quality rating. The rating system used was that specified by the OAQPS for the preparation of AP-42 sections. The data were rated as follows:

A
Multiple tests performed on the same source using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform to the methodology specified in EPA reference test methods, although these methods were certainly used as a guide for the methodology actually used.

B
Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.

C
Tests that were based on an untested or new methodology or that lacked a significant amount of background data.

D
Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following criteria were used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated is well documented In the report. The source was operating within typical parameters during the test.

2. Sampling procedures. The sampling procedures conformed to a generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurred, an evaluation was made of the extent such alternative procedures could influence the test results.

3. Sampling and process data. Adequate sampling and process data are documented in the report. Many variations can occur unnoticed and without warning during testing. Such variations can induce wide deviations in sampling results. If a large spread between test results cannot be explained by information contained in the test report, the data are suspect and were assigned a lower rating.

4. <u>Analysis and calculations</u>. The test reports contain original raw data sheets. The nomenclature and equations used were compared to those (if any) specified by the EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM

The quality of the emission factors developed from analysis of the test data was rated utilizing the following general criteria:

<u>A (Excellent)</u>
Developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

<u>B (Above average)</u>
Developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

<u>C (Average)</u>
Developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As in the A-rating, the source category is specific enough so that variability within the source category population may be minimized.

<u>D (Below Average)</u>
The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

<u>E (Poor)</u>
The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are always noted.

The use of these criteria is somewhat subjective and depends to an extent on the individual reviewer.

3.4 REFERENCES FOR CHAPTER 3

1. *Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections*, EPA-454/B-93-050, U.S. Environmental Protection Agency, Emission Inventory Branch, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 27711, October 1993.

2. *Compilation of Air Pollutant Emission Factors, Volume I: Stationary Sources*, Supplement A, Appendix C.2, "Generalized Particle Size Distributions." U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, October 1986.

4.0 POLLUTANT EMISSION FACTOR DEVELOPMENT

4.1 CRITERIA POLLUTANT EMISSIONS DATA

Total Non-Methane Organic Compounds

As is typical for the manufacture of petrochemicals in general, the primary pollutants of concern from the production of adipic acid are organic compounds. The raw material (cyclohexane) and the intermediates (cyclohexanol and cyclohexanone) associated with this process are nonmethane organic compounds, and the offgases from the primary oxidation process contain significant quantities of various C_2 to C_5 hydrocarbons. Emissions data found in Table 4.1-1 are derived from confidential gas stream analyses at the two duPont facilities. Emission factors for organic compounds from adipic acid refining and drying, cooling, and storage found in Section 5.1 (4th Edition of AP-42) were taken from a document that was not an original source of emissions test data. The data in this screening study were derived primarily from emission inventory questionnaire responses and could not be verified. As a result, the emission factors were copied into the revised section unchanged, but were downgraded from "B" to "E"-rated factors. The lack of documentation for the testing procedures utilized to develop the cited emissions data precluded assigning the factors a higher rating. See Section 4.3 for a more detailed review of the source of these data.

TABLE 4.1-1 (METRIC UNITS)
UNCONTROLLED TOTAL NONMETHANE ORGANIC COMPOUNDS

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	5.40
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	5.90
duPont - Sabine River			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	9.35
duPont - Victoria			
Cyclohexane oxidation:0 low-pressure scrubber	C	N/A	1.2
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	1.7
duPont - Sabine River			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	1.3
duPont - Victoria			
KA oxidation absorber	C	N/A	0.274
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	0.007
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.002

[a]Units in kg/Mg.

TABLE 4.1-1 (ENGLISH UNITS)
UNCONTROLLED TOTAL NONMETHANE ORGANIC COMPOUNDS

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	10.8
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	11.8
duPont - Sabine River			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	18.7
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	2.3
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	3.4
duPont - Sabine River			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	2.6
duPont - Victoria			
KA oxidation absorber	C	N/A	0.549
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	0.014
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.004

[a]Units in lb/ton.

Lead and sulfur dioxide

No data on emissions of these pollutants were expected nor found for the adipic acid manufacturing process.

Nitrogen oxides

The use of an aqueous solution of nitric acid in the oxidation of the intermediates cyclohexanone and cyclohexanol to adipic acid results in the presence of significant quantities of oxides of nitrogen in the gaseous effluent from the oxidation process and subsequent bleaching, purification, and crystallization steps. Alternatives to nitric acid oxidation have been explored as a result of concern over NO_x emissions, but none has been implemented commercially. Emissions data found in Table 4.1-2 are derived from confidential gas stream analyses and engineering estimates at the two duPont adipic acid production facilities. Emission factors for NO_x from adipic acid refining and drying, cooling, and storage found in Section 5.1 (4th Edition of AP-42) were taken from a document that was not an original source of emissions test data. The data in this screening study were derived primarily from emission inventory questionnaire responses and could not be verified. As a result, the emission factors were copied into the revised section unchanged, but were downgraded from "B" to "E"-rated factors. The lack of documentation for the testing procedures utilized to develop the cited emissions data precluded assigning the factors a higher rating. See Section 4.3 for a more detailed review of the source of these data.

Carbon monoxide

Carbon monoxide is emitted from both the primary and secondary oxidation processes in the manufacture of adipic acid from cyclohexane. Emissions data found in Table 4.1-3 are derived from confidential gas stream analyses and engineering estimates at the two duPont adipic acid production facilities. Emission factors for CO from adipic acid refining and drying, cooling, and storage found in Section 5.1 (4th Edition of AP-42) were taken from a document that was not an original source of emissions test data. The data in this screening study were derived primarily from emission inventory questionnaire responses and could not be verified. As a result, the emission factors were copied into the revised section unchanged, but were downgraded from "B" to "E"-rated factors. The lack of documentation for the testing procedures used to develop the cited emissions data precluded assigning the factors a higher rating. See Section 4.3 for a more detailed review of the source of these data.

TABLE 4.1-2 (METRIC UNITS)
NITROGEN OXIDES

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
KA oxidation absorber	B	N/A	7.0715
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	0.7935
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.428

[a]Units in kg/Mg.

TABLE 4.1-2 (ENGLISH UNITS)
NITROGEN OXIDES

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
KA oxidation absorber	B	N/A	14.143
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	1.587
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.856

[a]Units in lb/ton.

TABLE 4.1-3 (METRIC UNITS)
CARBON MONOXIDE

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	29.7
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	14.3
duPont - Sabine River			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	29.9
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	7.85
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	10.6
duPont - Sabine River			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	8.40
duPont - Victoria			
KA oxidation absorber	C	N/A	0.246
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	0.140
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.755

[a]Units in kg/Mg.

TABLE 4.1-3 (ENGLISH UNITS)
CARBON MONOXIDE

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	59.4
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	28.6
duPont - Sabine River			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	59.8
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	15.7
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	21.2
duPont - Sabine River			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	16.8
duPont - Victoria			
KA oxidation absorber	C	N/A	0.492
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	0.279
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.151

[a]Units in lb/ton.

Particulate Matter

Emissions of particulate matter occur at adipic acid manufacturing facilities as a result of the crystalline form of the finished product. These emissions are found at all steps within the process flow from the crystallizers to the product packaging and shipping operations. The test results shown in Table 4.1-4 were obtained from source test summaries found in the Air Pollutant Information System database maintained by the Florida Department of Environmental Regulation. No documentation of the testing procedures by which this data was obtained was available, and these data are therefore not rated and are not utilized in calculating emission factors for AP-42 section 6.2. These data represent total (including filterable, organic condensible, and inorganic condensible) particulate matter emissions, without regard to the portion of the sampling train the particulate was collected in or to particle size. Given with the control equipment are the nominal control efficiencies for each component tested; emission factors are on a controlled basis.

Emission factors for organic compounds from adipic acid refining and drying, cooling, and storage found in Section 5.1 (4th Edition of AP-42) were taken from a document that was not an original source of emissions test data. The data in this screening study were derived primarily from emission inventory questionnaire responses and could not be verified. As a result, the emission factors were copied into the revised section unchanged, but were downgraded from "B" to "E"-rated factors. The lack of documentation for the testing procedures used to develop the cited emissions data precluded assigning the factors a higher rating. See Section 4.3 for a more detailed review of the source of these data.

TABLE 4.1-4 (METRIC UNITS)
PARTICULATE MATTER

Plant/ Process	Control Device (nominal efficiency)	Average Production Rate[a]	Average Emission Rate[b]	Average Emission Factor[c]
Monsanto - Pensacola				
Product Screening	Baghouse (95%)	3.384	0.454	0.134
Monsanto - Pensacola				
Product Screening	Baghouse (95%)	2.797	0.346	0.124
Monsanto - Pensacola				
Product Dryer	Scrubber (99%)	2.095	0.120	0.0287
Monsanto - Pensacola				
Product Loading (Railcar)	Baghouse (96.7%)	4.3	2.87	0.34
Monsanto - Pensacola				
Product Loading (Railcar)	Baghouse (96.7%)	6.29	0.055	0.0044
Monsanto - Pensacola				
Product Packaging	Baghouse (96%)	6.85	0.0055	0.0008
Monsanto - Pensacola				
Product Dryer	Scrubber (99.4%)	2.22	0.073	0.0163

[a]Units in Mg/hr.
[b]Units in kg/hr.
[c]Units in kg/Mg.

TABLE 4.1-4 (ENGLISH UNITS)
PARTICULATE MATTER

Plant/ Process	Control Device (nominal efficiency)	Average Production Rate[a]	Average Emission Rate[b]	Average Emission Factor[c]
Monsanto - Pensacola				
Product Screening	Baghouse (95%)	3.731	1.00	0.268
Monsanto - Pensacola				
Product Screening	Baghouse (95%)	3.084	0.763	0.247
Monsanto - Pensacola				
Product Dryer	Scrubber (99%)	4.62	0.2652	0.0574
Monsanto - Pensacola				
Product Loading (Railcar)	Baghouse (96.7%)	9.4	6.33	0.673
Monsanto - Pensacola				
Product Loading (Railcar)	Baghouse (96.7%)	13.85	0.0122	0.0088
Monsanto - Pensacola				
Product Packaging	Baghouse (96%)	7.55	0.0122	0.0016
Monsanto - Pensacola				
Product Dryer	Scrubber (99.4%)	4.90	0.1600	0.0326

[a]Units in ton/hr.
[b]Units in lb/hr.
[c]Units in lb/ton.

4.2 NONCRITERIA POLLUTANT EMISSION DATA

Hazardous Air Pollutants

Hazardous air pollutants (HAPs) are defined in the 1990 Clean Air Act Amendments. Confidential process information from three separate facilities indicates that HAPs emitted from the adipic acid manufacturing process may include phenol (if used as the raw material rather than cyclohexane), methanol (if used to convert recovered dibasic acids to dibasic esters), benzene (if used in small quantities in conjunction with cyclohexane as a raw material), chlorine (if added to the adipic acid cooling tower), and compounds of cobalt and/or chromium (in the combustion offgas from burning the nonvolatile residue, if these metals are used as catalysts in the primary oxidation). No quantitative emissions data were available for any of these pollutants.

Global Warming Gases

Methane, carbon dioxide, and nitrous oxide are among the pollutants that have been found to contribute to overall global climate change. Emissions of carbon dioxide and methane from the high- and low-pressure scrubbers related to the primary oxidation process have been quantified, as have emissions of carbon dioxide from the oxidation reactor, absorber, and nitric acid tank fume sweep vent related to the secondary oxidation process. Emissions of nitrous oxide from the oxidation reactor, absorber, and nitric acid tank fume sweep associated with the secondary oxidation process have been quantified. The emissions data for methane in Table 4.2-1, carbon dioxide in Table 4.2-2, and nitrous oxide in Table 4.2-3 are derived from confidential gas stream analyses at the two duPont adipic acid manufacturing facilities. These data are the bases for the emission factors for global warming gases presented in the revised AP-42 Section 6.2. The resultant emission factors are all "C"-rated due to a lack of documentation of the testing methodologies utilized.

TABLE 4.2-1 (METRIC UNITS)
GLOBAL WARMING GASES: METHANE

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	0.050
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	0.12
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	0.02
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	0.065

[a]Units in kg/Mg.

TABLE 4.2-1 (ENGLISH UNITS)
GLOBAL WARMING GASES: METHANE

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	0.10
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	0.24
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	0.04
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	0.013

[a]Units in lb/ton.

TABLE 4.2-2 (METRIC UNITS)
GLOBAL WARMING GASES: CARBON DIOXIDE

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	21.0
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	8.65
duPont - Sabine River			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	11.9
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	3.2
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	3.8
duPont - Sabine River			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	4.2
duPont - Victoria			
KA oxidation: absorber	C	N/A	57.977
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	2.615
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.049

[a]Units in kg/Mg.

TABLE 4.2-2 (ENGLISH UNITS)
GLOBAL WARMING GASES: CARBON DIOXIDE

Plant/Process	Test Rating	Test Method	Average Emission Factor[a]
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	42.0
duPont - Victoria			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	17.3
duPont - Sabine River			
Cyclohexane oxidation: high-pressure scrubber	C	N/A	23.7
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	6.4
duPont - Victoria			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	7.6
duPont - Sabine River			
Cyclohexane oxidation: low-pressure scrubber	C	N/A	8.3
duPont - Victoria			
KA oxidation: absorber	C	N/A	115.954
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	5.230
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.098

[a]Units in lb/ton.

TABLE 4.2-3 (METRIC UNITS)
GLOBAL WARMING GASES: NITROUS OXIDE

Source Test #	Test Rating	Test Method	Average Emission Factor
duPont - Victoria			
KA oxidation: absorber	B	N/A	294.717
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	1.311
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	0.729

[a]Units in kg/Mg.

TABLE 4.2-3 (ENGLISH UNITS)
GLOBAL WARMING GASES: NITROUS OXIDE

Source Test #	Test Rating	Test Method	Average Emission Factor
duPont - Victoria			
KA oxidation: absorber	B	N/A	589.433
duPont - Victoria			
Nitric acid tank fume sweep	C	N/A	2.621
duPont - Sabine River			
Nitric acid tank fume sweep	N/A	Engineering Estimate	1.458

[a]Units in lb/ton.

Stratospheric Ozone-Depleting Gases

Pollutants such as chlorofluorocarbons, carbon tetrachloride, methyl chloroform, and hydrofluorocarbons have been found to contribute to depletion of the stratospheric ozone layer. None of these compounds or classes of compounds appear as raw materials or intermediates in the adipic acid manufacturing process, and thus no emissions data were expected nor found.

4.3 REVIEW OF SPECIFIC DATA SETS

Reference #1: *Screening Study for New Adipic Acid Plants*

This mid-1970's reference documents the results of a study examining the impact of New Source Performance Standards (NSPS) regulating emissions of hydrocarbons and carbon monoxide from adipic acid production facilities. The data contained within this report are taken from responses to emission inventory questionnaires, and the original sources of the data (i.e., emission test reports) are not available for review.

References #2-3: Letters from E.I. duPont deNemours & Co.

These letters from J.M. Rung of duPont Petrochemicals' Victoria, Texas, plant comprise the emissions data provided by duPont for the update of AP-42 Section 6.2. These data encompass both duPont adipic acid production facilities, and include data for global warming gases and criteria pollutants. Reference #2 includes tables summarizing the emission factors resulting from the enclosures to Reference #3. The enclosures to Reference #3 detail various emissions testing and gas stream analyses at the two facilities.

Reference #4: Fla. Dept. of Environmental Regulation *Air Pollutant Information System*

This reference provided emissions data based upon testing performed on the Monsanto adipic acid production facility in Pensacola. This data could not be used in developing emission factors for use in AP-42 because it is not an original source of raw emissions data, and the procedures used to conduct the testing could not be evaluated.

TABLE 4-3.1
LIST OF CONVERSION FACTORS

Multiply:	**by:**	**To obtain:**
mg/dscm	4.37×10^{-4}	gr/dscf
m^2	10.764	ft^2
m^3	35.3145	ft^3
m	3.281	ft
kg	2.205	lb
kPa	0.145	psia
kg/Mg	2.0	lb/ton
Mg	1.1023	ton

Temperature conversion equations:

Fahrenheit to Celsius:

$$°C = \frac{(°F - 32)}{1.8}$$

Celsius to Fahrenheit:

$$°F = 1.8(°C) + 32$$

4.4 REFERENCES FOR CHAPTER 4

1. *Screening Study to Determine Need for Standards of Performance for New Adipic Acid Plants: Final Report*, EPA Contract No. 68-02-1316, GCA Corporation, Bedford, MA, July 1976.

2. Letter from J.M. Rung, E.I. duPont de Nemours & Co., Inc., Victoria, TX, to D. Beauregard, U.S. Environmental Protection Agency, Research Triangle Park, NC, 30 April 1992.

3. Confidential letter from J.M. Rung, E.I. duPont de Nemours & Co., Inc., Victoria, TX, to D. Beauregard, U.S. Environmental Protection Agency, Research Triangle Park, NC, 30 April 1992.

4. *"Master Detail Report: Monsanto Chemical Co, Pensacola, Florida,"* Air Pollutant Information System, Florida Department of Environmental Regulation, April 1992.

APPENDIX A.

AP-42 SECTION 6.2