# SURVEY REPORTS
# ON ATMOSPHERIC EMISSIONS
# FROM THE PETROCHEMICAL
# INDUSTRY

# VOLUME III

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by

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# PETROCHEMICAL AIR POLLUTION STUDY

## INTRODUCTION TO SERIES

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry.

A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in these four volumes numbered EPA 450/3-73-005-a, -b, -c, and -d. The Tables of Contents of these reports list the processes that have been surveyed.

Those processes which have a significant impact on air quality are being studied in more detail by EPA. These in-depth studies will be published separately in a series of volumes entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006-a, -b, -c, etc.) At the time of this writing, a total of seven petrochemicals produced by 11 distinctly different processes has been selected for this type of study. Three of these processes, used to produce two chemicals (polyethylene and formaldehyde), were selected because the survey reports indicated further study was warranted. The other five chemicals (carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride and ethylene oxide) were selected on the basis of expert knowledge of the pollution potential of their production processes. One or more volumes in the report series will be devoted to each of these chemicals.

## ACKNOWLEDGEMENTS

## Table of Contents

## List of Tables and Figures

NOTE: There are numerous tables and figures in the Survey Reports that are included in the appendicies of this report. These tables and figures are separately listed in each appendix.

## SUMMARY

A study of air pollution as caused by the petrochemical industry has been undertaken in order to provide data that the Environmental Protection Agency can use in the fulfillment of their obligations under the terms of the Clean Air Amendments of 1970. The scope of the study includes most petrochemicals which fall into one or more of the classifications of (a) large production, (b) high growth rate, and (c) significant air pollution. The processes for the production of each of these selected chemicals have been studied and the emissions from each tabulated on the basis of data from and Industry Questionnaire. A survey report prepared for each process provides a method for ranking the significance of the air pollution from these processes. In-depth studies on those processes which are considered to be among the more significant polluters either have been or will be provided.

To date, drafts of in-depth studies on seven processes have been submitted. In addition, two further processes have been selected for in-depth study and work on these is in progress. All of these in-depth studies will be separately reported under Report Number EPA-450/3-73-006 a, b, c, etc.

A total of 33 Survey Reports have been completed and are reported here, or in one of the other three volumes of this report series.

I.  Introduction

A study has been undertaken to obtain information about selected pro-
duction processes that are practiced in the Petrochemical Industry.  The
objective of the study is to provide data that are necessary to support
the Clean Air Ammendments of 1970.

The information sought includes industry descriptions, air emission
control problems, sources of air emissions, statistics on quantities and
types of emissions and descriptions of emission control devices currently
in use.  The principal source for these data was an industry questionnaire
but it was supplemented by plant visits, literature searches, in-house
background knowledge and direct support from the Manufacturing Chemists
Association.

A method for rating the significance of air emissions was established
and is used to rank the processes as they are studied.  The goal of the
ranking technique is to aid in the selection of candidates for in-depth
study.  These studies go beyond the types of information outlined above
and include technical and economic information on "best systems" of emission
reduction, the economic impact of these systems, deficiencies in petrochemical
pollution control technology and potential research and development programs
to overcome these deficiencies.  These studies also recommend specific plants
for source testing and present suggested checklists for inspectors.

This final report presents a description of the industry surveys that
have been completed, as well as a status summary of work on the in-depth
studies.

The Appendicies of this report include each of the 33 Survey Reports
that were prepared during the course of the study.

II.  Discussion

A.  Petrochemicals to be Studied

There are more than 200 different petrochemicals in current production in the United States.  Many of these are produced by two or more processes that are substantially different both with respect to process techniques and nature of air emissions.  Although it may eventually become necessary to study all of these, it is obvious that the immediate need is to study the largest tonnage, fastest growth processes that produce the most pollution.

Recognizing this immediate need, a committee of Air Products' employees and consultants reviewed the entire list of chemicals and prepared a list of thirty chemicals which were recommended for primary consideration in the study and an additional list of fourteen chemicals that should receive secondary consideration.  Since this was only a qualitative evaluation it was modified slightly as additional information was received and after consultation with the Environmental Protection Agency (EPA).

The final modified list of chemicals to be studied included all but three from the original primary recommendations.  In addition, four chemicals were added and one was broken into two categories (namely low and high density polyethylene) because of distinct differences in the nature of the final products.  This resulted in thirty-two chemicals for study and fourty one processes which are sufficiently different to warrant separate consideration.  Hence, the following list of petro-chemicals is the subject of this study.

| | |
|---|---|
| Acetaldehyde (2 processes) | Nylon 6 |
| Acetic Acid (3 processes) | Nylon 6,6 |
| Acetic Anhydride | "Oxo" Alcohols and Aldehydes |
| Acrylonitrile | Phenol |
| Adipic Acid | Phthalic Anhydride (2 processes) |
| Adiponitrile (2 processes) | Polyethylene (high density) |
| Carbon Black | Polyethylene (low density) |
| Carbon Disulfide | Polypropylene |
| Cyclohexanone | Polystyrene |
| Ethylene | Polyvinyl Chloride |
| Ethylene Dichloride (2 processes) | Styrene |
| Ethylene Oxide (2 processes) | Styrene - Butadiene Rubber |
| Formaldehyde (2 processes) | Terephthalic Acid (1) |
| Glycerol | Toluene Di-isocyanate (2) |
| Hydrogen Cyanide | Vinyl Acetate (2 processes) |
| Maleic Anhydride | Vinyl Chloride |

(1)  Includes dimethyl terephthalate.
(2)  Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

B.  Preliminary Investigations

Immediately upon completion of the preliminary study lists, a literature review was begun on those chemicals which were considered likely candidates for study.  The purpose of the review was to prepare an informal "Process Portfolio" for each chemical.  Included in the portfolio are data concerning processes for producing the chemical, estimates of growth in production, estimates of production costs, names,

locations and published capacities of producers, approximations of overall plant material balances and any available data on emissions or their control as related to the specific process.

The fundamental purpose of these literature reviews was to obtain background knowledge to supplement what was ultimately to be learned from completed Industry Questionnaires. A second and very important purpose was to determine plant locations and names of companies producing each chemical. This information was then used to contact responsible individuals in each organization (usually by telephone) to obtain the name and address of the person to whom the Industry Questionnaire should be directed. It is believed that this approach greatly expedited the completion of questionnaires. The mailing list that was used is included as Appendix I of this report.

C. Industry Questionnaire

Soon after the initiation of the petrochemical pollution study, a draft questionnaire was submitted by Air Products to the Environmental Protection Agency. It had been decided that completion of this questionnaire by industry would provide much of the information necessary to the performance of the study. The nature and format of each question was reviewed by EPA engineers and discussed with Air Products engineers to arrive at a modified version of the originally proposed questionnaire.

The modified questionnaire was then submitted to and discussed with an Industry Advisory Committee (IAC) to obtain a final version for submission to the Office of Management and Budget (OMB) for final approval, as required prior to any U. S. Government survey of national industries. The following listed organizations, in addition to the EPA and Air Products, were represented at the IAC meeting:

Trade Associations

Industrial Gas Cleaning Institute
Manufacturing Chemists Association

Petrochemical Producers

B. F. Goodrich Chemical Company
E. I. duPont deNemours and Company
Exxon Chemical Company
FMC Corporation
Monsanto Company
Northern Petrochemical Company
Shell Chemical Company
Tenneco Chemicals, Inc.
Union Carbide Corporation

Manufacturers of Pollution Control Devices

John Zink Company
UOP Air Correction Division

State Pollution Control Departments

New Jersey
Texas

The questionnaire, along with a detailed instruction sheet and an example questionnaire (which had been completed by Air Products for a fictitious process that was "invented" for this purpose) were submitted to the OMB for approval. In due course, approval was received and OMB Approval Number 158-S-72019 was assigned to the questionnaire. Copies of the approved instruction sheet, example questionnaire are included as Appendix II of this report.

The questionnaires were mailed in accordance with the mailing list already discussed and with a cover letter that had been prepared and signed by the EPA Project Officer. The cover letter was typed in a manner that permitted the insertion of the name and address of the receipient at the top of the first page and the name of the process, the plant location and an expected return date at the bottom of the first page. A copy of this letter of transmittal is also included in Appendix II.

Understandably, because of the dynamic nature of the petrochemical industry, about 10 percent of the questionnaires were directed to plants which were no longer in operation, were still under construction, were out-of-date processes or were too small to be considered as typical. This did not present a serious problem in most cases because (a) 100 percent of the plants were not surveyed and (b) the project timing permitted a second mailing when necessary. Appendix III tabulates the number of questionnaires incorporated into each study.

One questionnaire problem that has not been resolved is confidentiality. Some respondents omitted information that they consider to be proprietary. Others followed instructions by giving the data but then marked the sheet (or questionnaire) "Confidential". The EPA is presently trying to resolve this problem, but until they do the data will be unavailable for inclusion in any Air Products' reports.

D. Screening Studies

Completed questionnaires were returned by the various respondents to the EPA's Project Officer, Mr. L. B. Evans. After reviewing them for confidentiality, he forwarded the non-confidential data to Air Products. These data form the basis for what has been named a "Survey Report". The purpose of the survey reports being to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". These reports are included as appendicies to this report.

Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for calculating a Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix IV of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emissions Summary Table that constitutes part of this report. This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes being studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process (Block) flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were established for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) are proposed.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR are proposed.

The bases for these ratings and example calculations are included in Appendix V of this report.

E. In-Depth Studies

The original performance concept was to select a number of petro-chemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furance Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional processes be "nominated" for in-depth study. The chemicals involved are phthalic anhydride, formaldehyde and ethylene oxide. Work on these indicated a need for four additional in-depth studies as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst.

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

Drafts of these have been submitted to the EPA and reviewed by the Industry Advisory Committee. The phthalic anhydride report also includes a section on production from naphthalene by air oxidation, a process which is considered to be a significant polluter in today's environment but without significant growth potential.

These seven in-depth studies will be separately issued in final report form, under Report Number EPA-450/3-73-006 a, b, c, etc.

An in-depth study, besides containing all the elements of the screening studies, delves into questions such as "What are the best demonstrated systems for emission reduction?", "What is the economic impact of emission control on the industry involved?", "What deficiencies exist in sampling, analytical and control technology for the industry involved?".

In striving to obtain answers to these questions, the reports include data on the cost effectiveness of the various pollution control techniques source testing recommendations, industry growth projections, inspection procedures and checklists, model plant studies of the processes and descriptions of research and development programs that could lead to emission reductions.

Much of the information required to answer these questions came from the completed Industry Questionnaires and the Process Portfolios. However, the depth of understanding that is required in the preparation of such a document can only be obtained through direct contact with the companies that are involved in the operation of the processes being studied. Three methods for making this contact were available to Air Products. The first two are self-evident, as follows: Each questionnaire contains the name, address and telephone number of an individual who can provide additional information. By speaking with him, further insight was obtained into the pollution control problems that are specific to the process being studied; or through him, a visit to an operating plant was sometimes arranged, thus achieving a degree of first hand knowledge.

However, it was felt that these two techniques might fall short of the level of knowledge desired. Thus, a third, and unique procedure was arranged. The Manufacturing Chemists Association (MCA) set up, through

its Air Quality Committee (AQC), a Coordinating Technical Group (CTG) for each in-depth process. The role of each CTG was to:

1. Assist in the obtaining of answers to specific questions.

2. Provide a review and commentary (without veto power) on drafts of reports.

The AQC named one committee member to provide liaison. In several cases, he is also one of the industry's specialists for the process in question. If not, one other individual was named to provide CTG leadership. Coordination of CTG activities was provided by Mr. Howard Guest of Union Carbide Corporation who is also on the EPA's Industry Advisory Committee as the MCA Representative. CTG leadership is as follows:

| Chemical | AQC Member | Other |
|---|---|---|
| Carbon Black | C. B. Beck<br>Cabot Corporation | None |
| Acrylonitrile | W. R. Chalker<br>Du Pont | R. E. Farrell<br>Sohio |
| Formaldehyde | W. B. Barton<br>Borden | None |
| Ethylene Dichloride | W. F. Bixby<br>B. F. Goodrich | None |
| Phthalic Anhydride | E. P. Wheeler<br>Monsanto | Paul Hodges<br>Monsanto |
| Ethylene Oxide | H. R. Guest<br>Union Carbide | H. D. Coombs<br>Union Carbide |

F. Current Status

Survey Reports on each of the 33 processes that were selected for this type of study have been completed, following review of the drafts by both the EPA and the Petrochemical Industry. These reports constitute the subject matter of this report.

In-depth studies of the seven processes mentioned above have been completed in draft form, submitted to the EPA for initial review, discussed in a public meeting with the Industry Advisory Committee and re-submitted to the EPA in revised form. They are currently receiving final EPA review and will be issued as final reports, following that review.

The EPA has now selected two additional processes for in-depth study and work on these is currently in progress. They are:

1. High Density Polyethylene via the Low and Intermediate Pressure Polymerization of Ethylene.

2. Low Density Polyethylene via the High Pressure Polymerization of Ethylene.

III. <u>Results</u>

The nature of this project is such that it is not possible to report any "results" in accordance with the usual meaning of the word. Obviously, the results are the Survey Reports and In-Depth Studies that have been prepared. However, a tabulation of the emission data collected in the study and summarized in each of these reports will be useful to the EPA in the selection of those processes which will be either studied in-depth at some future date, or selected for the preparation of new source standards. Such a tabulation, entitled "Emissions Summary Table", is attached.

IV.  Conclusions

As was stated above under "Results", the conclusions reached are specific to each study and, hence, are given in the individual reports. Ultimately, some conclusions are reachable relative to decisions on processes which require future in-depth studies or processes which warrant the promulgation of new source standards.

A firm basis for selecting these processes is difficult to achieve, but the data contained in the Emissions Summary Table can be of value in setting a basis, or selecting processes.

It is imperative, when using the table, to be aware of the following facts.

1. The data for some processes are based on 100 percent survey of the industry, while others are based on less than 100 percent with some as few as a single questionnaire.

2. Some of the reported data are based on stack sampling, others on continuous monitoring and still others on the "best estimate" by the person responsible for the questionnaire.

3. Air Products attempted to use sound engineering judgement in obtaining emission factors, industry capacities and growth projections. However, other engineering firms, using the same degree of diligence would undoubtedly arrive at somewhat different final values.

Thus, the tabulation should be used as a guide but not as a rigorous comparison of process emissions.

Furthermore, data on toxicity of emissions, odors and persistence of emitted compounds are not included in the tabulation. In addition, great care must be used when evaluating the weighted emission rates because of the wide range in noxiousness of the materials lumped together in the two most heavily weighted categories. For example, "hydrocarbons" includes both ethane and formaldehyde and "particulates" includes both phthalic anhydride and the permanent hardness of incinerated water.

Bearing all of these qualifications in mind, several "top 15" rankings of processes can be made, as in Tables II through V. Obviously, one of these tables could be used to select the more significant polluters directly. Of course, other rankings could be made, such as leading emitters of $NO_x$ or particulates, etc. Using these four tables, however, one analysis might be that the number of times a process appears in these tables is a measure of its pollution significance, or in summary:

| Appear in 4 Tables | Appear in 3 Tables |
|---|---|
| Carbon Black | Acrylonitrile |
| Low Density Polyethylene | Adiponitrile (Butadiene) |
| High Density Polyethylene | Ethylene Dichloride (Oxychlorination) |
| Cyclohexanone | Dimethyl Terephthalate |
| Polypropylene | Ethylene Dichloride (Direct) |
| Polyvinyl Chloride | Ethylene |
| Ethylene Oxide | |

| Appear in 2 Tables | Appear in 1 Table |
|---|---|
| Maleic Anhydride | Phthalic Anhydride |
| Isocyanates | Formaldehyde (Iron Oxide) |
| Phenol | Polystyrene |
| Formaldehyde (Silver) | Nylon 6 |
| | Nylon 6,6 |
| | Vinyl Chloride |

Thus, on this basis and in retrospect, it could be concluded that four of the selected in-depth studies (carbon black, ethylene oxide, and both low and high density polyethylene) were justified but that three of them (phthalic anhydride and both formaldehyde processes) were of lesser importance.

On the same basis, seven processes should be considered for future in-depth studies, namely:

    Cyclohexanone
    Polypropylene
    Polyvinyl Chloride
    Adiponitrile (Butadiene Process)
    Dimethyl Terephthalate (and TPA)
    Ethylene Dichloride (Direct)
    Ethylene

Obviously, many alternative bases could be established. It is not the function of this report to select a basis for initiating future studies because the priorities of the EPA are unknown. The most apparent of these bases are the ones suggested by Tables II through V, namely the worst total polluters, the worst polluters on a weighted basis, the greatest increase in pollution (total or weighted) or the largest numbers of new plants. In addition, noxiousness of the emissions (photo-chemical reactivity, toxicity, odor, persistence) could be considered in making a selection.

TABLE I
EMISSIONS SUMMARY

Page 1 of 3

ESTIMATED [1] CURRENT AIR EMISSIONS, MM LBS./YEAR

| | Hydrocarbons [3] | Particulates [4] | Oxides of Nitrogen | Sulfur Oxides | Carbon Monoxide | Total | Total Weighted [5] |
|---|---|---|---|---|---|---|---|
| Acetaldehyde via Ethylene | 1.1 | 0 | 0 | 0 | 0 | 1.1 | 86 |
| via Ethanol | 0 | 0 | 0 | 0 | 27 | 27 | 27 |
| Acetic Acid via Methanol | 0 | 0 | 0.01 | 0 | 0 | 0.01 | 1 |
| via Butane | 40 | 0 | 0.04 | 0 | 14 | 54 | 3,215 |
| via Acetaldehyde | 6.1 | 0 | 0 | 0 | 1.3 | 7.4 | 490 |
| Acetic Anhydride via Acetic Acid | 3.1 | 0 | 0 | 0 | 5.5 | 8.6 | 253 |
| Acrylonitrile (9) | 183 | 0 | 5.5 | 0 | 196 | 385 | 15,000 |
| Adipic Acid | 0 | 0.2 | 29.6 | 0 | 0.14 | 30 | 1,190 |
| Adiponitrile via Butadiene | 11.2 | 4.7 | 50.5 | 0 | 0 | 66.4 | 3,200 |
| via Adipic Acid | 0 | 0.5 | 0.04 | 0 | 0 | 0.54 | 30 |
| Carbon Black | 156 | 8.1 | 6.9 | 21.6 | 3,870 | 4,060 | 17,544 |
| Carbon Disulfide | 0.15 | 0.3 | 0.1 | 4.5 | 0 | 5.1 | 120 |
| Cyclohexanone | 70 | 0 | 0 | 0 | 77.5 | 148 | 5,700 |
| Dimethyl Terephthalate (+TPA) | 91 | 1.4 | 0.1 | 1.0 | 53 | 146.5 | 7,460 |
| Ethylene | 15 | 0.2 | 0.2 | 2.0 | 0.2 | 17.6 | 1,240 |
| Ethylene Dichloride via Oxychlorination | 95.1 | 0.4 | 0 | 0 | 21.8 | 117.3 | 7,650 |
| via Direct Chlorination | 29 | 0 | 0 | 0 | 0 | 29 | 2,300 |
| Ethylene Oxide | 85.8 | 0 | 0.3 | 0.1 | 0 | 86.2 | 6,880 |
| Formaldehyde via Silver Catalyst | 23.8 | 0 | 0 | 0 | 107.2 | 131 | 1,955 |
| via Iron Oxide Catalyst | 25.7 | 0 | 0 | 0 | 24.9 | 50.6 | 2,070 |
| Glycerol via Epichlorohydrin | 16 | 0 | 0 | 0 | 0 | 16 | 1,280 |
| Hydrogen Cyanide Direct Process | 0.5 | 0 | 0.41 | 0 | 0 | 0.91 | 56 |
| Isocyanates | 1.3 | 0.8 | 0 | 0.02 | 86 | 88 | 231 |
| Maleic Anhydride | 34 | 0 | 0 | 0 | 260 | 294 | 2,950 |
| Nylon 6 | 0 | 1.5 | 0 | 0 | 0 | 1.5 | 90 |
| Nylon 6,6 | 0 | 5.5 | 0 | 0 | 0 | 5.5 | 330 |
| Oxo Process | 5.25 | 0.01 | 0.07 | 0 | 19.5 | 24.8 | 440 |
| Phenol | 24.3 | 0 | 0 | 0 | 0 | 24.3 | 1,940 |
| Phthalic Anhydride via O-Xylene | 0.1 | 5.1 | 0.3 | 2.6 | 43.6 | 51.7 | 422 |
| via Naphthalene | 0 | 1.9 | 0 | 0 | 45 | 47 | 160 |
| High Density Polyethylene | 79 | 2.3 | 0 | 0 | 0 | 81.3 | 6,400 |
| Low Density Polyethylene | 75 | 1.4 | 0 | 0 | 0 | 76.4 | 6,100 |
| Polypropylene | 37.5 | 0.1 | 0 | 0 | 0 | 37.6 | 2,950 |
| Polystyrene | 20 | 0.4 | 0 | 1.2 | 0 | 21.6 | 1,650 |
| Polyvinyl Chloride | 62 | 12 | 0 | 0 | 0 | 74 | 5,700 |
| Styrene | 4.3 | 0.07 | 0.14 | 0 | 0 | 4.5 | 355 |
| Styrene-Butadiene Rubber | 9.4 | 1.6 | 0 | 0.9 | 0 | 12 | 870 |
| Vinyl Acetate via Acetylene | 5.3 | 0 | 0 | 0 | 0 | 5.3 | 425 |
| via Ethylene | 0 | 0 | TR | 0 | 0 | TR | TR |
| Vinyl Chloride | 17.6 | 0.6 | 0 | 0 | 0 | 18.2 | 1,460 |
| Totals | 1,227.6 | 49.1 | 94.2 | 33.9 | 4,852.6 | 6,225.9 [7] | 110,220 [7] |

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes $H_2S$ and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, $NO_x$ - 40, $SO_x$ - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

Page 2 of 3

ESTIMATED ADDITIONAL [2] AIR EMISSIONS IN 1980, MM LBS./YEAR

| | Hydrocarbons [3] | Particulates [4] | Oxides of Nitrogen | Sulfur Oxides | Carbon Monoxide | Total | Total Weighted [5,6] |
|---|---|---|---|---|---|---|---|
| Acetaldehyde via Ethylene | 1.2 | 0 | 0 | 0 | 0 | 1.2 | 96 |
| via Ethanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Acetic Acid via Methanol | 0 | 0 | 0.04 | 0 | 0 | 0.04 | 2 |
| via Butane | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| via Acetaldehyde | 12.2 | 0 | 0 | 0 | 2.5 | 14.7 | 980 |
| Acetic Anhydride via Acetic Acid | 0.73 | 0 | 0 | 0 | 1.42 | 2.15 | 60 |
| Acrylonitrile (9) | 284 | 0 | 8.5 | 0 | 304 | 596 | 23,000 |
| Adipic Acid | 0 | 0.14 | 19.3 | 0 | 0.09 | 19.5 | 779 |
| Adiponitrile via Butadiene | 10.5 | 4.4 | 47.5 | 0 | 0 | 62.4 | 3,010 |
| via Adipic Acid | 0 | 0.5 | 0.04 | 0 | 0 | 0.54 | 30 |
| Carbon Black | 64 | 3.3 | 2.8 | 8.9 | 1,590 | 1,670 | 7,200 |
| Carbon Disulfide | 0.04 | 0.07 | 0.03 | 1.1 | 0 | 1.24 | 30 |
| Cyclohexanone | 77.2 | 0 | 0 | 0 | 85.1 | 162 | 6,260 |
| Dimethyl Terephthalate (+TPA) | 73.8 | 1.1 | 0.07 | 0.84 | 42.9 | 118.7 | 6,040 |
| Ethylene | 14.8 | 0.2 | 0.2 | 61.5 | 0.2 | 77 | 2,430 |
| Ethylene Dichloride via Oxychlorination | 110 | 0.5 | 0 | 0 | 25 | 136 | 8,800 |
| via Direct Chlorination | 34.2 | 0 | 0 | 0 | 0 | 34.2 | 2,740 |
| Ethylene Oxide | 32.8 | 0 | 0.15 | 0.05 | 0 | 33 | 2,650 |
| Formaldehyde via Silver Catalyst | 14.8 | 0 | 0 | 0 | 66.7 | 81.5 | 1,250 |
| via Iron Oxide Catalyst | 17.6 | 0 | 0 | 0 | 17.0 | 34.6 | 1,445 |
| Glycerol via Epichlorohydrin | 8.9 | 0 | 0 | 0 | 0 | 8.9 | 700 |
| Hydrogen Cyanide Direct Process | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Isocyanates | 1.2 | 0.7 | 0 | 0.02 | 85 | 87 | 225 |
| Maleic Anhydride | 31 | 0 | 0 | 0 | 241 | 272 | 2,720 |
| Nylon 6 | 0 | 3.2 | 0 | 0 | 0 | 3.2 | 194 |
| Nylon 6,6 | 0 | 5.3 | 0 | 0 | 0 | 5.3 | 318 |
| Oxo Process | 3.86 | 0.01 | 0.05 | 0 | 14.3 | 18.2 | 325 |
| Phenol | 21.3 | 0 | 0 | 0 | 0 | 21.3 | 1,704 |
| Phthalic Anhydride via O-Xylene | 0.3 | 13.2 | 0.8 | 6.8 | 113 | 134 | 1,100 |
| via Naphthalene | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| High Density Polyethylene | 210 | 6.2 | 0 | 0 | 0 | 216 | 17,200 |
| Low Density Polyethylene | 262 | 5 | 0 | 0 | 0 | 267 | 21,300 |
| Polypropylene | 152 | 0.5 | 0 | 0 | 0 | 152.5 | 12,190 |
| Polystyrene | 20 | 0.34 | 0 | 1.13 | 0 | 21.47 | 1,640 |
| Polyvinyl Chloride | 53 | 10 | 0 | 0 | 0 | 63 | 4,840 |
| Styrene | 3.1 | 0.05 | 0.1 | 0 | 0 | 3.25 | 225 |
| Styrene-Butadiene Rubber | 1.85 | 0.31 | 0 | 0.18 | 0 | 2.34 | 170 |
| Vinyl Acetate via Acetylene | 4.5 | 0 | 0 | 0 | 0 | 4.5 | 360 |
| via Ethylene | 0 | 0 | TR | 0 | 0 | TR | TR |
| Vinyl Chloride | 26.3 | 0.9 | 0 | 0 | 0 | 27.2 | 2,170 |
| Totals | 1,547.2 | 55.9 | 79.5 | 80.5 | 2,588 | 4,351.9 | 134,213 (7) |

(1)  In most instances numbers are based on less than 100% survey.  All based on engineering judgement of best current control.  Probably has up to 10% low bias.
(2)  Assumes future plants will employ best current control techniques.
(3)  Excludes methane, includes $H_2S$ and all volatile organics.
(4)  Includes non-volatile organics and inorganics.
(5)  Weighting factors used are:  hydrocarbons - 80, particulates - 60, $NO_x$ - 40, $SO_x$ - 40, and CO - 1.
(6)  Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7)  Totals are not equal across and down due to rounding.
(9)  See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY                                                                      Page 3 of 3

| | Emissions [2], MM Lbs./Year | | Estimated Number of New Plants (1973 - 1980) | Total Estimated Capacity MM Lbs./Year | |
|---|---|---|---|---|---|
| | Total by 1980 | Total Weighted [5] by 1980 | | Current | By 1980 |
| Acetaldehyde via Ethylene | 2.3 | 182 | 6 | 1,160 | 2,460 |
| via Ethanol | 27 | 27 | 0 | 966 | 966 |
| Acetic Acid via Methanol | 0.05 | 3 | 4 | 400 | 1,800 |
| via Butane | 54 | 3,215 | 0 | 1,020 | 500 |
| via Acetaldehyde | 22 | 1,470 | 3 | 875 | 2,015 |
| Acetic Anhydride via Acetic Acid | 10.8 | 313 | 3 | 1,705 | 2,100 |
| Acrylonitrile (9) | 980 | 38,000 | 5 | 1,165 | 3,700 (8) |
| Adipic Acid | 50 | 1,970 | 7 | 1,430 | 2,200 |
| Adiponitrile via Butadiene | 128.8 | 6,210 | 4 | 435 | 845 |
| via Adipic Acid | 1.1 | 60 | 3 | 280 | 550 |
| Carbon Black | 5,730 | 24,740 | 13 | 3,000 | 5,000 (8) |
| Carbon Disulfide | 6.3 | 150 | 2 | 871 | 1,100 |
| Cyclohexanone | 310 | 11,960 | 10 | 1,800 | 3,600 |
| Dimethyl Terephthalate (+TPA) | 265 | 13,500 | 8 | 2,865 | 5,900 |
| Ethylene | 94 | 3,670 | 21 | 22,295 | 40,000 |
| Ethylene Dichloride via Oxychlorination | 253 | 16,450 | 8 | 4,450 | 8,250 (8) |
| via Direct Chlorination | 63 | 5,040 | 10 | 5,593 | 11,540 |
| Ethylene Oxide | 120 | 9,530 | 15 | 4,191 | 6,800 (8) |
| Formaldehyde via Silver Catalyst | 212.5 | 3,205 | 40 | 5,914 | 9,000 |
| via Iron Oxide Catalyst | 85 | 3,515 | 12 | 1,729 | 3,520 (8) |
| Glycerol via Epichlorohydrin | 25 | 2,000 | 1 | 245 | 380 |
| Hydrogen Cyanide Direct Process | 0.5 (10) | 28 (10) | 0 | 412 | 202 |
| Isocyanates | 175 | 456 | 10 | 1,088 | 2,120 |
| Maleic Anhydride | 566 | 5,670 | 6 | 359 | 720 |
| Nylon 6 | 4.7 | 284 | 10 | 486 | 1,500 |
| Nylon 6,6 | 10.8 | 650 | 10 | 1,523 | 3,000 |
| Oxo Process | 43 | 765 | 6 | 1,727 | 3,000 |
| Phenol | 46 | 3,640 | 11 | 2,363 | 4,200 |
| Phthalic Anhydride via O-Xylene | 186 | 1,522 | 6 | 720 | 1,800 (8) |
| via Naphthalene | 47 | 160 | 0 | 603 | 528 |
| High Density Polyethylene | 297 | 23,600 | 31 | 2,315 | 8,500 |
| Low Density Polyethylene | 343 | 27,400 | 41 | 5,269 | 21,100 |
| Polypropylene | 190 | 15,140 | 32 | 1,160 | 5,800 |
| Polystyrene | 43 | 3,290 | 23 | 3,500 | 6,700 |
| Polyvinyl Chloride | 137 | 10,540 | 25 | 4,375 | 8,000 |
| Styrene | 7.4 | 610 | 9 | 5,953 | 10,000 |
| Styrene-Butadiene Rubber | 14 | 1,040 | 4 | 4,464 | 5,230 |
| Vinyl Acetate via Acetylene | 9.8 | 785 | 1 | 206 | 356 |
| via Ethylene | TR | TR | 4 | 1,280 | 2,200 |
| Vinyl Chloride | 45 | 3,630 | 10 | 5,400 | 13,000 |
| Totals | 10,605 (7) | 244,420 (7) | | | |

(1)  In most instances numbers are based on less than 100% survey.  All based on engineering judgement of best current control.  Probably has up to 10% low bias.
(2)  Assumes future plants will employ best current control techniques.
(3)  Excludes methane, includes $H_2S$ and all volatile organics.
(4)  Includes non-volatile organics and inorganics.
(5)  Weighting factors used are:  hydrocarbons - 80, particulates - 60, $NO_x$ - 40, $SO_x$ - 20, and CO - 1.
(6)  Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7)  Totals are not equal across and down due to rounding.
(8)  By 1985.
(9)  See sheet 1 of 3
(10)  Due to anticipated future shut down of marginal plants.

## TABLE II

TOTAL ANNUAL EMISSIONS, ALL "POLLUTANTS", BY 1980 (MM LBS./YR.)*

| | |
|---|---|
| Carbon Black | 5,730 |
| Acrylonitrile | 980 |
| Maleic Anhydride | 566 |
| Low Density Polyethylene | 343 |
| Cyclohexanone | 310 |
| High Density Polyethylene | 297 |
| Dimethyl Terephthalate | 265 |
| Ethylene Dichloride | 253 |
| Phthalic Anhydride (Total) | 233 |
| Formaldehyde (Silver) | 212 |
| Polypropylene | 190 |
| Isocyanates | 175 |
| Polyvinyl Chloride | 137 |
| Adiponitrile (Butadiene Process) | 129 |
| Ethylene Oxide | 120 |

*Fifteen highest numbers, as summarized in Table I, for this category.

## TABLE III

TOTAL ANNUAL WEIGHTED EMISSIONS BY 1980 (MM LBS./YR.)*

| | |
|---|---|
| Acrylonitrile | 38,000 |
| Low Density Polyethylene | 27,400 |
| Carbon Black | 24,740 |
| High Density Polyethylene | 23,600 |
| Ethylene Dichloride (Oxychlorination) | 16,450 |
| Polypropylene | 15,140 |
| Dimethyl Terephthalate | 13,500 |
| Cyclohexanone | 11,960 |
| Polyvinyl Chloride | 10,540 |
| Ethylene Oxide | 9,530 |
| Adiponitrile (Butadiene Process) | 6,210 |
| Maleic Anhydride | 5,670 |
| Ethylene Dichloride (Direct) | 5,040 |
| Ethylene | 3,670 |
| Phenol | 3,640 |

*Fifteen highest numbers, as summarized in Table I, for this category.

## TABLE IV

### SIGNIFICANT EMISSION INDEX*

| | |
|---|---|
| Acrylonitrile | 23,000 |
| Low Density Polyethylene | 21,300 |
| High Density Polyethylene | 17,200 |
| Polypropylene | 12,190 |
| Ethylene Dichloride (Oxychlorination) | 8,800 |
| Carbon Black | 7,200 |
| Cyclohexanone | 6,260 |
| Dimethyl Terephthalate | 6,040 |
| Polyvinyl Chloride | 4,840 |
| Adiponitrile (Butadiene) | 3,010 |
| Ethylene Dichloride (Direct) | 2,740 |
| Maleic Anhydride | 2,720 |
| Ethylene Oxide | 2,650 |
| Ethylene | 2,430 |
| Vinyl Chloride | 2,170 |

*Fifteen higest numbers, as summarized in Table I, for this category.

TABLE V

NUMBER OF NEW PLANTS (1973-1980)*

| | |
|---|---|
| Low Density Polyethylene | 41 |
| Formaldehyde (Silver) | 40 |
| Polypropylene | 32 |
| High Density Polyethylene | 31 |
| Polyvinyl Chloride | 25 |
| Polystyrene | 23 |
| Ethylene | 21 |
| Ethylene Oxide | 15 |
| Carbon Black | 13 |
| Formaldehyde (Iron Oxide) | 12 |
| Phenol | 11 |
| Cyclohexanone | 10 |
| Isocyanates | 10 |
| Nylon 6 | 10 |
| Nylon 6,6 | 10 |
| Ethylene Dichloride (Direct) | 10 |

*Fifteen highest numbers, as summarized in Table I, for this category.

**Maleic Anhydride**

# Table of Contents

## List of Illustrations and Tables

I. Introduction

Maleic Anhydride is a white crystalline solid that is normally marketed in tablet form although some producers have a substantial bulk market in tank cars or wagons. Its major use, accounting for about 50% of total production, is in the formulation of polyester resins. Additionally, it is an intermediate in the production of fumaric acid and agricultural pesticides. Alkyd resins and other miscellaneous uses account for the remaining 25% of production.

With one exception, all U. S. maleic anhydride (direct) production is based on the vapor phase oxidation of benzene, as licensed by Scientific Design. Petro-tex, however, utilizes a feedstock of mixed butylene at their Houston plant. Lower yields and higher investment costs apparently tend to off-set the economic advantage offered by the cheaper $C_4$ charge material. Also, minor quantities of maleic anhydride are produced as a by-product with phthalic anhydride when the naphthalene based process is used.

## II. Process Description

Benzene in the presence of a suitable catalyst may be oxidized to maleic anhydride. The primary overall reaction is:

$$\text{Benzene} \quad + \quad 9/2\ O_2 \quad \longrightarrow \quad \text{Maleic Anhydride} \quad + \quad 2\ H_2O \quad + \quad 2\ CO_2$$

Benzene                                    Maleic Anhydride

78.11                                      98.06
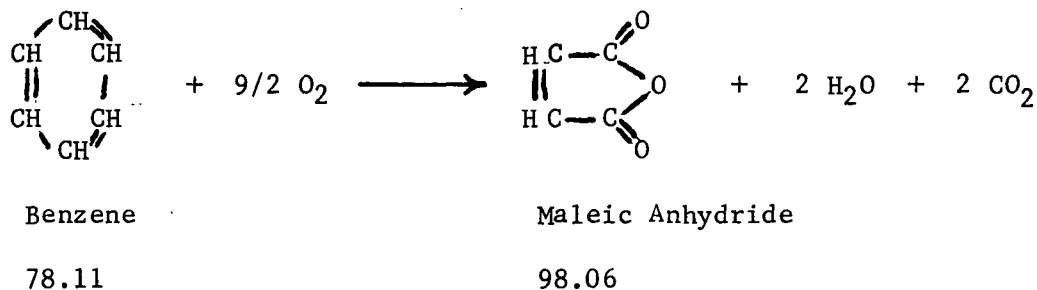
Standard commercial practice is to conduct the reaction in the vapor phase, utilizing a $V_2O_5$ based catalyst.

Benzene is either carbureted with air and preheated or vaporized and then mixed with an excess of preheated air prior to being admitted to a multi-tubular catalytic reactor. The vapors pass downward (or upward in some cases) through the tubes, which contain a pelleted $V_2O_5$ catalyst, and exit the reactor at a temperature in the range of 750 to 850° F. The very large heat of reaction (up to 2,600 BTU/lb. of MAN) is removed by the heat of transfer fluid - molten salt or boiling mercuy - that circulates around the outside of the tubes, and by air preheat.

The effluent vapors, consisting of maleic anhydride, maleic acid, carbon oxides, water and benzene, are cooled and then passed through a partial condenser and separator, where the bulk of the maleic anhydride is separated from the non-condensibles. The overhead material from the separator still contains some maleic anhydride, this material is recovered thru absoprtion in aqueous (or non-aqueous) solvents and recovered as maleic acid.

The crude maleic acid is converted to the anhydride by dehydration, usually by azeotropic distillation. This material is combined with the maleic anhydride recovered from the partial condenser and purified by vacuum and/or azeotropic distillation. The product is then either tableted or flaked and packaged or marketed in bulk.

The above described processing scheme is consistent with the presented flow diagram, Figure I (which see), and typical of the methods used by domestic producers. However, the reader should be cognizant of the fact that a wide variety of product recovery and purification techniques exist within the industry today.

III.  Plant Emissions

A.  Continuous Air Emissions

1.  Product Recovery Condenser Vent (Scrubber Exhaust)

This stream is the only source of emissions reported by four of the seven respondents.  Thus, it seems reasonable to categorize it as the single most important emission source for the subject process.  The two main components, of a polluting nature, are carbon monoxide and benzene.  The concentration of carbon monoxide varies from .87 lbs. CO/lb. of MAN to .44 lbs./lb, while the concentration of benzene varies from .20 lbs. benzene/lb. of MAN to .06 lbs./lb.  As mentioned in the process description section of this report, the vapors from the condenser are vented to a scrubber for recovery of uncondensed maleic anhydride, prior to venting the effluent gases to the atmosphere.  Many plants route streams from other sections of the unit to this same scrubber in order to minimize emissions and affect economy of operation through the utilization of a single large scrubber rather than several smaller ones.  Unfortunately, lack of data preclude calculation of scrubber efficiency.  A summary of emissions from this source are listed in Table III.

2.  Product Flaking, Pelleting, Packaging and Storage

Three respondents report emissions from this type of operation. Respondent 18-2 reports emitting .0002 lbs./lb. of maleic anhydride from his pelleting and packaging operation.  Respondent 18-6 reports 'losing' 0.6 lbs./hr. of maleic anhydride from his product storage area, however, a scrubbing device removes all of that material from the vent stream before atmospheric discharge.  Respondent 18-7 also reports emissions from the subject area, again he states water scrubbing results in the complete removal of pollutants from the vent.

3.  Aqueous Waste Incinerator Flue Gas

Only respondent 18-2 has reported an emission from this source. It results from the incineration of various plant generated aqueous waste streams.  The respondent indicates that the only pollutants discharged as a result of this operation are .0001 lbs. of particulates ($Na_2CO_3$)/lb. of product.

4.  Distillation and Dehydration Section Vent

Only respondent 18-2 reports emissions from this source.  This is so because most other operators direct the light ends resulting from these operations to the main scrubber (see Section III-A-1). Emissions reported consist of .0001 lbs./lb. of maleic anhydride plus varying quantities of non-polluting gases.  The emission is summarized in Table III.

B.  Intermittent Air Emissions

No intermittent air emissions were reported.

C. Continuous Liquid Wastes

   The following data relating to waste liquid production and disposal were reported by the respondents:

| Plant | Type of Waste Liquid | Amount MM Gal./Yr. | Treatment and/or Disposal Method |
|-------|----------------------|---------------------|----------------------------------|
| 18-1 | Still washing | 0.9 | Outside contractor |
| 18-2 | | 6.3 | Biological treatment |
| 18-3 | | 32.8 | Lime neutralization |
| 18-4 | | 34.0 | |
| 18-5 | Process water | 15.5 | |
| | Cooling tower water | 17.3 | |
| 18-6 | Total water outfall | 110.5 | To municipal sewer |
| 18-7 | Purification system wash water | 3.6 | To municipal sewer |

D. Solid Wastes

   Only three of the seven respondents reported the generation of solid waste materials. The only type of solid waste reported by the three was spent catalyst. The amounts and disposal method are reported below:

| Plant | Tons of Catalyst/Yr. | Disposal Method |
|-------|----------------------|-----------------|
| 18-3 | 18 | Landfill |
| 18-5 | 30 | Reprocessed |
| 18-6 | 53 | Landfill |

E. Fugitive Emissions

   None of the respondents have offered a quantitative estimate of fugitive emissions. Aside from the normal sources, such as leaking pump seals, packing gland, etc., there are two (probable) principal sources for emissions of this type in most maleic anhydride plants. They are:

   (1) Storage tank vents - very few of the respondents indicate the use of conservation vents on storage tanks. Since benzene is relatively volatile, it is reasonable to assume that moderate amounts of that material at least is 'lost' to the atmosphere.

   (2) Packaging, pelleting and flaking - most plants employing this type of solids handling equipment suffer at least some losses. It seems reasonable to assume, therefore, that these areas would represent emission sources.

F. Odors

   In general, the respondents indicate that maleic anhydride is not the cause of a significant odor problem. Only one respondent reported receiving a community odor complaint in the past 12 months. Maleic anhydride was identified as the source of odor in that instance. No other respondents reported the detection of odors off the plant site.

IV. Emission Control

The various emission control devices that have been reported as being utilized by operators of maleic anhydride plants are summarized in Table IV of this report, which is entitled 'Catalog of Emission Control Devices'. The control devices may be divided into two broad categories; (1) <u>Combustion Devices</u> - those devices which depend on thermal (or catalytic) oxidation of combustibles for emission control, and (2) <u>Non-Combustion Devices</u> - devices that do not depend on combustion for emission control. In Table IV, all devices are assigned efficiency ratings (when data permits). Efficiencies are defined in terms of:

(1) "CCR" - Completeness of Combustion Rating

$$CCR = \frac{\text{lbs. of } O_2 \text{ reacting (with pollutant in device feed)}}{\text{lbs. of } O_2 \text{ that theoretically could react}} \times 100$$

(2) "SE" - Specific Efficiency

$$SE = \frac{\text{specific pollutant in - specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(3) "SERR" - Significance of Emission Reduction Rating

$$SERR = \frac{(\text{pollutant x weighting factor})in - (\text{pollutant x weighting factor})out}{(\text{pollutant x weighting factor})in} \times 100$$

A more detailed discussion of these ratings may be found in Appendix V of this report.

Combustion devices are normally assigned a CCR and a SERR rating whereas non-combustion devices are assigned SE and SERR ratings. Unfortunately none of the respondents provided sufficient data to calculate the above indicated efficiencies. Therefore, only a few general observations about the expected device performance can be made.

Scrubbers

Most plants scrub the uncondensed portion of the reactor effluent after it passes through the partial condensor. This is done principally to recover maleic anhydride. Many plants utilize this same device to scrub vent gases from various areas of the plant. However, CO and hydrocarbon emissions from this device are quite high. Appreciably better control would be achieved by coupling the product scrubber with a combustion type device. One plant (18-4) plans such an installation They state total costs will be $1,000,000.

Plant 18-2 and 18-7 utilize separate scrubbers to control the emissions of MAN particles from their flaking, tableting packaging operations. One would expect scrubbing efficiencies to be quite high for this service — 98%+.

Incinerators

Only one plant employs an incineration device - plant 18-2. It is used to dispose of aqueous wastes. The respondent shows no hydrocarbons, CO or other pollutants in the incinerator flue gas. However, this does not

the device performs with 100 efficiency because incinerator effluents are difficult to sample or monitor. Considering that there are no sulfur, nitrogen or halogen bearing compounds used in the process, a high SERR rating is to be expected.

Developmental work directed toward reduction in emissions for the subject process falls into the following general areas, as has been suggested by questionnaire respondents and general literature.

(1) Substitution of oxygen for air; as the oxidizing agent.

(2) Development of fluid bed process to permit reduction of air/benzene feed ratio.

(3) Development of more selective catalyst.

(4) More efficient design and better utilization of pollution control devices currently being used.

(5) Investigate use of recycle air to improve yield and reduce emissions.

This list is by no means intended to be exhaustive, nor is knowledge available as to whether or not some of these types of work are in progress.

## V.  Significance of Pollution

It is recommended that no in-depth study of this process be undertaken at this time.  The predicted growth and emission rates are both moderate. Therefore, the resultant SEI is less than for other processes that are currently being survyed.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants. This work is summarized in Tables V and VI.

Published support for the annual growth rate upon which the Table V forecast of new plants is based may be found in the April 3, 1973 issue of Chemical Marketing, Chemical Profiles section.

On a weighted emission basis a Significant Emission Index of 2,721 has been calculated in Table VI.  Thus, this number, in part, is the basis for recommending the exclusion of this process from the in-depth portion of the overall petrochemical industry study that is scheduled for the near future.

## VI. Maleic Anhydride Producers

The following list shows the production capacity of the maleic anhydride producers and their location by plant.

| Name | Location | Capacity - MM Lbs./Year |
|---|---|---|
| Allied Chemical Corp. | Moundsville, W. Va. | 20 |
| Koppers Company | Bridgeville Pa. | 34 |
| Monsanto Company | St. Louis, Mo. | 105 |
| Petro-tex Chemical Corp. | Houston, Texas | 50 |
| Reichhold Chemical | Elizabeth, N. J. | 30 |
|  | Morris, Ill. | 60 |
| Tenneco Chemical | Fords, N. J. | 20 |
| USS Chemical Division | Pittsburgh, Pa. | 40 |
|  | Total - | 359* |

*1973 capacity is estimated to be 9% higher than 1972 capacity, i.e., 1.09 x 359 - 391 MM lbs./year.

| Stream I. D. No. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Component | Fresh Feed | Air | Scrubber Vent Gas | Vacuum Light Ends [1] | Product Maleic Anhydride | Refiner Heavy Ends |
| CO | | | 0.303 | | | |
| $CO_2$ | | | 1.189 | | | |
| $O_2$ | | 9.152 | 7.082 | | | |
| $N_2$ | | 30.124 | 30.124 | | | |
| Benzene | 1.331 | | 0.067 | | | |
| Maleic Anhydride | | | | | 1.000 | |
| $H_2O$ | | | 1.644 [2] | | | |
| Misc. HC's | | | | 0.133 [3] | | 0.066 [3] |
| | 1.331 | 39.276 | 40.409 | 0.133 | 1.000 | 0.066 |

(1)  In some units this stream is recycled to reactor.

(2)  Includes 1.001 T/T of water lost from water scrubber.  If other scrubbing medium such as dibutyl phthalate
     is employed, water in vent is reduced to 0.553 T/T.

(3)  Arbitrary split, contains oxygenated compounds rejected in waste water streams.

## TABLE MA-II
## MALEIC ANHYDRIDE
## EX
## BENZENE
## GROSS REACTOR HEAT BALANCE

| HEAT IN | BTU/LB. OF MAN |
|---|---|
| Benzene vaporizer and superheater | 250 |
| Exothermic heat of reaction | 18,000 |
| | Total - 18,250 |

| HEAT OUT | |
|---|---|
| Reactor heat loss | 25 |
| Reactor temperature control | 10,725 |
| Differential enthalpy* | 7,500 |
| | Total - 18,250 |

*Enthalpy Effluent - Enthalpy Feed

| EPA Code Number | 18-1 | | 18-2 | | |
|---|---|---|---|---|---|
| Date on stream | | | 1972 | | |
| Capacity - Tons Maleic Anhydride (MAN)/Yr. | 20,000 | | 22,000 | | |
| Average Production - Tons MAN/Yr. | | | | | |
| Range in Production - % of Max. | 0 | | 0 | | |

Emissions to Atmosphere

| | Scrubber Vent | Benzene and Product Recovery Vent | Vacuum System Vent | Scrubber Vent | Incinerator Vent |
|---|---|---|---|---|---|
| Stream | | | | | |
| Flow - SCFM | 42,000 | 43,100 | 16 | 2890 | 7400 |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous | Continuous |
| if Intermittent - Hrs./Yr. of Flow | | | | | |
| Composition - Tons/Ton of MAN | | | | | |
| Particulate | | | | | 0.0001 ($Na_2 CO_3$) |
| $O_2$ | 6.1280 | 5.6727 | 0 0030 | 0.5598 | 0.1091 |
| $N_2$ | 26.3280 | 26.7818 | 0.0100 | 1.8348 | 1.8000 |
| $CO_2$ | 1.8416 | 1.2800 | 0.0009 | | 0.3727 |
| CO | 0.8674 | 0.6109 | | | |
| $H_2O$ | 2.2354 | 0.8727 | | 0 0449 | 2 4764 |
| MAN (a) | | 0.0027 | 0 0001 | 0 0002 | |
| Maleic Acid | 0.0040 | | | | |
| Benzene | 0.0624 | 0.0033 | | | |
| Formaldehyde | 0.0154 | | | | |
| Formic Acid | 0 0012 | | | | |
| Xylene | | | | | |
| Sample Tap Location | Top of Stack | Stack | Top of Stack | Top of Stack | Top of Stack |
| Date or Frequency of Sampling | Benzene - 3/week   Others 1/week | | | | |
| Type of Analysis | MS, GLC, PT. Wet Chemical | Design Calc. | Design Calc. | Design Calc. | Design Calc |
| Odor Problems | Yes - In plant - No - Off Plant | No | No | No | No |
| Vent Stacks | | | | | |
| Flow - SCFM per stack | 21,000 | 43,100 | 16 | 2 890 | 7,400 |
| Number | 2 | 1 | 1 | 1 | 1 |
| Height - Feet | 79 and 99 | 90 | 85 | 20 | 36 |
| Diameter - Inches | 24 | 42 | 2 | 14 | 14 |
| Exit Gas Temperature - °F | 109 | 100 | 80 | 86 | 200 |
| Emission Control Device | | | | | |
| Type | Water Scrubber | Not Specified | Not Specified | Water Scrubber | Water Scrubber |
| Catalog I. D. Number | | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of MAN | 0.0830 | | 0.0062 | | |
| Total Particulate/Aerosol Emissions - Ton/Ton of MAN | 0 | | 0.0001 | | |
| Total $NO_x$ Emissions | | | | | |
| Total $SO_x$ Emissions | | | | | |
| Total CO Emissions | 0.8674 | | 0.6109 | | |

NOTES:  (See also sheets 2 and 3 of 3)

(a)  Often emitted as maleic acid, but common practice is to report it as the anhydride.

| | 18-3 | 18-4 | 18-5 |
|---|---|---|---|
| EPA Code Number | 18-3 | 18-4 | 18-5 |
| Date on stream | 1961 | | |
| Capacity - Tons Maleic Anhydride (MAN)/Yr. | 10,000 | 17,000 | 25,000 |
| Average Production - Tons MAN/Yr. | | | |
| Range in Production - % of Max. | 0 | 0 | 0 |
| Emissions to Atmosphere | | | |
| Stream | Scrubber Vent | Scrubber Vent | Scrubber Vent |
| Flow - SCFM | 17,000 | 30,000 | 42,000 |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous |
| if Intermittent - Hrs./Yr. of Flow | | | |
| Composition - Tons/Ton of MAN | | | |
| Particulate | | | |
| $O_2$ | 6.9296 | )        | 4.9550 |
| $N_2$ | 22.8232 | )32.1810 | 24.2656 |
| $CO_2$ | 0.8480 | )        | 1.3126 |
| CO | 0.6844 | 0.6706 | 0.4434 |
| $H_2O$ | 0.3928 | 1.5139 | 1.3642 |
| MAN (a) | 0.0020 | 0.0059 | |
| Maleic Acid | | | 0.0115 |
| Benzene | 0.1008 | 0.0616 | 0.0627 |
| Formaldehyde | | | )Incl. with |
| Formic Acid | | | )Maleic Acid |
| Xylene | 0.0116 | | |
| Sample Tap Location | Scrubber | Not Sampled | Not Specified |
| Date or Frequency of Sampling | Four since 1968 | Not Sampled | Infrequent |
| Type of Analysis | Gravimetric - Wet Chemical | Mat. Balance | Not Specified |
| Odor Problems | No | No | Yes |
| Vent Stacks | | | |
| Flow - SCFM per stack | 17,000 | 30,000 | 42,000 |
| Number | 1 | 1 | 1 |
| Height - Feet | 72 | 74 | 65 |
| Diameter - Inches | 24 | 24 | 36 |
| Exit Gas Temperature - °F | 65 | 100 | 100 |
| Emission Control Device | | | |
| Type | Water Scrubber | Water Scrubber | Water Scrubber |
| Catalog I. D. Number | | | |
| Total Hydrocarbon Emissions - Ton/Ton of MAN | 0.1144 | 0.0675 | 0.0742 |
| Total Particulate/Aerosol Emissions - Ton/Ton MAN | 0 | 0 | 0 |
| Total $NO_x$ Emissions | | | |
| Total $SO_x$ Emissions | | | |
| Total CO Emissions | 0.6844 | 0.6706 | 0.4434 |

| | 18-6 | | | 18-7 |
|---|---|---|---|---|
| EPA Code Number | 18-6 | | | 18-7 |
| Date on stream | | | | |
| Capacity - Tons Maleic Anhydride (MAN)/Yr. | 52,500 | | | 15,000 |
| Average Production - Tons MAN/Yr. | | | | |
| Range in Production - % of Max. | 0 | | | 0 |
| Emissions to Atmosphere | | | | |
| Stream | Scrubber Vent | Fume Scrubber Vent | Product Recovery Vent | Scrubber Vent |
| Flow - SCFM | 78,000 | 45 | 20,000 | 7,000 |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous |
| if Intermittent - Hrs./Yr. of Flow | | | | |
| Composition - Tons/Ton of MAN | | | | |
| Particulate | | | | |
| $O_2$ | 3.9896 | | 2.4587 | 1.8912 |
| $N_2$ | 19.7250 | 0.0015 | 19.0421 | 6.6232 |
| $CO_2$ | 1.0363 | | 1.0776 | |
| CO | 0.4703 | | 0.6859 | |
| $H_2O$ | 1.2219 | | 0.6541 | 0.2315 |
| MAN (a) | ) 0.0047 | | | |
| Maleic Acid | ) | | | |
| Benzene | 0.0879 | | 0.1976 | |
| Formaldehyde | )Incl. with | | | |
| Formic Acid | )MAN | | | |
| Xylene | | | | |
| Sample Tap Location | Not Sampled | Not Sampled | Not Specified | Not Sampled |
| Date or Frequency of Sampling | Not Sampled | Not Sampled | Bz. - 2-3/week, CO - 1/2 month | Not Sampled |
| Type of Analysis | Mat. Balance | Mat. Balance | GLC and Mat. Balance | Design Calc. |
| Odor Problems | No | No | No | No |
| Vent Stacks | | | | |
| Flow - SCFM per stack | Not Specified | 45 | 20,000 | 7,000 |
| Number | Not Specified | 1 | 1 | 1 |
| Height - Feet | Not Specified | 9.5 | 56.8 | 30 |
| Diameter - Inches | Not Specified | 3 | 24 | 24 |
| Exit Gas Temperature - °F | 140 | 100 | 104 | 77 |
| Emission Control Device | | | | |
| Type | Water Scrubber | Venturi Scrubber | Not Specified | Water Scrubber |
| Catalog I. D. Number | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of MAN | 0.0926 | | 0.1976 | |
| Total Particulate/Aerosol Emissions - Ton/Ton MAN | 0 | | 0 | |
| Total $NO_x$ Emissions | | | | |
| Total $SO_x$ Emissions | | | | |
| Total CO Emissions | 0.4703 | | 0.6859 | |

**WATER SCRUBBERS**

| | | | | | |
|---|---|---|---|---|---|
| Flow Diagram Stream I. D. | | | | | |
| Device I. D. No. | MAN-1 | MAN-2 | MAN-3 | MAN-3 | MAN-4 |
| EPA Code Number of plant | 18-1 | 18-2 | 18-2 | 18-2 | 18-3 |
| Purpose - Control Emission of | Maleic Anhydride | Benzene and Maleic Anhydride | Maleic Anhydride | Particulate | Maleic Anhydride |
| Type - Spray | Not Specified | Not Specified | | X | Not Specified |
| Packed Column | | | X | | |
| Trays - Type | | | | | |
| Number | | | | | |
| Plenum Chamber | | | | X | |
| Other | | | | Venturi | |
| Water Rate | Not Specified | Not Specified | 45 GPM | 110 GPM | Not Specified |
| Design or Operating Temp. - F° | 109 | 100 | 86 | 1600 | 65 |
| Gas Rate - SCFM (lb./hr.) | 42,000 | 43,100 | 3,600 | 4 600 | 17,000 |
| Height (T-T), Ft. | Not Specified | Not Specified | 16.5 | Not Specified | Not Specified |
| Diameter - Ft. | Not Specified | Not Specified | 42 | Not Specified | Not Specified |
| Washed Gases to Stack | | | | | |
| Stack Height - Ft. | 79 and 99 | 90 | 20 | 36 | 72 |
| Stack Diameter - Inches | 24 | 42 | 14 | 14 | 24 |
| Installed Cost - Mat'l. & Labor - $ | Not Specified | Not Specified (a) | Not Specified (a) | Not Specified (a) | Not Specified |
| Installed Cost - Mat'l. & Labor - c/lb. MAN/Yr. | | | | | |
| Operating Cost - Annual - $ | | | | | |
| Operating Cost - c/lb. MAN/Yr. | | | | | |
| Efficiency - % | | | | | |

(a)  Total cost of all pollution control devices plus incinerator is $610,000.

**WATER SCRUBBERS**

| | MAN-5 | MAN-6 | MAN-7 | MAN-8 | MAN-9 | MAN-10 |
|---|---|---|---|---|---|---|
| Flow Diagram Stream I. D. | | | | | | |
| Device I. D. No. | MAN-5 | MAN-6 | MAN-7 | MAN-8 | MAN-9 | MAN-10 |
| EPA Code Number of plant | 18-4 | 18-5 | 18-6 | 18-6 | 18-7 | 18-7 |
| Purpose - Control Emission of | Maleic Anhydride | Maleic Anhydride | Maleic Anhydride | Maleic Anhydride | Maleic Anhydride | Maleic Anhydride |
| Type - Spray | X | Not Specified | Not Specified | | Not Specified | X |
| Packed Column | | | | | | |
| Trays - Type | Bubble Cap | | | | | |
| Number | Not Specified | | | | | |
| Plenum Chamber | | | | | | |
| Other | | | | Venturi | | |
| Water Rate | 17 - 37 GPM | Not Specified | Not Specified | Not Specified | Not Specified | 20 - 30 GPM |
| Design or Operating Temp. - F° | 100 | 100 | 140 | 50 | 104 | 70 - 100 |
| Gas Rate - SCFM (lb./hr.) | 30,000 | 42,000 | 78,000 | 45 | 20,000 | 7,000 |
| Height (T-T), Ft. | 22.5 | Not Specified | Not Specified | Not Specified | Not Specified | 15 |
| Diameter - Ft. | 11 | Not Specified | Not Specified | Not Specified | Not Specified | 4 |
| Washed Gases to Stack | | | | | | |
| Stack Height - Ft. | 74 | 65 | Not Specified | 9.5 | | 30 |
| Stack Diameter - Inches | 24 | 36 | Not Specified | 3 | | 24 |
| Installed Cost - Mat'l. & Labor - $ | 80,000 | Not Specified | Not Specified | 11,000 | Not Specified | 50,000 |
| Installed Cost - Mat'l. & Labor - ¢/lb. MAN/Yr. | 0.24 | | | 0.01 | | 0.17 |
| Operating Cost - Annual - $ | 12,500 | | | 230 | | 7,800 |
| Operating Cost - ¢/lb. MAN/Yr. | 0.04 | | | | | 0.03 |
| Efficiency - % | Unknown | | | Unknown | | Unknown |

INCINERATION DEVICES

| | | |
|---|---|---|
| Flow Diagram Stream I. D. | | |
| Device I. D. No. | MAN-11 | Proposed |
| EPA Code Number of plant | 18-2 | 18-4 |
| Types of Compounds Incinerated | Aqueous Wastes | Organic Vapors. CO [b] |
| Type Device | Incinerator | Boiler & Incinerator |
| Materials Incinerated, SCFM (lb./hr.) | (3400) Includes Water | 30,000 Includes Air |
| Auxiliary Fuel Required (excl. pilot) | Yes | Yes |
| Auxiliary Fuel Type | Natural Gas | Natural Gas/Oil |
| Auxiliary Fuel Rate - MM BTU/Hr. | 12 (Max.) | Not Specified |
| Device Elevation - Ft. above grade | Not Specified | Not Specified |
| Installed Cost - Mat'l & Labor - $ | Not Specified [a] | 1,000,000 Total |
| Installed Cost - Mat'l. & Labor - c/lb. of MAN | | Not Applicable |
| Operating Cost - Annual - $ | | Not Available |
| Operating Cost - c/lb. of MAN | | Not Available |
| Efficiency - CCR - % | 99+ (Expected) | 99+ (Expected) |
| Efficiency - SERR - % | Near 100 (c) | Near 100 (c) |

(a) Total installed cost for all pollution control devices including scrubbers is $610,000.

(b) Scrubber vent will supply combustion air to new gas/oil fired boiler-incinerator, which will eliminate odors, hydrocarbon emissions and carbon monoxide from this source. New boiler-incinerator will replace existing coal-fired boiler for steam generation.

(c) Depends upon time/temperature relationship for NOx formation.

TABLE MA-V
NUMBER OF NEW PLANTS BY 1980

| Current Capacity | Marginal Capacity | Current Capacity on-stream in 1980 | Demand 1980 | Capacity 1980 | Capacity to be Added | Economic Plant Size | Number of New Plants |
|---|---|---|---|---|---|---|---|
| 390 | 30 | 360 | 720 | 720 | 360 | 60 | 6 |

NOTE:  All capacities in MM lbs./year.

TABLE MA-VI
EMISSION SOURCE SUMMARY*
TON/TON MALEIC ANHYDRIDE

| Emission | Source | |
| --- | --- | --- |
| | Scrubber Vent | Storage Losses and Fugitive Emissions |
| Hydrocarbons | .086 | Note (1) |
| Particulates | .. | Note (2) |
| $NO_x$ | | |
| $SO_x$ | | |
| CO | .670 | |

NOTES:

(1) There will be small amounts of hydrocarbon emissions from storage tanks but the amount is not available.

(2) Fugitive dust emissions will mostly be composed of maleic anhydride powder from the pelletizing, handling and storage operations of maleic anhydride. The amount is not indicated and will vary from plant to plant depending on operations.

TABLE MA-VII
WEIGHTED EMISSION RATES

Chemical _____ Maleic Anhydride _____

Process _____ Oxidation of Benzene _____

Increased Capacity by 1980 ___ 360 MM Lbs./Year _____

| Pollutant | Emissions, Lb./Lb. | Increased Emissions MM Lbs./Year | Weighting Factor | Weighted Emissions MM Lbs./Year |
|---|---|---|---|---|
| Hydrocarbons | .086 | 31 | 80 | 2,480 |
| Particulates | | | 60 | |
| $NO_x$ | | | 40 | |
| $SO_x$ | | | 20 | |
| CO | .670 | 241 | 1 | 241 |

Significant Emission Index = 2,721

**Nylon 6**

## Table of Contents

## List of Illustrations and Tables

I. Introduction

Nylon 6, $H[HN(CH_2)_5CO]_nOH$, is a linear aliphatic polyamide. It can be either spun into a fiber or made into a molding resin. The fiber is used for apparel, home furnishings, tire cord and industrial applications, while the resin is used for films, coatings for wires and cables, automotive parts and numerous other industrial and consumer applications.

Nylon 6 is produced commercially by the continuous polymerization of caprolactam, $HN(CH_2)_5CO$.

In the old process the polymer was produced by batch polymerization, but because the reaction produces no water it was relatively easy to put the process on a continuous basis. Small quantities of the polymer are still produced by the old method.

Today, nylon 6 capacity stands at around 500 MM lbs./year. It is expected that by 1980 the capacity will reach 1.5 billion lbs./year, requiring about ten new nylon 6 plants each having a capacity of 100 MM lbs./year.

Air emissions associated with nylon 6 polymerization are caused by small vents from numerous process operations. In general, the process could be characterized as a moderately low polluter.

## II.  Process Description

Nylon 6 is produced by the continuous polymerization of caprolactam.

$$n \; HN(CH_2)_5CO \quad \xrightarrow{\;+\;H_2O\;} \quad H\left[HN(CH_2)_5CO\right]_n OH$$
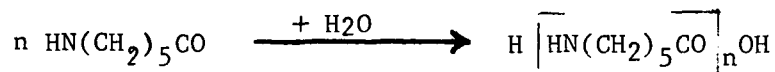
The mechanism of the reaction is considered to involve an addition reaction of an open lactam ring into the growth chain initiated by the combined catalytic effect of water and acid groups.  Contrary to amino acid polymerization, the reaction does not involve any significant removal of water since only small amounts are used as catalyst.  The overall reaction is an equilibrium reaction with conversions of monomer of 85 to 90%.  A substantial amount of oligomers (5%) are formed and they must be removed in part (1-2% of product) if high quality polymer is desired.

The following is a description of a typical process to produce nylon 6 (see Figure NYL 1).

Molten caprolactam is mixed with water, catalysts, stabilizer and delusterant (if fibers are to be made) and is fed into a reactor which is operated at about 500° F.  The mass slowly proceeds down the reactor which is usually divided into several zones.  The overall reaction is slightly exothermic and heat exchange is provided by dowtherm.  The reactor effluent consists of molten polymer, monomer, oligomers and water.  Monomer and oligomer constitute 10-15% of the reactor effluent.

There are two methods being used to purify the crude polymer and recover unreacted polymer.  In the first, the polymer is cast into ribbon form, quenched and cut into chips.  Unreacted monomer and some oligomer are removed from the chips by extraction with hot water.  The water is sent to monomer recovery where the oligomers are depolymerized and the monomer is dehydrated and returned to the system.  The chips are dried and are then ready for melting and spinning or bagging.

In the second method, the molten polymer exiting from the reactor is sent to a vacuum distillation column where monomer, water and oligomers are removed overhead.  The molten polymer can then be spun directly into fibers or cut into chips for bagging.

III.  Plant Emissions

    A.  Continuous Air Emissions

        A majority of the air pollution associated with nylon 6 polymerization is caused by small vents from a number of process units.  Although plant 19-3 was the only respondent to report any emission control devices from these sources, it is believed that other producers use vent condensers to recover some caprolactam   The following is a description of the sources of air emissions from the nylon 6 process.

        1. 'Mix and Spin Tank Vents

        Only respondent 19-4 reports losses due to the mixing of molten caprolactam with water and catalysts prior to reaction.  Since the system is nitrogen padded, the main constituent of this vent is nitrogen.  The only noxious emission is .00012 lbs./lb. nylon 6 of caprolactam.

        2.  Polymerization Vent

        Nitrogen present as an inert in the reaction chamber along with some water is purged from the system by venting from the polymerization reactor.  Some caprolactam is carried with the gases to the atmosphere.  Emission rates vary from plant to plant but on the average, about .00034 lbs./lb. nylon 6 of caprolactam enters the atmosphere from this source.

        3.  Chip Formation Vent

        When the molten polymer ribbon is quenched with either cold water or an inert gas, some caprolactam vapor is lost to the atmosphere before the polymer solidifies.  Plant 19-3 reports significant emissions of .00337 lbs./lb. of nylon 6 of caprolactam.

        4.  Nylon Chip Slurry Tank

        Plant 19-4 reports small losses of caprolactam from the slurry tank prior to the extraction system.

        7.  Depolymerizer Vent

        Oligomers extracted from the product are in many plants depolymerized to caprolactam.  Some caprolactam is usually vented to the atmosphere from the depolymerizing reactor.  The quantity released varies from insignificant to significant quantities.

        6.  Pellet Drying

        Small amounts of caprolactam are lost when the extracted pellets are dried with an inert gas or air.  The quantity released to the atmosphere is small.

        8.  Caprolactam Recovery Vent

        Plant 19-3 reports that trace amounts of caprolactam are lost during the caprolactam recovery distillation process.

B. Intermittent Air Emissions

    1. Equipment Cleaning Furnaces

    Equipment such as filters, etc., which become fouled with polymer and oligomers are cleaned, in some operations, in a furnace. The two respondents which report such operations claim that only carbon dioxide and water are emitted. One of the plants reports an afterburner, without which, smoking will probably occur.

C. Continuous Liquid Waste

    1. Waste Water

    Waste water discharges and methods of treatment used by nylon 6 producers are summarized below,

| Plant Code No. | Waste Water - GPM | Treatment Used |
|---|---|---|
| 19-1 | .12 | Not Specified |
| 19-3 | 20-50 (cooling water) | Chlorine Treated Evaporative Ponds (Reclaimed) |
| 19-4 | .5 (process) | Untreated |
|  | 1.8 (cooling) | Untreated |

D. Solid Wastes

    Solid waste in the form of oligomers and waste polymer is produced at many installations. The waste can be disposed of in a land fill.

E. Odor

    There are no community odor problems associated with the nylon 6 polymerization process.

F. Fugitive Emissions

    No sources of air emissions due to leaks, spills, etc., were reported. It is assumed that such losses exist but are not significant.

G. Noise

    Although not reported, or requested in the questionnaire, it has been reported by industry that noise from cutters may be an environmental problem.

IV. Emission Control

Details on emission control devices reported by the respondent can be found in Table IV, Catalog of Emission Control Devices. A brief description of the devices follows:

### Condensers

Plant 19-3 employs vent condensers to lower emissions and increase recovery of caprolactam from the polymerization reactor vent and the caprolactam recovery column vent.

### Scrubbers

Spray type scrubbers are employed in plant 19-3 to reduce emissions from the pelletizer vent and the depolymerizer vent.

### Afterburner

Plant 19-3 employs an afterburner to insure that only carbon dioxide and water exit from the equipment cleaning furnace. The operator reports that the exhaust is smokeless and odorless so complete combustion is assumed.

V. <u>Significance of Pollution</u>

It is recommended that no in-depth study be made of the subject process. The quantity of air emissions released as air pollutants is less for this process than for processes currently under in-depth study.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980 and to estimate the total weighted annual emission of pollutants from these new plants. This work is summarized in Tables V, VI and VII.

On a weighted emission basis, a Significant Emission Index of 194 has been calculated in Table VII. Hence, the recommendation to exclude an in-depth study of Nylon 6 Polymerization from the overall scope of work for this project.

VI. <u>Nylon 6 Producers</u>

| <u>Company</u> | <u>Location</u> | <u>Capacity - MM Lbs./Year</u> |
|---|---|---|
| Allied Chemical Co. | Chesterfield, Va. | 238 |
| American Enka Corp. | Enka, N. C. | 79 |
|  | Lowland, Tenn. | 20* |
| Dow Badische Co. | Freeport, Texas | 80 |
| Firestone Tire & Rubber Co. | Hopewell, Va. | 47 |
|  | Pottstown, Pa. | 2* |
| Foster Grant Co. | Leominster, Mass. | 5* |
| Gulf Oil Corp. | Henderson, Ky. | 5* |
| Rohm & Haas Co. | Fayetteville, N. C. | 10* |
|  |  | Total - 486 |

*Capacities are approximate.

TABLE NYL-I
MATERIAL BALANCE
NYLON 6 (1)
T/T NYLON 6

| Fresh Caprolactam | Recycle Caprolactam (2) | Polymer | | Waste (Oligomers & Waste Polymer) |
|---|---|---|---|---|
| | | Nylon 6 | Oligomers | |
| 1.147 | .146 | .985 | .015 | .001 |

(1)  Based on information found in literature and respondents comments.

(2)  Unreacted caprolactam and caprolactam recovered from oligomer depolymerization.

TABLE NYL-II
HEAT BALANCE
NYLON 6

There is insufficient information available on which to base an overall energy balance for Nylon 6 polymerization.

| | Hot Melt Filter Vent | Wash Water Recovery Vacuum Jet Exhaust | Pellet Drying | Vaporized Benzene from Waste Water | Equipment Cleaning Furnace Afterburner Exhaust |
|---|---|---|---|---|---|
| Plant EPA Code Number | | | 19-1 | | |
| Capacity - Tons/Yr. of Nylon 6 | | | 40,000 | | |
| Production - Tons/Yr. of Nylon 6 | | | 40,000 | | |
| Emissions to Atmosphere | | | | | |
| Stream I. D. No. (Figure NYL-I) | | | D | | |
| Stream | | | | | |
| Flow - Lbs./Hr. | 6200 SCFM | Never Measured | 1363 | | ~318 SCFM |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous | Intermittent |
| if Intermittent - Hrs./Yr. | | | | | 416 |
| Composition - Ton/Ton of Nylon 6 | | | | | |
| Caprolactam | .000001 | | | | |
| Benzene | | + | | .003852 | |
| Nitrogen | | | .143169 | | |
| Air | (1) | (2) | | | |
| Water | (1) | | .005618 | | (3) |
| Carbon Dioxide | | | | | (3) |
| Oligomer | | | | | |
| Phosphoric Acid | | | | | |
| Hydrogen | | | .000153 | | |
| Vent Stacks | Yes | Yes | | | |
| Number | 1 | 1 | | | |
| Height - Feet | 36 | 46 | | | |
| Diameter - Inches | 19.5 by 14.5 | 2 | | | |
| Exit Gas Temp. - F° | 100 | 90 | | | |
| Flow - SCFM | 6200 | | | | |
| Emission Control Devices | No | No | | | |
| Type | | | | | |
| Analysis | Yes | None | | | |
| Sample Tap Location | None | | | | |
| Date or Frequency of Sampling | March, 1972 | | | | |
| Type of Analysis | Chromatograph | None | | | |
| Odor Problem | No | No | | | |
| Summary of Air Pollutants | | | | | |
| Hydrocarbons - Ton/Ton of Nylon 6 | | | 003852 | | |
| *Particulates & Aerosols - Ton/Ton of Nylon 6 | | | .000001 | | |
| $NO_x$ - Ton/Ton of Nylon 6 | | | 0 | | |
| $SO_x$ - Ton/Ton of Nylon 6 | | | 0 | | |
| $CO_x$ - Ton/Ton of Nylon 6 | | | 0 | | |

*Caprolactam vapors are considered as aerosols.

(1) Mostly water and air.
(2) Mostly air.
(3) Complete combustion to $CO_2$ and $H_2O$ reported.

| | | | |
|---|---|---|---|
| Plant EPA Code Number | | 19-2 | |
| Capacity - Tons/Yr. of Nylon 6 | | Confidential (1) | |
| Production - Tons/Yr. of Nylon 6 | | Confidential | |
| Emissions to Atmosphere | | | |
|     Stream I. D. No. (Figure NYL-I) | B | B | B |
|     Stream | Melt Polymerizer | Chip Polymerizer | Depolymerizer Vent |
|     Flow - Lbs./Hr. | 260 | 22 | 477 |
|     Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous |
|       if Intermittent - Hrs./Yr. | | | |
|     Composition - Ton/Ton of Nylon 6 | | | |
|       Caprolactam | + | + | + |
|       Benzene | | | |
|       Nitrogen | Nearly 100% | Nearly 100% | |
|       Air | | | |
|       Water | | | Nearly 100% |
|       Carbon Dioxide | | | |
|       Oligomer | | | |
|       Phosphoric Acid | | | |
|       Hydrogen | | | |
|     Vent Stacks | Yes | Yes | Yes |
|       Number | 1 | 1 | 1 |
|       Height - Feet | 70 | 70 | 70 |
|       Diameter - Inches | 1.44 | 1 44 | .33 |
|       Exit Gas Temp. - F° | 260 | 250 | 212 |
|       Flow - SCFM | | | |
|     Emission Control Devices | Yes | Yes | Yes |
|       Type | Vent Condenser | Vent Condenser | Vent Condenser |
|     Analysis | None | None | None |
|       Sample Tap Location | | | |
|       Date or Frequency of Sampling | | | |
|       Type of Analysis | Material Balance | Material Balance | Material Balance |
|       Odor Problem | No | No | No |
|     Summary of Air Pollutants | | | |
|       Hydrocarbons - Ton/Ton of Nylon 6 | | 0 | |
|       *Particulates & Aerosols - Ton/Ton of Nylon 6 | | + | |
|       $NO_x$ - Ton/Ton of Nylon 6 | | 0 | |
|       $SO_x$ - Ton/Ton of Nylon 6 | | 0 | |
|       CO - Ton/Ton of Nylon 6 | | 0 | |

(1)  Published capacity is 45 MM lbs./year.

Plant EPA Code Number      19-3
Capacity - Tons/Yr. of Nylon 6      119,000
Production - Tons/Yr. of Nylon 6      119,000
Emission to Atmosphere

| | | | | | |
|---|---|---|---|---|---|
| Stream I. D. No. (Figure NYL-I) | B | C | | F | E |
| Stream | Reactor Vent | Pelletizer Vent | Nylon Chip Slurry Tank Vent | Caprolactam Recovery Distillation Column Vent | Depolymerization Reactor Vent |
| Flow - Lbs./Hr. | | | | | |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous | Intermittent |
|   if Intermittent - Hrs./Yr. | | | | | 1800 |
| Composition - Ton/Ton of Nylon 6 | | | | | |
|   Caprolactam | .000960 | .003374 | .000062 | + | Unknown (Small) |
|   Benzene | | | | | |
|   Nitrogen | .064991 | | | | |
|   Air | | .472925 | | | |
|   Water | .041780 | | .001797 | .008605 | Unknown |
|   Carbon Dioxide | | | | | |
|   Oligomer | | | | | |
|   Phosphoric Acid | | | | | |
|   Hydrogen | | | | | |
| Vent Stacks | Yes | Yes | Yes | Yes | Yes |
|   Number | 1 | 1 | 1 | 1 | 1 |
|   Height - Feet | 90 | 95 | Unknown | 90 | 65 |
|   Diameter - Inches | Unknown | 12 | Unknown | Unknown | 12 by 12 |
|   Exit Gas Temp. - F° | 80 | 80 | 78 | ~200° F | Ambient to 120° F |
|   Flow - SCFM | 685 | 2400 | 20 | 235 lbs /hr | 1800 |
| Emission Control Devices | Yes | Yes | No | Yes | Yes |
|   Type | Condenser | Water Spray | | Condenser. Steam Ejector | Water Spray |
| Analysis | No | No | No | No | No |
|   Sample Tap Location | | | | | |
|   Date or Frequency of Sampling | | | | | |
|   Type of Analysis | Estimated | Estimated | Estimated | Estimated | None |
|   Odor Problem | No | No | No | No | No |
| Summary of Air Pollutants | | | | | |
|   Hydrocarbons - Ton/Ton of Nylon 6 | | | 0 | | |
|   *Particulates & Aerosols - Ton/Ton of Nylon 6 | | | .004396 | | |
|   $NO_x$ - Ton/Ton of Nylon 6 | | | 0 | | |
|   $SO_x$ - Ton/Ton of Nylon 6 | | | 0 | | |
|   CO - Ton/Ton of Nylon 6 | | | 0 | | |

| | A | | B | | D |
|---|---|---|---|---|---|
| Plant EPA Code Number | | | | 19-4 | |
| Capacity - Tons/Yr. of Nylon 6 | | | | 39,275 | |
| Production - Tons/Yr. of Nylon 6 | | | | 39,275 | |
| Emissions to Atmosphere | | | | | |
| Stream I. D. No. (Figure NYL-I) | A | | B | | D |
| Stream | Mix Tank Vents | Spin Tank Vents | Polymerization Reactor Vent | Part Cleaning Furnace Off-Gas | Depolymerization Reactor Vent |
| Flow - Lbs./Hr. | | | | | |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Intermittent | Continuous |
| if Intermittent - Hrs./Yr. | | | | Not Specified | |
| Composition - Ton/Ton of Nylon 6 | | | | | |
| Caprolactam | .000005 | .000118 | .000100 | | (2) |
| Benzene | | | | | |
| Nitrogen | .000195 | .001433 | .003233 | | |
| Air | | | | | 254220 |
| Water | | + | .000016 | (1) | |
| Carbon Dioxide | .000001 | | | | |
| Oligomer | | | | (1) | (2) |
| Phosphoric Acid | | | | | (2) |
| Hydrogen | | | | + | |
| Vent Stacks | Not Specified | Not Specified | Not Specified | Not Specified | Not Specified |
| Number | | | | | |
| Height - Feet | | | | | |
| Diameter - Inches | | | | | |
| Exit Gas Temp. - F° | | | | | |
| Flow - SCFM | | | | | |
| Emission Control Devices | No | No | No | No | No |
| Type | | | | | |
| Analysis | None | None | None | No | No |
| Sample Tap Location | | | | | |
| Date or Frequency of Sampling | | | | | |
| Type of Analysis | Estimate | Estimate | Estimate | None | None |
| Odor Problem | | | | | |
| Summary of Air Pollutants | | | | | |
| Hydrocarbons - Ton/Ton of Nylon 6 | | | 0 | | |
| *Particulates & Aerosols - Ton/Ton of Nylon 6 | | | .0262 | | |
| NO$_x$ - Ton/Ton of Nylon 6 | | | 0 | | |
| SO$_x$ - Ton/Ton of Nylon 6 | | | 0 | | |
| CO - Ton/Ton of Nylon 6 | | | 0 | | |

(1) Composition unknown.
(2) A total of 3 vol. %, approximately .026 lbs./lb. nylon 6 (not considered typical).

INCINERATION DEVICES

| | |
|---|---|
| EPA Code No. for plant using | 19-1 |
| Device I. D. No. | IN-I |
| Type of Compound Incinerated | Hydrocarbon and CO (1) |
| Type of Device | After Burner |
| Material Incinerated - SCFM | 800 |
| Auxiliary Fuel - Excluding Pilot | Yes |
| Type | Methane |
| Rate - BTU/hr. | |
| Device or Stack Height - Feet | 9.6 |
| Installed Cost - Mat'l. & Labor - $ | 7,700 |
| Installed Cost based on "year" - dollars | 1971 |
| Installed Cost - c/lb. of Nylon 6/year | .0096 |
| Operating Cost - Annual - $ (1972) | 1900 |
| Net Value of Recovered Heat | |
| Net Operating Cost - $/year | 1900 |
| Net Operating Cost - c/lb. of Nylon 6 | .0024 |
| Efficiency - CCR (1) | 100% |

(1)  For explanation and definition see Appendix V.

SCRUBBERS

| | | |
|---|---|---|
| EPA Code No. for plant using | 19-3 | 19-3 |
| Flow Diagram (Fig. Nylon 1) Stream No. | C | E |
| Device I. D. No. | SC-I | SC-II |
| Control Emission of | Caprolactam | Caprolactam |
| Scrubber Type | Spray Eductor | Duct Spray |
| Scrubbing Liquid | Water | Water |
| Scrubbing Liquid Rate - GPM | | |
| Operating Temp. - F$^o$ | | |
| Gas Rate - SCFM | | |
| Washed Gases to Stack | Yes | Yes |
|     Stack Height - Ft. | 95 | 65 |
|     Stack Diameter - Inches | 12 | 12 by 12 |
| Installed Cost - Mat'l. & Labor - $ | 45,000 | 40,200 |
| Installed Cost based on "year" - dollars | 1973 | 1961 |
| Installed Cost - c/lb. of Nylon 6/year | .018 | .017 |
| Operating Cost - Annual - $ | 2200 | |
| Value of Recovered Product - $ | | |
| Net Operating Cost - c/lb. Nylon 6 | .009 | |
| Efficiency - % - SE (1) | | |
| Efficiency - % - SERR (1) | | |

CONDENSERS

| | | |
|---|---|---|
| Type | Heat Exchanger | Stream Ejector and Condenser |
| EPA Code No. for plant using | 19-3 | 19-3 |
| Flow Diagram (Fig. Nylon 1) Stream No. | B | F |
| Device I. D. No. | CON-I | CON-II |
| Control Emission of | Caprolactam | Caprolactam |
| Cooling Liquid | Water | Steam |
| Cooling Liquid Rate | | |
| Gas Rate - SCFM | ~700 | |
| Temperature to Condenser - F$^o$ | | |
| Temperature out of Condenser - F$^o$ | | |
| Quantity Condensed - lbs./hr. | | |
| Non-Condensibles - SCFM | | Trace |
| Installed Cost - Mat'l. & Labor - $ | 60,000 | 1,500 |
| Installed Cost based on "year" - dollars | 1961 - 1970 | 1968 |
| Installed Cost - c/lb. of Nylon 6/year | .025 | .006 |
| Operating Cost - Annual - Annual - $ (1972) | 11,000 | 1400 |
| Value of Recovered Product - $ | 340,000 | |
| Net Operating Cost - Annual - $ | 329,000 | 1400 |
| Net Operating Cost - c/lb. of Nylon 6 | (.138) | (.006) |
| Efficiency - % - SE (1) | | Near 100% |
| Efficiency - % - SERR (1) | | Near 100% |

TABLE NYL-V
NUMBER OF NEW PLANTS BY 1980
NYLON 6

| Current Capacity (1) | Marginal Capacity | Current Capacity on-stream in 1980 | Demand 1980 | Capacity to be Added | Economic Plant Size | Number of New Units |
|---|---|---|---|---|---|---|
| 486 | 0 | 486 | 1500 (2) | 1014 | 100 | 10 |

(1)  MM lbs./year.

(2)  Process Research, Inc., report for the EPA.

TABLE NYL-VI
EMISSION SOURCE SUMMARY
NYLON 6
T/T NYLON 6

| Pollutant | Source | | | | | Total |
|---|---|---|---|---|---|---|
| | Mixing Tank Vents | Reactor Vent | Pellet Formation Washing & Drying Vents | Furnace Cleaning | Caprolactam Recovery | |
| Hydrocarbon | 0 | 0 | 0 | 0 | 0 | 0 |
| Aerosols & Particulates [1] | .00012 | .00034 | .00172 | 0 | 0.001 | 0.00318 |
| $NO_x$ | 0 | 0 | 0 | Trace | 0 | Trace |
| $SO_x$ | 0 | 0 | 0 | 0 | 0 | 0 |
| CO | 0 | 0 | 0 | 0 | 0 | 0 |

(1)  Caprolactam is considered an aerosol.

TABLE NYL-III
WEIGHTED EMISSION RATES

Chemical _____ Nylon 6 _____

Process _____ Continuous Polymerization of Caprolactam

New Added Capacity _____ 1,014 MM Lbs./Year _____

| Pollutant | Emissions, Lb./Lb. | Increased Emissions MM Lbs./Year | Weighting Factor | Weighted Emissions MM Lbs./Year |
|---|---|---|---|---|
| Hydrocarbons | 0 | 0 | 80 | 0 |
| Aerosols & Particulates [1] | .00318 | 3.2 | 60 | 194 |
| $NO_x$ | Trace | 0 | 40 | 0 |
| $SO_x$ | 0 | 0 | 20 | 0 |
| CO | 0 | 0 | 1 | 0 |

Significant Emission Index = 194

# Nylon 6,6

# Table of Contents

I.  Introduction

Nylon 6,6 is synthesized from its monomer, hexamethyl diammonium adipate or nylon salt, by polymerizing the monomer to a molecular weight of 12,000 to 20,000 under temperature and pressure.  Nylon salt is made by neutralization of aqueous solutions of its components, hexamethylene diamine and adipic acid.

There are two processes used to make nylon 6,6.  The older process is batch polymerization, which usually ends with the nylon  6,6 as a flake or pellet, which may then be remelted and spun to yarn.  The second process, the newer of the two, is a continuous polymerization and spinning process, which produces a nylon yarn or filament directly.

Although there is a large installed capacity for nylon 6,6 production, some 1.5 billion pounds annually, the amount of air pollution associated with these plants is comparatively small on a mass emission basis.  However, depending on plant size, the emissions which can produce a "blue haze" may become sufficiently significant to make their abatement desirable.  In such circumstances the most conventional abatement approach is scrubbing.  This produces a biodegradable liquid waste.  One plant estimates a $4  million investment in its combined air-liquid abatement facilities.  A modest amount of solid waste is generated which has no commercial value .

## II.  Process Description

Nylon 6,6 is made by polymerization of nylon salt (hexamethylene diammonium adipate) from an aqueous suspension at elevated temperature and pressure. Two processes are  in general use, batch and continuous.  Nylon salt is usually stored as a 10 - 20% aqueous solution and can easily be made from aqueous solutions of adipic acid and hexamethylene diamine.

Batch Process - the reaction is:

(a)  Neutralization

$$HOOC \cdot (CH_2)_4 \cdot COOH + H_2N \ (CH_2)_6 \cdot NH_2 \longrightarrow OOC \cdot (CH_2)_4 \cdot COO^- \ \ ^+H_3N \cdot (CH_2)_6 \cdot NH_3^+$$

| Adipic Acid | Hexamethylene Diamine | Hexamethylene Diammonium Adipate (Nylon Salt) |
|---|---|---|
| Mol. Wt.    146.1 | 116.2 | 262.3 |

(b)  Polymerization

$$Nylon\ Salt \longrightarrow \left[ \overset{O}{\overset{..}{C}} \ (CH_2)_4 - \overset{O}{\overset{..}{C}} - \overset{H}{N} - (CH_2)_6 - \overset{H}{N} \right]_n + 2n\ H_2O$$

Nylon 6,6
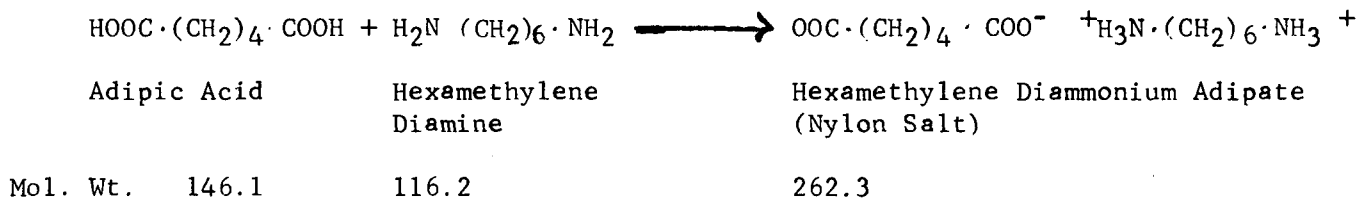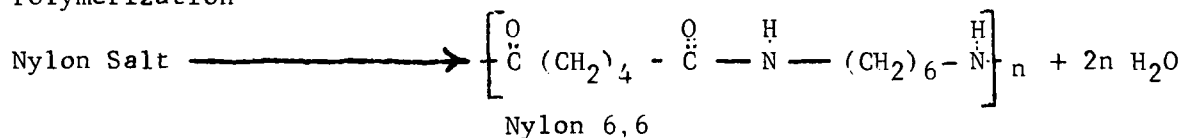
Mol. Wt. (repeat unit)  226.8

Nylon monomer (nylon salt) is usually fed as a water suspension or homogeneous mixture to an evaporator where it is concentrated to a 50 - 60% aqueous slurry by removal of water.  This aqueous slurry together with additives such as 0.5% by weight acetic acid as a chain terminator (viscosity, m. wt. control), $TiO_2$ as a delusterant, are pumped to an autoclave reactor. Here temperature is increased to $260^o$ - $280^o$ C ($\sim520^o$ F) and pressure is allowed to build to 250 PSIG by controlled venting of the  steam produced from the condensation polymerization.  Any water remaining after this point is reached is then removed by lowering the pressure to atmospheric while maintaining a constant temperature.  The polymer (12,000 - 20,000 m.w.) is a clear melt which is removed from the reactor under nitrogen, cooled and cast (pelletized) quickly as it is not stable at high temperatures.  The solid nylon 6,6 resin is flaked or chipped and can then go to product storage.  These flakes can be remelted and spun into filaments or molded to various shapes.

### Continuous Process

A more recent development in nylon 6,6 manufacture is the continuous process.  The chemistry of this reaction is identical to the batch process. However, where it may take 2 - 4 hours to convert nylon salt to finished polymer in the batch process, monomer goes to polymer in the continuous process in about 5 minutes, but with a relatively higher investment per unit produced.

Nylon salt solution is fed to a thin film evaporator at about $230^o$ F, where the bulk of the water of solution is removed.  Any additives needed are generally added after the evaporation stage and these plus the dewatered monomer are fed to another thin film evaporator held at $450^o$ F and elevated pressure where the condensation polymerization takes place and the water is removed as steam.  Molten polymer goes  to a "flasher" at atmospheric pressure to remove more water of condensation.  The polymer may be put thru a finishing

step at 540° F to be sure polymerization is complete or it may by-pass this step.  In any event the hot molten polymer goes directly to spinning, drawing and beaming operations rather than cooling and casting into resin as in the batch process.

III. Plant Emissions

A. Continuous Air Emissions - Batch & Continuous Processes

1. Evaporator Off-Gas - Code Letter (A) on drawing

Both respondents report essentially all steam from this source with very small traces of hexamethylene diamine present. No scrubbing or incinerator devices are used. No odors were reported.

2. Reactor or Polymerizer Off-Gas - Code Letter (B) on drawing

Again the main constituent of this vent stream is steam with small amounts of hexamethylene diamine. The presence of monomer and polymer is noted as detectable and has the potential for causing off-plant odors. One plant is installing scrubbers to control this potential odor source and the attendant "blue haze" which periodically forms.

3. Flasher or Separator Off-Gas - Continuous Process - Vent (C)

This stream is reported to be similar in composition to the reactor off-gas (code letter C) but much less in terms of lb. gas per lb. finished product. No odors were reported.

4. Finisher Exhaust - Code Letter (D) - Continuous Process

Not all continuous processes employ a finishing step after the high pressure reaction - atmospheric pressure flashing step. Those that do, report very small emissions compared to the other stages. This stream is normally not scrubbed although one respondent scrubs this stream with a water spray in some of his units. No odor problems were reported.

5. Miscellaneous Streams

(a) When the flaked nylon resin is pneumatically conveyed, the conveying gas can be a source of emissions to the atmosphere. The one piece of data on this stream, a cyclone exhaust shows only minimal traces of water vapor, hexamethylene diamine and nylon.

(b) One respondent showed an emission from the spinning operation. Presumably this is cooling air contaminated with infinitesimal quantities of particulates, hydrocarbons and nylon 6,6. The stream was not scrubbed and no estimate of quantity was available.

(c) Nylon scraps (see also D-Solid Wastes). One respondent reports incineration of about 0.003 lb. nylon scraps per lb. nylon 6,6. Complete incineration of the scraps would give roughly 0.00123 lb. $NO_x$ per lb. nylon 6,6. No data on this incineration are available.

B. Intermittent Air Emissions

No intermittent air emissions were reported.

C. Continuous Liquid Wastes

Only one respondent reported waste water quantities from the processes as follows:

| Process Type | Waste Water from | GPM | Treatment |
|---|---|---|---|
| Batch | Casting | 36 | in-plant |
| Continuous | Not Specified | 135 | in-plant |

D. Solid Wastes

Operator of plant EPA code 20-1 reports production of 1,160 lbs. per day of casting scraps (nylon polymer), which are incinerated. Plant code EPA 20-3, a continuous process reports "no solid wastes associated with this process". No comment was available from another respondent.

E. Odors

The polymerization of nylon salt to nylon 6,6 is a process for which no odor problems or complaints were reported. The odor of hexamethylene diamine is detectable at times on site and under some atmospheric conditions it may also be detected beyond the plant borders.

F. Fugitive Emissions

Neither respondent reports any fugitive losses. The only comment was that there are "no other known emissions although minor leakages probably occur".

G. Other Emissions

Fuel oil for heating was reported by only one respondent. About 56 million lbs. of fuel oil are consumed at amaximum of 3% sulfur (estimated average is 2.5%). At the maximum level, this is 1.7 million lbs. of S per year or 3.4 million lbs. $SO_2$ per year, the largest single reported source of pollution in the process (0.0093 lbs. $SO_2$/lb. nylon 6,6).

Dowtherm is used for a heat transfer medium. Losses here are 75 gal./year (one source of data), which is insignificant.

IV. Emission Control

Two plants report using emission control devices. One instance is a water scrubber used on the exhaust from the finishing operations. Water is the scrubbing medium and the effluent is treated in-plant before discharge to the sewer. The following efficiencies were calculated on the basis of reported data.

SE* - Specific Efficiency - 99.7%.

SERR* - Significance of Emission Reduction Rating - 99.7%.

The other plant is in the process of adding scrubbers to their polymerizer equipment which they consider to be the major source of air pollution from the process ("blue haze" and hexamethylene diamine odor).

*See Appendix V for explanation of these terms.

## V. Significance of Pollution

It is recommended that no in-depth study of this process be made. Emissions are low and roughly equal to the combustion product emissions from the fuels used in some of the plants.

A modest 10% per year growth is projected for the period up to 1980. Even if this growth were off by 50 to 100%, the Significance of Emission Index* would still be low. An SEI of 318 has been calculated for this process. Doubling this figure would still leave the process in the low pollution category. Emissions consist mostly of particulates (hexamethylene diamine is the major component), which could easily be removed by water scrubbing (as one respondent is doing) should this ever be necessary.

*See Appendix IV for an explanation of this term.

## VI.  Producers of Nylon 6,6 Resins and Fibres from Monomer

The capacities and plant locations listed below are based on information provided in the questionnaire and in the literature.

| Company | Location | MM Lbs. 1971 Capacity |
|---|---|---|
| **Fibre Producers** | | |
| Allied Chem. Fibres Div. | W. Conshohocken, Pa. | N. A. |
| E. I. duPont | Camden, S. C. | 40 |
| | Chattanooga, Tenn. | 140 |
| | Martinsville  Va. | 100 |
| | Richmond, Va. | 200 |
| | Seaford, Del. | 365 |
| Beaunit Corporation | Etowah, Tenn. | |
| | Odessa, Texas | 100 |
| Fibre Industries, Inc. | Greenville  S. C. | 80 |
| | Guazama, P. R. | 60 |
| Monsanto | Greenwood, S. C. | 100 |
| | Pensacola, Florida | 240 |
| Rohm & Haas, Sauquoit Fibres Div. | Scranton, Pa. | 4 |
| | | Sub - 1,429 |
| **Resin Producers** | | |
| Celanese Corporation | La Porte, Texas | 12 |
| DuPont Plastics Department | Parkersburg, W. Va. | 70 |
| Beaunit Corporation | Etowah, Tenn. | 2 |
| Monsanto Corporation | Pensacola, Florida | 10 |
| | | Total - 1,523 |

PAGE NOT

AVAILABLE

DIGITALLY

TABLE N6,6-I
MATERIAL BALANCE

The conversion of nylon 6,6 salt (hexamethylene diammonium adipate) to nylon 6,6 polymer is almost 100% of theoretical according to the literature and data surveyed. A comparison of actual reported yields vs theoretical is shown below:

| Source | Lb. Adipic Acid per Lb. Nylon 6,6 | Lb. Hexamethylene Diamine per Lb. Nylon 6,6 | Lb. Nylon 6,6 Polymer | Lb. Water per Lb. Nylon 6,6 |
|--------|------------------------|--------------------------------|-----------------|------------------|
| Theory | 0.646 | 0.513 | 1.000 | 0.159 |
| Actual | 0.653 | 0.521 | 1.000 | 0.174* |

*includes waste products which are reported minimal.

TABLE N6,6-II
GROSS REACTOR HEAT BALANCE

There are not sufficient published data available to permit the construction
of a detailed heat balance for this proces.

| | 20-1 | | | 20-2 | |
|---|---|---|---|---|---|
| Plant Code No. | | | | | |
| Capacity - Tons Nylon 6,6/Year | | 75,000 | | 93,500 | |
| Range in Production - % of Max. | None | None | None | None | None |
| Emissions to Atmosphere | | | | | |
| Stream | (A) - Evaporator Off-Gas | (B) Autoclave Off-Gas | (C) Conveyor Air Exhaust | (IA) - Evaporator Off-Gas | (IB) - Autoclave Off-Gas |
| Flow - Lbs./Hr. | 4700 | 540 | 7500 | 4708 | 610 |
| Flow Characteristic | Continuous | Continuous | Continuous | Continuous | Continuous |
| Composition, Ton/Ton Nylon 6,6 | | | | | |
| Nylon Salt | + | + | | + | + |
| Water | 0.274700 | 0.031480 | + | 1.10500 | 0.61000 |
| Hexamethylene Diamine | 0.000175 | 0.000090 | + | 0.00090 | 0.00200 |
| Adipic Acid | + | + | | | |
| Nylon 6,6 Polymer | | | + | | + |
| Cyclopentanone | | | | | |
| Halides | | | | | |
| Tot. Organic Carbon | | | | | |
| Sulfonamide | | | | | |
| Vent Stacks | | | | | |
| Number | 1 | 1 | 1 | 5 | 21 |
| Height - Feet | 10 | 26 | Cyclone | 86 | 88 |
| Diameter - Inches | 8 | 4 | | 8 | 4 |
| Exit Gas Temp., °F | 155° | 400° | 129° | 360° | 300° |
| SCFM/Stack | 1665 | 178 | 5400 | 1650 | 216 |
| Emission Control Devices | | | | | |
| Type | None | None | None | None | None |
| Analyses | | | | | |
| Date or Frequency of Sampling | Never | Never | Never | Occasional | Occasional |
| Sample Location | | | | | |
| Type of Analysis | Calc'd. | Calc'd. | Calc'd. | TIT, GC, GRAV, TOC | TIT, GC, GRAV, TOC |
| Odor Problem | No | No | No | No | No |
| Summary of Air Pollutants | | | | | |
| Hydrocarbons, Ton/Ton Nylon 6,6 | | 0 | | | 0 |
| Particulates & Aerosols - Ton/Ton Nylon 6,6 | | 0.000265 | | | 0.002900 |
| $NO_x$ - Ton/Ton Nylon 6,6 | | 0 | | | 0 |
| $SO_x$ - Ton/Ton Nylon 6,6 | | 0 | | | 0 |
| CO - Ton/Ton Nylon 6,6 | | 0 | | | 0 |

| | | | | |
|---|---|---|---|---|
| Plant Code No. | ←——————————————— 20-2 ————————————————→ | | | |
| Capacity - Tons Nylon 6,6/Year | 36,500 | | | |
| Range in Production - % of Max. | None | None | None | None |
| Emissions to Atmosphere | | | | |
|   Stream | (IIA) - Evaporator Off-Gas | (IIB) - Reactor Off-Gas | (IIC) - Separator Off-Gas | (IID) Finisher Exhaust |
|   Flow - Lbs./Hr. | 1422 | 4554 | 980 | 730 |
|   Flow Characteristic | Continuous | Continuous | Continuous | Continuous |
|   Composition, Ton/Ton Nylon 6,6 | | | | |
|     Nylon Salt | + | + | + | + |
|     Water | 0.34100 | 1.09300 | 0.23500 | 0.17500 |
|     Hexamethylene Diamine | 0.00009 | 0.00350 | 0.00350 | 0.00013 |
|     Adipic Acid | | | | |
|     Nylon 6,6 Polymer | | + | + | + |
|     Cyclopentanone | | | | |
|     Halides | | | | |
|     Tot. Organic Carbon | | | | |
|     Sulfonamide | | | | |
| Vent Stacks | | | | |
|   Number | 2 | 2 | 2 | 2 |
|   Height - Feet | 88 | 95 | 83 | 88 |
|   Diameter - Inches | 4 | 12 | 2½ | 4 |
|   Exit Gas Temp., °F | 265° | 330° | 600° | 300° |
|   SCFM/Stack | 450 | 1490 | 325 | 240 |
| Emission Control Devices | | | | |
|   Type | None | None | None | None |
| Analyses | | | | |
|   Date or Frequency of Sampling | Occasional | Occasional | Occasional | Occasional |
|   Sample Location | | | | |
|   Type of Analysis | TIT, GRAV, TOC | TIT, GRAV, TOC | TIT, GRAV, TOC | ? |
|   Odor Problem | No | No | No | No |
| Summary of Air Pollutants | | | | |
|   Hydrocarbons - Ton/Ton Nylon 6,6 | | 0 | | |
|   Particulates & Aerosols - Ton/Ton Nylon 6,6 | | 0.007200 | | |
|   $NO_x$ - Ton/Ton Nylon 6,6 | | 0 | | |
|   $SO_x$ - Ton/Ton Nylon 6,6 | | 0 | | |
|   $CO_x$ - Ton/Ton Nylon 6,6 | | 0 | | |

| | | | | |
|---|---|---|---|---|
| Plant Code No. | ←———————— | 20-2 | ———————— | —→ |
| Capacity - Tons Nylon 6,6/Year | | 38,000 | | |
| Range in Production - % of Max. | None | None | None | |
| Emissions to Atmosphere | | | | |
| Stream | (IIIA) Evaporator Off-Gas | (IIIB) Reactor Off-Gas | (IIIC) Separator Off-Gas | (IIID) Finisher Exhaust |
| Flow - Lbs./Hr. | 6080 | 6080 | 1130 | 560 |
| Flow Characteristic | Continuous | Continuous | Continuous | Continuous |
| Composition - Ton/Ton Nylon 6,6 | | | | |
| Nylon Salt | + | + | + | + |
| Water | 0.70200 | 0.70200 | 0.13050 | 0.064700 |
| Hexamethylene Diamine | 0.00016 | 0.00180 | 0.00066 | 0.000003 |
| Aidpic Acid | | | | |
| Nylon 6,6 Polymer | | + | + | + |
| Cyclopentanone | | | | |
| Halides | | | | |
| Tot. Organic Carbon | | | | |
| Sulfonamide | | | | |
| Vent Stacks | | | | |
| Number | 1 | 1 | 1 | 1 |
| Height - Feet | 101 | 112 | 101 | 101 |
| Diameter - Inches | 6 | 12 | 2 | 2 |
| Exit Gas Temp., $^{\circ}$F | 300$^{\circ}$ | 570$^{\circ}$ | 590$^{\circ}$ | 300$^{\circ}$ |
| SCFM/Stack | 2000 | 2000 | 370 | 185 |
| Emission Control Devices | | | | |
| Type | None | None | None | None |
| Analyses | | | | |
| Date or Frequency of Sampling | Occasional | Occasional | Occasional | Never |
| Sample Location | | | | |
| Type of Analysis | TIT, GRAV, TOC | TIT, GRAV, TOC | TIT, GRAV, TOC | |
| Odor Problem | No | No | No | No |

| Summary of Air Pollutants | |
|---|---|
| Hydrocarbons - Ton/Ton Nylon 6,6 | 0 |
| Particulates & Aerosols - Ton/Ton Nylon 6,6 | 0.00262 |
| NO$_x$ - Ton/Ton Nylon 6,6 | 0 |
| SO$_x$ - Ton/Ton Nylon 6,6 | 0 |
| CO - Ton/Ton Nylon 6,6 | 0 |

TABLE N6,6-III
NATIONAL EMISSIONS INVENTORY
NYLON 6,6 FROM NYLON SALT

| | 20-2 | | | | 20-3 | | |
|---|---|---|---|---|---|---|---|
| Plant Code No. | | | | | | | |
| Capacity - Tons Nylon 6,6/Year | 10,000 | | | | 62,500 | | |
| Range in Production - % of Max. | None | None | None | None | None | None | None |
| Emissions to Atmosphere | | | | | | | |
| Stream | (IVA) Evaporator Off-Gas | (IVB) Reactor Off-Gas | (IVC) Separator Off-Gas | (A) Evaporator Off-Gas | (B) Reactor Off-Gas | (C) Separator Off-Gas | (E) Finisher Off-Gas |
| Flow - Lbs./Hr. | 1780 | 3100 | 273 | 11,500 | 8800 | 410 | 40 |
| Flow Characteristic | Continuous | Continuous | Continuous | Continuous | Continuous | Continuous | Continuous |
| Composition - Ton/Ton Nylon 66, | | | | | | | |
| Nylon Salt | + | + | + | | | | |
| Water | 0.78070 | 1.36000 | 0.1197 | 0.781800 | 0.626700 | 0.029135 | 0.002857 |
| Hexamethylene Diamine | 0.00048 | 0.00250 | 0.00041 | 0.000180 | 0.002500 | 0 000070 | + |
| Adipic Acid | | | | | | | |
| Nylon 6,6 Polymer | | + | + | | | 0.000001 | + |
| Cyclopentanone | | | | 0.000008 | 0.000063 | 0.000002 | + |
| Halides | | | | 0.000002 | 0.00002 | Nil | + |
| Tot. Organic Carbon | | | | 0.000510 | 0.001800 | 0.000033 | + |
| Sulfonamide | | | | | | 0.000045 | + |
| Vent Stacks | | | | | | | |
| Number | 1 | 1 | 1 | ? | ? | ? | 1 |
| Height - Feet | 98 | 110 | 95 | | | | |
| Diameter - Inches | 4 | 12 | 4 | | | | |
| Exit Gas Temp., °F | 230° | 400° | 610° | | | | |
| SCFM/Stack | 580 | 560 | 90 | | | | |
| Emission Control Devices | | | | | | | |
| Type | None | None | None | None | None | None | Scrubber |
| Analyses | | | | | | | |
| Date or Frequency of Sampling | Occasional | Occasional | Never | Occasional | Occasional | Occasional | Once |
| Sample Location | | | | | | | |
| Type of Analysis | TIT, GRAV, TOC | TIT, GRAV, TOC | | TIT, GC, TOC | TIT, GC, TOC | TIT, GC, TOC | TIT, GC, TOC |
| Odor Problem | No | No | No | No | No | No | No |
| Summary of Air Pollutants | | | | | | | |
| Hydrocarbons - Ton/Ton Nylon 6,6 | | 0 | | | | 0 | |
| Particulate & Aerosols - Ton/Ton Nylon 6,6 | | 0.00339 | | | | 0.002891 | |
| $NO_x$ - Ton/Ton Nylon 6,6 | | 0 | | | | 0 | |
| $SO_x$ - Ton/Ton Nylon 6,6 | | 0 | | | | 0 | |
| CO - Ton/Ton Nylon 6,6 | | 0 | | | | 0 | |

NOTES

1.  Composition  +  symbol means presence of compound as a trace.

2.  Type of Analysis, symbols mean:

    TIT - Titration
    GC - Gas Chromatography
    TOC - Total Organic Carbon
    GRAV - Gravimetric Analysis

3.  Particulates/Aerosols

    Counts the following compounds:  Hexamethylene Diamine, Adipic Acid,
    Nylon Salt, Nylon 6,6 Polymer, Cyclopentanone, Halide, Sulfonamide.

TABLE N6,6-IV
CATALOG OF EMISSION CONTROL DEVICES
NYLON 6,6

| Absorber/Scrubber | | |
|---|---|---|
| EPA Code | 20-3 | 20-2 |
| Flow Diagram Stream I. D. | (E) | (B) |
| Device I. D. No. | | |
| Control Emission of | Hexamethylene Diamine and others | Hexamethylene Diamine |
| Scrubbing/Absorbing Liquid | Water | Water |
| Type | Spray Column | * |
| | | |
| Scrubbing/Absorbing Liquid Rate GPM | 15 | |
| Design Temp. (Operating Temp.)°F | (100° F) | |
| Gas Rate SCFM (lb./hr.) | (40) | |
| T-T Height - Feet | | |
| Diameter - Feet | | |
| Washed Gases to Stack | | |
| Stack Height - Feet | | |
| Stack Diameter- Feet | | |
| Installed Cost, Mat'l. & Labor - $ | 89,000 | |
| Installed Cost Based on - "year" - dollars | 1968 | |
| Installed Cost - ¢/lb. Nylon 6,6/Yr. | 0.071 | |
| Operating Cost - Annual - $ | 19,850 | |
| Value of Recovered Product, $/Yr. | 0 | |
| Net Operating Cost, ¢/lb. Nylon 6,6 | 0.016 | |
| Efficiency - % - SE | 99.7 | |
| Efficiency - % - SERR | 99.7 | |

*Details not available - equipment in process of being designed for addition in near future.

| Current Installed Capacity | Marginal Capacity | Current Capacity on-stream in 1980 | Demand* 1980 | Capacity 1980 | Capacity to be Added | Economic Plant Size | Number of New Units |
|---|---|---|---|---|---|---|---|
| 1,523 | 0 | 1,523 | 2,400 | 3,000 | 1,477 | 150 | 10 |

Notes:

1. All capacities in MM lbs./year (million lbs./year).
2. Demand estimated at 80% of installed capacity.
3. Growth rate of 10%/year assumed.

TABLE N6,6-VI
EMISSION SOURCE SUMMARY
TON/TON NYLON 6,6

| Emission | Source | | | | | Total |
|---|---|---|---|---|---|---|
| | Evaporation Section | Reactor Section | Flasher Section | Finishing | Fugitive | |
| Hydrocarbons | 0 | 0 | 0 | 0 | 0 | 0 |
| Particulates & Aerosols | 0.000333 | 0.002100 | 0.001100 | 0.000044 | 0 | 0.003577 |
| $NO_x$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $SO_x$ | 0 | 0 | 0 | 0 | 0 | 0 |
| CO | 0 | 0 | 0 | 0 | 0 | 0 |

TABLE N6,6-VII
WEIGHTED EMISSION RATES

Chemical _____ Nylon 6,6 _____

Process _____ Batch and Continuous Polymerization _____

Increased Capacity by 1980 ___1,480 MM Lbs./Year_____

| Pollutant | Emissions, lb./lb. Nylon 6,6 | Increased Emissions MM lbs./year | Weighting Factor | Weighted Emissions MM lbs./year |
|---|---|---|---|---|
| Hydrocarbons | 0 | 0 | 80 | 0 |
| Particulates & Aerosols | 0.003577 | 5.294 | 60 | 317.6 |
| $NO_x$ | 0 | 0 | 40 | 0 |
| $SO_x$ | 0 | 0 | 20 | 0 |
| CO | 0 | 0 | 1 | 0 |

Significant Emission Index = 318

Oxo Process

# Table of Contents

## List of Illustrations and Tables

I.  Introduction

One of the processes which gained world wide importance during recent years is the so called Oxo synthesis for the production of aldehydes and alcohols from olefins and synthesis gas (CO + $H_2$).  Although the oxo synthesis or hydroformylation was discovered in 1938, the big industrial success has been only recently - within the last 15 to 20 years.

In terms of production capacity the oxo process (combined with an aldol condensation to double molecular weight) is the largest process for producing alcohols from the butanols ($C_4$) up through the hexadecanols ($C_{16}$) and higher.

Hydrocarbons and particulates are the main air pollutants associated with these plants.  To a lesser degree, CO is a problem but a very minor one.  The main odor problem appears to be trace quantities of aldehydes and alcohols in vents from distillation columns and tanks.  Unfortunately, even trace quantities of these compounds are enought to create a local odor problem in the plant.  Particulates arise from loss of catalyst (metallic oxides) from the system in vent gases but these losses are very small and constitute no apparent problem.  Off-gases from the process consist of CO, $H_2$ and hydrocarbons, chiefly $C_1$ to $C_4$ paraffins.  These gases are either flared or sent to refinery fuel gas.  In either event, proper combustion should give $CO_2$ and water.[1]  Combustion efficiencies are estimated at 98 to 100 percent and CO and hydrocarbon release to the air is under control almost all of the time.

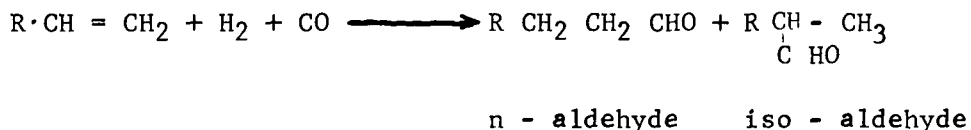Current oxo alcohol production is about 1727 million lbs./year.  Assming a growth of 8 - 9 percent per year, an installed capacity of 3000 million lbs. is predicted by 1980 which will be equal to the demand by then.  This is based on current use of plasticizers in PVC plastics and as bases for surfactants.  Both these uses should increase up through 1980.

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(1)  Although the flaring will produce small quantities of $NO_x$.
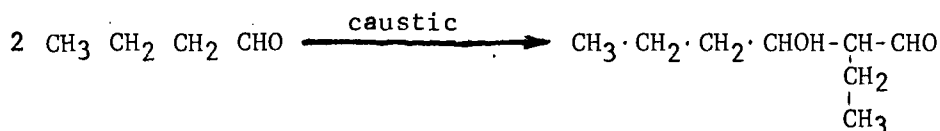
II.  Process Description

The oxo process is the commercial application of a chemical reaction
called oxonation or, more properly, hydroformylation.  In this reaction,
hydrogen and carbon monoxide are added across an olefinic bond (C=C) to
produce aldehydes containing one more carbon atom than the olefin.  Several
reactions are involved but for simplicity, we shall mention only the three
basic reactions taking place.

(1)  Hydroformylation of an olefin to an aldehyde (Oxo Process).

$$R \cdot CH = CH_2 + H_2 + CO \longrightarrow R\ CH_2\ CH_2\ CHO + R\ \underset{\underset{C\ HO}{|}}{CH} - CH_3$$

                                         n - aldehyde      iso - aldehyde

The straight chain n - aldehyde is the preferred product.

(2)  Aldol Condensation - Doubling of the molecular weight of an aldehyde.
     Example - n - butyraldehyde.

$$2\ CH_3\ CH_2\ CH_2\ CHO \xrightarrow{\text{caustic}} CH_3 \cdot CH_2 \cdot CH_2 \cdot \underset{\underset{CH_3}{\underset{|}{CH_2}}}{\overset{|}{CHOH-CH-CHO}}$$

     n - butyraldehyde                    n - butyraldol

The n - butyraldol may be dehydrated and hydrogenated to an alcohol,
2 ethyl hexanol.

(3)  Hydrogenation of the aldehydes to the corresponding alcohol.

$$R \cdot CH_2\ CH_2\ C \overset{O}{\underset{}{\diagup}} - H \xrightarrow{\text{Cat, H2}} R \cdot CH_2 \cdot CH_2\ \overset{OH}{\underset{}{\overset{|}{CH_2}}}$$

     a n - aldehyde                    a n - alcohol
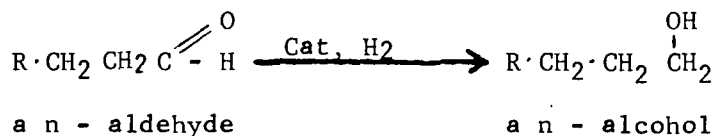
In commercial practice all three of these reactions are used individually
or in common as follows:

Oxo Process

The reaction of an olefin (propylene, octenes, etc.) with carbon
monoxide and hydrogen (syn gas made by steam reforming of methane, ethane,
etc.) at 200 - 400° F and 500 - 5000 PSI pressure, in the presence of a
cobalt catalyst produces a mixture of aldehydes and alcohols with one
more carbon atom than the starting olefin.  This reaction is properly
known as oxonation (hence "oxo") or more accurately, hydroformylation.
Following removal of the catalyst (decobalting) the reaction mixture is
catalytically hydrogenated.  The resulting product is then fractionated
to yield the finished "oxo" alcohol.  Except when ethylene is used as
the starting olefin, a mixture of straight chain and branched chain
alcohols are produced.  With propylene and higher molecular weight linear
olefins, the percentage of normal alcohol product can be significantly
increased by modifying the cobalt catalyst system, e.g. with phosphine
ligands.  All alcohols produced by this technique are primary, regardless
of the feedstock usd.

OA-3

## Aldol Process

N - butyraldehyde in the presence of caustic condenses to form
2 - ethyl hexeneal which on hydrogenation and distillation yields pure
2 - ethyl - 1 - hexanol (2 EH). This alcohol was the first large
volume synthetically produced higher aliphatic primary alcohol and is
still today the most important member of the group. N - butyraldehyde
may be made by subjecting propylene to the oxo reaction. The aldol
condensation doubles the number of carbon atoms in the alcohol precursor
made in the oxo reaction.

## Oxo Aldol (Combined) Process

In the combined process, with propylene as the feedstock and a
special catalyst system, 2 - ethyl hexanol is produced via the oxo -
aldol route in one operation. One of the special catalyst systems is
a tributyl phosphine cobalt carbonyl complex (plus KOH) which
promotes a high degree of linearity of the intermediate butyraldehyde and
hence high yields of 2 - ethyl hexanol. Branched chain hexadecyl
alcohol is also made by a combined oxo - aldol process. In this case
branched chain heptenes are the feedstock and the cobalt catalyst is
modified by the addition of metal organic compounds such as zinc,
cadmium or lead stearates.

Plants covered by this report include plain oxo plants with subsequent
hydrogenation to alcohols and plants with oxo - aldol routes to higher
molecular weight alcohols.

## III.  Plant Emissions

No two oxo alcohol plants are exactly alike or even closely alike. The comments below refer to the generalized flow diagram OA-1 in this report which gives all the basic steps which most of these plants possess.

A.  Continuous Air Emissions

1.  Reforming Furnaces Vent Gas $^{(A)}$

Some respondents gave data on operation of their steam reforming furnaces (to CO + $H_2$ "syn gas") and hydrogen production facilities. Emissions from this source represent emergency flarings of gases due to upsets.  The figures given are probably low since all plants have these furnaces but data was not given for all plants.

2.  Oxo Reactor System Off-Gas $^{(C)}$

All plants have a reactor system off-gas which is normally flared. Usual composition is steam, $N_2$, CO, $H_2$ and light hydrocarbons.  Gases are burned to $CO_2$ and $H_2O$ with better than 98% efficiency.  Some hydrocarbons and CO may escape unburned and these are shown on Table III.  One respondent had a measure of the small quantity of $NO_x$ found in the flare gas from $N_2$ present in the combustion air. Very small quantities of particulates (catalyst - metallic oxides) were reported in several streams and this has been noted also on Table III.

3.  Catalyst System Vent Gas $^{(D)}$, $^{(E)}$

Chief emission here is water as steam but small quantities of hydrocarbons are reported (aldehydes, alcohols) and these represent a minor in-plant odor problem.  Also trace quantities of particulates (catalyst - metal oxide) are present in this stream.

4.  Compressor Engine Exhaust

One respondent uses methane fueled engines to drive his compressors which are used to feed syn gas and hydrogen to the process.  Since all the plants using the oxo process are pressure plants (1500 - 6500 PSIG) in the reaction section, they all must have compressors. Others may be methane or gas fueled also but were not reported. Since engine exhaust is a pollutant, we reported this source. Even though it is small, it is an inherent part of the process. The figure shown is probably low since other plants may well have gas fueled engines on their compressors also.

5.  Distillation Purification System Vents $^{(F)}$, $^{(I)}$

Gases here are chiefly steam and hydrocarbon (aldehyde and alcohol in this case) and represent a local odor problem.

6.  Heavy Liquids Incinerator Stack Gas $^{(L)}$, $^{(H)}$

Some plants burn the heavy by-products made in an incinerator, others send them to disposal in refinery fuel oil where we have no

data. Those incinerating this stream report practically complete combustion but in every case trace amounts of aldehydes and alcohols can be detected in the stack gas. This stream also represents a local odor problem.

Many of the respondents have only one or two emissions listed. Other vent streams go into the refinery fuel system and are not counted as emissions in this report. One respondent (21-3) reports no emissions at all - everything being sent to the refinery fuel system. One cannot help but wonder that there must be some emergency venting to a flare or the atmosphere in this plant too - every other plant reports some of this but no emission data were forthcoming from 21-3. Nevertheless, this plant was averaged in with all the others and in effect diluted the emissions shown in Table III because of the claimed 100% purity.

B. Intermittent Air Emissions (see A-1)

Some plants vent the reforming furnaces continuously and some report only intermittent emissions due to upsets or start-up.

C. Continuous Liquid Wastes (L), (M)

All plants have liquid waste consisting of heavy organics which are incinerated, burned in refinery fuel, or reprocessed. (See Section A-6.)

Waste Water (J)

Every plant has a waste water stream which varies from 0.06 gal/lb. product to 1.7 gal/lb. product. Five of seven respondents treat this water at least thru primary treatment. The remaining two have no treatment other than oil skimming.

D. Solid Wastes (K)

Five of seven respondents report periodic removal of solid wastes from the process in the form of spent catalyst. They are disposed of by landfill in the plant or sold to an outside firm for reclamation. Amounts vary from 0.000053 lb./lb. product to 0.001680 lb./lb. product but the data is sketchy.

E. Odors

Some respondents reported the odor of heavy aldehydes and alcohols in plant but no one reported any outside odor complaints. As stated earlier, these compounds have odors enduring enough that they could probably be detected off-site if the wind and atmospheric conditions were right.

F. Fugitive Emissions

None of the respondents report any fugitive emissions or even offer an estimate.

G. Other Emissions

None reported.

IV.  Emission Control

Emission control devices used in this process are summarized in Table IV.
All plants have flares which are used to burn excess gas or gases emitted due
to process upset or start-up.  In all cases, using the data reported,
combustion efficiency is better than 98% and all components could burn
completely to $CO_2$ and $H_2O$.  No nitrogen compounds are present although traces
of $NO_x$ have been reported in the flared gas, presumably from $N_2$ present in
small quantities in the syn gas and from the air required for complete
combustion in the flare.  No sulfur compounds are used in these plants.
Emissions to the air, when they occur, are hydrocarbons (chiefly $C_1$ - $C_4$
aliphatics), particulate and CO and take place generally during an upset or
start-up with the resultant surge of feed to the flare.

Heavy residual liquids are incinerated and the only source of emissions
here are trace quantities of heavy aldehydes and alcohols which are detectable
by their odor in the stack gas.  This source represents a minor local odor
problem at the plants.

One respondent has a water scrubber on his aldehyde and alcohol column vents
to attempt to reduce the odor of gases emitted.  The scrubbed gases still present
an odor problem although the aldehyde and alcohol content can only be reported
as "trace".  The major constituent is air.  Since actual quantitative data
are not available for the flared and incinerated gases, a Completeness of
Combustion Rating ("CCR") and Significance of Emission Reduction Rating ("SERR")
cannot be calculated.  From the sparse and incomplete data available, however,
we estimate a 98+% for both these ratings and generally rather close to 100%.

The one water scrubber used removes trace quantities of aldehydes and
alcohols from distillation column vent gases.  Since the odor of aldehydes
and alcohols is still detectable in the scrubbed off-gas, one must conclude
that the efficiency of this device is not 100% but a lesser figure.  Lack of
quantitative data precludes calculation of an exact efficiency.

## V. Significance of Pollution

It is recommended that no in-depth study of this process be made. Reported emissions on a weighted basis (Table VII, SEI = 325) put the plants on the lower end of the emission spectrum. It should be mentioned that several plants reported a local in-plant odor problem with heavy alcohols and aldehydes in storage tank breathers and distillation column vents. Although no odor complaints were reported, these odors are tenacious enough that they probably could be detected off-site if the wind were in the proper direction.

Methods outlined in Appendix IV of this report have been used to estimate the total weighted annual emissions from new plants. This work is summarized in Tables V, VI and VII.

The projected increase in oxo alcohol production has been estimated from literature comments on possible future uses. Published support for this forecast has not been found. Assumptions made were:

1. A major use of $C_6$ - $C_{12}$ alcohols will continue to be as bases for plasticizers for polyvinyl chloride plastics. PVC plastics are projected to grow 9 - 12 percent per year through 1980.

2. A major use of $C_{12}$ - $C_{18}$ alcohols will be as bases for surfactants and this market is projected to grow also.

3. No more natural fatty alcohol plants will be built.

4. The recent oversupply of oxo alcohols has now been alleviated by increased demand. Supply and demand will be about equal in 1980.

Using the above assumptions, it was projected that the oxo alcohol market will increase from 1,727 million lbs./year to about 3,000 million lbs by 1980. One marginal oxo unit has already been shut down. All the others apparently will keep on running until at least 1980. New plants (six required) will have a capacity averaging 200 million lbs./year. On a weighted emission basis, an SEI of 325 was calculated for this project and as such it is recommended that no in-depth study be made.

## VI. Producers of Oxo Alcohols

The capacities and plant locations listed below are based on information provided in the questionnaires and in the literature.

| Company | Location | Capacity MM Lbs./Yr. | Type* |
|---|---|---|---|
| Dow Badische | Freeport, Texas | 180 | i & n $C_4$, i & n butal, 2 EH |
| Eastman Kodak, Eastman Chem. Prod. | Longview, Texas | 435 | i & n $C_4$, i & n butal, 2 EH, prop. ald. |
| Getty Oil | Del. City, Del. | 42 | i $C_8$, i $C_{10}$, i $C_{13}$ |
| Gulf Oil | Phila. Pa. | 40 | i $C_{13}$ |
| Monsanto | Texas City, Texas | 200 | n - $C_7$, $C_9$, $C_{11}$ |
| Shell | Deer Park, Texas | 150 | i & n $C_4$, i & n butal, 2 EH |
| | Geismar, La. | 150 | n - $C_{12}$, $C_{13}$, $C_{14}$, $C_{15}$ |
| Exxon Corp. | Baton Rouge, La. | 160 | i - $C_8$, $C_9$, $C_{10}$ $C_{13}$, $C_{16}$ |
| Union Carbide Corp. | Seadrift, Texas | 100 | i & n $C_4$, n - butal i $C_6$, $C_8$, $C_{10}$, $C_{13}$ prop. ald. |
| | Texas City, Texas | 200 | Same as Seadrift plant & n $C_3$ & $C_5$ |
| U. S. Steel | Haverhill, Ohio | 70 | i - $C_8$ - $C_{10}$ |

Total = 1,727 million lbs/year

*Key to type of alcohol

| | |
|---|---|
| i & n $C_4$ | = iso & normal butyl alcohol |
| i $C_6$ | = iso hexyl alcohol |
| i $C_8$ etc. | = iso octyl alcohol |

| | |
|---|---|
| i & n butal | = iso & normal butyraldehyde |
| 2 EH | = 2 ethyl - 1-hexanol |
| n $C_6$ - $C_{11}$ | = normal $C_6$ to $C_{11}$ alcohols (linear) |
| prop - ald. | = normal propionaldehyde |

PAGE NOT

AVAILABLE

DIGITALLY

TABLE OA-I
ALCOHOLS FROM THE OXO PROCESS
MATERIAL BALANCE - T/T ALCOHOL

There are insufficient data for a good material balance on this complex process. A partial balance can be made on olefins charged to the process vs alcohol made. Data given below do not account for either syn. gas ($CO + H_2$) charged or gaseous products leaving the process.

1.578 lb. olefin [1] ------------------------- 1.000 lb. alcohol [2]
                                               0.264 light oxo "gasoline"
                                               0.133 heavy liquid ends
                                               0.181 light ends (gas) [3]

It should be noted that this is an "average" balance and does not apply to any individual product or grade of products.

---

(1) $C_3$ to $C_{12}$.
(2) $C_4$ to $C_{16}$.
(3) By difference.

TABLE OA-II
ALCOHOLS VIA THE OXO PROCESS
REACTOR HEAT BALANCE

There are not sufficient data available to permit the construction of a detailed heat balance for this complex series of reactions. The literature lists the following:

(1)  The reaction is highly exothermic once initiated.
(2)  The reaction is first order relative to the olefin charge.
(3)  Heat release.

   (a)  50,000 BTU/lb. mol olefin converted to alcohol.
   (b)  62,500 BTU/lb. mol ethylene converted to alcohol.
   (c)  Ethylene $\longrightarrow$ propionaldehyde + 34.8 kcal./mol released.

| | 21-1 | | | | 21-2 | |
|---|---|---|---|---|---|---|
| Plant EPA Code No. | | | | | | |
| Capacity - Tons Alcohols/Year | 90,000 | | | | 75,000 | |
| Range of Production - % of Max. | 0 | | | | 0 | |
| Emissions to Atmosphere | | | | | | |
| Stream | Ald., Alc., Heavy Liquids to Incinerator | Compressor Engine Exhausts | Oxo Reactor Vent Gas | Alc. Distn. Section Vent | Ald., Alc., Heavy Liquids to Incinerator | Up-set Gas to Emergency Flare |
| Flow - Lbs./Hr. (SCFM) | 9879 | 9000 | 3112 | 2808 | (50,000) | (228 Avg.) |
| Flow Characteristic | Continuous | Continuous | Continuous | Continuous | Continuous | Variable |
| If Intermittent | | | | | | |
| Composition - Ton/Ton Alc. | (a) | (c) | | | (a) | (b) |
| Hydrogen | | | 0.00006 | 0.00003 | 0.32959 | 0.00012 |
| Nitrogen (Air) | 0.01113 | | | 0.00118 | | 0.00009 |
| CO | | 0.07609 | 0.00044 | | | 0.00006 |
| $CO_2$ | 0.28483 | 0.11956 | 0.15268 | | 0.08789 | 0.00132 |
| Steam | 0.13356 | 0.19565 | 0.01092 | 0.14054 | 0.02199 | 0.00035 |
| $NO_x$ | | | | | | |
| $C_1$ - $C_4$ & Higher Hydrocarbons | | | 0.00006 | 0.02002 | | 0.00006 |
| Aldehydes & Alcohols | Trace | | | 0.00076 | Trace | |
| Particulates | | | | | Trace | |
| Vent Stacks | | | | | | |
| Number | 1 | 4 | 1 | 6 | | 1 |
| Height - Feet | 18 | 14' & 10.5" | 20 | 20 - 200 | | 100 |
| Diameter, Inches | 60 | 24" & 16" | 4 | 2 - 4 | | 14 |
| Exit Gas Temp. °F | ? | 850° F | 100° | 90° - 200° | | 1000° |
| SCFM/Stack | | 750 | 470 | 4 - 200 | | 228 |
| Emission Control Devices | Incinerator | None | None | None | Incinerator | Flare |
| Analysis | | | | | | |
| Date or Frequency of Sampling | Never | Never | Never | Once | Never | Never |
| Tap Location | | | | Vent | | |
| Type Analysis | | Estimate | Mat'l. Balance | M.S. | Estimate | Estimate |
| Odor Problem | At times | No | No | No | Yes | No |
| Summary of Air Pollutants | | | | | | |
| Hydrocarbons - Ton/Ton Alc. | | Trace | | | | 0.02090 |
| Aerosols - Ton/Ton Alc. | | | | | | |
| $NO_x$ - Ton/Ton Alc. | | | | | | |
| $SO_x$ - Ton/Ton Alc. | | | | | | |
| CO - Ton/Ton Alc. | | 0.07609 | | | | 0.00050 |

| | 21-4 | 21-5 | | 21-6 |
|---|---|---|---|---|
| Plant EPA Code No. | 21-4 | 21-5 | | 21-6 |
| Capacity - Tons Alcohols/Year | 48,000 | 217,500 | | 35,000 |
| Range of Production - % of Max. | 0 | 0 | | 0 |
| Emissions to Atmosphere | | | | |
| Stream | Oxo Reactor Vent Gas | Oxo Reactor Vent Gas | Cat. Regenerator Vent Gas | Oxo Reactor Vent Gas |
| Flow - Lbs./Hr. (SCFM) | 119,026 | 2072 | (1800) | 18,240 |
| Flow Characteristic | Continuous | Continuous | Continuous | Continuous |
| if Intermittent, Hrs./Yr. | | | | |
| Composition - Ton/Ton Alc. | (b) | (b) | | (b) |
| Hydrogen | | 0.00002 | | |
| Nitrogen (Air) | | 0.00026 | | 0.02589 |
| CO | | 0.00030 | | |
| $CO_2$ | 6.9287 | 0.02827 | | 1.7295 |
| Steam | 3.8915 | 0.01287 | 0.08102 | 0.95710 |
| $NO_x$ | 0.00027 | | | |
| $C_1$ - $C_4$ & Higher Hydrocarbons | | | 0.00012 | |
| Aldehydes & Alcohols | | | 0.00012 | |
| Particulates | 0.00002 | | Trace | |
| Vent Stacks | | | | |
| Number | 1 | 1 | 1 | 1 |
| Height - Feet | 120 | 100 | 60 | 125 |
| Diameter - Inches | | 20 | 14 | 16 |
| Exit Gas Temp. °F | | | 212° | 213° |
| SCFM/Stack | | | 1800 | 360,000 |
| Emission Control Devices | Flare | Flare | None | Flare |
| Analysis | | | | |
| Date or Frequency of Sampling | Never | 12/Day | 1/Month | Once |
| Tap Location | | in-line | in-line | in-line |
| Type of Analysis | Est. from Feed | G. C. | Mat. Bal., TOC,TIT | G. C. |
| Odor Problem | No | No | Yes | No |
| Summary of Air Pollutants | | | | |
| Hydrocarbons - Ton/Ton Alc. | | | 0.00024 | |
| Aerosols - Ton/Ton Alc. | 0.00002 | | Trace | |
| $NO_x$ - Ton/Ton Alc. | 0.00027 | | | |
| $SO_x$ - Ton/Ton Alc. | | | | |
| CO - Ton/Ton Alc. | | | 0.00030 | |

Plant EPA Code No. — 21-7
Capacity - Tons Alcohols/Year — 80,000
Range of Production - % of Max. — 0

Emissions to Atmosphere

| Stream | Hyd. Reformer Vent | $CO_2$ Removal Vent | Cat. Recovery System Vent | Cat. Regenerator System Vent |
|---|---|---|---|---|
| Flow - Lbs./Hr. (SCFM) | (7 Avg.) | 302 | 730 | 19 |
| Flow Characteristic | Intermittent | Continuous | Continuous | Continuous |
| if Intermittent, Hrs./Yr. | 8 | | | |
| Composition - Ton/Ton Alc. | | | | |
| Hydrogen | 0.000032 | 0.000063 | | |
| Nitrogen (Air) | | | 0.022260 | 0.00058 |
| CO | 0.000002 | | | |
| $CO_2$ | 0.000178 | 0.009404 | | |
| Steam | 0.000577 | | | |
| $NO_x$ | | | | |
| $C_1$ - $C_4$ & Higher Hydrocarbons | 0.000006 | | | |
| Aldehydes & Alcohols | | | Trace | Trace |
| Particulates | | | | |
| Vent Stacks | | | | |
| Number | 2 | 1 | 1 | 1 |
| Height - Feet | | | | |
| Diameter - Inches | | | | |
| Exit Gas Temp. °F | | | | |
| SCFM/Stack | | 42 | 151 | 4 |
| Emission Control Devices | None | None | None | None |
| Analysis | | | | |
| Date or Frequency of Sampling | Never | Once | Never | Never |
| Tap Location | | in-line | | |
| Type of Analysis | Estimate | G.C. | Calculated | Calculated |
| Odor Problem | No | No | Yes | Yes |
| Summary of Air Pollutants | | | | |
| Hydrocarbons - Ton/Ton Alc. | | | | |
| Aerosols - Ton/Ton Alc. | | | | |
| $NO_x$ - Ton/Ton Alc. | | | | |
| $SO_x$ - Ton/Ton Alc. | | | | |
| CO - Ton/Ton Alc. | | | | |

Plant EPA Code No. — 21-7
Capacity - Tons Alcohols/Year — 80,000
Range of Production - % of Max. — 0

| Emissions to Atmosphere | Compressor | Distn. Column | Storage Tank | Oxo Reactor |
|---|---|---|---|---|
| Stream | Flush Lines | Vent | Vents | Vent Gas, Etc. |
| Flow - Lbs./Hr. (SCFM) | (0.01 Avg.) | 110 | 96 | 3544 |
| Flow Characteristic | Intermittent | Continuous | Continuous | Continuous |
| if Intermittent, Hrs./Yr. | 1 | | | |
| Composition - Ton/Ton Alc. | | | | (b) |
| Hydrogen | Trace | | | 0.000113 |
| Nitrogen (Air) | Trace | | 0.00301 | 0.017857 |
| CO | Trace | | | 0.000940 |
| $CO_2$ | Trace | | | 0.53571 |
| Steam | | 0.00338 | | 0.038496 |
| $NO_x$ | | | | |
| $C_1$ - $C_4$ & Higher Hydrocarbons | Trace | 0.00006 | | |
| Aldehydes & Alcohols | Trace | | Trace | |
| Particulates | | | | |
| Vent Stacks | | | | |
| Number | 3 | 1 | | 1 |
| Height - Feet | | | | 200 |
| Diameter - Inches | | | | 24 |
| Exit Gas Temp. °F | | | | ? |
| SCFM/Stack | | 35 | | 606 |
| Emission Control Devices | None | None | None | Flare |
| | | | | |
| Analysis | | | | |
| Date or Frequency of Sampling | Never | Never | Never | 3 times/year |
| Tap Location | | | | line to flare |
| Type of Analysis | | Calculated | Calculated | M.S. |
| Odor Problem | No | No | No | No |
| Summary of Air Pollutants | | | | |
| Hydrocarbons - Ton/Ton Alc. | | | | 0.000066 |
| Aerosols - Ton/Ton Alc. | | | | |
| $NO_x$ - Ton/Ton Alc. | | | | |
| $SO_x$ - Ton/Ton Alc. | | | | |
| CO - Ton/Ton Alc. | | | | 0.000942 |

# EXPLANATION OF NOTES
## TABLE OA-III
## NATIONAL EMISSIONS INVENTORY
## ALCOHOLS VIA THE OXO PROCESS

(a) Respondents furnished composition of liquid to incinerator. Figures shown are calculated combustion products assuming complete combustion to $CO_2$ and water unless other data were available. Usually trace quantities of alcohols, aldehydes or particulates were noted in the incinerator stack gases and usually there is a minor odor problem associated with these incinerators.

(b) Respondents furnished composition of gas streams to the flare. Figures shown are calculated on 98% complete combustion to $CO_2$ and $H_2O$ unless other data were available. In most cases, some pollutants appear to be in the flared gas but they were so low that no odor problem was reported. Small quantities of $NO_x$ are present in the flared gas from $N_2$ in the combustion air.

   Type of Analysis  M.S. = Mass Spectrograph
   
                         G.C. = Gas Chromatograph
   
                         TOC = Total Organic Carbon
   
                         TIT = Titration

(c) Plant 21-1 gives large volume of methane as fuel to gas compressors. Compressor exhaust estimated by an arbitrary choice of 50% $CH_4$ going to $CO_2$ and 50% to CO in the engines.

Many plants vent gas streams to refinery fuel systems and use the flare only in cases of upset or emergency. Hence, some plants listed show no flared gas at all or low flow to the flare. One respondent showed all gas streams going to plant fuel line and no atmospheric emissions at all. This appears overly optimistic and this data was taken with a grain of salt.

TABLE OA-IV
CATALOG OF EMISSION CONTROL DEVICES
ALCOHOLS VIA THE OXO PROCESS

## INCINERATION DEVICES

| | | | |
|---|---|---|---|
| EPA Code No. for plant using | 21-1 | 21-1 | 21-2 |
| Flow Diagram (Fig. I) Stream I. D. | (L) (M) | (C) | (A) (C) |
| Device I. D. No. | 101 | 102 | 101 |
| Type of Compound Incinerated | Heavy Alcohols & Aldehydes & Misc. Waste Liquid | Syn. Gas & Hydrocarbons | Syn. Gas & Hydrocarbons |
| Type of Device | Incinerator | Flare | Flare |
| Material Incinerated, Lb./Hr. (SCFM) | 2350 | 1019 | 38 |
| Auxilliary Fuel Req'd. (excl. pilot) | | | |
| Type | | | Natural Gas |
| Rate - BTU/Hr. | | | $5.5 \times 10^6$ |
| Device or Stack Height - Feet | 18 | 75 | 100 |
| Installed Cost - Mat'l. & Labor - $ | $12,700 | $10,365 | $145,000 |
| Installed Cost Based on "year" - $ | 1967 - 1972 | ca. 1967 | 1941 to 1972 |
| Installed Cost - ¢/lb. Alcohol - Yr. | 0.0071 | 0.0058 | 0.0967 |
| Operating Cost - Annual (1972) - $/Yr. | $5,800 | $5,600 | $40.000 |
| Operating Cost - ¢/lb. Alcohol | 0.0032 | 0.0031 | 0.0267 |
| Efficiency - % - CCR | Approximately 99% | 100 [1] | 66 - 100 [2] |
| Efficiency - % - SERR | Approximately 99% | 100 [1] | 15 - 100 [2] |

## INCINERATION DEVICES

| | | | |
|---|---|---|---|
| EPA Code No. for plant using | 21-2 | 21-4 | 21-5 |
| Flow Diagram (Fig. I) Stream I. D. | (L) (M) | (A) (C) | (A) (C) |
| Device I. D. No. | 102 | 101 | 101 |
| Type of Compound Incinerated | Butanol, Butyl Ether, Heavy Ends, Cat. Salts | Syn. Gas & Hydrocarbons | Syn. Gas & Hydrocarbons |
| Type of Device | Incinerator | Flare | Flare |
| Material Incinerated, Lb./Hr. (SCFM) | 1920 | 35281 | 754 |
| Auxilliary Fuel Req'd. (excl. pilot) | | | |
| Type | Natural Gas | | |
| Rate - BTU/Hr. | $10 \times 10^6$ | | |
| Device or Stack Height - Feet | ? | 120 | 100 |
| Installed Cost - Mat'l. & Labor - $ | $155,000 | $9,077 [3] | $97,000 |
| Installed Cost Based on "year" - $ | 1959 - 1970 | 1971 - 1972 | 1968 - 1969 |
| Installed Cost - ¢/lb. Alcohol - Yr. | 0.1033 | 0.00946 | 0.0223 |
| Operating Cost - Annual (1972) - $/Yr. | $51,200 | $20,284 | $16,000 |
| Operating Cost - ¢/lb. Alcohol | 0.034 | 0.02113 | 0.00368 |
| Efficiency - % - CCR | Approximately 99% | 100 [1] | 98 [1] |
| Efficiency - % - SERR | Approximately 99% | 100 [1] | 98 [1] |

(1) So reported by respondent.
(2) Worst case based on no burning of hydrocarbons during up-sets. Best case assumes all go to $CO_2$ & $H_2O$ actual performance lies between these extremes, not enough data to pin down any closer.
(3) Tip only and steam line on existing flare tower.

TABLE OA-IV
CATALOG OF EMISSION CONTROL DEVICES
ALCOHOLS VIA THE OXO PROCESS

## INCINERATION DEVICES

| | | |
|---|---|---|
| EPA Code No. for plant using | 21-6 | 21-7 |
| Flow Diagram (Fig. I) Stream I. D. | (A) (C) | (A) (C) |
| Device I. D. No. | 101 | 101 |
| Type of Compound Incinerated | Syn. Gas | Syn. Gas & Hydrocarbons |
| Type of Device | Flare | Flare |
| Material Indincerated, Lb./Hr. (SCFM) | (6000) | 631 |
| Auxilliary Fuel Req'd. (excl. pilot) | | |
| Type | | |
| Rate - BTU/Hr. | | |
| Device or Stack Height - Feet | 125 | 200 |
| Installed Cost - Mat'l. & Labor - $ | $50,000 | $245,000 |
| Installed Cost Based on "year" - $ | 1962 | 1966 |
| Installed Cost - c/lb. Alcohol - Yr. | 0.0714 | 0.1531 |
| Operating Cost - Annual (1972) - $/Yr. | $4,220 | $61,500 |
| Operating Cost - c/lb. Alcohol | 0.00603 | 0.0384 |
| Efficiency - % - CCR | 100 [1] | Approximately 98 |
| Efficiency - % - SERR | 100 [1] | Approximately 98 |

(1) So reported by respondent.
(2) Worst case based on no burning of hydrocarbons during up-sets. Best case assumes all go to $CO_2$ & $H_2O$ actual performance lies between these extremes, not enough data to pin down any closer.
(3) Tip only and steam line on existing flare tower.

ABSORBERS/SCRUBBERS

| | |
|---|---|
| EPA Code No. for plant using | 21-1 |
| Flow Diagram (Fig. I) Stream I. D. | (F) (I) |
| Device I. D. No. | 103 |
| Controls Emission of | Alcohol & Aldehyde Vapors |
| Scrubbing/Absorbing Liquid | Water |
| Type | Scrubber |
| Scrubbing/Absorbing Liquid Rate GPM | 2 |
| Gas Rate - SCFM (lb./hr.) | ? |
| T-T Height, Feet | 7.5 |
| Diameter, Feet | 1.5 |
| Washed Gases to Stack | ? |
| Stack Height - Feet | 15 |
| Stack Diameter - Inches | 3 |
| Installed Cost - Mat'l. & Labor - $ | $1,680 |
| Installed Cost - Based on "year" - $ | 1967 - 1972 |
| Installed Cost - ¢/lb. Alcohol/Yr. | 0.00093 |
| Operating Cost - Annual - $ (1972) | $3,600 |
| Value of Recovered Product, $/Yr. | 0 |
| Net Operating Cost - ¢/lb. Alcohol | 0.0020 |
| Efficiency - % - SE | $\angle 100$ |
| Efficiency - % - SERR | $\angle 100$ |

TABLE OA-V
NUMBER OF NEW PLANTS BY 1980

| Current Capacity | Marginal Capacity | Current Capacity on-stream in 1980 | Demand 1980 | Capacity* 1980 | Capacity to be Added | Economic Plant Size | Number of New Units |
|---|---|---|---|---|---|---|---|
| 1727 | 0 | 1727 | 3000 | 3000 | 1273 | 200 | 6 |

NOTE: All capacities in million lbs./year.

*Based on use of alcohols as plasticizers in PVC and detergents and assuming that no new natural fatty alcohol plants will be built. Current over capacity of oxo alcohols should be over well before 1980 and new plants or expansion of existing facilities necessary to meet a growth rate of 8.9%/year.

| Emission | Source | | | | | | Total |
|---|---|---|---|---|---|---|---|
| | Reforming Furnaces Vent Gas | Oxo Reactor System Off-Gas | Catalyst System Vent Gas | Compressor Engine Exhausts | Distillation Purification System Vents | Heavy Liquid Incinerator Stack Gas | |
| Hydrocarbons | 0.000009 | 0.000010 | 0.000040 | | 0.002970 | TR | 0.003029 |
| Particulates/Aerosols | | 0.000003 | TR | | | TR | 0.000003 |
| $NO_x$ | | 0.000040 | | | | | 0.000040 |
| $SO_x$ | | | | | | | |
| CO | 0.000009 | 0.000240 | | 0.011000 | | | 0.011249 |

## TABLE OA-VII
## WEIGHTED EMISSION RATES

Chemical _____ Alcohols _____

Process _____ Oxo _____

Increased Capacity by 1980 __ 1273 MM lbs./year _____

| Pollutant | Emissions Lb./Lb. | Increased Emissions MM Lbs./Year | Weighting Factor | Weighted Emissions MM Lbs./Year |
|---|---|---|---|---|
| Hydrocarbons | 0.003029 | 3.856 | 80 | 308.5 |
| Particulates | 0.000003 | 0.0038 | 60 | 0.3 |
| $NO_x$ | 0.000040 | 0.0509 | 40 | 2.0 |
| $SO_x$ | | | 20 | 0 |
| CO | 0.011249 | 14.320 | 1 | 14.3 |

Significant Emission Index = 325.1

# Table of Contents

## List of Illustrations and Tables

I.  Introduction

Half the phenol produced goes into phenolic resins, while a substantial proportion is used to make the nylon-6 intermediate caprolactam.  Natural phenol capacity accounts for only 2% of present day production, and the cumene process has replaced other synthetic phenol processes to such an extent that over 90% of U. S. capacity involves the use of cumene charge stock today.

In common with other air oxidation processes, venting of "spent air" accounts for a major portion of the emissions from the cumene derivation phenol process. In addition, since acetone is a major by-product, there is a roughly equivalent quantity of primarily low molecular weight hydrocarbon emissions associated with the product recovery and purification sections of the plant.  Emissions of phenolic material is low, in keeping with the recognized toxicity of these materials, though respondents have noted phenolic odors are detectable at times, usually only within the plant.  In general, air pollutant emissions from these phenol plants can be characterized as low to moderate.

This air pollution study report includes information provided by eight of the ten cumene process producers in the United States.  According to Chemical Marketing Reporters' June 19, 1972 Chemical Profile, only three plants with a total capacity of 310 million pounds annually continue to produce phenol using other than the cumene process.  Current cumene process capacity is approximately 2.5 billion pounds of phenol per year and is expected to increase to some 4.2 billion pounds per year by 1980.

No change in emission rate (i.e., tons emission/ton  phenol) is forseen except that, based on indications from respondents utilizing activated carbon for recovery of cumene from vented "spent air", other producers may find such pollution control equipment economically justified, and average hydrocarbon rate of emissions will actually be less in the future.

II. <u>Process Description</u>

The cumene process was developed by Hercules, and Distillers, Ltd. of England and concurrently, independently by Allied Chemical Corporation. First commercial production began in the early 1950's, with the cumene route taking over 50% of the market by 1968 and roughly 90% at the present time.

There are essentially two steps in the liquid phase production of phenol from cumene (see Table I and Figures PH-1 and PH-2). (i, ii, iii, iv, v ref.).

1. Air is introduced to a vigorously stirred, slightly alkaline aqueous sodium carbonate emulsion with purified cumene to produce cumene hydroperoxide (CHP).

2. Dilute sulfuric acid is added to a second agitated reactor to effect cleavage of the cumene hydroperoxide directly into phenol and acetone.

In the oxidation step, oil-soluble heavy metal catalyst and promoters may be present, and an emulsifying agent such as sodium stearate may be used. With a sodium carbonate solution pH in the range 8.5 to 10.5, and water-to-oil ratio between 2 and 5, reaction is carried out using about 0.5 pounds of oxygen per pound of phenol, and cumene recycle ratio of $\sim$2:1, at temperatures up to 260° F and atmospheric or moderate superatmospheric pressure. Cooling is required (see Table II-A) to avoid thermal decomposition of the cumene hydroperoxide, and with conversion maintained in the range of 30 to 50%, "spent air" is vented through an effective refrigerated condensing system and other equipment for recovery and recycle of unconverted cumene. During this oxidation step, some formaldehyde is produced (along with some lesser quantities of other reaction products), indicating that the minor by-product acetophenone is also being formed.

Some producers elect to use a vacuum concentrator on the oxidation reactor effluent at this point, and to recycle separated overhead cumene to the oxidizer. In any case, precautions must be taken to avoid explosive concentrations of peroxides.

The cleavage step, which follows, involves intimate contact with dilute sulfuric acid ($\sim$5 - 25%) at temperatures in the range of 130 to 150° F and pressure slightly above atmospheric. Considerable heat is generated, and again it is important to provide adequate cooling to avoid thermal decomposition. There are undoubtedly a number of minor side reactions which occur in the cleavage reactor; it appears likely that the small amount of alpha methyl styrene produced results from loss of oxygen from CHP to form cumyl alcohol, followed by dehydration of the alcohol in the presence of sulfuric acid (see reactions III (A) and III (B) in Table I).

An aqueous acid phase from the cleavage reaction effluent separation is recycled back to the cleavage reactors with makeup acid, and the oil phase is water washed with appropriate means for selective extraction where required. The oil layer is sent on through a distillation train for recovery and purification of product acetone, recycle cumene, alpha methyl styrene (part or all of which may be hydrogenated and recycled), product phenol, and acetophenone, which may be purified for marketing or simply left with the residual oil for use as fuel, or for incineration.

III.  **Plant Emissions**

   A.  Continuous Air Emissions

      1.  Feed Purification Vent

         Literature references indicate the necessity for "clean" cumene
         feed and certainly those who find alpha methyl styrene unmarketable
         must hydrogenate this material for recycle.  However, only respondent
         22-1 mentions feed purification, and his information suggests that
         emissions here are negligible.

      2.  Oxidizer Vent

         "Spent air" exhausted from the oxidizer is the largest single
         source of emissions from cumene process phenol plants.  Although not
         all respondents provided details, it appears that multiple stage
         condensing systems involving refrigeration under moderate pressures
         up to 70 or 80 psig are virtually integral to the oxidation section.
         Variations in emissions are found because individual producers operate
         at a different pressure, cool to a different temperature, use a
         scrubber, rely on an activated carbon adsorber, or send the vent stream
         to an incinerator.  Reported emissions, running from "trace" through
         .0015 up to .0067 tons/ton phenol normally (with occasional 1 to 4
         hour equipment failure breaks, in one case up to .049 tons/ton phenol),
         are summarized in Table III.

      3.  Concentrator Vent

         Where respondents reported emission for a post oxidizer cumene
         hydroperoxide concentrator vent (22-1, 22-6 and 22-6), emission levels
         were low, in the range .0003 tons/ton of phenol and less.  Reported
         emissions summarized in Table III.

      4.  Cleavage Section Vent

         Respondent information on cleavage section vent emissions is very
         meagre, with only one actual figure of .0002 tons/ton phenol reported.
         However, the fact that acetone is produced here, together with one
         respondent's design calculation figure of .0024 tons of acetone plus
         .0013 tons of aldehydes per ton of phenol indicates that low to
         moderate light hydrocarbon emissions from cleavage may be "normal".
         Reported emissions are summarized in Table III.

      5.  Distillation Train Vents

         Acetone is the prominent emission component from this section of
         the plant, with some formaldehyde.  Respondent 22-6 has calculated
         on the basis of vapor pressure over the analysed condensed liquid,
         and finds emissions at .0043 tons of acetone and .0003 tons of
         formaldehyde per ton of phenol from an acetone topping tower, and
         22-4 uses design calculations to show acetone .0012 and formaldehyde
         .0009 tons/ton of phenol similarly.  No other emissions of any
         consequence are reported, though trace amounts of cumene, mesityl oxide,
         and phenol are mentioned.  See Table III for details.

      6.  Plant Flares and Boiler Operations

         In some cases, waste "light oil", "heavy oil", or "heavy ends"

are sold or transferred to refinery sections of the overall plant for use as fuel. Respondent 22-3 reports continuous delivery of light and heavy oil waste to boilers for fuel, where excess air is reported to result (design basis) in complete combustion so that no significant air pollution occurs. Respondent 22-8 accumulates phenolic heavy ends and about once a month sends this liquid to a fuel gas fired flare, again with reported (design basis) complete combustion.

B. Intermittent Air Emissions

Aside from the intermittent flaring of liquid waste (see 6 above) the only intermittent air emissions involved are those associated with atmosphere venting during start-ups and plant emergencies, or in those cases where equipment changeover or refill is required, as with spent activated carbon sorbent. An example of the latter is mentioned by respondent 22-6 with regard to the infrequent direct venting of the oxidizer off-gas (averaging $\sim .04$ and up to .049 tons of hydrocarbon emission/ton of phenol) when spent activated carbon sorber is taken off the line. Another example is given by respondent 22-8, again with regard to venting of the oxidizer off-gas (hydrocarbon emissions up to as high as .004 tons/ton of phenol for 1 to 4 hour periods possibly ten times per year when "recovery equipment (may) fail"). Emissions in this category may be expected to vary greatly, and no valid "normal" figure can be inferred from the information at hand.

C. Continuous Liquid Wastes

1. Heavy Ends

"Phenolic heavy ends" or "light" and "a heavy oil" or "residual fuel" bottoms from the distillation train most certainly have to be disposed of one way or another. Literature information indicates that the amount of heavy oil waste is roughly 0.1000 tons per ton of phenol product. The six respondents providing information on this point gave figures running from .05 to .26, with a comparable average of 0.11 tons per ton of phenol, though accompanying charge stock or product components considered not worth recovering would raise the actual amount of "waste" perhaps 50%, or even more, in some cases.

Only three respondents actually indicated how their residual oil was handled, and in each case incineration or flaring with fuel gas was reported. Complete combustion, with no significant air pollution emissions is the design basis, although some $NO_x$ probably forms.

2. Aqueous Waste

Acidic waste wash water from the cleavage reactor separator has been combined together with aqueous phenolic waste streams and other waste water in figures supplied by the respondents, though presumably some selective handling is practiced in disposal. The total amounts handled and method of disposal was reported as follows:

| Respondent Code | Tons waste water per ton phenol | Disposal Method |
|---|---|---|
| 22-1 | 15.9 | Refinery treating system |

| Respondent Code | Tons waste water per ton phenol | Disposal Method |
|---|---|---|
| 22-3 | 1.6 | Injection well |
| 22-4 | 2.2 | – |
| 22-5 | ? | Injection well |
| 22-6 | 1.6 | In-plant waste treatment |
| 22-7 | 4.3 | – |
| 22-8 | 0.33 | In-plant waste treatment |
| 22-9 | 0.13 | Refinery waste treatment |

D. Solid Wastes

Only respondents reporting solid wastes were 22-7, with an undefined 81,000 lb./month, 22-8, with 50,000 lb./year of diatomaceous earth for water filtration  sent to in-plant land fill, and 22-9, with 100 lb. waste solid disposed of on company property.

E. Odors

There was no mention of odor complaints during the past year by any of the eight respondents.  Six of the respondents reported in-plant odor problems associated with the oxidation section (mainly cumene), with no complaints mentioned, and only infrequent off-plant odors noted from this source by two of those reporting.  Respondents 22-4 and 22-6 mentioned in-plant odor from the acetone topping unit, with the latter referring to infrequent off-plant odor being observed from this source, though again, no complaints.  The 22-6 alpha methyl styrene tower had in-plant odor problems, again infrequently off-plant.  Only respondent 22-8 mentioned odor from the cleavage section, and this was in-plant.  Only respondent 22-1 mentioned phenolic type odors, and these were said to be associated with a phenolic water sump and a process bottoms transfer pump, detectable only on plant property.  Respondent 22-8 reported that on occasions when the fuel gas fired incinerator was used to burn liquid phenol waste, there was an odor (not identified) on the plant property, and infrequently off-plant, though no complaints had been noted.

F. Fugitive Emissions

Most producers made no attempt to estimate fugitive emissions. Respondents who did make estimates provided figures which compare as shown here in the right hand column.

| Respondent Code No. | Identified Emissions total tons/ton phenol | Fugitive or "other emissions" total tons/ton phenol |
|---|---|---|
| 22-1 | .0028 | .0005 |
| 22-4 | .0091 | .0003 |
| 22-6 | .0046 | .0010 |

In some cases, mention was made of fugitive emissions involving leaks from pump seals, valve stems, packing glands, waste oil end water sumps, etc., with no attempt at an estimate.  One respondent lumped all emissions and leakage together without distinguishing air

PH-6

or water pollutants, by suggesting approximately 2% losses according
to weight balance on cumene charge, a figure equivalent to .0285
tons per ton of phenol. This figure is high, but perhaps has meaning
in terms of potential for air and water pollution together.

Calculations based on vapor pressure and tank volume and turnovers
per year provide an upper limit estimate for losses to atmosphere
from storage tanks. The total hydrocarbon figures obtained in this
way vary greatly, from less than .00001 tons/ton of phenol to as
much as .0018 tons/ton, in most cases the major portion being acetone.
In many cases, producers have floating roof tanks or have installed
$N_2$ blanket or other type conservation vents, or else the tanks are
normally kept filled. The one respondent from California had
apparently provided floating roof or vapor seal devices so that
tankage vapor losses were virtually eliminated.

None of the respondents gave any figures for appreciable
actual phenol emissions, and with its low vapor pressure, one would
not expect much loss to the atmosphere. However, phenol is highly
toxic, and does have an extremely low TLV or threshold limit value
in air, set by the American Conference of Governmental Industrial
Hygienists, as recorded by N. Irving Sax in "Dangerous Properties
of Industrial Materials", 3rd Edition, (1968). Sax gives
a recommended 5 ppm TLV for phenol, compared to a recommended
25 ppm for benzene or a tentative 50 ppm for cumene. Sax points
out (page 3) that literal application of TL values is dangerous
for a number of reasons.* Nevertheless, one can calculate that
considerable quantities of air would be "contaminated" to the TLV
level when, for example, a large phenol tank held at 130° F is
filled with liquid phenol with vapor escaping through an unprotected
vent to the atmosphere. For one respondent's tank conditions,
assuming complete purging of the vapor space for each reported tank
fill, the average daily phenol emission would be sufficient to
bring a 400 x 400 foot square, 1000 foot depth layer of air to the
5 ppm TLV level. For another respondent, the volume of air brought
to the 5 ppm phenol TLV level each day would correspond to 570 x 570
feet square and 1000 foot depth. Thus, on general principles, for
a toxic material such as phenol, one might well recommend the
installation of protected vent systems for storage tanks and other
vessels whereever feasible.

*One of these being, of course, that material which is picked up by skin contact
is included and thus makes establishment of air limits difficult.

## IV. Emission Control

Table IV of this report, "Catalog of Emission Control Devices", provides a summary of the devices reported by operators of cumene process phenol plants. The control devices may be divided into two broad categories: (1) Combustion Devices - those which depend on thermal or catalytic oxidation of combustibles for emission control, and (2) Non-Combustion Devices - Those that do not depend on combustion. In Table IV, all combustion devices will be assigned two efficiency ratings (when data are available):

(1) CCR - Completeness of Combustion Rating

$$CCR = \frac{\text{lbs. of } O_2 \text{ that react with pollutants in feed to device}}{\text{lbs. of } O_2 \text{ that theoretically could react with these pollutants}} \times 100$$

(2) SERR - Significance of Emission Reduction Rating

$$SERR = \frac{\text{weighted pollutants in } - \text{ weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

A more detailed discussion of these ratings may be found in Appendix V of this report.

Most non-combustion devices will be assigned a Specific Efficiency, SE, based on percent reduction of a specific compound with that compound defined. A few non-combustion devices will receive SERR ratings.

In some cases, respondents included helpful information on a venting device which, when carefully maintained, provided effective emission control, but they were quick to point out that the device was really an economically necessary integral part of the plant equipment, therefore, not legitimately an emission control cost item. In other cases, the large amount of hydrocarbon recovery attributable to the device made it obvious that it was an economic necessity, but the difficult-to-assess incremental cost of further reducing condensate temperature, or maintaining a slightly higher pressure in a knock-out drum, or more frequent change over to a freshly reactivated carbon sorbent tower, or the like, might well be considered part of the expense of emission control.

Undoubtedly due, at least in part, to the strict attention being paid to environmental considerations in California, the one cumene process phenol producer responding to the questionnaire from that state has installed devices on virtually every vent, outlet, or tank to keep air emissions low. It appears that emissions are indeed low for this plant, which is a small one, but unfortunately the respondent does not have quantitative data to provide a means for comparison with other plants.

The following is a brief summation of the various emission control devices identified by respondents in this survey. Details are to be found in Table IV with accompanying footnotes for that table.

### Sorbers/Scrubbers

Activated carbon sorber beds are identified as effective emission control devices for recovering cumene from spent air from the oxidizer, by both 22-6 and 22-7 respondents; respondent 22-3 likewise mentions that activated carbon is used to advantage in the same location, but

ordinarily relies on a gas fired incinerator for further clean-up
of this high volume effluent stream (see below).

Pressure and temperature conditions for the stream entering the
PH-VII carbon bed are such that a relatively high cumene content is
present, and the device, with a specific efficiency of 91%, is shown to
recover sufficient cumene in one year's time to pay off the installed
cost. Carbon sorber PH-VIII is also effective, though its Specific
Efficiency is only 82% and the respondent had no operating cost figures.

"Scrubber" device PH-I listed by 22-1 is merely a water seal leg
trap on the feed purification system, and water "scrubber" tank PH-XIV
is a "catch-all" emergency relief provision which also serves to scrub
normal wash section vents from several plant locations.

The "Scrubber-Cooler" device, which is part of the PH-II combination
emission control used by 22-1 to recover cumene from the oxidizer
off-gas, must really be considered an integral part of the plant, an
economic necessity. It involves circulation of cooled cumene condensate
down a 15 tray column to recover cumene in the vent stream and return
to the oxidizer.

## Condensers and K. O. Drums

Respondents 22-1, 22-4 and 22-5 all rely on refrigerated condensing
equipment with knock-out drums under moderate pressure to achieve sub-
stantial removal of cumene from the oxidizer off-gas, with PH-II, PH-V
and PH-VI respectively. In all three cases, the equipment is primarily
needed for returning cumene to the oxidizer and only secondarily is an
emission control device. Respondent 22-1 used a three stage water condenser,
PH-III to control emission from the post oxidation concentrators, obtaining
65% Specific Efficiency, incurring a net cost in the operations.
Respondent 22-4, with water condenser PH-IX above a post-oxidation wash
unit, really considers this an economic necessity, hence, provided no
recovery or operating cost data.

Respondent 22-1 shows single cold water condensers with knock-out
drums PH-X and PH-XI for the cleavage reactor and an acetone tower,
respectively; two-stage cold water condensers with steam jet ejectors and
knock-out drums (PH-XII and PH-XIII) for acetone purification and phenol
recovery, respectively. In each case the equipment is a legitimate
emission control cost item, but there is insufficient data provided to
allow an estimate of efficiency.

## Incineration Devices

Producer 22-3 identifies a gas-fired incinerator PH-IV normally*, serving
to virtually eliminate hydrocarbon emissions from the oxidizer off-gas that
has already passed through what appears to be fairly efficient activated
carbon beds. Analytical data given indicate no unburned hydrocarbon or
pollutant other than a trace of $NO_x$ in the effluent, hence, virtually
100% Specific Efficiency.

Respondent 22-8 lists PH XV gas fired flare for periodic burning of
heavy ends waste, and reports that on equipment design basis, combustion
is complete, so 100% efficiency is indicated (though an infrequent off-plant

_____

*Out of service for extensive repairs at the time of responding to the
questionnaire, August, 1972.

odor problem is mentioned). Respondent 22-3 reports that both light and heavy oil waste is sent to plant boilers as fuel, but no information is provided to indicate efficiencies. Both of these incinerators probably cause the formation of at least traces of $NO_x$.

Future Possibilities

Among items mentioned by respondents for improvement in emission control were these:

1. Installation of vapor recovery or vapor conservation equipment on tanks.

2. Improvement in pump seals for phenolic stocks.

3. General process improvements. Areas for investigation in this regard include the following:

    (a) Reexamination of proposals to use oxygen in place of air, with due emphasis on safety and economic considerations.

    (b) Further use of refrigerated condenser equipment.

    (c) Further use of hydrocarbon recovery systems like activated carbon.

## V. Significance of Pollution

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980, and to estimate total weighted annual emissions of pollutants from these new plants. The results are summarized in Tables V, VI and VII.

On a weighted emission basis, a Significant Emission Index of 1,704 has been calculated in Table VII. This is well below the SEI's anticipated for other processes in the study.

Because of the relatively low SEI, it is recommended that no in-depth study of the Cumene Oxidation Process for the production of Phenol be undertaken in the current study. Although, a review of this recommendation may be justified at a future date. The reasons for review are somewhat subjective in nature, and no one of them would be justification on its own for an in-depth study. However, taken together they might be sufficiently important to warrant the collection of data that are pertinent to the setting of emission standards on new stationary sources. Briefly, these reasons are:

1) The reported oxidizer emissions factors range from a trace to nearly 0.01 with an emergency factor of nearly .05 reported in one instance. This is understandable since pollution control devices range from simple condenser systems through scrubbers to carbon absorbers and incinerators.

2) The reported oxidizer emissions include pollutants such as formaldehyde, acetophenone and cumene. If traces of cumene hydroperoxide are also present in this stream, it could be acid cleaved in the surroundings to form phenol.

3) Cleavage vents also contain noxious substances such as aldehydes.

4) Emission factors alone do not tell the story since some plants report emissions in terms of hundreds of pounds per hour of hydrocarbons or aldehydes.

5) An amount of liquid waste which is equivalent to about 10% of the production capacity is typically incinerated, which if uncontrolled could produce significant air pollution, expecially $NO_x$ or products of incomplete combustion.

6) Occasional off-plant odors are reported.

7) Phenol is highly toxic.

8) The process is clearly a growth one. Thus, economics of scale and new design might force shut downs of more marginal plants than were assumed in the prediction of the numbers of new plants. Hence, a greater number of candidates for new source standards would exist.

9) Phenol storage techniques are such that significant quantities of the substance could be emitted.

## VI. Phenol Producers (vi, vii, viii)

Natural phenol hardware capacity was about 60 MM pounds of phenol per year in 1972, but actual capacity was somewhat lower because of a scarcity of feedstocks for coal-tar derived material. Producers in this natural product category include Kaiser Steel, Fontana, California, Koppers Co., Inc., Follansbee, W. Va., Merichem Co., Houston, Texas, Productol Chemical, Santa Fe Springs, California, Stinson Lumber Co., Anacortes, Washington and U. S. Steel Corporation, Clairton, Pa.

Synthetic phenol, as mentioned previously, is derived from cumene for the most part, other processes being found unable to compete except for certain special circumstances. For example, as noted by Stanford Research Institute in "Chemical Economics Handbook", Dow Chemical maintains a benzene chlorination plant, Kalama Chemical, Inc. a toluene oxidation plant and Reichhold Chemicals, Inc. a benzene sulfonation plant because of special by-products obtained. Following is a list of companies and locations where synthetic phenol is now being produced (see CEH, July, 1972). In many cases, a large proportion of the capacity is committed for captive use.

Published Synthetic Phenol Capacity [1].

| Company | Location | Manufacturing Process | 1972 Capacity MM Lb./Yr. |
|---|---|---|---|
| Allied Chemical Corp. | Frankford, Pa. | Cumene | 500 |
| Clark Oil & Refining Corp. | Blue Island, Ill. | Cumene | 75 |
| Dow Chemical Co. | Oyster Creek, Texas | Cumene | 400 |
| | Midland, Mich. | Chlorina. Benzene | 100 |
| Georgia-Pacific Corp. | Palquemine, La. | Cumene | 200 |
| Kalama Chemical, Inc. | Kalama, Wash. | Toluene | 48 |
| Monsanto Co. | Chocolate Bayou, Texas | Cumene | 375 |
| Reichhold Chemicals | Tuscaloosa, Ala. | Sulfonation | 135 |
| Shell Chemical Co. | Houston, Texas | Cumene | 60 |
| Skelly Oil Co. | El Dorado, Kansas | Cumene | 50 |
| Std. Oil Co. of California | Richmond, Cal. | Cumene | 55 |
| Union Carbide Corp. | Bound Brook, N. J. | Cumene | 150 |
| | Penuelas, P. R. | Cumene | (2) |
| United States Steel Corp. | Haverhill, Ohio | Cumene | 215 [3] |
| | | Total | 2,363 |

(1)  As given by J. L. Blackford, July, 1972, Chemical Economics Handbook, Stanford  Research Institute.

(2)  Union Carbide Penuelas, Puerto Rico, 200 MM Lb./Yr. new capacity, scheduled by January, 1973.

(3)  U. S. Steel, Haverhill plant capacity expansion up to 305 MM Lbs./Yr. in progress, see CW 1/31/73, page 19.

## MAIN REACTION

### I. Step A. Oxidation

Cumene + Oxygen $\longrightarrow$ Cumene Hydroperoxide

120.2       32       152.2

### I. Step B. Cleavage

Cumene Hydroperoxide    $\xrightarrow{H^+}$    Phenol + Acetone

152.2       94.1       58.1
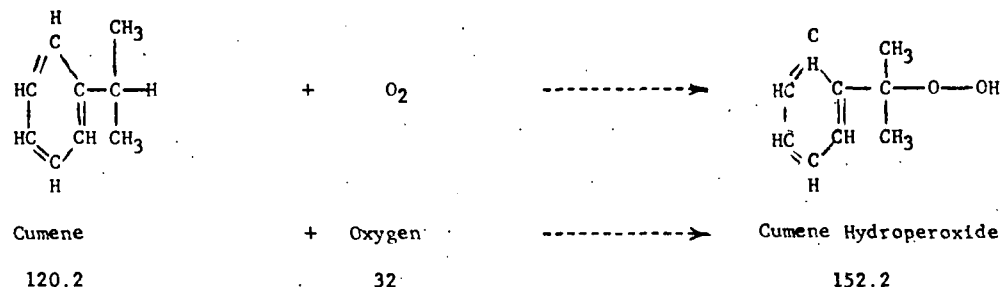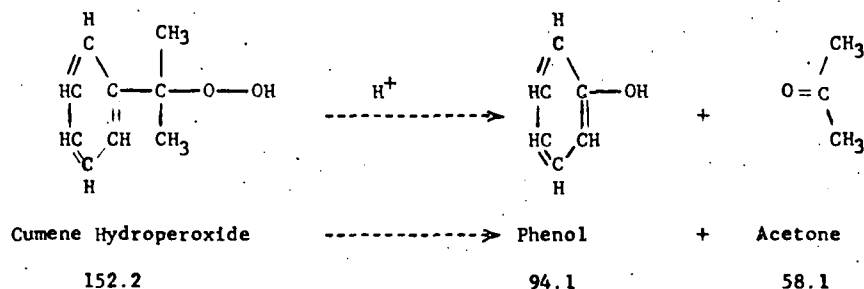
## SECONDARY REACTIONS

### II. Production of Acetophenone

Cumene Hydroperoxide $+ \frac{1}{2} O_2 \longrightarrow$ Acetophenone + Formaldehyde + Water

152.2       16       120.2       30       18
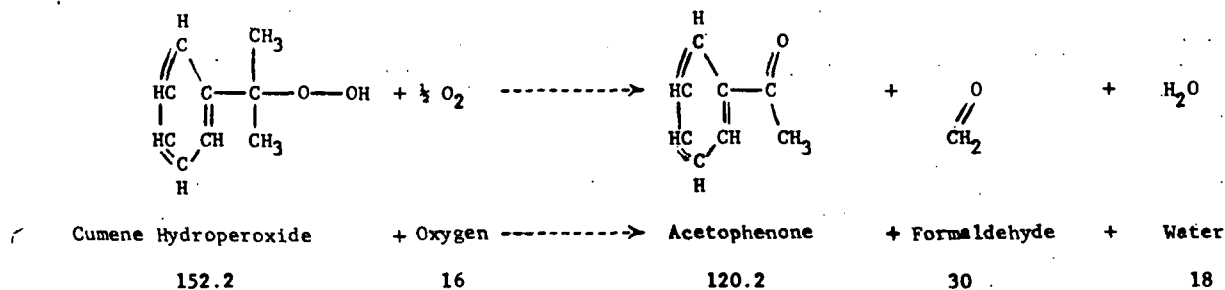
### III. Production of αMethylstyrene

Cumene Hydroperoxide $\longrightarrow$ Cumyl Alcohol + Oxygen $\xrightarrow{(B)}$ αMethyl Styrene + Water

152.2       136.2       16       118.2       9
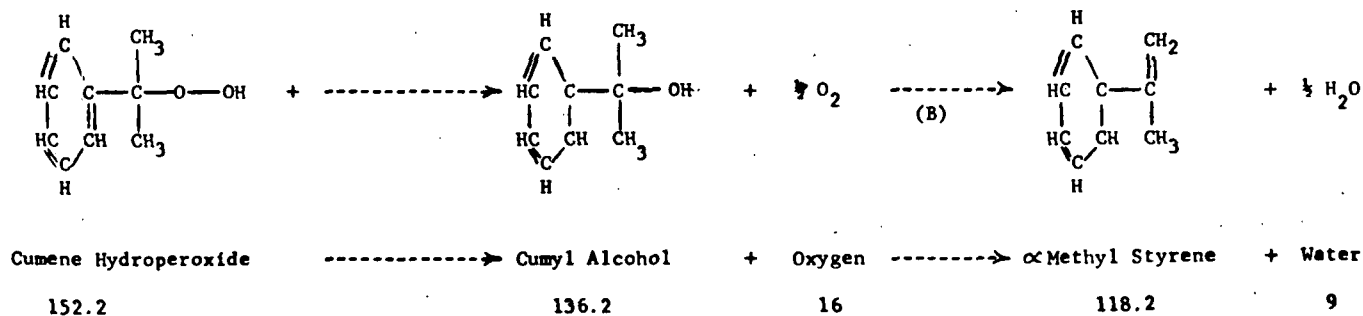
## TABLE PH-II
## PHENOL PRODUCTION EX CUMENE

### MATERIAL BALANCE* TONS/TON OF PRODUCT

| Stream No. (Fig. II) | (1) | (2) | (3) | (1, 2 & 3) | (5) | (6) | (7) | (8) |
|---|---|---|---|---|---|---|---|---|
| Stream Name | Oxidizing Air | Feed | Recycle | Gross Oxidizer Feed | Oxidizer Effluent | Vent | Cleavage Effluent | Acetone Twr. Ovhd. |
| Cumene | | 1.4450 | 3.2611 | 4.7061 | 3.2611 | .0029 | 3.2611 | |
| Cumene Hydroperoxide | | | | | 1.7621 | | | |
| Phenol | | | | | | | 1.0091 | |
| Acetone | | | | | | | .6230 | .6204 |
| αMe-Styrene | | | | | | | .1009 | |
| Acetophenone | | | | | .0505 | | .0505 | |
| Formaldehyde | | | | | | .0126 | | |
| Oxygen | .5007 | | | .5007 | | .1100 | .0137 | |
| Nitrogen | 1.7319 | | | 1.7319 | | 1.7319 | | |
| Water | | | | | .0052 | .0024 | .0206 | |
| Total | 2.2326 | 1.4450 | 3.2611 | 6.9387 | 5.0789 | 1.8598 | 5.0789 | .6204 |

| Stream No. (Fig. II) | (9) | (10) | (11) | (12) | (13) | (14) | (15) | (16) | (17) |
|---|---|---|---|---|---|---|---|---|---|
| Stream Name | Acetone Tower Vent | Cumene Tower Ovhd. | αMe Styrene Tower Ovhd. | Phenol Tower Btms. | Phenol Product | Alkali To Oxidizer | Make-up Acid | Wash Water | Wash Tower Btm. |
| Cumene | | 3.2611 | | | | Not Defined – See Note "A" | Not Defined – See Note "B" | Not Defined – See Note "C" | Not Defined – See Note "D" |
| Cumene Hydroperoxide | | | | | | | | | |
| Phenol | | | | .0091 | 1.0000 | | | | |
| Acetone | .0026 | | | | | | | | |
| αMe-Styrene | | | .1009 | | | | | | |
| Acetophenone | | | | .0505 | | | | | |
| Formaldehyde | | | | | | | | | |
| Oxygen | | | | | | | | | |
| Nitrogen | | | | | | | | | |
| Water | | | | | | | | | |
| Total | .0026 | 3.2611 | .1009 | .0596 | 1.000 | | | | |

Notes: "A" Oxidation is facilitated thru the use of an alkaline - aqeous emulsion - PH of 8.5 - 10.0 - a Na2CO3 solution is normally used with emulsifying agents, H2O/oil ratio is thought to be in the range of 2/1 to 5/1 (vol.).

"B" Dilute (~10%) sulfuric acid is recycled for cleavage - make-up rate is unknown.

"C" Wash water to remove residual acid, rate unspecified.

"D" Consists of wash water and residual H2SO4.

*See notes "A" & "B" and Phenol Table II Material Balance Limitations.

PHENOL TABLE II MATERIAL BALANCE LIMITATIONS

1. Cumene conversion is set @ 30.7%; conversion usually reported between 25 and 45%.

2. Selectivity (moles phenol formed/moles cumene converted expressed as %) is set @ 88.4%. If methyl styrene is hydrogenated and recycled so that ½ goes to phenol, selectivity would be 92%. Since demand for ∝MS is less than ½ rated capacity, recycle is often preferred.

3. A review of respondents data reveals that heavy residual material amounting to ~ .1000 tons/ton of phenol is produced. This is not included in the material balance shown here because definitive composition information is lacking. If it be assumed that a like amount of cumene (0.1000 tons/ton of phenol) be consumed producing this heavy material, along with recycle of methyl styrene (see 2 above) a selectivity of 86 mole % would be realized, in line with the average figure reported by the eight respondents in the present study.

4. Oxidizing air fixed at 50 lb./100 lb. product phenol, which is ~140% of theoretical for conversion and selectivity shown.

5. Hydrocarbons are shown only for the two vent streams (6) and (9) where emissions are appreciable, though other vent streams do contain measurable emissions, as indicated in Table III.

6. All cumene recycle here is shown in cleavage section effluent, though, as indicated in Figure II, some proportion is usually taken out for recycle following oxidation and/or concentration.

7. Water amounts shown here represent only reaction product as indicated in Table I where formaldehyde and methyl styrene are produced. Substantial quantities of water are required for the alkaline aqueous emulsion in the oxidation section (2 to 5 times hydrocarbons present), for the dilute sulfuric acid (~10% concentration) in the cleavage section, and in the subsequent wash tower.

TABLE PH-IIA
PRODUCTION OF PHENOL FROM CUMENE
GROSS HEAT BALANCE (xiii, xiv, xv)

BASIS MATERIAL BALANCE TABLE II
AND REACTIONS IN TABLE I

| OXIDATION REACTOR | BTU/Lb. Phenol Product | |
| --- | --- | --- |
| | Exothermic (Cooling Req'd.) | Endothermic (Heating Req'd.) |
| Reaction I (A) producing cumene hydroperoxide | 483 | |
| "     II      "        acetophenone | 58 | |
| Heating cumene charge from 90 to 250° F | | 346 |
| Heating $N_2$ & $O_2$ from 90 to 250° F | | 87 |
| Totals | 541 | 433 |
| Net heat exchange requirement (difference) | 108 | |

| CLEAVAGE REACTOR | | |
| --- | --- | --- |
| Reaction I (B) producing phenol & acetone | 991 | |
| Reactions III (A) producing cumyl alcohol and III (B) producing  methyl styrene | 31 | |
| Cooling cumene from 250° F to 140° F | 165 | |
| Cooling cumene hydroperoxide & acetophenone to 140° F | 120 | |
| Totals | 1,307 | 0 |
| Net heat exchange requirement (difference) | 1,307 | |

TABLE PH-III
NATIONAL EMISSIONS INVENTORY
PHENOL PRODUCTION FROM CUMENE

Plant - EPA Code Number — 22-1
Capacity - Tons of Phenol/Yr. — 26,500
Average Production - Tons of Phenol/Yr. — 26,500
Quarterly Production Variation - % of Max. — 0

Emissions to Atmosphere

| Stream | Feed Purification Section Vent | Oxidation Section Vent | Concentration Section Vapor Condenser Vent | Cleavage Section Vapor Condenser Vent |
|---|---|---|---|---|
| Flow - Lb./Hr. | Unknown [1] | 21,800 [2] | 51.3 [2] | Unknown |
| Flow Characteristics - Continuous or Intermittent if Intermittent - Hrs/Yr. Flow | Continuous | Continuous | Continuous | Continuous |
| Composition - Tons/Ton of Phenol [5] | | | | |
| Cumene | (+) | (+) | .00001 [3] | |
| Cumene Hydroperoxide | | | | |
| Phenol | | | | |
| Acetone | | | | (+) |
| ⍺-Methyl Styrene | | | | |
| Acetophenone | | | | (+) |
| Acetaldehyde | | | | (+) |
| Formaldehyde | | (+) | (+) | |
| Mesityl Oxide | | | | |
| Dimethyl Benzyl Alcohol | | | | |
| Benzene | | | | |
| Toluene | | | + | |
| Ethyl Benzene | | | + | |
| Misc. Hydrocarbons | (+) | .0025 [2] | .00025 [2] | + (5%) |
| Cumyl Phenol & Phenolic Tars | | | | |
| Water | | + | + | + |
| Carbon Dioxide | | + | + | + |
| Nitrogen | | + | + | + |
| Oxygen | | + | + | + |
| Sample Tap Location | 12' up [7] | Elevated [7] | Elevated [7] | Elevated [7] |
| Date or Frequency of Sampling | Never | Twice | Twice (1970 & 1972) | Once (1972) |
| Type of Analysis | | G.C. ±5% | G.C. ±10% | G.C. ±10% |
| Odor Problems | No | Yes (in plant) | No | No |
| Vent Stacks | | | | |
| Flow - SCFM/stack | | 4350 [2] | 10.2 [2] | |
| Number | 1 | 1 | 1 | 1 |
| Height - Feet | 112 | 125 | 40 | 20 |
| Diameter - Inches | 2 | 10 | 2 | 2 |
| Exit Gas Temp. °F | Ambient | Ambient | Ambient | Ambient |
| Emission Control Devices | Yes | Yes | Yes | Yes |
| Type - Incinerator | | | | |
| Flare | | | | |
| Scrubber | | | | |
| Other | Liquid Trap | Scrubber-Cooler | Vapor Condenser | Vapor Condenser |
| Catalog I. D. Number | PH-I | PH-II | PH-III | PH-X |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | (+) | .0025 [2] | .0003 [2] | + |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | 0 | 0 | 0 | 0 |
| Total $NO_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total $SO_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | |

| | | | | |
|---|---|---|---|---|
| Plant - EPA Code Number | 22-1 | | | |
| Capacity - Tons of Phenol/Yr. | 26,500 | | | |
| Average Production - Tons of Phenol/Yr. | 26,500 | | | |
| Quarterly Production Variation - % of Max. | 0 | | | |
| Emissions to Atmosphere | | | | |
| Stream | Phenol & Acetone Sep'n/Purification Section Vapor Cond. Vents | Phenol Recovery & Sep'n. Section Vapor Cond. Vent | Residual Oil Sump Vent | Phenolic Water Sump Vent |
| Flow - Lb./Hr. | Unknown | Unknown | Unknown | Unknown |
| Flow Characteristics - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous |
| if Intermittent - Hrs./Yr. Flow | | | | |
| Composition - Tons/Ton of Phenol [5] | | | | |
| Cumene | | | | |
| Cumene Hydroperoxide | | | | |
| Phenol | | (+) | | (+) |
| Acetone | + | | | |
| $\alpha$ Methyl Styrene | | | | |
| Acetophenone | | | | |
| Acetaldehyde | (+) | | | |
| Formaldehyde | | | | |
| Mesityl Oxide | | | | |
| Dimethyl Benzyl Alcohol | | | | |
| Benzene | | | | |
| Toluene | | | | |
| Ethyl Benzene | | | | |
| Misc. Hydrocarbons | (+) | (+) | (+) | (+) |
| Cumyl Phenol & Phenolic Tars | | | | |
| Water | | | | |
| Carbon Dioxide | | | | |
| Nitrogen | | | | |
| Oxygen | | | | |
| Sample Tap Location | Elevated [7] | Elevated [7] | No port [7] | No port [7] |
| Date or Frequency of Sampling | Never | Never | Never | Never |
| Type of Analysis | | | | |
| Odor Problems | No | No | No [6] | Yes [8] |
| Vent Stacks | | | | |
| Flow - SCFM/stack | | | | |
| Number | 1 | 1 | 1 | 1 |
| Height - Feet | 120 | 125 | 30 | 24 |
| Diameter - Inches | 3 | 3 | 2 | 6 |
| Exit Gas Temp. °F | Ambient | Ambient | Ambient | Ambient |
| Emission Control Devices | Yes | Yes | Yes | None |
| Type - Incinerator | | | | |
| Flare | | | | |
| Scrubber | | | Yes | |
| Other | Vapor Condenser | Vapor Condenser | (6) | |
| Catalog I. D. Number | PH-XI, XII | PH-XIII | PH-XIV | |
| Total Hydrocarbon Emission - Ton/Ton of Phenol | (+) [4] | (+) | (+) | (+) |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | 0 | 0 | 0 | 0 |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | |

| | Oxidation Concentration Cleavage Section Pump Drain Sampling Vent | Misc Vent Water Scrubber Stack [10] | Process Bottoms Transfer Pump |
|---|---|---|---|
| Plant - EPA Code Number | | 22-1 | |
| Capacity - Tons of Phenol/Yr. | | 26,500 | |
| Average Production - Tons of Phenol/Yr. | | 26,500 | |
| Quarterly Production Variation - % of Max. | | 0 | |
| Emissions to Atmosphere | | | |
| Stream | | | |
| Flow - Lb./Hr. | 1.455 | Unknown | Unknown |
| Flow Characteristics - Continuous or Intermittent | Continuous | Continuous | Occasional |
| if Intermittent - Hrs./Yr. Flow | | | |
| Composition - Tons/Ton of Phenol [5] | | | |
| Cumene | | (+) | |
| Cumene Hydroperoxide | | | |
| Phenol | | | |
| Acetone | | (+) | |
| α-Methyl Styrene | | | |
| Acetophenone | | | |
| Acetaldehyde | | (+) | |
| Formaldehyde | | | |
| Mesityl Oxide | | | |
| Dimethyl Benzyl Alcohol | | | |
| Benzene | | | |
| Toluene | | | |
| Ethyl Benzene | | | |
| Misc. Hydrocarbons | .0000009 [9] | (+) | |
| Cumyl Phenol & Phenolic Tars | | | |
| Water | + | (+) | |
| Carbon Dioxide | + | | |
| Nitrogen | + | (+) | |
| Oxygen | + | (+) | (+) |
| Sample Tap Location | At grade [7] | Need platform [7] | Hot stack [7] |
| Date or Frequency of Sampling | Once (1972) | Never | Not Sampled |
| Type of Analysis | G.C. ±5% | | |
| Odor Problems | No | No | Occasional [8] |
| Vent Stacks | | | |
| Flow - SCFM/stack | .29 | | |
| Number | 1 | 1 | |
| Height - Feet | 70 | 87 | |
| Diameter - Inches | 2 | 14 | |
| Exit Gas Temp. °F | Ambient | Ambient | |
| Emission Control Devices | None | | |
| Type - Incinerator | | | |
| Flare | | | |
| Scrubber | | Yes | |
| Other | | | |
| Catalog I. D. Number | | PH-XIV | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | .0000009 [9] | (+) [11] | (+) |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | 0 | 0 | 0 |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | |

| | | | | |
|---|---|---|---|---|
| Plant - EPA Code Number | | 22-3 | | |
| Capacity - Tons of Phenol/Yr. | | 200,000 | | |
| Average Production - Tons of Phenol/Yr. | | 200,000 | | |
| Quarterly Production Variation - % of Max. | | 0 | | |
| Stream | Oxidation Section Vent | Oxidation Section Incinerator Stack | Gases (Calc.) ex Incineration of Light Oil Waste | Gases (Calc.) ex Incineration of Heavy Oil Waste |
| Flow - Lb./Hr. | 114,300 [13] | 128,600 [13], [15] | 47,100 [16] | 142,000 [17] |
| Flow Characteristics - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous |
| if Intermittent - Hrs./Yr. Flow | | | | |
| Composition - Tons/Ton of Phenol [5] | | | | |
| Cumene | 0 to .005 | | | |
| Cumene Hydroperoxide | | | | |
| Phenol | | | | |
| Acetone | | | | |
| α Methyl Styrene | | | | |
| Acetophenone | | | | |
| Acetaldehyde | | | | |
| Formaldehyde | (+) | | | |
| Mesityl Oxide | | | | |
| Dimethyl Benzyl Alcohol | | | | |
| Benzene | | | | |
| Toluene | | | | |
| Ethyl Benzene | | | | |
| Misc. Hydrocarbons | "trace" (orgs.) | (+) | | |
| Cumyl Phenol & Phenolic Tars | | | | |
| Water | 0 to .0024 | Trace | .0522 | .0833 |
| Carbon Dioxide | | | .1521 | .3583 |
| Nitrogen | 2.2625 | + | .6679 | 2.1813 |
| Oxygen | .1190 | + | .1093 | .3354 |
| Sample Tap Location | Stairway access | Difficult | None [18] | None [18] |
| Date or Frequency of Sampling | at original start-up | Never | | |
| Type of Analysis | Org. G.C. ±20% | | | |
| Odor Problem | Yes (in plant) [14] | No [15] | | |
| Vent Stacks | | | | |
| Flow - SCFM/stack | 25,700 | 20,250 | | |
| Number | | 1 | | |
| Height - Feet | | 55 | | |
| Diameter - Inches | | 72 | | |
| Exit Gas Temp. °F | 50° | 450° | | |
| Emission Control Devices | | | | |
| Type - Incinerator | | Yes [15] | | |
| Flare | | | | |
| Scrubber | | | Boiler (Fuel) | Boiler (Fuel) |
| Other | Activa. Carbon [12] | | Boiler #1 | Boiler #2 |
| Catalog I. D. Number | | PH-IV | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | 0 to .005 [12] | (+) | | |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | "trace" | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | 0 | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | |

| | | | | |
|---|---|---|---|---|
| Plant - EPA Code Number | | 22-4 [21] | | |
| Capacity - Tons of Phenol/Yr. | | 125,000 | | |
| Average Production - Tons of Phenol/Yr. | | 125,000 | | |
| Quarterly Production Variation - % of Max. | | 0 | | |
| Stream | Oxidizer Section Vent | Post Oxidizer Washer, Surge Tank Combination Vent | Cumene Stripper Jet Condenser Vent | Acetone Topping Column Overhead Accumulator |
| Flow - Lb./Hr. | 53,500 [19] | 790 [19] | Unknown | 64 [19] |
| Flow Characteristics - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous |
| if Intermittent - Hrs./Yr. Flow | | | | |
| Composition - Tons/Ton of Phenol [5] | | | | |
| Cumene | .0020 | .0003 | + | |
| Cumene Hydroperoxide | | | | |
| Phenol | | | | |
| Acetone | | | | .0012 |
| α Methyl Styrene | | | | |
| Acetophenone | | | | |
| Acetaldehyde | | | | .0009 |
| Formaldehyde | .0032 | | | (+) |
| Mesityl Oxide | | | | |
| Dimethyl Benzyl Alcohol | | | | |
| Benzene | .0015 | | | |
| Toluene | | | | |
| Ethyl Benzene | | | | |
| Misc. Hydrocarbons | | | + | |
| Cumyl Phenol & Phenolic Tars | | | | |
| Water | .0017 | | | |
| Carbon Dioxide | | | | |
| Nitrogen | 1.6550 | + | | (+) |
| Oxygen | .1000 | + | | (+) |
| Sample Tap Location | Easily arranged | | Could arrange | Could arrange |
| Date or Frequency of Sampling | Never [19] | Never [19] | Never | Never [19] |
| Type of Analysis | | | | |
| Odor Problem | No | Yes (in plant) | No | Yes (in plant) |
| Vent Stacks | | | | |
| Flow - SCFM/stack | 12,000 | 180 | Unknown | 7.8 |
| Number | 1 | 1 | 1 | 1 |
| Height - Feet | 70 | 30 | 40 | 80 |
| Diameter - Inches | 14 | 4 | 6 | 10 |
| Exit Gas Temp. °F | 45° | 85° | 130° | 110° |
| Emission Control Devices | | | | |
| Type - Incinerator | | | | |
| Flare | | | | |
| Scrubber | | | | |
| Other | Refrig. 73 psig Cond. [20] | 18 psig Chiller [20] | C. W Condenser | C. W. Condenser |
| Catalog I. D. Number | PH-V | PH-IX | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | .0067 | .0003 | + | .0021 |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | |

| | | Post Cleavage Reactor Vapor Condenser Vent | Post Cleavage Washer Vent | Phenol-Acetone Still Vapor Condenser Vent | Acetone Column Vapor Condenser Vent | Phenol Recovery Overhead Accumulator Section Vent |
|---|---|---|---|---|---|---|
| Plant - EPA Code Number | 22-4 [21] | | | | | |
| Capacity - Tons of Phenol/Yr. | 125,000 | | | | | |
| Average Production - Tons of Phenol/Yr. | 125,000 | | | | | |
| Quarterly Production Variation - % Of Max. | 0 | | | | | |
| Stream | | | | | | |
| Flow - Lb./Hr. | | Unknown | Unknown | Unknown | Unknown | Unknown |
| Flow Characteristics - Continuous or Intermittent | | Continuous | Continuous | Continuous | Continuous | Continuous |
| if Intermittent - Hrs./Yr. Flow | | | | | | |
| Composition - Tons/Ton of Phenol [5] | | | | | | |
| Cumene | | | | | | |
| Cumene Hydroperoxide | | | | | | |
| Phenol | | | | | | (+) |
| Acetone | | (+) | | (+) | (+) | |
| α Methyl Styrene | | | | | | |
| Acetophenone | | | | | | |
| Acetaldehyde | | (+) | | | | |
| Formaldehyde | | (+) | | | | |
| Mesityl Oxide | | | | | | |
| Dimethyl Benzyl Alcohol | | | | | | |
| Benzene | | | | | | |
| Toluene | | | | | | |
| Ethyl Benzene | | | | | | |
| Misc. Hydrocarbons | | (+) | (+) | (+) | (+) | (+) |
| Cumyl Phenol & Phenolic Tars | | | | | | |
| Water | | | (+) | | | |
| Carbon Dioxide | | | | | | |
| Nitrogen | | (+) | | | | |
| Oxygen | | (+) | | | | |
| Sample Tap Location | | | | | | |
| Date or Frequency of Sampling | | | | | | |
| Type of Analysis | | | | | | |
| Odor Problem | | | | | | |
| Vent Stacks | | | | | | |
| Flow - SCFM/stack | | | | | | |
| Number | | | | | | 1 |
| Height - Feet | | | | | | ? |
| Diameter - Inches | | | | | | |
| Exit Gas Temp. °F | | | | | | |
| Emission Control Devices | | | | | | |
| Type - Incinerator | | | | | | |
| Flare | | | | | | |
| Scrubber | | | | | | |
| Other | | C. W. Condenser | | C. W. Condenser | Condenser | |
| Catalog I. D. Number | | | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | | (+) | (+) | (+) | (+) | + |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | | | |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | | | | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | | | |

| | 22-5 | | 22-6 | | |
|---|---|---|---|---|---|
| Plant - EPA Code Number | 22-5 | | 22-6 | | |
| Capacity - Tons of Phenol/Yr. | 107,500 | | 100,000 | | |
| Average Production - Tons of Phenol/Yr. | 107,500 | | 100,000 | | |
| Quarterly Production Variation - % of Max. | 0 | | 0 | | |
| Emissions to Atmosphere | | | | | |
| Stream | Spent Oxidation Air Vent | Oxidizer Off-gas Vent (23) | Post Oxidizer Cumene Recovery Spent Air Vent | Post Oxidizer Concentration Condenser Vent | Cleavage Condenser Vent |
| Flow - Lb./Hr. | 48,080 (22) | 36,995 | 33,973 | 6.0 | 6.5 |
| Flow Characteristics - Continuous or Intermittent if Intermittent - Hrs./Yr. Flow | Continuous | (See note) | Continuous | Continuous | Continuous |
| Composition - Tons/Ton of Phenol (5) | | | | | |
| Cumene | .0015 (22) | .0383 | .0020 | .00002 | |
| Cumene Hydroperoxide | | | | | |
| Phenol | | | | | |
| Acetone | | | | | .0002 |
| α Methyl Styrene | | | | | |
| Acetophenone | | | | | |
| Acetaldehyde | | | | | (+) |
| Formaldehyde | (+) | .0015 | .0014 | .000007 | (+) |
| Mesityl Oxide | | | | | |
| Dimethyl Benzyl Alcohol | | | | | |
| Benzene | (+) | (+) | | .000002 | |
| Toluene | | | | .000001 | |
| Ethyl Benzene | | | | .0000002 | |
| Misc. Hydrocarbons | (+) | (+) | (+) | (+) | |
| Cumyl Phenol & Phenolic Tars | | | | | |
| Water | .0015 | .0295 | .0408 | .00001 | .00003 |
| Carbon Dioxide | | | | | |
| Nitrogen | 1.6642 | 1.3022 | 1.2203 | .00013 | .00003 |
| Oxygen | .1309 | .1032 | .0951 | .00007 | .00002 |
| Sample Tap Location | Could install | Easy access | Easy access | Easy, 10' up | Easy, 5' up |
| Date or Frequency of Sampling | Never | Monthly from 9/71 | 3 x/month from 9/71 | 9/18 & 9/20/72 | Never |
| Type of Analysis | None | Acetone Scrub. GLC | Acetone Scrub. GLC | G.C. ± 20% | Design Calc., ± 20% |
| Odor Problems | No | Yes (in plant) | No | No | No |
| Vent Stacks | | | | | |
| Flow - SCFM/stack | 10,190 | 7576 | 7576 | 1.1 | 0.83 |
| Number | 1 | | 1 | 1 | 1 |
| Height - Feet | 86 | | 86 | 76 | 76 |
| Diameter - Inches | 10 | | 12 | 2 | 2 |
| Exit Gas Temp. °F | 40° | 100° @ 28 psig | 140° | 105° | 95° |
| Emission Control Devices | | | | | |
| Type - Incinerator | | | | | |
| Flare | | | | | |
| Scrubber | | | | | |
| Other | Refrig. 70 psig Condenser | | Carbon Absorber | | |
| Catalog I. D. Number | PH-VI | | PH-VII | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | .0015 (22) | .0398 (23) | .0034 (24) | .00003 | .0002 |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | | |
| Total NO_x Emissions - Ton/Ton of Phenol | | | | | |
| Total SO_x Emissions - Ton/Ton of Phenol | | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | | |

Plant - EPA Code Number                                        22-6
Capacity - Tons of Phenol/Yr.                                  100,000
Average Production - Tons of Phenol/Yr.                        100,000
Quarterly Production Variation - % of Max.                     0
Emissions to Atmosphere

| Stream | Acetone Topping Column Vent | Acetone Tower Vent | αMethyl Styrene Tower Vent | Natural Gas Fired Reboiler Stack |
|---|---|---|---|---|
| Flow - Lb./Hr. | 115 (25) | Unknown | 11 | |
| Flow Characteristics - Continuous or Intermittent | Continuous | Intermittent | Continuous | |
| if Intermittent - Hrs./Yr. Flow | | ~1600 (26) | | |
| Composition - Tons/Ton of Phenol (5) | | | | |
| Cumene | | | .0001 | |
| Cumene Hydroperoxide | | | | |
| Phenol | | | | |
| Acetone | .0043 | + | | |
| αMethyl Styrene | | | | |
| Acetophenone | | | | |
| Acetaldehyde | .0003 | | | |
| Formaldehyde | (+) | | | |
| Mesityl Oxide | | | .00005 | |
| Dimethyl Benzyl Alcohol | | | | |
| Benzene | | | | |
| Toluene | | | .00004 | |
| Ethyl Benzene | | | .0002 | |
| Misc. Hydrocarbons | | | (+) | |
| Cumyl Phenol & Phenolic Tars | | | | |
| Water | | + | | |
| Carbon Dioxide | | | | |
| Nitrogen | (+) | + | | |
| Oxygen | (+) | + | | |
| Sample Tap Location | Easy access | Remove drain bell | Difficult | |
| Date or Frequency of Sampling | Daily (liquid) | Never | Daily for >1 year | |
| Type of Analysis | Calc. ex G.C. on equil. liquid | Calc. | Calc. ex G.C. on equil. liquid | |
| Odor Problems | Yes, Infrequently off plant | No | Yes, Infrequently off plant | |
| Vent Stacks | | | | |
| Flow - SCFM/stack | 12.8 | | 0.70 | |
| Number | 1 | 1 | 1 | |
| Height - Feet | 86 | 86 | 70 | |
| Diameter - Inches | 6 | 18 | 4 | |
| Exit Gas Temp. °F | 130° | 95° | 289° | |
| Emission Control Devices | | | | |
| Type - Incinerator | | | | |
| Flare | | | | |
| Scrubber | | | | |
| Other | | | | |
| Catalog I. D. Number | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | .0046 (25) | + (26) | .0004 | (27) |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | | | .00000004 |
| Total CO Emissions - Ton/Ton of Phenol | | | | |

Plant - EPA Code Number — 22-7
Capacity - Tons of Phenol/Yr. — 40,000
Average Production - Tons of Phenol/Yr. — 40,000
Quarterly Production Variation - % of Max. — 0

Emissions to Atmosphere

| Stream | Post Oxidizer Carbon Sorber Vent | Post Oxidizer Steam Jet Vent | Phenol Recovery Purification Vent | Product Recovery Section Steam Jet Vent | Acetone Recovery Section Vent |
|---|---|---|---|---|---|
| Flow - Lb./Hr. | 23,800 [28] | No data | No data | No data | No data |
| Flow Characteristics - Continuous or Intermittent | Continuous | Continuous | | | |
| if Intermittent - Hrs./Yr. Flow | | | | | |
| Composition - Tons/Ton of Phenol [5] | | | | | |
| Cumene | .0029 | (+) | | | |
| Cumene Hydroperoxide | | | | | |
| Phenol | | | (+) | | |
| Acetone | | | | | (+) |
| ∝ Methyl Styrene | | | | | |
| Acetophenone | | | | | |
| Acetaldehyde | | | | | |
| Formaldehyde | | (+) | | | |
| Mesityl Oxide | | | | | |
| Dimethyl Benzyl Alcohol | | | | | |
| Benzene | | | | | |
| Toluene | | | | | |
| Ethyl Benzene | | | | | |
| Misc. Hydrocarbons | (+) | (+) | (+) | (+) | |
| Cumyl Phenol & Phenolic Tars | | | | | |
| Water | | (+) | | | |
| Carbon Dioxide | | | | | |
| Nitrogen | | (+) | | | |
| Oxygen | | (+) | | | |
| Sample Tap Location | Difficult | | | | |
| Date or Frequency of Sampling | 4 times per year | | | | |
| Type of Analysis | GLC on cond. liq. | | | | |
| Odor Problems | Undetermined | | | | |
| Vent Stacks | | | | | |
| Flow - SCFM/stack | 5330 | | | | |
| Number | Not given | 1 | 1 | 1 | 1 |
| Height - Feet | | 50 | 70 | 75 | 75 |
| Diameter - Inches | | 4 | 4 | 4 | 4 |
| Exit Gas Temp. °F | 41° | 70° | 70° | 70° | 70° |
| Emission Control Devices | | | | | |
| Type - Incinerator | | | | | |
| Flare | | | | | |
| Scrubber | | | | | |
| Other | Carbon Adsorber | | | | |
| Catalog I. D. Number | PH-VIII | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | .0029 | (+) | (+) | (+) | (+) |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | | |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | | |

| | Product Recovery Section Vent | ∝ Methyl Styrene Recovery Section Steam Jet Vent | ∝ Methyl Styrene Recovery Section Vent | Residual Fuel Recovery Section Vent |
|---|---|---|---|---|
| Plant - EPA Code Number | | 22-7 | | |
| Capacity - Tons of Phenol/Yr. | | 40,000 | | |
| Average Production - Tons of Phenol/Yr. | | 40,000 | | |
| Quarterly Production Variation - % of Max. | | 0 | | |
| Emissions to Atmosphere | | | | |
| Stream | | | | |
| Flow - Lb./Hr. | No data | No data | No data | No data |
| Flow Characteristics - Continuous or Intermittent | | | | |
| if Intermittent - Hrs./Yr. Flow | | | | |
| Composition - Tons/Ton of Phenol (5) | | | | |
| Cumene | | (+) | (+) | |
| Cumene Hydroperoxide | | | | |
| Phenol | | | | |
| Acetone | | | | |
| ∝ Methyl Styrene | | | | |
| Acetophenone | | | | |
| Acetaldehyde | | | | |
| Formaldehyde | | | | |
| Mesityl Oxide | | (+) | (+) | |
| Dimethyl Benzyl Alcohol | | | | |
| Benzene | | | | |
| Toluene | | (+) | (+) | |
| Ethyl Benzene | | (+) | (+) | |
| Misc. Hydrocarbons | (+) | (+) | (+) | + |
| Cumyl Phenol & Phenolic Tars | | | | |
| Water | | | | |
| Carbon Dioxide | | | | |
| Nitrogen | | | | |
| Oxygen | | | | |
| Sample Tap Location | | | | |
| Date or Frequency of Sampling | | | | |
| Type of Analysis | | | | |
| Odor Problems | | | | |
| Vent Stacks | | | | |
| Flow - SCFM/stack | | | | |
| Number | 1 | 1 | 1 | 1 |
| Height - Feet | 75 | 50 | 50 | 75 |
| Diameter - Inches | 4 | 4 | 4 | 4 |
| Exit Gas Temp. °F | 70° | 70° | 70° | 70° |
| Emission Control Devices | | | | |
| Type - Incinerator | | | | |
| Flare | | | | |
| Scrubber | | | | |
| Other | | | | |
| Catalog I. D. Number | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | (+) | (+) | (+) | (+) |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | |
| Total $NO_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total $SO_x$ Emissions - Ton/Ton of Phenol | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | |

Plant - EPA Code Number    22-8
Capacity - Tons of Phenol/Yr.    30,000
Average Production - Tons of Phenol/Yr.    30,000
Quarterly Production Variation - % of Max.    7.5%
Emissions to Atmosphere

| Stream | Oxidizer Section Vent | Concentration Section Combined Vents | Cleavage Section Combined Vents | Product Recovery Section Combined Vents | Phenolic Heavy Ends Flare |
|---|---|---|---|---|---|
| Flow - Lb./Hr. | 14,220 | 18 | 48 | 47.5 | 72,800 [31] |
| Flow Characteristics - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous | Intermittent |
| if Intermittent - Hrs./Yr. Flow | | | | | 168 |
| Composition - Tons/Ton of Phenol [5] | | | | | |
| Cumene | .0040 [29] | .00005 | | | |
| Cumene Hydroperoxide | | | | | |
| Phenol | | | | .0000007 | |
| Acetone | | .00003 | .0024 | | |
| α Methyl Styrene | | | | | |
| Acetophenone | | | | | |
| Acetaldehyde | | (+) | ) | | |
| Formaldehyde | (+) | (+) | ).0013 | | |
| Mesityl Oxide | | | | | |
| Dimethyl Benzyl Alcohol | | | | | |
| Benzene | (+) | | | | |
| Toluene | | | | | |
| Ethyl Benzene | | | | | |
| Misc. Hydrocarbons | | | | (+) | (+) |
| Cumyl Phenol & Phenolic Tars | | | | | (+) |
| Water | .0040 | .0019 | .0026 | .0062 | .0217 |
| Carbon Dioxide | | | | | .0241 |
| Nitrogen | 1.7711 | ).0005 | | ).00003 | .1371 |
| Oxygen | .0959 | ) | | ) | .0210 |
| Sample Tap Location | None (difficult) | None (difficult) | None (difficult) | None (difficult) | Very difficult |
| Date or Frequency of Sampling | Never | Never | Never | Never | Never |
| Type of Analysis | Design Calc. (+20%) | Design Calc. (+30%) | Design Calc. (+50%) | Design (+40%) | Design Calc. (+20%) |
| Odor Problems | Yes, in plant | No | Yes, in plant | No | Yes, in plant |
| Vent Stacks | | | | | |
| Flow - SCFM/stack | 3200 | .89  4.85  .06 | .2  3.8  6.6 | 0.5  16.63 | 16,500 |
| Number | 1 | 1  1  1 | 1  1  1 | 1  1 | 1 |
| Height - Feet | 50 | 67  15  50 | 60  93  15 | 2  15 | 4 |
| Diameter - Inches | 6 | 20  2  3 | 1  16  3 | 1  4 | 15 |
| Exit Gas Temp. °F | 65° | ~125°(30) 215° 100° | 150° ~125 (30) 215° | 140° (30) 215° | 1000° |
| Emission Control Devices | | | | | |
| Type - Incinerator | | | | | Yes |
| Flare | | | | | Yes |
| Scrubber | | | | | |
| Other | | | | | |
| Catalog I. D. Number | | | | | PH-XV |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | .0040 [29] | .0001 | .0037 | .0000007 | (+) |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | | |
| Total NO$_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total SO$_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | | |

Plant - EPA Code Number — 22-9
Capacity - Tons of Phenol/Yr. — 28,500
Average Production - Tons of Phenol/Yr. — 28,500
Quarterly Production Variation - % of Max. — 29%

Emissions to Atmosphere

| | Post Oxidizer Cumene Recovery Section Vent | CHP Conc'n. & Decomp. Section Steam Eductor Vent | Raw Acetone Column Vent | Cumene Column Steam Eductor Vent | ∝Methyl Styrene Column Steam Eductor Vent |
|---|---|---|---|---|---|
| Flow - Lb./Hr. | 11,270 (32) | Unknown | Unknown | Unknown | Unknown |
| Flow Characteristics - Continuous or Intermittent if Intermittent - Hrs./Yr. Flow | Continuous | Continuous | Continuous | Continuous | Continuous |
| Composition - Tons/Ton of Phenol (5) | | | | | |
| Cumene | + | | | (+) | (+) |
| Cumene Hydroperoxide | | | | | |
| Phenol | | | | | |
| Acetone | | | + | | |
| ∝ Methyl Styrene | | | | | |
| Acetophenone | | | | | |
| Acetaldehyde | | | (+) | | |
| Formaldehyde | | (+) | (+) | | |
| Mesityl Oxide | | | | | (+) |
| Dimethyl Benzyl Alcohol | | | | | |
| Benzene | | | | | |
| Toluene | | | | | (+) |
| Ethyl Benzene | | | | | (+) |
| Misc. Hydrocarbons | + | + | | + | + |
| Cumyl Phenol & Phenolic Tars | | | | | |
| Water | | + | | + | + |
| Carbon Dioxide | | | | | |
| Nitrogen | }1.6744 | + | (+) | + | + |
| Oxygen | | + | (+) | + | + |
| Sample Tap Location | None, difficult | Very difficult | Very difficult | Very difficult | Very difficult |
| Date or Frequency of Sampling | Never | Never | Never | Never | Never |
| Type of Analysis | None | None | None | None | None |
| Odor Problems | Yes, off plant infreq. | No | "Not applicable" | No | No |
| Vent Stacks | | | | | |
| Flow - SCFM/stack | 2500 | | | | |
| Number | 1 | 2 | 1 | 1 | 1 |
| Height - Feet | 45 | 57 | 80 | 105 | 95 |
| Diameter - Inches | 14 | 1.5 | 3 | 1.5 | 1.5 |
| Exit Gas Temp. °F | 70° | 200° | 70° | 200° | 200° |
| Emission Control Devices | | | | | |
| Type - Incinerator | | | | | |
| Flare | | | | | |
| Scrubber | | | | | |
| Other | | | | | |
| Catalog I. D. Number | | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | + | + | + | + | + |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | | |
| Total $NO_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total $SO_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | | |

Plant - EPA Code Number — 22-9
Capacity - Tons of Phenol/Yr. — 28,500
Average Production - Tons of Phenol/Yr. — 28,500
Quarterly Production Variation - % of Max. — 29%

Emissions to Atmosphere

| Stream | Phenol Column Steam Eductor Vent | Residue Stripper Steam Eductor Vent | Acetone Dilution Column Vent | Acetone Concentration Column Vent | Acetophenone Purification Batch Still Steam Eductor |
|---|---|---|---|---|---|
| Flow - Lb./Hr. | Unknown | Unknown | Unknown | Unknown | Unknown |
| Flow Characteristics - Continuous or Intermittent if Intermittent - Hrs./Yr. Flow | Continuous | Continuous | Continuous | Continuous | Intermittent |
| Composition - Tons/Ton of Phenol [5] | | | | | |
| Cumene | | | | | |
| Cumene Hydroperoxide | | | | | |
| Phenol | (+) | (+) | | | |
| Acetone | | | + | + | |
| ∝ Methyl Styrene | | | | | |
| Acetophenone | | | | | (+) |
| Acetaldehyde | | | | (+) | |
| Formaldehyde | | | | | |
| Mesityl Oxide | | | | | |
| Dimethyl Benzyl Alcohol | | | | | |
| Benzene | | | | | |
| Toluene | | | | | |
| Ethyl Benzene | | | | | |
| Misc. Hydrocarbons | + | + | | | + |
| Cumyl Phenol & Phenolic Tars | | | | | |
| Water | + | + | | | + |
| Carbon Dioxide | | | | | |
| Nitrogen | + | + | (+) | (+) | + |
| Oxygen | + | + | (+) | (+) | + |
| Sample Tap Location | Very difficult | Very difficult | Very difficult | None, Very difficult | None, Very difficult |
| Date or Frequency of Sampling | Never | Never | Never | Never | Never |
| Type of Analysis | None | None | None | None | None |
| Odor Problems | No | No | "Not applicable" | "Not applicable" | No |
| Vent Stacks | | | | | |
| Flow - SCFM/stack | | | | | |
| Number | 1 | 1 | 1 | 1 | 1 |
| Height - Feet | 65 | 65 | 80 | 93 | 95 |
| Diameter - Inches | 1.5 | 1.5 | 3 | 3 | 2 |
| Exit Gas Temp. °F | 200° | 200° | 70° | 70° | 200° |
| Emission Control Devices | | | | | |
| Type - Incinerator | | | | | |
| Flare | | | | | |
| Scrubber | | | | | |
| Other | | | | | |
| Catalog I. D. Number | | | | | |
| Total Hydrocarbon Emissions - Ton/Ton of Phenol | + | + | + | + | + (33) |
| Total Particulate & Aerosol Emissions - Ton/Ton of Phenol | | | | | |
| Total $NO_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total $SO_x$ Emissions - Ton/Ton of Phenol | | | | | |
| Total CO Emissions - Ton/Ton of Phenol | | | | | |

# EXPLANATION OF NOTES
## TABLE PH-III
### NATIONAL EMISSIONS INVENTORY
### PHENOL PRODUCTION FROM CUMENE

(1)  No information given for estimating emissions, device presumably
     releases some small quantities of hydrocarbons.

(2)  Since sampling involved plant operation @ 85% of capacity, stream flow
     has been adjusted in simple proportion to correspond to 100% capacity
     rate,

(3)  Toluene, ethyl benzene and cumene here accounted for as cumene.

(4)  Vents from PH-XI and PH-XII are combined and presumably carry acetone
     vapor, but the amount is unknown, and no odor problem is indicated.

(5)  The (+) notations shown here were not reported by the particular
     respondent, but indicate probable presence of at least a trace emission
     as judged from specific process step, in line with other respondents
     information on a like stream.

(6)  Sump seal and vent improved in 1970 to eliminate a previous occasional
     in-plant odor emission.

(7)  Hazardous area, protective clothing and gear required.

(8)  Phenolic odor occasionally detectable on plant property.

(9)  Sampled during capacity operation.

(10) Vents from acetone purification, post-cleavage neutralizing and wash
     section and phenolic water stripper, together with occasional emergency
     relief, delivered to scrubber PH-XIV.

(11) Total for other emissions, including occasional pump seal and other
     minor leakages estimated by respondent at 30,000 lbs. total hydrocarbons
     per year, equivalent to 0.0006 tons/ton phenol.

(12) Freshly regenerated active carbon beds (not specifically identified by
     respondent) prevent organics in effluent to incinerator; spent carbon
     permits up to 0.2% organics in gas and stream to incinerator.

(13) Sampled at ~70% production rate; stream flow proportionately adjusted
     to level corresponding to normal production rate of 48,000 lbs. phenol/hr.;
     stream for incinerator stack similarly adjusted.

(14) Odor off property only one time when equipment malfunctioned.

(15) Incinerator damaged by fire, undergoing repairs, but not in operation as
     of August 4, 1972.

(16) Light oil liquid waste stream of 2,500 lbs./hr. from cleavage and distillation
     section (tons/ton of phenol amounts: .0260 cumene, .0078 AMS, .0078 acetone
     and .0104 other oils) pumped to boiler, and for present purpose assumed
     to undergo complete combustion with 100% excess air.

(17) Heavy oil liquid waste stream of 6,000 lb./hour from cleavage and distillation section (tons/ton of pehnol amounts: .00625 cumene, .0375 phenol, .01875 acetophenone and .0625 liquid "heavies") pumped to second boiler, and for present purpose assumed to undergo complete combustion with 100% excess air.

(18) Liquid streams analysed before pumping to boilers.

(19) Data calculated from engineering design using known vapor pressures of components, with exception of $O_2$ which is continuously metered and analysed.

(20) System primarily designed for material recovery, hence, not listed as an air pollution control cost.

(21) Vent streams believed to be carrying less than 10 lbs. of organic flow per hour were not surveyed in answer to the questionnaire; only two of these streams involved have measurable organic flow, and these together were estimated at 11 lbs./hour, equivalent to about 0.0003 tons/ton of phenol.

(22) Figures given calculated from design material balances supplied by original contractor.

(23) This vent stream, which can have as high as .049 tons organic emissions/ton of phenol, is sent to PH-VII activated charcoal adsorption recovery system, which normally is in service and removes about 90% of organics present.

(24) Depending on time since last regeneration, PH-VII effluent can go to .0109 tons organic emissions/ton phenol.

(25) Higher in warm weather, $\pm$ 40% over year.

(26) Flow (rate unknown) has been observed ~6 times/month over 4 months, or 20% the time, while operating @ 100 - 110% of design capacity, the stream consists primarily of acetone.

(27) Other emissions believed to be insignificant relative to thru-put ($<0.1%$ or $<0.0010$ tons/ton phenol).

(28) Sampled at ~93.8% of capacity, figures adjusted.

(29) Hydrocarbons can reach 0.0240 tons/ton phenol ten times per year for ~1 - 4 hours each time, when recovery system failure occurs.

(30) Combined concentration section vents ~125° F exit gas temperature, cleavage section ~125° F, recovery section ~150° F.

(31) Flare operated to burn an annual total of 500,000 lbs. phenolic heavy ends @ 3,000 lb./hour, 12 times per year for ~14 hours each occurrence at (intermittent) flow rate shown. Design burner feed operation with 100% excess $O_2$ assumed together with steam injection ratio of 2 lb. steam per 1 lb. hydrocarbon fuel, assuming complete combustion.

(32)  Design calculation.

(33)  Other emissions not known, total loss for unit may be approximately
      2 wt. % of cumene charged as determined by material balance.  (Equiva-
      lent to 0.0200 tons/ton phenol).

| Plant Section | Feed Purification | | Oxidation | | |
|---|---|---|---|---|---|
| Device Class | Scrubber | Scrubber Condenser [2] | Condenser [6] | Incinerator [7] | Condenser [8] |
| EPA Code No. for plant using | 22-1 | 22-1 | 22-1 | 22-3 | 22-4 |
| Flow Diagram (Fig. II) Stream I. D. | A | B | C | B | B |
| Device I. D. No. | PH-I | PH-II | PH-III | PH-IV | PH-V |
| Purpose - Control Emission of | Hydrocarbons | Hydrocarbons | Hydrocarbons | Hydrocarbons | Hydrocarbons |
| **SCRUBBING/SORBING MEDIUM** | Water [1] | Cumene | | | |
| Type - Spray | | | | | |
| Packed Column(s) | | | | | |
| Trays - Type | | ? | | | |
| Number | | 15 | | | |
| Plenum Chamber | | | | | |
| Other | Seal Leg Trap | | | | |
| Scrubbing/Sorbing Medium Usage - GPM (lbs./lb. phenol) | ~1000 GP Yr. | | | | |
| Design Temp. (operating temp.) °F | Ambient | 100 [3]  40 [3]  40 | | | |
| Gas Rate - SCFM (lb./hr.) | Unknown | -  3700  - | 8.7 | (80,000) | (73,300) |
| T-T Height - Ft. | ? | 43  6 | | | |
| Diameter - Ft. | .167 | 3.5  3 | | | |
| Wash/Vent Gases to stack | Yes | Vent | | Stack | Vent |
| Stack Height - Ft. | 112 | 125 | | 55 | 70 |
| Stack Diameter - Ft. | .167 | .84 | | 6 | 1.17 |
| **K. O. TYPE - CONDENSER & K. O. DRUM** | | Yes | | Yes | Yes |
| Demister | | | | | |
| Degasser | | | | | |
| Other | | | | | |
| Design Pressure (operating pressure) PSIG | 0 | ~80  ~80  80 | | | — 73 — |
| Flow Rate of Treated Stream | | | | | |
| Liquid - lb./hr. (GPM) | | Unknown (recy.) | 1.4 | | |
| Gas - lb./hr. (SCFM) | | — (3700) — | (8.7) | | |
| SCFM/Stack | | — 3700 — | 8.7 | | |
| Primary Condenser Refrigeration Liquid | | Fre-12 | Water [6] | | Water  NH$_3$ [8] |
| Capacity of Refrigeration Unit - Tons | | .75 | | | |
| Temperature to Condenser - (Sorber) - °F | | 100 | 130 | | |
| Temperature out of Condenser - (Sorber) - °F | | 40 | Ambient | | |
| Compound Types Incinerated | | | | Hydrocarbons | |
| Combustion Device - Flare | | | | | |
| Incinerator | | | | Yes | |
| Other | | | | | |
| Materials to Incinerator - SCFM (lb./hr.) | | | | (80,000) | |
| Auxilliary Fuel Req'd. (Excl. pilot) | | | | Yes | |
| Type | | | | Nat. Gas | |
| Rate BTU/Hr. | | | | Not given | |
| Installed Cost - Mat'l. & Labor $ | 800 | 100,000 | 20,000 | 75,000 | 300,000 |
| Installed Cost Based on "year" - dollars | 1953 | 1953 | 1953 | 1971 | 1970 |
| Installed Cost - Mat'l. & Labor - ¢/lb. of Phenol/Yr. | .0015 | .1887 | .0377 | .0188 | .1200 |
| Operating Cost - Annual - $ (1972, excl. depreciation) | 150 | 15,800 | 7,500 | 66,000 [7] | (8) |
| Value of Recovered - $/Yr. | 0 | 3,000 [4] | 1,000 | 0 | |
| Net Operating Cost - Annual - $ (excl. depreciation) | 150 | 12,800 | 6,500 | ~56,000 [7] | |
| Net Operating Cost - ¢/lb. of Phenol | .0003 | | .0123 | .0140 [7] | |
| Efficiency - % SE     (% CCR) | Virtual 100 | 87 [5] | 65 | 100 | (8) |
| Efficiency - % SERR | Virtual 100 | 87 | 65 | 100 | |

| Plant Section | Oxidation | | | | Cleavage Reaction |
|---|---|---|---|---|---|
| Device Class | Condenser [8] | Carbon Sorber [9] | Carbon Sorber [9] | Condenser | Condenser |
| EPA Code No. for plant using | 22-5 | 22-6 | 22-7 | 22-4 | 22-1 |
| Flow Diagram (Fig. II) Stream I. D. | /B\ | /B\ | /B\ | /C\ | /D\ |
| Device I. D. No. | PH-VI | PH-VII | PH-VIII | PH-IX | PH-X |
| Purpose - Control Emission of | Hydrocarbons | Hydrocarbons | Hydrocarbons | Hydrocarbons | Hydrocarbons |
| SCRUBBING/SORBING MEDIUM | | | | | |
| Type - Spray | | Activa. Carbon | Activa. Carbon | | |
| Packed Column (s) | | 2 (alternate) | 2 (alternate) | | |
| Trays - Type | | | | | |
| Number | | | | | |
| Plenum Chamber | | | | | |
| Other | | | | | |
| Scrubbing/Sorbing Medium Usage - GPM (lbs./lb. phenol) | | | | | |
| Design Temp. (operating temp.) °F | | ~120 | 41 | | |
| Gas Rate - SCFM (lb./hr.) | (66,670) | (36,995) | 5,000 | 172 | Unknown |
| T-T Height - Ft. | | 9 | Not given | | |
| Diameter - Ft. | | 8 | " " | | |
| Wash/Vent Gases to stack | Vent | Vent | Vent | | Vent |
| Stack Height - Ft. | 86 | 86 | | | 20 |
| Stack Diameter - Ft. | .855 | 1.0 | | | .167 |
| K. O. TYPE - CONDENSER & K. O. DRUM | Yes   Yes | | | | Yes |
| Demister | | | | | |
| Degasser | | | | | |
| Other | | | | | |
| Design Pressure (operating pressure) PSIG | 73   70 | ~14 | ~0.5 | 33 | 2 |
| Flow Rate of Treated Stream | | | | | |
| Liquid - lb./hr. (GPM) | | 908 recycle | 129 recycle | Unknown | Unknown |
| Gas - lb./hr. (SCFM) | | (7576) | (5000) | (172) | " |
| SCFM/Stack | | 7576 | 5000 | 172 | |
| Primary Condenser Refrigeration Liquid | Water   NH$_3$ [8] | | | Water | Water |
| Capacity of Refrigeration Unit - Tons | | | | | |
| Temperature to Condenser - (Sorber) - °F | 226   110 | 100 | 41 | Not given | 170 |
| Temperature out of Condenser - (Sorber) - °F | 110   140 | 140 | 41 | 85 | Ambient |
| Compound Types Incinerated | | | | | |
| Combustion Device - Flare | | | | | |
| Incinerator | | | | | |
| Other | | | | | |
| Materials to Incinerator - SCFM (lb./hr.) | | | | | |
| Auxilliary Fuel Req'd. (Excl. pilot) | | | | | |
| Type | | | | | |
| Rate BTU/Hr. | | | | | |
| Installed Cost - Mat'l. & Labor - $ | 179,000 (est.) | 220,000 | 18,000 [10] | 30,000 | 18,000 |
| Installed Cost Based on "year" - dollars | 1969 | 1970 | 1969 | 1970 | 1953 |
| Installed Cost - Mat'l. & Labor - ¢/lb. of Phenol/Yr. | .0833 | .1100 | .0225 | | .0340 |
| Operating Cost - Annual - $ (1972, excl. depreciation) | 24,600 | 120,000 | Unknown | (13) | 2,600 |
| Value of Recovered - $/Yr. | | 340,000 | 48,310 | Unknown | 1,000 |
| Net Operating Cost - Annual - $ (excl. depreciation) | | -220,000 [11] | | | 1,600 |
| Net Operating Cost - ¢/lb. of Phenol | | -.1100 [11] | -.0604 [12] | | .0030 |
| Efficiency - % SE    (% CCR) | (8) | 91 | 82 | ? | ? |
| Efficiency - % SERR | | 91 | 82 | ? | ? |

| Plant Section | Acetone Tower Condenser | Acetone Purification Condenser [14] | Phenol Recovery Condenser [14] | Wash & Emergency Relief (Misc) Scrubber | Product Recovery Incinerator |
|---|---|---|---|---|---|
| Device Class | | | | | |
| EPA Code No. for plant using | 22-1 | 22-1 | 22-1 | 22-1 | 22-8 |
| Flow Diagram (Fig. II) Stream I. D. | ▲F | ▲G | ▲H | E\G\J | T |
| Device I. D. No. | PH-XI | PH-XII | PH-XIII | PH-XIV | PH-XV |
| Purpose - Control Emission of | Hydrocarbons | Hydrocarbons | Hydrocarbons | Phenolics & HC's | Heavy Ends [17] |
| | | | | | |
| SCRUBBING/SORBING MEDIUM | | | | Water | |
| Type - Spray | | | | | |
|     Packed Column(s) | | | | | |
|     Trays - Type | | | | | |
|         Number | | | | | |
|     Plenum Chamber | | | | | |
|     Other | | | | Tank | |
| Scrubbing/Sorbing Medium Usage - GPM (lbs./lb. phenol) | | | | .03 | |
| Design Temp. (operating temp.) °F | | | | Ambient | |
| Gas Rate - SCFM (lb./hr.) | Unknown | Unknown | Unknown | Unknown | (3,000 liquid) [17] |
| T-T Height - Ft. | | | | 12 | |
| Diameter - Ft. | | | | 18 | |
| Wash/Vent Gases to stack | Vent [15] | Vent [15] | Vent | Wash/Stack | Stack |
|     Stack Height - Ft. | 120 | 120 | 125 | 86.5 | 4 |
|     Stack Diameter - Ft. | .25 | .25 | .25 | 1.17 | 1.25 |
| | | | | | |
| K. O. TYPE - CONDENSER & K. O. DRUM | Yes | | Yes | | |
|     Demister | | | | | |
|     Degasser | | | | | |
|     Other | | (14) | | | |
| Design Pressure (operating pressure) PSIG | 1 | 10 psia | 1 psia | 1 | |
| Flow Rate of Treated Stream | | | | | |
|     Liquid - lb./hr. (GPM) | Unknown | Unknown | Unknown | Unknown | |
|     Gas - lb./hr. (SCFM) | " | " | " | " | |
|     SCFM/Stack | " | " | " | " | |
| Primary Condenser Refrigeration Liquid | Water | Water | Water | | |
| Capacity of Refrigeration Unit - Tons | | | | | |
| Temperature to Condenser - (Sorber) - °F | 135 | 105 | 85 | | |
| Temperature out of Condenser - (Sorber) - °F | ~85 | Ambient | Ambient | | |
| Compound Types Incinerated | | | | | Heavy phenols, tars [17] |
| Combustion Device - Flare | | | | | Yes |
|     Incinerator | | | | | |
|     Other | | | | | |
| Materials to Incinerator - SCFM (lb./hr.) | | | | | 16,500 [18] |
| Auxilliary Fuel Req'd. (Excl. pilot) | | | | | |
|     Type | | | | | Fuel Gas |
|     Rate BTU/Hr. | | | | | |
| Installed Cost - Mat'l. & Labor - $ | 5,000 | 15,000 | 10,000 | 18,000 | 155,000 |
| Installed Cost Based on "year" - dollars | 1953 | 1953 | 1953 | 1953 | 1959 - 1970 |
| Installed Cost - Mat'l. & Labor - c/lb. of Phenol/Yr. | .0094 | .0283 | .0189 | .0340 | .2583 |
| Operating Cost - Annual - $ (1972, excl. depreciation) | 1,150 | 2,900 | 3,500 | 2,000 | 51,200 |
| Value of Recovered - $/Yr. | 100 | 500 | 500 | 100 | 0 |
| Net Operating Cost - Annual - $ (excl. depreciation) | 1,050 | 2,400 | 3,000 | 1,900 | 51,200 |
| Net Operating Cost - c/lb. of Phenol | .0020 | .0045 | .0057 | .0036 | .0853 |
| Efficiency - % SE (% CCR) | ? | ? | ? | ? | 100 |
| Efficiency - % SERR | ? | ? | ? | ? | 100 |

# EXPLANATION OF NOTES
## TABLE PH-IV
### CATALOG OF EMISSION CONTROL DEVICES
### PRODUCTION OF PHENOL FROM CUMENE

(1) Effluent water is sent to phenolic water stripper, which is vented through PH-XIV.

(2) Device PH-II involves a combination of a water-cooled vent gas scrubber-cooler and a knock-out drum operating at 80 PSIG.

(3) Outlet temperatures for scrubber-cooler and subsequent refrigerated condenser respectively (PH-II).

(4) Vapor pressure calculation for temperatures indicated around this PH-II device show very good agreement with the amount of cumene reported leaving the oxidizer, but consistent vapor pressure calculations for cumene leaving the scrubber and then escaping the post refrigeration knock-out drum suggest a cumene recovered value (@ $.032/lb.) for the latter (refrigerated condenser) of ∿$39,000, it may be that recovery costs do not allow full credit.

(5) Specific efficiency (SE) calculated using vapor pressure data around the refrigerated condenser and knock-out drum. SE for the entire scrubber-condenser unit is 99.4%, but at least the scrubber section must be considered an economically necessary integral part of the process equipment.

(6) Three-stage water condenser with steam jet ejectors.

(7) Incinerator PH-IV, normally operating @ $1400^{\circ}$ F with $400^{\circ}$ F exit gas, was out of service for repairs when the questionnaire was filled out in August, 1972, due to damage by fire. Operating costs for 1972 include $20,000 maintenance, high due to repairs needed; net operating cost given here assumes $10,000 maintenance for normal year. Respondent 22-3 reports that the oxidizer section effluent stream normally sent to PH-IV incinerator actually comes from activated carbon beds, which can allow as much as 0.2% organics (= up to .0033 tons cumene/ton phenol) emissions when activated carbon bed recovery equipment is near exhaustion.

(8) Two-stage cooling system, with a water-cooled and a refrigerated condenser, each followed by 73 PSIG knock-out drums, with final release of uncondensable gas to atmosphere; this PH-VI unit is an economic necessity (respondent 22-4 reports recovery of 99% of the 20,000 lb./hour hydrocarbon content) and only secondarily an emission control device, hence, no assignable operating costs for emission control as such.

(9) Two beds down-flow operation ($\Delta$P ∿28 PSI for PH-VII 22-6) alternately, with upflow low-pressure steam regeneration, recondensation and recyle of recovered cumene.

(10) Figure given is double the installed cost of a new adsorber installed by 22-7 in 1969; cost of original PH-VIII adsorbers unknown.

(11) Negative numbers here indicate credit.

(12) Credit shown does not take 22-7 PH-VIII operating costs (unknown) into account.

(13)  This PH-IX condenser, according to 22-4 respondent, is primarily designed for material recovery, thus considered inappropriate as an air pollution control cost.

(14)  Two-stage vapor condenser with steam jet ejectors (PH-XII).

(15)  Common vent for acetone tower and purification section of PH-XI and PH-XII of 22-1.

(16)  Up to once per year, PH-XIV of 22-1 serves as an emergency relief tank for oxidation, concentration and other sections, as well as providing normal venting from wash section; normal water level is 6 foot depth.

(17)  Cumyl phenol and phenolic tar (~60 wt. %), acetophenone (30 wt. %) and phenol (8 wt. %) liquid stream burned at rate shown about 12 times a year for ~14 hours each time, for a total of 500,000 lbs./year.

(18)  Flow of 16,500 SCFM for PH-XV of 22-8 assumes design operation of two identical burners in parallel with 100% excess $O_2$, together with steam injection rate of 2 lbs. steam/lb. of hydrocarbon fuel, using 10,000 SCFH fuel gas and 10,000 lb./hr. steam while flare is being operated to burn liquid waste.

TABLE PH-V
NUMBER OF NEW PLANTS BY 1980
CAPACITIES MM LBS./YR.

| Current Capacity | Marginal Capacity | Current Capacity On-stream in 1980 | Demand 1980 | Capacity 1980 | Capacity to be added by 1980 | Plant Size | Number of New Units |
|---|---|---|---|---|---|---|---|
| 2,363 (a) | 233 (b) | 2,130 | 3,800 | 4,200 | 2,070 (c) | 200 | 10 - 11 |

Notes:

(a) See Section VI, Phenol Producers, for source.

(b) Arbitrary 50% of 1972 non-cumene and smaller plants.

(c) Including replacement for marginal capacity.

TABLE PH-VI
EMISSION SOURCE SUMMARY
TON/TON OF PHENOL PRODUCT

| Emissions | Source | | | | Total |
|---|---|---|---|---|---|
| Location in Plant | Oxidation Section | Concentration Cleavage Section | Distillation Section | Fugitive Emissions | |
| Hydrocarbons | .0038 | .0021 | .0038 | .0006 | .0103 |
| Particulates & Aerosols | None | None | None | None | None |
| $NO_x$ | None | None | None | None | None |
| $SO_x$ | None | None | None | None | None |
| CO | None | None | None | None | None |

## TABLE PH-VII
## WEIGHTED EMISSION RATES

Chemical _____ Phenol _____

Process _____ Air Oxidation of Cumene _____

Increased Capacity by 1980  2,070  MM Lbs./Yr. _____

| Pollutant | Current Capacity Emissions, Lb./Lb. | Projected New Capacity Increased Emissions MM Lbs./Yr. | Weighting Factor | Projected New Capacity Weighted Emissions MM Lbs./Yr. |
|---|---|---|---|---|
| Hydrocarbons | .0103 | 21.3 | 80 | 1,704 |
| Particulates | 0 | | 60 | |
| $NO_x$ | 0 | | 40 | |
| $SO_x$ | 0 | | 20 | |
| CO | 0 | | 1 | |

Significant Emission Index = 1,704 MM Lbs./Yr.

## TABLE PH-VIII - REFERENCES

i       P. W. Sherwood, Pet. Proc. <u>8</u>, p 1348 (September, 1953).

ii      J. Gordon, Hydr. Proc. & Pet. Ref. <u>40</u>, p 193 (June, 1961).

iii     M. Sittig, "      "      "      "   <u>41</u>, p 129 (August, 1962).

iv      R. B. Stobaugh, Hydr. Proc.          <u>45</u>, p 143 (January, 1966).

v       Kirk-Othmer, 2nd Ed. Vol. 15, p 147 (1968).

vi      Processes Research. Inc. Task Order No. 14, Final Report Air Pollution Control in Phenol Industry (8/13/71).

vii     Chemical Profile, Chemical Marketing Reporter "Phenol", (6/19/72).

viii    J. L. Blackford "Chemical Economics Handbook", Stanford Research Institute, (July, 1972).

ix      G. P. Armstrong, et al  J. Chem. Soc. p 666 (1950).

x       A. C. Davies, et al      "      "      "   p 2204 (1954).

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xii     Alwyn C. Davies, "Organic Peroxides" Butterworths, London (1961).

xiii    P. Cray & A. Williams. Chem. Reviews <u>59</u>, p 239 (1959).

xiv     Perry, "Chemical Engineers Handbook, 4th Ed., Mc Graw Hill (1969).

xv      S. W. Benson, et al, "Additivity Rules for the Estimation of Thermo-chemical Properties", Chem. Reviews <u>69</u>, p. 279 - 324 (1969).

High Density Polyethylene

## Table of Contents

## List of Illustrations & Tables

I. Introduction

More polyethylene is produced in the United States than any other plastic. Several types of polyethylene are produced. The two most important basic types are High Density Polyethylene (HDPE) - the subject of this survey report - Low Density Polyethylene (LDPE). HDPE currently holds roughly one-third of the total polyethylene market; however, due to a higher predicted growth rate, it is expected to significantly increase its share of the market by 1980. The major portion of the noxious emissions resulting from the production of HDPE is related to the separation and repurification of solvents and unreacted monomers from the virgin polymer. Significant emissions may also emmanate from the pneumatic conveyor vent system - the pneumatic conveyors being used to transport the HDPE granules to various blending and storage facilities. In addition the the vapor emissions, waste water, spent catalysts and off-spec HDPE are 'produced' and must be disposed of by the operator. Also some plants produce a relatively low molecular weight 'wax' which, if incinerated, would add to the volume of air emissions.

There are three basic types of process, namely solution, slurry and vapor phase. The slurry process, as licensed by Phillips, accounts for most of today's capacity and as such is the primary subject of this report. Union Carbide is now offering licenses on a vapor phase process but none is yet in operation in the U.S. Total U.S. capacity for HDPE is expected to reach 8.5 billion pounds by 1980.

## II. Process Description

Any description of current commercial ethylene polymerization techniques/ processes will necessarily be quite sketchy since the details of these processes are closely guarded trade secrets. Hence, the following section is more abbreviated than in most of the survey reports.

There is great variety in the various HDPE processes utilized today. Processes of similar design may be grouped together if classification is determined by the types of phases present in the polymerization reactor. Accordingly, there are three major categories: (1) solution, (2) slurry, and (3) vapor phase. These categories may be further subdivided according to the physcial state of the catalyst, but that detail will not be discussed here. The solution process is thought by many to be on the way out. Union Carbide has recently shut down the solution line at its Seadrift, Texas plant. The vapor phase process, may be of more importance in the future. The slurry process, as exemplified by Phillips Particle Form (PF) process, accounts for the bulk of the HDPE produced in the U.S. Indeed, Phillips claim (1) that their process accounts for more HDPE capacity in the U.S. than all other processes combined. Consequently, this process description will confine itself to that variation.

The mechanism of ethylene polymerization on a metal oxide surface - Phillips uses a chromic oxide catalyst - is quite complex (2). The simplified net reaction is:

$$n \quad \begin{matrix} H \\ \diagdown \\ C \\ \diagup \\ H \end{matrix} = \begin{matrix} H \\ \diagup \\ C \\ \diagdown \\ H \end{matrix} \quad \longrightarrow \quad \begin{bmatrix} H & H \\ | & | \\ -C- & C- \\ | & | \\ H & H \end{bmatrix}_n$$

The ethylene feed plus any co-monomer are treated to remove catalyst poisons; primarily $CO_2$, $O_2$, and $H_2O$; prior to their dissolution in an appropriate solvent - such as pentane. The solution of monomers and pentane is then heated and pumped to a bank of stirred or loop-type reactors, where it is mixed with a previously activated, powdered catalyst that has been slurried in the $C_5$ solvent. The monomers polymerize around the fine catalyst particles, which are kept in suspension by agitation. The heat of polymerization is absorbed by the water-cooled reactor jacketing. Polymer molecular weight or chain length is controlled by the addition of small amounts of hydrogen or other telogens.

After a suitable residence time in the reactor, the effluent slurry is pumped (continuously or batch-wise) to the 'flash' section where part of the solvent, unreacted monomers, oligomers-'waxes', and light gases are flashed overhead. The flash gases are separated and purified, with the solvent and monomers being recycled. The 'waxes' are rejected and incinerated or disposed of in some other manner.

The HDPE 'granules' may be dissolved in hot solvent and the catalyst particles filtered out, however, it is believed that current practice is to allow the small amount of catalyst now required for polymerization to remain in the HDPE. Then the polymer is stripped of the remaining solvent, dried and conveyed to a blending or storage area.

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(1)   C.W. 5/10/72, pp 42.
(2)   See "Crystalline Olefin Polymers" - Part I by Raff & Doak for discussion.

III. Plant Emissions

    A. Continuous Air Emissions

        1. Flue Gas

        Two operators (EPA Code No 24-10 and 24-9) report using natural gas as fuel. Operator 24-9 specifies that the fuel is used in a catalyst activation heater. The amounts of fuel; 6 and 40 mm scf/year, respectively; and the quantity of sulfur, 1 to 3 ppm, are such that $SO_2$ emissions are negligible.

        2. Monomer and Solvent Recovery Vents

        All producers recycle solvent and most recycle unreacted monomer. These recycled streams require purification. The light and heavy ends from the purifaction process are either vented, flared, or sent to another process or a pollution control device. This operation is one of the main sources of air pollution in the production of HDPE. The reported vent streams in this category, along with their pollution control devices, are summarized in Tables III and IV.

        3. Conveyor Losses

        Semi-finished and finished HDPE granules are transported in-plant via pneumatic conveyors, by at least one operator (EPA Code No. 24-9). The various atmospheric vents that are associated with such a system are a source of hydrocarbon and particulate emissions. These emissions represent a significant portion of the total emissions dispite employment of various pollution control devices. The emission and device data are summarized in Tables III and IV.

    B. Intermittent Air Emissions

        1. Catalyst Activation

        The Phillips type catalysts require activation prior to use. Activation is accomplished by blowing hot air over/through the catalyst. Operator EPA Code No. 24-9 states that this is a batch-type operation. The emissions resulting from this operation are listed in Table III.

        2. Feed Treatment

        Polar substances poison Phillips type catalysts; consequently, water must be removed from the feed. This is accomplished through the use of mole seive absorbers. The absorbers are periodically regenerated and eventually dumped. During these operations the vessels are purged with the vent stream blowing to the atmosphere. These relatively small emissions are summarized in Table III.

        3. Reactor Catalyst Charging/Dumping

        One operator (EPA Code No. 24-1) who uses a supported Zeigler type catalyst reports weekly emissions of a nitrogen-alumina stream. This apparently occurs during catalyst dumping operations, but it is not perfectly clear. The emissions resulting from this operation are summarized in Table IV.

4. Start-Up and Emergency Vents

   This type of discharge is universally encountered in the
petrochemical industry and will vary from process-to-process,
from operator-to-operator, and from year-to-year. According to
the responses received to the HDPE questionnaires, all of these
vents are flared. This need not necessarily be the case for the
entire industry but since they are primarily hydrocarbon streams,
it is probable that they are flared.

   Flaring is a very effective method of reducing air pollution,
especially in situations such as this where the only products of
complete combustion are carbon dioxide and water. The only problem
with flares is that they must have a finite design limitation,
beyond which they will not achieve complete combustion and thus
are no longer "smokeless". In extreme emergencies they are apt to
receive entrained liquids or excessive gas flows, resulting in
smoky effluents.

   One respondent (EPA Code 24-9) reported the smokeless design
rate at 122,900 lbs./hour. This is nearly five times their hourly
production rate of polyethylene so it is probably an adequate safety
margin for most situations. However, the solvent circulation rate
is probably six or more times the production rate and vessel
capacities are even a greater multiple of capacity, therefore, it
is possible that some smoky flare conditions could be encountered.

   One additional point, about which all respondents were silent is
$NO_x$. The reaction between atmospheric nitrogen and oxygen is known
to produce these pollutants at high temperatures. Hence, it is
probable that some small concentration of $NO_x$ is produced in the
flame.

C. Liquid Wastes

   The only liquid waste reported was water. Operator EPA Code No.
24-10 reported discharging 330 gpm of waste water. Operator EPA
Code No. 24-9 reported discharging 100 to 150 gpm of water after
primary treatment. It was stated that this water was used for cooling
and as a HDPE pellet transfer medium. Operator EPA Code No. 24-1
reported a waste water stream of 1000 gph containing 15 ppm
cyclohexane. This concentration of cyclohexane represents $<.000001$
ton/ton of HDPE.

D. Solid Wastes

1. Spent Catalysts

   Depending on the process used, catalyst may or may not be
removed from the polymer. One operator who obviously does remove
it (EPA Code No. 24-1) reports the disposal of $1 \times 10^6$ lbs./yr.
of this material. It is hauled away by a waste disposal contractor.

2. Polyethylene Waste

   The amount of non-specification HDPE produced is a function of
the process used, the stringency of product molecular weight

range specifications, and many other factors. The actual amount reported varied from $2 \times 10^5$ to $2 \times 10^6$ lbs./yr. Some of this material may be applied in lower specification uses, but the remainder is either incinerated or removed by contract haulage.

3. Waxes

Varying amounts of relatively low molecular weight 'waxes' are produced by most HDPE processes. One operator (EPA Code No. 24-1) reported that $2 \times 10^5$ lbs./yr. are produced and disposed of by a contractor. Another operator (Code 24-10) reports "considerably less" than this amount.

E. Odors

No odors are reported by any of the questionnaire respondents. However, many of the reported vent streams contain materials that have odors.

F. Fugitive Emissions

Two of the four respondents reported fugitive emissions, both of fairly significant proportions, as follows:

Code 24-10 "Assuming 50% of unaccounted for non-methane hydrocarbons to flare and 50% to atmosphere - 5,900 tons/year fugitive loss".

Code 24-4 "Fugitive losses amounting to 7 MM lbs./year occur. These include ethylene, butene, cyclohexane, pentane and iso-butane and are equivalent to 0.5% of throughput."

These are each of the order of 0.03 lbs./lb. of product and thus are significant, being about equal to the total of all other reported hydrocarbon emissions. Yet, the other respondent reports no fugitive emissions, "other than small leaks".

Two rather obvious questions occur as a result of these reports, namely:

Are these estimates of losses real or can they be attributed to metering inaccuracies or material balance non-closure caused by small differences between very large members?

If these losses are real, are they air emissions or do most of them enter the flare header because of leaking relief valves?

It is assumed that the losses are in fact atmospheric emissions resulting and are of the order of 200 SCFM per plant.

## IV. Emission Control

The various emission control devices that have been reported as being employed by operators of high density polyethylene plants are summarized in the Catalog of Emission Control Devices - Table IV. In general, no quantitative information on the device performance has been made available. (In some instances, approximate numerical efficiencies have been assigned to these devices, see Table IV - on the basis of the operator's estimate of effluent composition). Never-the-less, certain generalizations about the performance of the devices utilized can be made:

### Water Scrubbers

Only one water scrubber was reported as being used. That is, operator EPA Code No. 24-1's device HP-2, which is used to remove "small quantities of alumina dust" from the exhaust gates of a reactor vent cyclone during weekly catalyst transferrals. The effluent from the device is described as being "essentially dust free". Since the device in question is a multi-tray scrubber working on what may be assumed to be a stream only lightly laden with particulate matter; its efficiency should be reasonably high. However, it would be imprudent to attempt to characterize the performance of all the scrubbers used by the industry on the basis of that single report.

### Cyclones

In high density polyethylene production these devices are used to remove or reduce the amount of HDPE dust emitted from the pneumatic conveyor vent system. The size of the particles being removed is reported as varying from 10 to 150 microns. The device efficiencies cannot be calculated from the data reported; but one may infer, from the variations in the description of cyclone exhaust gases, that there are significant differences in the performances of existing equipment. For example the operator of device HP-1 reports that the effluent from that device is "essentially dust free", whereas the operator of device HP-7a states that there are visible particulate emissions exhausting from it. The operator of device HP-7a (Plant EPA Code No. 24-9) further states that the currently existing cyclones will be replaced in the future - with higher efficiency cyclones and bag filters.

### Bag Filters

In general, bag filters are utilized for the same type of service as cyclones. The single exception is device HP-5 which is used by the operator of plant EPA Code No. 24-9 to remove catalyst fines from the atmospheric vent stream resulting from catalyst activation operations. The device is reported to remove all of the 10 to 200 micron particles which comprise its (particulate) feed.

Bag filters, when used to service pneumatic conveyor vent streams, apparently exhibit the same variation in performance that was reported for cyclones. Descriptions of filter exhaust streams range from "no particulates" to "visible (particulate) emissions". Unfortunately more quantitative data are lacking. Operator EPA Code No. 24-9 states that single compartment bag filters used in this service will be replaced with more efficient multi-compartment bag filters.

### Incinerators & Flares

All HDPE plant operators report the employment of a flare system. Again, the data necessary to calculate efficiencies have not been reported. Where

specified, all flares are associated with the reactor section. Only one plant operator, (EPA Code No. 24-1) reports incinerating off-spec HDPE. No details are given as to the type of incineration used or the amount of HDPE incinerated, except that the total amount of off-spec HDPE produced is 2 x $10^5$ lbs./yr. with a part being incinerated and part removed by a solid waste disposal contractor.

## Possible Methods for Emission Reduction

It seems unlikely that any change in operating conditions could be made within a given process, that would reduce air emissions without affecting various product qualities. However, it is conceivable that the choice of solvents could have a significant effect in overall emissions. Additionally, catalysts (or processes) that produce less 'wax' and off-spec HDPE will lessen pollution resulting from the production of HDPE.

Development work directed toward reductions in emissions from this process falls into the following general categories:

(1) Design and utilization of closed-loop pneumatic conveying systems, i.e., no atmospheric vents.

(2) Development of catalysts that produce no wax and minimize off-spec HDPE.

(3) Determination of solvent system that reduces emissions without adversely affecting the HDPE quality.

(4) Controlled combustion of hydrocarbon vent streams to minimize formation of $NO_x$ and to recover heat, where justified.

V.  Significance of Pollution

It is recommended that an in-depth study of this process be undertaken. Both the growth rate and quantity of pollutants emitted to the atmosphere are significant.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980, and to estimate the total weighted annual emissions of pollutants from these new plants. This work is summarized in Tables V, VI and VII.

The Table V forecast of new plants is based on the assumption that the HDPE growth experienced from 1965 to 1972 will extend to 1980. This is supported in part by the forecast in the final report, task order No. 15, page B-12, prepared for the EPA by Process Research, Incorporated. On the other hand Chemical Marketing of January 18, 1971, predicts a growth rate of 10% per year until 1975. If this rate were extrapolated to 1980, HDPE capacity at that time would be only 60% of the rate that Table V is based on. Obviously, there are serious differences of opinion on the future of HDPE.

A Significant Emissions Index (SEI) of 17,196 has been calculated in Table VII. However, as explained above, the basis for the SEI calculation, i.e., the 1980 capacity is subject to question. Furthermore, more than half of the total SEI is attributable to "fugitive emissions", yet some respondents have reported only minimal losses in this category. It is only by means of an in-depth study that these uncertainties can be clarified and the need for new source standards evaluated. Hence, the recommendation for such a study has been made.

## VI.  High Density Polyethylene Producers

The following tabulation of producers of high density polyethylene indicates published capacity:

| Company | Location | Capacity MM Lbs./Yr. |
|---|---|---|
| Allied Chemical Corp. | Baton Rouge, La. | 225 |
| Amoco Chemicals Corp. | Chocolate Bayou, Texas | 100 |
| Celanese Corporation | Deer Park, Texas | 225 |
| Chemplex Co. | Clinton, Iowa | 125 |
| Dow Chemical Co. | Freeport, Texas | 100 |
|  | Plaquemine, La. | 100 |
| E. I. DuPont deNemours & Company | Orange, Texas | 180 |
| Gulf Oil Corporation | Orange, Texas | 100 |
| Hercules, Inc. | Lake Charles, La. | 90 |
| Monsanto Company | Texas City, Texas | 180 |
| National Petro Chemicals Corporation | La Porte, Texas | 220 |
| Phillips Petroleum Co. | Pasadena, Texas | 300 |
| Sinclair-Koppers Co. | Port Arthur, Texas | 200 |
| Union Carbide | Seadrift, Texas | 140 |

Total - 2,315

TABLE HP-I
TYPICAL* HIGH DENSITY POLYETHYLENE UNIT
MATERIAL BALANCE, T/T OF HDPE

| Stream No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| | Fresh Feed | Make-up Solvent | Catalyst | Recycle | Gross Reactor*** Feed | Reactor Effluent | Solvent Recovery Vent & Losses | Heavy Reject | HDPE Handling Losses | Product |
| Ethylene | 1.0156 | | | 0.1144 | 1.1300 | 0.1147 | 0.0003 | | | |
| Butene-1 | 0.0086 | | | 0.0258 | 0.0344 | 0.0258 | | | | |
| Polyethylene | | | | | | 1.0010 | | | .0010 | 1.0000 |
| Solvent | | .0340 | | 5.6999 | 5.7339 | 5.7339 | .0340 | | | |
| Low M. Wt. 'wax' | | | | | | 0.0229 | | .0229 | | |
| Catalyst | | | .000002 | | | | | | | |
| | 1.0242 | .0340 | .000002 | 5.8401 | 6.8983 | 6.8983 | .0343 | .0229 | .0010 | 1.0000 |

*No single material balance can be truly typical of the various processes used to produce HDPE.
The above balance is an approximation (from sparse published data) of the Phillips Suspension
Process which has been represented** as the process accounting for the major portion of HDPE
capacity in the U. S. today.

**C.W. 5-10-72, pp 41

***There is considerable variation in the solvent/ethylene ratio reported in the literature. It
is possible that it is considerably higher than shown in the material balance.

<u>TABLE HP-II</u>
<u>HIGH DENSITY POLYETHYLENE</u>
<u>VIA</u>
<u>ETHYLENE POLYMERIZATION</u>
<u>GROSS HEAT BALANCE</u>

The exothermic heat of ethylene homopolymerization is 1450 BTU/LB. [1] (of ethylene).

There are not sufficient published data available to permit the construction of a typical commercial reactor section gross heat balance for this process.

(1)    Chem. Eng. 73 (16) 68 - August 1st, 1966.

| | | | | | | |
|---|---|---|---|---|---|---|
| Company | | | | | | |
| Location | | | | | | |
| EPA Code No. | 24-1 | | | | | |
| Capacity - Tons of H.D. Polyethylene/Yr. | 90,000 | | | | | |
| Average Production - Tons of H.D. P. E./Yr. | 90,500 | | | | | |
| Range in Production - % of Max. | 0 | | | | | |
| Emissions to Atmosphere | | | | | | |
| Stream | P.E. Stripping & Blending Vent | Reactor Vent | Emergency Vent ex. Distillation | Equipt. Purge & Emergency Vent ex. Compress Sect. | Equipt. Purge & Emergency Vent ex. Reactor Sect | Equipt. Purge & Emergency Vent ex. Polymer Recovery Section |
| Flow - Lb./Hr. | 200,400 | 3,540 | Not Specified | Not Specified | Not Specified | Not Specified |
| Flow Characteristic - Continuous or Intermittent | Continuous | Intermittent | Intermittent | Intermittent | Intermittent | Intermittent |
| if Intermittent - Hrs./Yr. Flow | | 1,250 | (3 min/incident) | Not Specified | Not Sepcified | Not Specified |
| Composition - Ton/Ton of H.D. P.E. | | | | | | |
| Hydrogen | | | | | | |
| Ethylene | | | + | + | + | + |
| Butene | | | | | | |
| Isobutane | | | | | | |
| Isopentane | | | | | | |
| Hexene | | | | | | |
| Polyethylene | | | | | | |
| Cyclohexane | .01768 | | | + | + | + |
| Air | 8.83978 | + | | | | |
| Alumina | | + | | | | |
| Co-Monomers | | | + | + | + | + |
| | | | | | | |
| Sample Tap Location | Up-stream of HP-1 | None | None | None | None | None |
| Date or Frequency of Sampling | Continuous | Not Sampled | Not Sampled | Not Sampled | Not Sampled | Not Sampled |
| Type of Analysis | "Flammability" anal. | | | | | |
| Odor Problem | No | No | No | No | No | No |
| Vent Stacks | Not Specified | Not Specified | | | | |
| Flow SCFM per stack | | | | | | |
| Number | | | | 1 | | |
| Height - Feet | | | | 235 | | |
| Diameter - Inches | | | | 30 | | |
| Exit Gas Temperature - F° | | | | Not Specified | | |
| Emission Control Devices | Yes | Yes | | Yes | | |
| Type - Flare | | | | X | | |
| Bag House | | | | | | |
| Cyclone | | | | | | |
| Water Scrubber | | X | | | | |
| Other | "Dust Precipitator" | | | | | |
| Catalog I. D. Number | HP-1 | HP-2 | | HP-3 | | |
| Total Hydrocarbon Emissions - ton/ton H.D. P. E. | Cannot be determined but >.01768 | | | | | |
| Total Particulate - ton/ton | Cannot be determined | | | | | |
| Total NO$_x$ - ton/ton | " " " | | | | | |
| Total SO$_x$ - ton/ton | " " " | | | | | |
| Total CO$_x$ - ton/ton | " " " | | | | | |

| | | Feed Prep | Solvent Recov. | Emergency Vent | Emergency Vent |
|---|---|---|---|---|---|
| Company | | | | | |
| Location | | | | | |
| EPA Code Number | 24-9 | | | | |
| Capacity - Tons of H.D. Polyethylene/Yr. | 110,000 | | | | |
| Average Production - Tons of H.D. P.E./Yr. | 103,500 | | | | |
| Range in Production - % of Max. | 0 | | | | |
| Emissions to Atmosphere | | | | | |
| Stream | | Feed Prep | Solvent Recov. | Emergency Vent | Emergency Vent |
| | | Section Purge | Section Purge | ex. Reactor | ex Solvent Processi |
| Flow - lb./hr. | | Not Specified | Not Specified | 80,000 | 200-1500 |
| Flow Characteristic - Continuous or Intermittent | | Intermittent | Intermittent | Intermittent | Intermittent |
| if Intermittent - hrs./yr. flow | | Not Specified | Not Specified | (15 min/incident) | Not Specified |
| Composition - ton/ton of H.D. P.E. | | | | | |
| Hydrogen | | | | + | + |
| Ethylene | | + | + | + | + |
| Butene | | + | + | + | |
| Isobutane | | + | + | + | + |
| Isopentane | | + | + | + | + |
| Hexene | | + | + | + | |
| Polyethylene | | - | | | |
| Cyclohexane | | | | | |
| Air | | | | | |
| Alumina | | | | | |
| Co-Monomer | | | | | |
| Nitrogen | | + | + | | + |
| Fuel Gas | | + | + | | |
| Silica Gel | | | | | |
| Sample Tap Location | | Not Sampled | Not Sampled | Not Sampled | Not Sampled |
| Date or Frequency of Sampling | | | | | |
| Type of Analysis | | Mat'l Bal. | Mat'l Bal. | Mat'l Bal. | Mat'l Bal. |
| Odor Problem | | No | No | No | No |
| Vent Stacks | | | Yes | | |
| Flow SCFM per stack | | | Not Specified | | |
| Number | | | 1 | | |
| Height - Feet | | | 150 | | |
| Diameter - Inches | | | | | |
| Exit Gas Temperature - F° | | | | | |
| Emission Control Devices | | | Yes | | |
| Type - Flare | | | + | | |
| Bag House | | | | | |
| Cyclone | | | | | |
| Water Scrubber | | | | | |
| Other | | | | | |
| Catalog I. D. Number | | | HP-4 | | |
| Total Hydrocarbon Emissions - ton/ton HDPE | | | | | |
| Total Particulate - ton/ton HDPE | | | | | |
| Total NO$_x$ Emissions ton/ton HDPE | | | | | |
| Total SO$_x$ Emissions ton/ton HDPE | | | | | |
| Total CO Emissions ton/ton HDPE | | | | | |

See Continuation of This Table

| | 24-9 | | | |
|---|---|---|---|---|
| Company | | | | |
| Location | | | | |
| EPA Code Number | 24-9 | | | |
| Capacity - Tons of H.D. Polyethylene/Yr. | 110,000 | | | |
| Average Production - Tons of H.D. P.E./Yr. | 103,500 | | | |
| Range in Production - % of Max. | 0 | | | |
| Emissions to Atmosphere | | | | |
| Stream | Catalyst Activation Section Vent | HDPE Conveying ex. Blending Vent | Intermed. Stg. Conveying Vent | Packaging Conveyor |
| Flow - lb./hr. | 200 | 42,172 (A) | 6800 (C) | 96,400 (E) |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous |
| if Intermittent - hrs./yr. flow | | | | |
| Composition - ton/ton of H.D. P.E. | Downstream of HP-5 | Downstream of HP-6 | Downstream of HP-7 | Downstream of HP-8 |
| Hydrogen | | | | |
| Ethylene | | | | |
| Butene | | | | |
| Isobutane | | | | |
| Isopentane | | | | |
| Hexene | | | | |
| Polyethylene | | + | + | + |
| Cyclohexane | | | | |
| Air | .00850 | (Total) 1.79280 | (Total) .27200 | (Total) 3.85600 |
| Alumina | | | | |
| Co-Monomer | | | | |
| Nitrogen | | | | |
| Fuel Gas | | | | |
| Silica Gel | + | | | |
| Sample Tap Location | Not Sampled | Not Sampled | Not Sampled | Not Sampled |
| Date or Frequency of Sampling | | | | |
| Type of Analysis | Mat'l Bal. | Mat'l Bal. | Mat'l Bal. | Mat'l Bal. |
| Odor Problem | No | No | No | No |
| Vent Stacks | Not Specified | Not Specified | Not Specified | Not Specified |
| Flow SCFM per stack | | | | |
| Number | | | | |
| Height - Feet | | | | |
| Diameter - Inches | | | | |
| Exit Gas Temperature - F° | | | | |
| Emission Control Devices | Yes | Yes | Yes | Yes |
| Type - Flare | + | | | |
| Bag House | | + | + | |
| Cyclone | | | + | + |
| Water Scrubber | | | | |
| Other | | | | |
| Catalog I. D. Number | HP-5 | HP-6 (B) | HP-7 (D) | HP-8 (F) |
| Total Hydrocarbon Emissions - ton/ton HDPE | } .035564 | | | |
| Total Particulate - ton/ton HDPE | | | | |
| Total NO$_x$ Emissions ton/ton HDPE | | | | |
| Total SO$_x$ Emissions ton/ton HDPE | | | | |
| Total CO Emissions ton/ton HDPE | | | | |

| | Plt. II Stripper System Vent | Plt. III Conveyor Purge Vent | Plt. III Conveyor Purge Vent | Plt. IV Purge Column Vent | Plant Flare | Fugitive Emissions | Not Specified |
|---|---|---|---|---|---|---|---|
| Company | | | | | | | |
| Location | | | | | | | |
| EPA Code No. | | 24-10 | | | | | 24-4 |
| Capacity - Tons of H.D. Polyethylene/Yr. | | 151,000 | | | | | |
| Average Production - Tons of H.D. P.E./Yr. | | 151,000 | | | | | |
| Range in Production - % of Max. | | 0 | | | | | 27% |
| Emissions to Atmosphere | | | | | | | |
| Stream | | | | | | | |
| Flow - Lb./Hr. | 1040 | 25 | 110 | 2)0 | Not Specified | | |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Continuous | Continuous | Intermittent | |
| if Intermittent - Hrs./Yr. Flow | | | | | | | |
| Composition - Ton/Ton of H.D. P.E. | | | | | | | |
| Hydrogen | | | | | | | |
| Ethylene | .00185 | | | .00008 | | | G |
| Butene | .00044 | | | | | | |
| Isobutane | | | | | | | |
| Isopentane | | | | | | | |
| Hexene | | | | .00007 | | | |
| Polyethylene | | | | | | | |
| Cyclohexane | | | | | | | |
| Air | .02188 | | | ($N_2$) .00249 | | | |
| Alumina | | | | | | | |
| CO-monomers | | | | | | | |
| Methane | | | | | | | |
| Carbon Monoxide | | | | | | | |
| Carbon Dioxide | .00107 | | | .00089 | | | |
| Unspecified Hydrocarbons | .00198 | .00065 | .00290 | .00190 | | .03907 | |
| Sample Tap Location | | | | | | | |
| Date or Frequency of Sampling | 1966 | 1963 | 1963 | 1972 | | | |
| Type of Analysis | GLC | GLC | GLC | GLC | | Estimate | |
| Odor Problem | No | No | No | No | | | |
| Vent Stacks | Yes | Yes | Yes | Yes | Yes | No | |
| Flow SCFM per Stack | 218 | | | 35 | | | |
| Number | 1 | 1 | 1 | 1 | 1 | | |
| Height-Feet | 86 | 36 | 95 | 160 | 100 | | |
| Diameter-Inches | 2 | 2 | 2 | 2 | 16 | | |
| Exit Gas Temperature - F° | 90 | Ambient | Ambient | Ambient | | | |
| Emission Control Devices | No | No | No | No | Yes | No | Yes |
| Type - Flare | | | | | X | | X |
| Bag House | | | | | | | |
| Cyclone | | | | | | | |
| Water Scrubber | | | | | | | |
| Other | | | | | | | |
| Catalog I. D. No. | | | | | HP-9 | | HP-10 |
| Total Hydrocarbon Emissions - Ton/Ton H.D. P.E. | | .04894 | | | | | Not Specified but 0.0206 if calculated on basis of publi- shed capacity |
| Total Particulate - ton/ton | | 0 | | | | | |
| Total $NO_x$ - Ton/Ton | | 0 | | | | | |
| Total $SO_x$ - Ton/Ton | | 0 | | | | | |
| Total CO - Ton/Ton | | 0 | | | | | |

| Note | Comment |
|------|---------|
| A | Total maximum flow for four separate streams. |
| B | Device HP-6 consists of 14 separate bag filters with an average of four compartments per filter and 15 bags per compartment. |
| C | Reported data interpreted as meaning stated flow is total for eight separate streams. |
| D | Device HP-7 consists of 34 cyclones and 11 bag filters. Table IV lists the cyclones under HP-7a and the bag filters under HP-7b. |
| E | Reported data interpreted as meaning stated flow is total for four separate streams. |
| F | Device HP-8 consists of four cyclones. |
| G | Respondent has verbally reported that his conveyor emission factors are camparable to those reported by respondent 24-10. |

## Reactor Section

**FLARE SYSTEM**

| | | | | |
|---|---|---|---|---|
| Flow Diagram Stream I. D. Letter | (B) | (B) | (B) | |
| Device I. D. Number | HP-3 | HP-4 | HP-9 | HP-10 |
| EPA Code No. for plant using | 24-1 | 24-9 | 24-0 | 24-4 |
| Types of compounds incinerated | Various Lt. H.C. | Various Lt. H.C. | Various Lt. H.C. | Not Specified |
| Amount incinerated - lb./hr. (SCFM) | | | | |
| Device or stack height - ft. | 235 | 150 | 100 | 149 |
| Stack diameter @ tip - inches | 30 | | 16 | 24 |
| Installed Cost - Mat'l & Labor - $ | 76,000 | 22,600 | 9,500 | 55,000 |
| Installed Cost - Mat'l & Labor - c/lb. of HDPE - Yr. | .04199 | .01092 | .00315 | |
| Operating Cost - Annual - $ | 5,000 | 12,250 | 26,500 | 11,300 |
| Operating Cost - Annual - c/lb. of HDPE - Yr. | .00276 | .00592 | .00878 | |
| Efficiency (V) CCR - % | | | | |
| Efficiency (V) SERR - % | | | | |

**WATER SCRUBBERS** - Device I. D. Number

| | | | | |
|---|---|---|---|---|
| WATER SCRUBBERS - Device I. D. Number | HP-2 | | | |
| Flow Diagram Stream I. D. Letter | (B) | | | |
| EPA Code No. for plant using | 24-1 | | | |
| Purpose - Control emission of | Alumina Dust | | | |
| Type - Spray | X | | | |
|     Packed column | | | | |
|     Trays - Type | X | | | |
|         Number | | | | |
|     Plenum chamber | | | | |
|     Other | | | | |
| Water rate - GPM | 10 | | | |
| Design (operating) Temp. - F° | | | | |
| Gas Rate - SCFM | 800 | | | |
| TT - Height - ft. | 12.75 | | | |
| Diameter - ft. | 2 | | | |
| Installed Cost - Mat'l & Labor, $ | 20,000 | | | |
| Installed Cost - Mat'l & Labor, c/lb. of HDPE/Yr. | .01105 | | | |
| Operating Cost - Annual - $ | 4,000 | | | |
| Operating Cost - c/lb. of HDPE/Yr. | .00221 | | | |
| Efficiency | | | | |

| | Catalyst Activation Section | Reactor Section | HDPE Stripping & Blending Sect. | Product Conveying Vent | Product Packaging Vent |
|---|---|---|---|---|---|
| **BAG FILTERS** | | | | | |
| Flow Diagram Stream I. D. Letter | (A) | | (C) | (D) | |
| Device I. D. Number | HP-5 | | HP-6 (I) | HP-7b (II) | |
| EPA Code No. for plant using | 24-9 | | 24-9 | 24-9 | |
| Purpose - control emission of | Catalyst Dust | | HDPE Dust | HDPE Dust | |
| Number of compartments | 1 | | 4 | Not Specified | |
| Bags per compartment | | | 15 | | |
| Type cloth used for bags | Orlon | | | | |
| Total bag area - ft.$^2$ | 200 | | | | |
| Design (operating) temp - F$^o$ | 250 | | | | |
| Design (operating) pressure - PSIG | | | | | |
| Installed Cost - Mat'l & Labor - $ | 3640 | | (Total) 101,000 | (Total) 31 800 | |
| Installed Cost - ¢/lb. of HDPE - Yr. | .00176 | | (Total) .04879 | .01536 | |
| Operating Cost - Annual - $ | 250 | | (Total) 3,500 | 0 | |
| Operating Cost - Annual - ¢/lb. of HDPE - Yr. | .00012 | | (Total) .00169 | 0 | |
| Efficiency - % | 100 | | 100 | | |
| | | | | | |
| **CYCLONES** | | | | | |
| Flow Diagram Stream I. D. Letter | | | (C) | (D) | (E) |
| Device I. D. Number | | | HP-1 | HP-7a (III) | HP-8 (IV) |
| EPA Code No. for plant using | | | 24-1 | 24-9 | 24-9 |
| Purpose - control emission of | | | HDPE Dust | HDPE Dust | HDPE Dust |
| TT - Height - Ft. | | | Not Specified | 5 | Not Specified |
| Diameter - Ft. | | | | 1.8 | |
| No of Stages | | | | 1 | |
| Installed Cost - Mat'l & Labor - $ | | | 30,000 | (Total) 43,200 | (Total) 9,700 |
| Installed Cost - ¢/lb. of HDPE - Yr. | | | .01658 | .02087 | (Total) .00469 |
| Operating Cost - Annual - $ | | | 6,000 | 0 | (Total) 1,500 |
| Operating Cost - ¢/lb. of HDPE - Yr. | | | .00332 | 0 | (Total) .00073 |
| Efficiency | | | ~100 (on particulates) | | ~ '100' |

| Note | Comment |
|------|---------|
| I | Device HP-6 consists of 14 separate bag filters with an average of four compartments/filter and 15 bags/compartment. |
| II | Device HP-7b consists of 11 individual bag filters. |
| III | Device HP-7b consists of 34 individual cyclones. |
| IV | Device HP-8 consists of four separate cyclones. |
| V | See Appendix V of this report for explanation of CCR and SERR efficiencies. |

## TABLE HP-V
## NUMBER OF NEW PLANTS BY 1980

| Current Capacity | Marginal Capacity | Current Capacity on-stream in 1980 | Demand 1980* | Capacity 1980 | Capacity to be Added | Economic Plant Size | Number of New Units |
|---|---|---|---|---|---|---|---|
| 2,315 | 0 | 2,315 | 8,500 | 8,500 | 6,186 | 200 | 30 - 31 |

NOTE:  All capacities in MM lbs./yr.

*1980 demand based on Stanford Research Institute's 'Chemical Economics Handbook', Section 580.1330.

See also discussion on page HP-8.

TABLE HP-VI
EMISSION SOURCE SUMMARY*
TON/TON HDPE

| Emissions | Catalyst Prep. | Reactor | Solvent Recovery | Polymer Stripping | Product Conveying | Fugitive | Flare | Total |
|---|---|---|---|---|---|---|---|---|
| | | | | | Source | | | |
| Hydrocarbons | | | .0020 | .0090 | .0030 | .0200 | | .0340 |
| Particulates | | | | | .0010 | | | .0010 |
| $NO_x$ | Negligible | Negligible | | | | | .0001 | 0 |
| $SO_x$ | | | | | | | | 0 |
| CO | | | | | | | | 0 |

*All quantities used in this table are based on data reported in questionnaires from plants with EPA Code Nos. 20-0, 20-1, 20-4, and 20-9. Most numbers have been subject to some adjustment - as dictated by the demands of engineering judgement.

<div align="center">

TABLE HP-VII
WEIGHTED EMISSIONS RATES

</div>

Chemical ___High Density Polyethylene_____

Process ____Intermediate and Low Pressure Polymerization_

Increased Capacity by 1980 _6,185 MM Lbs./Year_____

| Pollutant | Emissions, Lbs./Lb. | Increased Emissions MM Lbs./Year | Weighting Factors | Weighted Emissions MM Lbs./Year |
|---|---|---|---|---|
| Hydrocarbons | .034 | 210.3 | 80 | 16,824 |
| Particulates | .001 | 6.2 | 60 | 372 |
| $NO_x$ | TR | TR | 40 | TR |
| $SO_x$ | 0 | 0 | 20 | 0 |
| CO | 0 | 0 | 1 | 0 |

Significant Emission Index = 17,196 (MM lbs./yr.)

Low Density Polyethylene

# Table of Contents

## List of Illustrations & Tables

I. <u>Introduction</u>

More polyethylene is produced in the United States than any other plastic. Several types of polyethylene are produced. The two most important types are High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE). The screening effort in this report is based on questionnaires returned by seven LDPE manufacturers.

As of January, 1971, approximately 5,300,000,000 lbs./year of LDPE capacity existed in domestic facilities. Emissions arising from these facilities come primarily from materials handling; purges and venting of equipment and lines; gas separation and other recovery operations; and fugitive emissions. The pollutants are predominantly hydrocarbon vapors and fine polymer particulates. Relative to pollution significance, LDPE projections to the year 1980 indicate an SEI* of about 21,300. This index rating places LDPE in the ranks of petrochemicals which qualify for in-depth studies.

Note: Questionnaire response Code No. 24-8 came to review status just prior to issuance of this screening report. Therefore, the information in response 24-8 does not participate in the detailed structuring of this report. It can be stated, however, that - except for minor nuances such as in emission stream component concentrations - the 24-8 report content in general, fits the pattern of previous reports on LDPE.
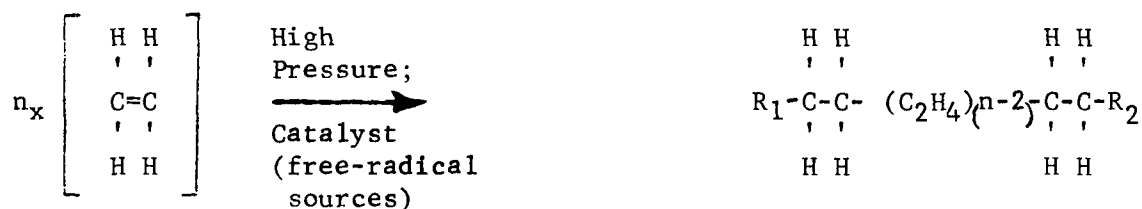
*See Appendix IV for explanation.

## II. Process Description

This is a simplified description of a modern high pressure ethylene polymerization process for the production of low density polyethylene (LDPE). A detailed technological description is 1) not necessary to fulfill the objectives of this screening report, and 2) not possible from information currently available in published form.

A simplified composite flow diagram is attached. Please see fold-out Drawing No. R-209. (Figure LD-I)

The characterizing variable in the LDPE reaction is pressure, which normally ranges from 10,000 to 30,000 PSIG, and can reach levels as high as 45,000 PSIG. The mechanism of ethylene polymerization on the catalyst surface is quite complex. The simplified net reaction:

$$n_x \begin{bmatrix} \begin{array}{cc} H & H \\ | & | \\ C=C \\ | & | \\ H & H \end{array} \end{bmatrix} \quad \begin{array}{c} \text{High} \\ \text{Pressure;} \\ \xrightarrow{\hspace{2cm}} \\ \text{Catalyst} \\ \text{(free-radical} \\ \text{sources)} \end{array} \quad \begin{array}{cc} H & H \\ | & | \\ R_1 -C-C- \\ | & | \\ H & H \end{array} (C_2H_4)_{n-2} \begin{array}{cc} H & H \\ | & | \\ C-C-R_2 \\ | & | \\ H & H \end{array}$$

$R_1$ and $R_2$ represent chain-terminations resulting from the introduction of "telogens" specifically chosen to accomplish this end. (Although not shown above, LDPE polymer structures are usually characterized by branched chains.) The ethylene monomer polymerizes in a stirred autoclave or a tubular reactor. During the reaction sequence, temperature is controlled at predetermined levels by a heat transfer system which can add or remove heat in exact accord with processing requirements. (Copolymers and other variations are commercially important; e.g., the vinyl acetate copolymer, "EVA".)

After a suitable residence time in the reactor, the monomer-polymer mix continues to the flash section where unreacted monomers and some "waxy" material are flashed overhead. The flash vapor components are separated and purified. Recovered monomers are recycled, and the waxy materials are buried, incinerated or handled by some other suitable means of disposal.

The crude LDPE is extruded and pelletized (or otherwise mechanically prepared) so that it can be fed to the materials handling and finishing sytem which follows.

The most common form of materials handling system for the pellets is airveying. This type of system permits intermediate and pre-shipment storage in an effectively deployed network of silos.

III. __Plant Emissions__

    A. Continuous Air Emissions

        1. Flue Gas

        No process fuel usage is reported.

        2. Purification and Recovery Vents

        All producers recycle unreacted monomer. The recovery streams require purification. The light and heavy ends from the purification process are either vented, flared, sent to another process, or to a pollution control device. These operations can be one of the sources of air pollution in the production of LDPE. The reported vent streams in this category, along with their pollution control devices, are summarized in Tables III and IV.

        3. Materials Handling Losses

        Semi-finished and finished LDPE granules are most often transported in-plant via pneumatic conveying systems. The various atmospheric vents that are associated with these systems are a source of hydrocarbon and particulate emissions. The hydrocarbon content of these emissions arises from a significant monomeric ethylene residual in the pellets. The ethylene diffuses from the pellets into the conveying air and silo purge air. Continuous particulate emissions are presumed not significant with suitable retention means such as cyclones and bag filters. Emission and control device data are summarized in Tables III and IV.

    B. Intermittent Air Emissions

        1. Catalyst Activation, Feed Treatment and Reactor Charging and Dumping

        These operations are accompanied by significant intermittent emissions in the case of __high__ density polyethylene production. These categories of operations are, therefore, mentioned here and are excluded as significant intermittent emissions sources in the case of LDPE production.

        2. Start-Up and Emergency Vents

        According to the responses received to the LDPE questionnaires, these vents are normally tied into flare systems. The products of combustion are carbon dioxide and water, except in certain emergencies when the flares receive entrained liquids or excessive gas flows, and may briefly show smoky effluents.

        The LDPE respondents' reports indicate that smokeless flare designs contain adequate safety margin for most situations. However, extreme swings in design parameters occasionally lead to upset conditions; e.g., pilot flame-out; excessive turndown demands; low or zero steam pressure.

        $NO_x$ formation resulting from the above start-up and emergency vent

flaring is not considered appreciable, relative to the national emissions inventory.

C. Waste Water

Water is used in the extrusion steps for cooling; as a pellet transfer medium; and as a means of "floating: oily liquids. However, no waste water was reported by any respondent.

D. Solid Wastes

1. Spent Catalysts

In contrast to HDPE operations, LDPE catalyst does not pose a solid waste problem.

2. Polyethylene Waste

The amount of non-specification and scrap LDPE produced is a function of the process used, the stringency of product molecular weight range specifications, and many other factors. The material is disposed of via incineration, landfill or contract haulage.

3. Waxes

Varying amounts of relatively low molecular weight solid waxes are produced by LDPE processes. Disposal is by methods similar to those employed for waste polyethylene.

E. Odors

No significant odors are reported by the questionnaire respondents. However, many of the reported vent streams contain materials that have odors.

F. Fugitive Emissions

The respondents indicate fugitive emissions (= "other emissions") of significant proportions, as shown quantitatively in the tabular portions of this report. It is assumed for the purposes of this screening study that all LDPE operations have significant fugitive emissions.

Liquid storage is 1) padded, 2) pressurized, 3) refrigerated, 4) or low volatility atmospheric tankage. The respondents are presumed to allot any liquid storage losses to "other emissions", Section VIII of the questionnaires, which they, in general, have calculated from their overall material balance.

IV. <u>Emission Control</u>

The various emission control devices that have been reported as being employed by operators of low density polyethylene plants are summarized in the Catalog of Emission Control Devices - Table IV. In general, no quantitative information on the device performance has been made available. Never-the-less, certain generalizations about the performance of the devices utilized can be made.

<u>Water Scrubbers</u>

No water scrubber or similar device was reported.

<u>Cyclones</u>

In low density polyethylene production, these devices are used to remove or reduce the amount of LDPE dust emitted from the pneumatic conveyor and silo vent systems. The device efficiencies cannot be calculated from the data reported. But the conclusion may be tentatively drawn that future installations may be teamed up with bag filters.

<u>Bag Filters</u>

Although none were reported, bag filters appear to be the ultimate final-step device for the LDPE plant of the future. A properly chosen device, according to data collected in this study and reported in Report No. EPA-450/3-006a, should remove substantially all LDPE particulate dust escaping the cyclones.

<u>Flares & Incinerators</u>

All LDPE plant operators are presumed to make use of a flare system. Data necessary to calculate combustion efficiencies of existing flares have not been reported. Where specified, flares are mainly associated with the purification and recovery sections. It is likely that some $NO_x$ is formed in these flares.

Most operators are presumed to employ incinerators for the (relative small) combustible liquid waste effluents. Existing incinerators, where reported, appear to make no contribution to the national emissions inventory.

## V. Significance of Pollution

It is recommended that LDPE be placed in the ranks of petrochemicals which qualify for in-depth studies. The projected LDPE capacity and the corresponding quantity of pollutants emitted to the atmosphere are significant. The significance lies principally in the large cumulative production capcity, rather than in the emissions from any single installation.

The methods outlined in Appendix IV of this report have been used to forecast the number of new plants that will be built by 1980, and to estimate the total weighted annual emissions of pollutants from these new plants. This work is summarized in Tablve V, VI, and VII.

The Table V forecast of new plants is based on the assumption that the LDPE growth rate experienced from 1960 to 1969 will extend to 1980. A Significant Emissions Index (SEI) of 21,300 has been calculated. See Table VII, although the bulk of this is in the category of "fugitive emissions". This fact, along with uncertainties in the growth forecast are reasons why an in-depth study is required to determine the applicability of new source standards to the LDPE process.

## VI. Low Density Polyethylene Producers

The following tabulation of producers of low density polyethylene indicates published production capacity:

| Company | Location | As of 1970, Installed Capacity, MM Lbs./Yr. |
|---|---|---|
| Allied Chemical Corp. | Orange, Texas | 25 |
| Chemplex Co. | Clinton, Iowa | 300 |
| Cities Service Co. | Lake Charles, La. | 220 |
| Columbian Carbon Co. | Lake Charles, La. | 220 |
| Cosden Oil & Chemical Co. | Calumet City, Ill. | 20 |
| Dart Industries, Inc. | Odessa, Texas | 365 |
| Dow Chemical Co. | Freeport, Texas | 300 |
| | Plaquemine, La. | 200 |
| E. I. DuPont deNemours & Co. | Orange, Texas | 425 |
| | Victoria, Texas | 200 |
| Eastman Kodak Co. | Longview, Texas | 250 |
| Exxon Chemical Co. - U.S.A. | Baton Rouge, La. | 330 |
| Gulf Oil Corp. | Cedar Bayou, Texas | 200 |
| | Orange, Texas | 300 |
| Monsanto Co. | Texas City, Texas | 140 |
| National Distillers & Chemical Corp. | Tuscola, Ill. | 150 |
| | Deer Park, Texas | 300 |
| Phillips Petroleum Co. | Houston, Texas | 39 |
| Sinclair-Koppers Co. | Port Arthur, Texas | 220 |
| Union Carbide | Seadrift, Texas | 360 |
| | South Charleston, W. Va. | 120 |
| | Texas City, Texas | 225 |
| | Torrence, Calif. | 120 |
| | Whiting, Indiana | 240 |
| | Total | 5,269 |

PAGE NOT

AVAILABLE

DIGITALLY

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TABLE LP-I
COMPOSITE LOW DENSITY POLYETHYLENE
NET MATERIAL BALANCE
(TONS/TON OF LDPE CAPACITY)

</div>

|  | Stream No. on Simplified Flow Diagram | Tons/Ton LD |
|---|---|---|
| **INPUT** | | |
| Ethylene | 1 | 1.0105 |
| Catalysts | 2 | 0.0004 |
| Modifiers & Co-monomers* | 3 | 0.0179 |
| Misc. Other Additives | 4 | 0.0071 |
| Mineral Spirits | 5 | 0.0046 |
| Total Input | | 1.0405 |
| **OUTPUT** | | |
| Polyethylene Resin Product | 6 | 1.0000 |
| Waste Solids | 7 | 0.0196 |
| Fugitive Emissions | 8 | 0.0100 |
| Compressor Pot Liquids | 9 | 0.0046 |
| Misc. Atmospheric Vents | - | 0.0063 |
| Total Output | | 1.0405 |

*Including telogens (chain terminators).
**Includes vinyl acetate, propylene, iso-butane and organic peroxides.

<u>TABLE LP-II</u>
<u>LOW DENSITY POLYETHYLENE</u>
<u>GROSS HEAT BALANCE</u>

The exothermic heat of ethylene homopolymerization is 1450 BTU/LB. [1] of monomer.

A commercial reactor section gross heat balance for this process cannot be suitably estimated from the available published data.

---

(1)  Chem. Eng. 73 (16) 68 - August 1st, 1966

# TABLE LP-III
## NATIONAL EMISSIONS INVENTORY
### LOW DENSITY POLYETHYLENE PRODUCTION

Company
Location

| | 24-2 | 24-3 | | 24-5 | | 24-6 | |
|---|---|---|---|---|---|---|---|
| EPA Code No. | 24-2 | 24-3 | | 24-5 | | 24-6 | |
| Capacity - Tons of LD Polyethylene/Yr. | 150,000 | 110,000 | | 180,000 | | 110,000 | |
| Average Production - Tons of LDPE/Yr. | 112,750 | 110,000 | | 180,000 | | 110,000 | |
| Seasonal Range in Production - % of Max. | 0 | 0 | | 0 | | 0 | |
| Emissions to Atmosphere | | | | | | | |
| Stream - Letter on Flow Diagram | C | C | A | B | C | B | C |
| Description | Other Emissions | Other Emissions | Iso-Col. Emission | Storage Vent | Other Emissions | Storage Vent | Other Emissions |
| Flow - Lb./Hr. of Pollutants | 514* | 3** | 28 | 92 | 360* | < 1 | 6 |
| Flow Characteristic - Continuous or Intermittent if Intermittent - Hrs./Yr. Flow | Continuous | Continuous | Continuous | Continuous | Continuous | Continuous | Continuous |
| Composition - Ton/Ton of LDPE | | | | | | | |
| Ethylene | | | | 0.002 | | 0.00003 | |
| Polyethylene | | | | **** | | | |
| Air | | | | | | 0.03 | |
| Hydrocarbons | 0.0143 | 0.0001 | 0.0006 | | 0.008 | | 0.005 |
| Sample Location | None | None | Open Vent | Not Sampled | None | None | None |
| Date or Frequency of Sampling | | | Not Routinely | *** | | Not Sampled | |
| Type of Analysis | | | Mass Spectrograph | Not Analyzed | | Indirect | |
| Odor Problem | | | No | Not Applicable | | Not Applicable | |
| Vent Stacks | None indicated except for emergency reactor overpressure | None Indicated | Not Specified | None Indicated | None Indicated | Yes | None Indicated |
| Flow SCFM per stack | | | | | | 160 Total | |
| Number | | | | | | Not Indicated | |
| Height - Feet | | | | | | 75 | |
| Diameter - Inches | | | | | | 10 | |
| Exit Gas Temperature - F° | | | | | | Ambient | |
| Emission Control Device | No | No | No | Not Indicated | No | No | No |
| Type - Flare | | | | | | | |
| Bag House | | | | | | | |
| Cyclone | | | | | | | |
| Water Scrubber | | | | | | | |
| Other | | | | | | | |
| Catalog I. D. Number | | | | | | | |
| Total Hydrocarbon Emissions - ton/ton LDPE | 0.0143 | 0.0001 | 0.0006 | 0.002 | 0.008 | 0.00003 | 0.0005 |
| Total Particulate - ton/ton LDPE | None Listed | None | None | **** | None Listed | None Listed | None Listed |
| Total $NO_x$ - ton/ton LDPE | None | None | None | None | None | None | None |
| Total $SO_x$ - ton/ton LDPE | None | None | None | None | None | None | None |
| Total CO - ton/ton LDPE | None | None | None | None | None | None | None |

*From material balance.
**Assumption
***"Tests have been conducted at several (other) locations with good agreement".
****"Polyethylene fines may also be entrained in the air stream."

Note: For non-polluting streams, please see Simplified Flow Diagram Figure LD-1, (Drawing R-209) and Table IV.

TABLE LP-III
NATIONAL EMISSIONS INVENTORY
LOW DENSITY POLYETHYLENE PRODUCTION

Company
Location
EPA Code Number                                                                    24-7
Capacity - Tons of LD Polyethylene/Yr.                                             182,500
Average Production - Tons of LDPE/Yr.                                              182,500
Seasonal Range in Production - % of Max.                                              0
Emissions to Atmosphere

| | | | |
|---|---|---|---|
| Stream Letter on Flow Diagram | D | B | E |
| Description | Compressor Purge | Storage Vent | Intermediate Storage Vent**** |
| Flow - lb./hr. of Pollutants | 23 | 180 | 48 |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous |
| if Intermittent - hrs./yr. flow | | | |
| Composition - Ton/Ton of LDPE | | | |
| Ethylene | 0.0005 | 0.0039 | 0.001 |
| Polyethylene | | | |
| Air | | 0.54 | 1.08 |
| Hydrocarbons | | | |
| Sample Location | Not Sampled | Top of pellet bins | Not Sampled |
| Date or Frequency of Sampling | | ** | |
| Type of Analysis | None* | ** | Composition Estimated |
| Odor Problem | None | No | No |
| Vent Stacks | Yes | Yes | Yes |
| Flow SCFM per stack | 0.243 Ave. | 186 | 345*** |
| Number | 21 | 29 | 31 |
| Height - Feet | 50 | 25 | 50 |
| Diameter - Inches | 4 | 8 | 20 |
| Exit Gas Temperature - F° | 100 | 90 | 90 |
| Emission Control Devices | None | None | None |
| Type - Flare | | | |
| Bag House | | | |
| Cyclone | | | |
| Water Scrubber | | | |
| Other | | | |
| Catalog I. D. Number | | | |
| Total Hydrocarbon Emissions - Ton/Ton LDPE | 0.0005 | 0.0039 | 0.001 |
| Total Particulate - ton/ton LDPE | None | None | None |
| Total NOₓ Emissions Ton/Ton LDPE | None | None | None |
| Total SOₓ Emissions Ton/Ton LDPE | None | None | None |
| Total CO Emissions Ton/Ton LDPE | None | None | None |

*"Equipment volume plus purge procedure" used to determine composition and flow.
**Samples taken during the last revisions to the purge air system, about 1968.
***Flow determined from purge air system capacity.
****In addition, there are "compounding" and "fines removal" vents which total less than 2 lbs./hr. LDPE fines

Note: For non-polluting streams, please see Simplified Flow Diagram Figure LD-1, (Drawing R-209) and Table IV.

| | F | C | E | D |
|---|---|---|---|---|
| Company | | | | |
| Location | | | | |
| EPA Code No. | 24-11*** | | 24-12 | |
| Capacity - Tons of LD Polyethylene/Yr. | 150,000 | | 150,000 | |
| Average Production - Tons of LDPE/Yr. | 150,000 | | 150,000 | |
| Seasonal Range in Production - % of Max. | 0 | | 0 | |
| Emissions to Atmosphere | | | | |
| Stream Letter on Flow Diagram | F | C | E | D |
| Description | Purification & Recovery Flare | Other Emissions | Materials Handling Vent**** | Depressuring Vents***** |
| Flow - Lb./Hr. of Pollutants | 2 | 211 | 44 | 8 |
| Flow Characteristic - Continuous or Intermittent | Continuous | Continuous | Continuous | Intermittent |
| if Intermittent - Hrs./Yr. Flow | | | | 54 |
| Composition - Ton/Ton LDPE | | | | |
| Ethylene | | | 0.0008 | 0.0002 |
| Polyethylene | | | 0.0003 | |
| $NO_x$ | 0.00006 | | | |
| Water Vapor | 0.042 | | | |
| Carbon Dioxide | 0.095 | | | |
| Hydrocarbons | | 0.006 | | |
| Sample Tap Location | None | None | None | None |
| Date or Frequency of Sampling | | | | |
| Type of Analysis | * | ** | | |
| Odor Problem | None Indicated | None Indicated | No | Odor, but no problem |
| Vent Stacks | Yes | Not Indicated | Yes | Yes |
| Flow SCFM per Stack | 1,500 | | 725 Ave | 250 |
| Number | 1 | | 69 | 50 |
| Height - Feet | 100 | | 60 | 35 |
| Diameter - Inches | 20 | | 24 | 1 to 3 |
| Exit Gas Temperature - F° | 3500 | | 100 | 50 - 200 |
| Emission Control Devices | Yes | None Indicated | No | None Indicated |
| Type - Flare | + | | | |
| Bag House | | | | |
| Cyclone | | | | |
| Water Scrubber | | | | |
| Other | | | | |
| Catalog I. D. No. | 24-11 101 | | | |
| Total Hydrocarbon Emissions - Ton/Ton LDPE | None | 0.006 | 0.0008 | 0.0002 |
| Total Particulate - ton/ton LDPE | None | None | 0.0003 | None |
| Total $NO_x$ - Ton/Ton LDPE | 0.00006 | None | None | None |
| Total $SO_x$ - Ton/Ton LDPE | None | None | None | None |
| Total CO - Ton/Ton LDPE | None | None | None | None |

*Composition calculated.
**Estimate based on plant-wide material balance.
***Combustion products from a liquids incinerator also exist, in addition to "other emissions". These combustion products
   present no emissions inventory contribution (the $NO_x$ and CO are so low that they have no significance as pollutants).
****Composition & flow estimated from material balance and estimated pneumatic conveyor blower capacity.
*****"Composition based on process composition - flow estimated".

Note: For non-polluting streams, please see Simplified Flow Diagram Figure LD-1 (Drawing R-209) and Table IV.

## FLARE SYSTEM

| Device I. D. Number* | 24-12 102 | 24-3 101 | 24-11 101 |
|---|---|---|---|
| Types of Compounds Flared | Various Lt. H.C. | Various Lt. H.C. | Various Lt. H.C. |
| Amount Flared - lb./hr. | Normally zero (5*) | 14,000** | 1,067 |
| Device or Stack Height - Ft. | 120 | 115 | 100 |
| Stack Diameter @ tip - inches | 36 | 10 | 20 |
| Installed Cost - Mat'l. & Labor - $ | 530,000 | 83,000 | 165,660 |
| Installed Cost - Mat'l. & Labor - c/lb. of LDPE Production | **** | 0.0377 | 0.0552 |
| Operating Cost - Annual - $ (1972) | 16,000 | 9,400 | 3,500 |
| Operating Cost - Annual - c/lb. of LDPE Production | **** | 0.0043 | 0.0012 |
| Efficiency - CCR - % | Presumed near 100% | Presumed near 100% | Presumed near 100% |
| Efficiency - SERR - % | Presumed over 99.5% | Presumed over 99.5% | Presumed over 99.5% |
| Years Installed | 1961-1969 | 1967-1970 | 1960-1968 |
| Source | John Zink tip Minneapolis Tank Stack | John Zink*** | In-house |

## MISCELLANEOUS

| Device I. D. Number * | 24-2 100 | 24-5 101 | 24-11 102 | 24-12 101 |
|---|---|---|---|---|
| Purpose - Control Emission of | LDPE Dust | Various Lt. H.C. | Combustible waste liquids | Combustible waste liquids |
| Type | Cyclone, tangential, central pipe w/top outlet (no dimension indicated) | Collection, storage compression, and recycle to process | Incinerator**** w/25 HP air blower 2,400 CFM | Incinerator**** w/pressurized liquid to firing gun and steam atomization |
| Rate | 1,810 SCFM/88 units (Total) | Not Indicated | 200 GPH capacity | Capacity not indicated |
| Installed Cost - Mat'l. & Labor, $ | 141,200 | 100,353 | 97,000 | 9,500 |
| Installed Cost - Mat'l. & Labor, c/lb. of LDPE Production | 0.0554 | 0.0279 | 0.0323 | 0.0032 |
| Operating Cost - Annual - $ (1972) | 5,100 | (11,650 credit) | 5,500 | 1,000 |
| Operating Cost - c/lb. of LDPE Production | 0.002 | (0.0032 credit) | 0.0018 | 0.0003 |
| Efficiency | Presumed near 100% | Not Indicated | Presumed Near 100% | Presumed near 100% |
| Years Installed | 1959-1965 | 1955-1957 | 1969-1971 | 1971 |
| Source | Nat'l. Conveyors Co. & Fuller Co. | In-house | Hauck, Mod. JBO-6125 | Nat'l, Airoil Burner Co. Size 3S single pedastal burner w/No. 3 SAR gun |

*EPA code number for questionnaire respondent followed by emission control device number used by the respondent.
**Design rate; ethylbenzene unit normally operates to keep this stream = zero.
***Ignitor system and steam ring.
****These items are included as reported by the two respondents, 24-11 and 24-12; the resultant combustion products make no significant contribution as pollutants relative to the national emissions inventory.
*****Flare serves entire plant, no apportionment was made relative to LDPE plant emergencies.

Note: Respondents 24-6 and 24-7 indicate that there is no emission control device.

TABLE LP-V
NUMBER OF NEW PLANTS BY 1980

| Current Capacity | Marginal Capacity | Current Capacity on-stream in 1980 | Demand 1980* | Capacity 1980 | Capacity to be Added by 1980 | Economic Plant Size** | Number of New Units |
|---|---|---|---|---|---|---|---|
| 5,269 | 564 | 4,705 | 19,000 | 21,100 | 16,395 | 400 | 41 |

Note:  All capacities in MM LBS./YR.

*1980 demand based on Stanford Research Institute's
 'Chemical Economics Handbook', Section 580.1330.

**Estimated.

## TABLE LP-VI
## EMISSION SOURCE SUMMARY*
## TON/TON OF LDPE

| Emissions | Source | | | | | Total |
|---|---|---|---|---|---|---|
| | Compressor Purge | Reactor | Materials Handling | Gas-Separation Recovery Operation, Fugitive Emissions** | Flare*** | |
| Hydrocarbons | 0.001 | ↑ | 0.005 | 0.010 | TR | 0.016 |
| Particulates | | | 0.0003 | None | None | 0.0003 |
| $NO_x$ | | Negligible | None | None | $< .0001$ | $< 0.0001$ |
| $SO_x$ | | | None | None | None | 0 |
| CO | | ↓ | None | None | None | 0 |

*At the time that this report was written, there were seven questionnaires on hand, with EPA Code No's. 24-2, 24-3, 24-5, 24-6, 24-7, 24-11, 24-13.  The entries in the above table are adjudged to represent a modern plant with adequate capture and non-release of emissions candidates, and efficient particulate (polyethylene fines) removal means.

**The expressions "fugitive emissions" and "other emissions" are currently used interchangeably.  "Other emissions" is the label used in the questionnaire form, Section VIII.

***Flares, where used are either intermittent, or also served other plant processes.

Chemical    Low Density Polyethylene

Process    High Pressure Polymerization

New Added Capacity by 1980    16,395 MM Lbs./Yr.

| Pollutant | Emissions, Lbs./Lb. | Increased Emissions MM Lbs./Year | Weighting Factors | Weighted Emissions MM Lbs./Year |
|---|---|---|---|---|
| Hydrocarbons | 0.016 | 262 | 80 | 21,000 |
| Particulates | 0.0003 | 5 | 60 | 300 |
| $NO_x$ | Negligible | Negligible | 40 | |
| $SO_x$ | None | 0 | 20 | |
| CO | None | 0 | 1 | |

Significant Emission Index = 21,300 (MM Lbs./Year)

FINAL ADDRESS LIST

Air Products & Chemicals, Inc.
P. O. Box 97
Calvert City, Kentucky

Attention: Mr. Howard Watson

Allied Chemical Corp.
Morristown, New Jersey

Attention:   Mr. A. J. VonFrank
             Director Air & Water
             Pollution Control

American Chemical Corp.
2112 E. 223rd
Long Beach, California   90810

Attention:   Mr. H. J. Kandel

American Cyanamid Company
Bound Brook, New Jersey

Attention:   Mr. R. Phelps

American Enka Corporation
Enka, North Carolina   28728

Attention:   Mr. Bennet

American Synthetic Rubber Corp.
Box 360
Louisville, Kentucky   40201

Attention:   Mr. H. W. Cable

Amoco Chemicals Corporation
130 E. Randolph Drive
Chicago, Illinois

Attention:   Mr. H. M. Brennan, Director
             of Environomental Control Div.

Ashland Oil Inc.
1409 Winchester Ave.
Ashland, Kentucky   41101

Attention:   Mr. O. J. Zandona

Borden Chemical Co.
50 W. Broad Street
Columbus, Ohio   43215

Attention:   Mr. Henry Schmidt

Celanese Chemical Company
Box 9077
Corpus Christi, Texas   78408

Attention:   Mr. R. H. Maurer

Chemplex Company
3100 Gulf Road
Rolling Meadows, Illinois   60008

Attention:   Mr. P. Jarrat

Chevron Chemical Company
200 Bush Street
San Francisco, California   94104

Attention:   Mr. W. G. Toland

Cities Service Inc.
70 Pine Street
New York City, NY   10005

Attention:   Mr. C. P. Goforth

Clark Chemical Corporation
Blue Island Refinery
131 Kedzie Avenue
Blue Island, Illinois

Attention:   Mr. R. Bruggink, Director
             of Environmental Control

Columbia Nitrogen Corporation
Box 1483
Augusta, Georgia   30903

Attention:   Mr. T. F. Champion

Continental Chemical Co.
Park 80 Plaza East
Saddlebrook, NJ   07662

Attention:  Mr. J. D. Burns

Cosden Oil & Chemical Co.
Box 1311
Big Spring, Texas   79720

Attention:  Mr. W. Gibson

Dart Industries, Inc.
P. O. Box 3157
Terminal Annex
Los Angeles, California   90051

Attention:  Mr. R. M. Knight
            Pres. Chemical Group

Diamond Plastics
P. O. Box 666
Paramount, California   70723

Attention:  Mr. Ben Wadsworth

Diamond Shamrock Chem. Co.
International Division
Union Commerce Building
Cleveland, Ohio   44115

Attention:  Mr. W. P. Taylor, Manager
            Environ. Control Engineering

Dow Badische Company
Williamsburg, Virginia   23185

Attention:  Mr. L. D. Hoblit

Dow Chemical Co. - USA
2020 Building
Abbott Road Center
Midland, Michigan   48640

Attention:  Mr. C. E. Otis
            Environmental Affairs Div.

E. I. DuPont de Nemours & Co.
Louviers Building
Wilmington, Delaware   19898

Attention:  Mr. W. R. Chalker
            Marketing Services Dept.

Eastman Chemicals Products, Inc.
Kingsport, Tennessee

Attention:  Mr. J. A. Mitchell
            Executive Vice President
            Manufacturing

El Paso Products Company
Box 3986
Odessa, Texas   79760

Attention:  Mr. N. Wright,
            Utility and Pollution
            Control Department

Enjay Chemical Company
1333 W. Loop South
Houston, Texas

Attention:  Mr. T. H. Rhodes

Escambia Chemical Corporation
P. O. Box 467
Pensacola, Florida

Attention:  Mr. A. K. McMillan

Ethyl Corporation
P. O. Box 341
Baton Rouge, Louisiana   70821

Attention:  Mr. J. H. Huguet

Fibre Industries Inc.
P. O. Box 1749
Greenville, South Carolina   29602

Attention:  Mr. Betts

Firestone Plastics Company
Box 699
Pottstown, Pennsylvania   19464

Attention:  Mr. C. J. Kleinart

Firestone Synthetic Rubber Co.
381 W. Wilbeth Road
Akron, Ohio   44301

Attention:  Mr. R. Pikna

Firestone Plastics Company
Hopewell, Virginia

Attention:  Mr. J. Spohn

FMC - Allied Corporation
P. O. Box 8127
South Charleston, W. VA   25303

Attention:  Mr. E. E. Sutton

FMC Corporation
1617 J.F.K. Boulevard
Philadelphia, PA

Attention: Mr. R. C. Tower

Foster Grant Co., Inc.
289 Main Street
Ledminster, Mass.   01453

Attention. Mr. W. Mason

G.A.F. Corporation
140 W. 51st Street
New York, NY   10020

Attention:  Mr. T. A. Dent, V.P.
            of Engineering

General Tire & Rubber Company
1 General Street
Akron, Ohio   44309

Attention:  Mr. R. W. Laundrie

Georgia-Pacific Company
900 S.W. 5th Avenue
Portland, Oregan   97204

Attention:  Mr. V. Tretter
            Sr. Environmental Eng.

Getty Oil Company
Delaware City, Delaware   19706

Attention:  Mr. Gordon G. Gaddis

B. F. Goodrich Chemical Co.
6100 Oak Tree Blvd.
Cleveland, Ohio   44131

Attention:  Mr. W. Bixby

Goodyear Tire & Rubber Co.
1144 E. Market Street
Akron, Ohio   44316

Attention:  Mr. B. C. Johnson, Manager
            Environmental Engineering

Great American Chemical Company
650 Water Street
Fitchburg, Mass.

Attention:  Dr. Fuhrman

Gulf Oil Corporation
Box 1166
Pittsburgh, Pennsylvania

Attention:  Mr. D. L. Matthews
            Vice President -
            Chemicals Department

Hercules Incorporated
910 Market Street
Wilmington, Delaware

Attention:  Dr. R. E. Chaddock

Hooker Chemical Corporation
1515 Summer Street
Stamford, Conn.   06905

Attention:  Mr. J. Wilkenfeld

Houston Chemical Company
Box 3785
Beaumont, Texas   77704

Attention:  Mr. J. J. McGovern

Hystron Fibers Division
American Hoechst Corporation
P. O. Box 5887
Spartensburg, SC   29301

Attention:  Dr. Foerster

Jefferson Chemical Company
Box 53300
Houston, Texas   77052

Attention:  Mr. M. A. Herring

Koch Chemical Company
N. Esperson Building
Houston, Texas   77002

Attention:  Mr. R. E. Lee

Koppers Company
1528 Koppers Building
Pittsburgh, Pennsylvania   15219

Attention:  Mr. D. L. Einon

Marbon Division
Borg-Warner Corporation
Carville, Louisiana   70721

Attention:  Mr. J. M. Black

Mobay Chemical Corporation
Parkway West & Rte 22-30
Pittsburgh, Pennsylvania   15205

Attention:  Mr. Gene Powers

Mobil Chemical Company
150 E. 42nd Street
New York, NY   10017

Attention:  Mr. W. J. Rosenbloom

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri   63166

Attention:  Mr. J. Depp, Director of
            Corp. Engineering

National Distillers & Chem. Corp.
U.S. Industrial Chem. Co. Div.
99 Park Avenue
New York, NY   10016

Attention:  Mr. J. G. Couch

National Starch & Chem. Co.
1700 W. Front Street
Plainfield, New Jersey   07063

Attention:  Mr. Schlass

Northern Petrochemical Company
2350 E. Devon Avenue
Des Plaines, Illinois   60018

Attention:  Mr. N. Wacks

Novamont Corporation
Neal Works
P. O. Box 189
Kenova, W. Virginia   25530

Attention:  Mr. Fletcher

Olin Corporation
120 Long Ridge Road
Stamford, Conn.

Attention:  Mr. C. L. Knowles

Pantasote Corporation
26 Jefferson Street
Passaic, New Jeresy

Attention:  Mr. R. Vath

Pennwalt Corporation
Pennwalt Building
3 Parkway
Philadelphia, PA  19102

Attention:  Mr. J. McWhirter

Petro-Tex Chemical Corporation
Box 2584
Houston, Texas  77001

Attention:  Mr. R. Pruessner

Phillips Petroleum Co.
10 - Phillips Bldg.
Bartlesville, Oklahoma  74004

Attention:  Mr. B. F. Ballard

Polymer Corporation, Ltd.
S. Vidal Street
Sarnia, Ontario
Canada

Attention:  Mr. J. H. Langstaff
            General Manager
            Latex Division

Polyvinyl Chemicals Inc.
730 Main Street
Wilmington, Mass.  01887

Attention:  Mr. S. Feldman, Director of
            Manufacturing - Engineering

PPG Industries Inc.
One-Gateway Center
Pittsburgh, Pennsylvania  15222

Attention:  Mr. Z. G. Bell

Reichold Chemicals Inc.
601-707 Woodward Hts. Bldg.
Detroit, Michigan  48220

Attention:  Mr. S. Hewett

Rohm & Haas
Independence Mall West
Philadelphia, PA  19105

Attention:  Mr. D. W. Kenny

Shell Chemical Co.
2525 Muirworth Drive
Houston, Texas  77025

Attention:  Dr. R.L. Maycock
            Environ. Eng. Div.

Sinclair-Koppers Chem. Co.
901 Koppers Building
Pittsburgh, Pennsylvania  15219

Attention:  Mr. R. C. Smith

Skelly Oil Company
Box 1121
El Dorado, Kansas  67042

Attention:  Mr. R. B. Miller

Standard Brands Chem. Industries
Drawer K
Dover, Delaware  19901

Attention:  Mr. E. Gienger, Pres.

Stauffer Chemical Co.
Westport, Connecticut

Attention:  Mr. E. L. Conant

Stepan Chemical Company
Edens & Winnetka Road
Northfield, Illinois  60093

Attention:  Mr. F. Q. Stepan
            V.P. - Industrial Chemicals

Tenneco Chemicals Inc.
Park 80 Plaza - West 1
Saddlebrook, NJ  07662

Attention:  Mr. W. P. Anderson

Texas - U.S. Chemical Company
Box 667
Port Neches, Texas  77651

Attention:  Mr. H. R. Norsworth

Thompson Plastics
Assonet, Mass.  02702

Attention:  Mr. S. Cupach

Union Carbide Corporation
Box 8361
South Charleston, W. Virginia  25303

Attention:  Mr. G. J. Hanks, Manager
            Environ. Protection
            Chem. & Plastics Division

Uniroyal Incorporated
Oxford Management &
Research Center
Middlebury, Conn.  06749

Attention:  Mr. F. N. Taff

The Upjohn Company
P. O. Box 685
La Porte, Texas

Attention:  Mr. E. D. Ike

USS Chemicals Division
U.S. Steel Corporation
Pittsburgh, Pennsylvania  15230

Attention:  Mr. Gradon Willard

W. R. Grace & Company
3 Hanover SquarNew York, NY  10004

Attention:  Mr. Robt. Goodall

Wright Chemical Corporation
Acme Station
Briegelwood, North Carolina  28456

Attention:  Mr. R. B. Catlett

Wyandotte Chemical Corp.
Wyandotte, Michigan  48192

Attention:  Mr. John R. Hunter

Vulcan Materials Company
Chemicals Division
P.O. Box 545
Wichita, Kansas  67201

Attention:  H.M. Campbell
            Vice-President, Production

ENVIRONMENTAL PROTECTION AGENCY

Office of Air Programs
Research Triangle Park, North Carolina 27711

Dear Sir:

The Environmental Protection Agency, Office of Air Programs is
engaged in a study of atmospheric emissions from the Petrochemical
Industry. The primary purpose of this study is to gather information
that will be used to develop New Stationary Source Performance Standards
which are defined in Section 111 of the Clean Air Act as amended
December 31, 1970 (Public Law 91604). These new source standards will
not be set as part of this study but will be based (to a large extent)
on the data collected during this study.

A substantial part of the work required for this study will be per-
formed under contract by the Houdry Division of Air Products and Chemicals.
Several other companies not yet chosen will assist in the source sampling
phase of the work.

Very little has been published on atmospheric emissions from the
petrochemical industry. The first part of this study will therefore
rank the most important petrochemical processes in their order of importance
in regard to atmospheric emissions. The Petrochemical Emissions Survey
Questionnaire will be the primary source of data during the first phase.
This ranking will be based on the amount and type of emissions from the
process, the number of similar processes and the expected growth of the
process. A second in-depth phase of the study to document emissions more
completely will be based on information obtained through actual stack
sampling.

Attached you will find a copy of the petrochemical questionnaire
which you are requested to complete and return to the Enviromental
Protection Agency within forty-two (42) calender days.

You are required by Section 114 of the Clean Air Act to complete each applicable part of this questionnaire except for question II.4. and II.5. These two questions are concerned with the water and solid waste generated by the process itself not with that generated by the emission control equipment. This information would be of a value to the EPA and your answers will be appreciated.

This questionnaire is to be completed using the information presently available to your company. We are not asking that you perform special non-routine measurements of emissions streams. We are asking for results of measurements that you have made or for estimates when measurements have not been made. Where requested information is not available, please mark sections "not available". Where the requested information is not applicable to the subject process, mark the questionnaire sections "not . applicable". A sample questionnaire, filled out for a fictitious process is enclosed for your guidance.

It is the opinion of this office that for most processes it should be possible to answer all survey questions without revealing any confidential information or trade secrets. However, if you believe that any of the information that we request would reveal a trade secret if divulged you should clearly identify such information on the completed questionnaire. Submit, with the completed questionnaire, a written justification explaining the reason for confidential status for each item including any supportive data or legal authority. Forward a duplicate of your claim and supporting material, without the questionnaire data, to our counsel, Mr. Robert Baum, Assistant General Counsel, Air Quality and Radiation Division, Environmental Protection Agency, Room 17B41, 5600 Fishers Lane, Rockville, Maryland 20852. Emission data cannot be considered confidential.

Final authority for determining the status of the information resides with the Enviromental Protection Agency. A reply describing the decision reached will be made as soon as possible after receipt of the claim and supporting information. During the period before the final determination this office will honor any request to treat the questionnaire information as confidential.

Information declared to be a trade secret is subject to protection from being published, divulged, disclosed or made known in any manner or to any extent by Section 1905 of Title 18 of the United States Code. The disclosure of such information, except as authorized by law, shall result in a fine of not more than $1,000 or imprisonment of not more than one year, or both; and shall result in removal of the individual from his office or employment.

Although it should be noted that Section 114, Subsection C of the Clean Air Act allows such information to be disclosed "to other officers, employees, or authorized representatives of the United States concerned with carrying out the Act or when relevant in any proceeding under this Act," no confidential information will be revealed to any private concern employed by the Environmental Protection Agency to assist in this study.

The handling and storage of information for which the determination is pending or information which has been determined to be of a confidential nature is carefully controlled. Preliminary control procedures require that the material be labeled confidential and stored in a locked file.

The complete form should be mailed to:

> Mr. Leslie B. Evans
> Environmental Protection Agency
> Office of Air Programs
> Applied Technology Division
> Research Triangle Park, NC 27711

It is possible that additional copies of this questionnaire which will request information covering other petrochemical processes or other plants using the same process and operated by your organization will be sent to you in the course of this study. Clarification of items contained in the questionnaire may be obtained from Mr. Evans by telephone at 919/688-8146. Thank your for your help in this matter.

Sincerely,

*Leslie B. Evans*

Leslie B. Evans
Industrial Studies Branch

## Petrochemical Questionnaire

### Instructions

I.  **Capacity.** Describe capacity of process by providing the following:

   1.  **Process capacity.** Give capacity in units per year and units
       per hour. An "actual" capacity is preferred but "published"
       or "name plate" capacity will be satisfactory if such capa-
       city is reasonably correct. Do not give production.

   2.  **Seasonal variation.** Describe any significant seasonal
       variations in production.

       As example an ammonia plant might produce more during
       spring and winter quarters:

       | quarter | Jan-Mar | April-June | July-Sept | Oct-Dec | Year Total |
       |---------|---------|------------|-----------|---------|------------|
       | %       | 40      | 20         | 10        | 30      | 100%       |

II. **Process.** Describe the process used to manufacture the subject
    chemical by providing the following:

   1.  **Process name.** If the process has a common name or description,
       give this. If any portion of the process (e.g., product
       recovery method) has a common name, give this.

   2.  **Block Diagram.** Provide a block diagram of the process showing
       the major process steps and stream flows.

       (a) Show on block diagram all streams described below.
           Identify each required stream by letter. (A,B,C, etc.)
           In general the streams that must be identified are
           (1) the gaseous emissions streams before and after
           any control device and (2) the gaseous or liquid
           streams which, after leaving the process site, produce
           gaseous emissions during further processing or com-
           bustion.

           (1)   Any gaseous waste streams before and after any
                 pollution device should be shown and identified.

           (ii)  Streams from rupture disks or pressure relief
                 valves which protect equipment from operating
                 upsets but discharges less than once every year
                 need not be shown.

           (iii) Emissions from pressure relief systems that
                 normally discharge during power failures or
                 other emergencies should be shown, identified
                 by letter and labeled "emergency".

(iv)   Emissions from fueled heaters such as "heat
transfer medium" heaters, steam generators,
or cracking furnaces need not be shown if
they are fueled completely by fuels listed in
Question VII and are not used to incinerate by-
products or off gases.

(v)    Emissions from Claus units associated with
process need not be shown.  Stream to Claus
unit should be shown and identified with letter.

(vi)   Emissions from a central power plant (or steam
plant) which burns a liquid fuel produced as a
by-product of this process need not be shown.
Such liquid fuel should be shown and identified
by letter.

(vii)  Emissions from a central power plant (or steam
plant) which burns a gaseous fuel produced as
a by-product of this process need not be shown.
Such gaseous fuel should be shown and identified
by letter.

(b)  Show all gaseous emission control devices.  Identify
each control device on the block diagram by a three
digit number (101, 102, 103, etc.)

(c)  Show all stacks or vents that vent streams listed in
(a) and (b) above.  It a stack to vent discharges
emissions from more than one source, label this stack
or vent with a letter in sequence started in II.2.a.
(D,E,F, etc.)  If a stack or vent discharges emissions
from only one source label the stack with the same
letter as the emission stream.

3.  Raw material and product.  Give approximate chemical com-
position and approximate amount (on yearly basis and at
capacity given in I.1) of all raw-materials, products
and by-products.  If composition or amounts vary, give
ranges.  Composition may be given in commonly accepted
terms when a chemical analysis would be inappropriate.
The description "light straight-run naphtha" would be
adequate.

4.  Waste water.  Is there a waste water discharge from this
process which is (eventually) discharged to a receiving
body of water?  Is this waste water treated by you or
by others?  Give the approximate volume and indicate
whether this is measured or estimated.

-3-

5. <u>Waste solids.</u> Is there a waste solids discharge from this process? How is it disposed of? Give the approximate daily total of waste solids and indicate if this is measured or estimated.

III. <u>Emissions (composition and flow)</u>: For each stream requested in II.2.a. and shown on the block diagram by letter provide the following: (Use separate sheets for each identified location - 6 copies are provided). All of the questions will not be applicable for each stream.

As an example, question 10, <u>odor problem</u>, applies only to streams which are emitted to the atmosphere.

1. <u>Chemical composition and flow.</u> Give composition as completely as possible from information you have available. Do not omit trace constituents if they are known. If anything (e.g. fuel) is added upstream of any emission control devices, give the chemical composition and flow prior to the addition, and give the quantity and composition of the added material. If liquids or solids are present (in gas stream) provide the composition and amount of these also. Give flow volume (SCFM), temperature (F°) and pressure (psig or inches $H_2O$).

2. <u>Variation in chemical composition and flow.</u> If average stream composition or flow varies significantly over some period of time during normal or abnormal operation, discuss this variation and its frequency. Relate this to the average and range of composition given in III.1.

As examples:

"During start-up (once a month) the benzene is about 12% by volume for one hour" or "the benzene can be expected to go from 5% to 9% by volume during life of catalyst, the 'average' figure given is about average over the catalyst life" or "power failures occur about once each winter causing stream A to increase from 0 to (initially) 50,000 lbs/hr., and about 8,000 lbs is vented over a 15 minute period."

3. <u>Production rate during sampling.</u> If stream composition and volume flow rates given in answer to questions III.1. and III.2. were measured at a plant production rate different than the capacity of the plant given in I.1. give the rate at which the measurements were made.

As example:

Figures given for this stream (A) were made when plant was operating at 90% of capacity given in I.1.

4.   Methods used to determine composition and flow.  Is information
     from material balance, from sample and analysis, or other?
     Describe briefly.

5.   Sampling procedure.  If samples have been taken, give summary
     description of sampling procedure or give reference if
     described in open literature.

6.   Analytical procedure.  If samples have been taken, give sum-
     mary description of analytical procedure or give reference if
     described in open literature.

7.   Sampling frequency.  How often is the stream sampled?

     As Examples:

     "continuous monitor" or "twice a shift for last 18 months"
     or "once in the fall of 1943".

8.   Confidence level.  Give some idea how confident you are in
     regard to compositions in III.1.

     As examples:

     "probably correct $\pm$ 20%" or "slightly better than wild guess".

9.   Ease of sampling.  How difficult is it to sample this stream?

     As examples:

     "sample line runs into control room" or "sample port provided
     but accessible only with 20-ft. ladder."

10.  Odor problem.  Is the odor of this emission detectable at
     ground level on the plant property or off the plant property?
     If odors carry beyond the plant property are they detectable
     frequently or infrequently?  Have you received a community
     odor complaint traceable to this source in the past year?
     Has the odorous material been chemically identified?  What
     is it?

IV.  **Emission control device.**  Supply the following information for each control device shown on the block diagram.  (Use separate sheets for each - 3 copies are provided).

1.  **Engineering description.**  Give brief description and process sketch of the control device.  Attach print or other description if you prefer.  Show utilities used, steam produced, product recovered, etc.  Give manufacturer, model number and size (if applicable).  Give complete (applicable) operating conditions, i.e. flows, temperatures, pressure drops, etc.

2.  **Capital cost of emission control system.**

    (a)  Give capital cost for the emission control device as it is described in IV.1. above; i.e., if equipment has been modified or rebuilt give your best estimate of capital cost of equipment now in service.  For the total installed cost give the approximate breakdown by year in which cost was incurred.

        As example:

        Major equipment cost  $155,000
        Total installed cost  $250,000
        Year        Cost
        1963        $160,000
        1964          40,000
        1971          50,000
                    $250,000

    (b)  On the check list given mark whether the items listed are included in total cost as given above.  Give one sentence explanation when required but do not give dollar amounts.

    (c)  Was outside engineering contractor used and was cost included in capital cost?

    (d)  Was in-house engineering used and was cost included in capital cost?

    (e)  Was emission control equipment installed when plant was built?

3.  **Operating cost of emission control system.**  Give the best estimate of cost of operating emission control system in dollars per year with process operated at capacity given in I.1.  Other disposal (g) would include, as example, the cost of incinerating a by-product stream which has no value.

V.  Stack or vent description.  Each stack or vent should have been identified by letter on the block diagram.  Provide the requested information for each stack.  Stack flow, V.4. should be entered only when it is not possible to calculate this number by adding gas flows given in III.1.

An example would be when an off gas from the process is discharged into a power plant stack.

VI.  Tankage.  Give information requested for all tankage larger than 20,000 gallons associated with the process and normally held at atmospheric pressure (include raw material, process, product and by-product tankage).  Method of vapor conservation (3.) might include, as examples:

"none, tank vents to air"
"floating roof"
"vapor recovery by compression and absorption".

VII.  Fuels.  If fuels are used in the process give the amount used on a yearly basis at capacity given in I.1.  Do not include fuel used in steam power plants.  Give sulfur content.  Identify each fuel as to its source (natural gas pipeline, process waste stream, Pennsylvania soft coal).  Is the fuel used only as a heat source (as with in-line burner)?

VIII.  Other emissions.  If there is a loss of a volatile material from the plants through system leaks, valve stems, safety valves, pump seals, line blowing, etc., this loss is an emission.  In a large complex high pressure process this loss may be several percent of the product.  Has this loss been determined by material balance or other method?  What is it?  Give best estimate.

IX.  Future plans.  Describe, in a paragraph, your program for the future installation of air pollution control equipment for this unit or for future improvements in the process which will reduce emissions.

OMB Approval Number 158 S 72019

This example questionnaire has been
completed for a fictitious company
and process.

Example
Questionnaire

Air Pollution Control Engineering and Cost Study of the Petrochemical Industry

Please read instructions before completing questionnaire.

Subject chemical: _____ Pyrrole

Principal by-products: _ Pyrrolidone

Parent corporation name: Orivne Petrochemical Co.

Subsidiary name: _____ Noissime Division

Mailing address: _____ P.O. Box 1234

_____ Rianaelc, North Carolina, 27700

Plant name: _____ Rianaelc Plant

Physical location: _____ 30 miles N.W. Durham, North Carolina

(include county and
air quaility control
region)_ Orange County; Eastern Piedmont Intrastate (Region IV)

Person EPA should contact regarding information supplied in this questionnaire

Name: _____ John Doe

Title: _____ Supervisor of Process Development

Mailing address: _____ Noissime Division of O.P.C.

_____ P.O. Box 1234

_____ Rianaelc, North Carolina, 27700

Telephone number: _____ 919  XXX  XXXX

Date questionnaire completed: _____ May 30, 1972

I. <u>Capacity</u>.

    1. <u>Process capacity</u>. (not production)

       <u>80,000,000 lbs.</u>        per year

       <u>10,000 lbs.</u>        per hour
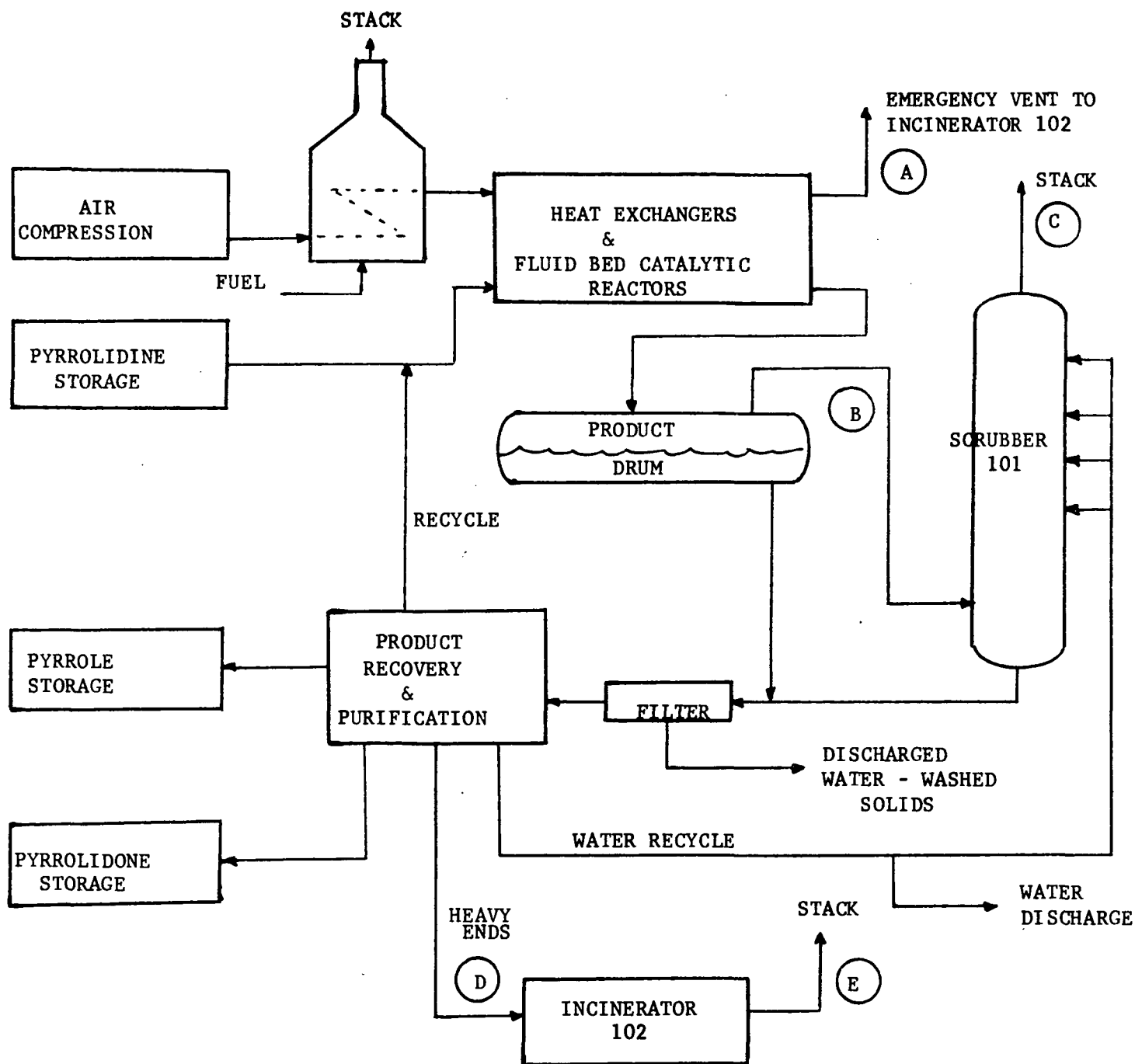
    2. <u>Seasonal variation</u>. (of production)

| quarter | 1 | 2 | 3 | 4 | year total |
|---------|-----|-----|-----|-----|------|
| %       | 30  | 20  | 20  | 30  | 100% |

II. Process.

1. Process name.

Relvrep – Process (oxidative dehydrogenation of pyrrolidine)

2. Block diagram.

II. Process. (Continued)

    3. Raw materials and products

        <u>Raw materials</u>

| <u>Name</u> | <u>Quantity</u> | <u>Composition</u> | |
|---|---|---|---|
| Pyrrolidine | 130,000,000 lbs/yr. | pyrrolidine | 98% |
| | | other amines | 2% |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

<u>Product and by-products</u>

| <u>Name</u> | <u>Quantity</u> | <u>Composition</u> | |
|---|---|---|---|
| Pyrrole | 80,000,000 lbs/yr. | pyrrole | 99.5% |
| | | | |
| | | | |
| Pyrrolidone | 20,000,000 lbs/yr. | pyrrolidone | 99.5% |
| | | | |
| | | | |
| | | | |
| | | | |

II.  Process.  (Continued)

    4.  Waste water.

       750 gal/hr. treated by us, measured in treatment unit.

    5.  Waste solids.

       200 lbs/hr. catalyst dust from filter.  Estimated average quantity hauled away by solids waste disposal contractor.

III.1.Emissions (composition and flow).                    Six copies provided
                                                           this section


Stream flow shown on block diagram by letter___A___.

1.  Flow___?___Temperature___?___Pressure_____.

| Component Name | Formula | State | Average amount or composition | Composition Range |
|---|---|---|---|---|
| Particulate | * | Solid | | |

Depending upon cause of emergency, emissions could range from contaminated feed to contaminated product. Upset durations seldom exceed 15 minutes during which time incinerator operation would be modified. For initial 1-2 minutes after upset pollutants might leave incinerator stack. Following that, stack gases will be nearly 100% $CO_2$, $H_2O$ & $N_2$. On average, such upsets occur two or three times per year. Particulates are possible, depending upon cause of upset. One such upset occurred in 1969.

* Particulate matter should be described as fully as possible._____
_____
_____

III. Continued    For stream flow shown on block diagram by letter____A____.

    2. <u>Composition variation</u>.

      See III-1

    3. <u>Production rate during sampling</u>.

      Never Sampled

    4. <u>Method used to determine composition and flow</u>.

      Not applicable

III.  Continued  For stream flow shown on block diagram by letter_____A_____.

     5.  Sampling procedure.

        Not Applicable

     6.  Analytical procedure.

        Not Applicable

     7.  Sampling frequency.

        Never

III. Continued  For stream flow shown on block diagram by letter __A__ .

       8. Confidence level.

        Not Applicable

       9. Ease of sampling.

        Impossible

      10. Odor problem.  (Circle yes or no or mark "not applicable")

        Is the odor of this emission ever detectable at ground level

        on the plant property? Yes/no  Off the plant property?  Yes/no

        If odors carry beyond the plant property are they detectable

        infrequently? Yes/no Frequently?  Yes/no  Have you received a

        community odor complaint traceable to this source in the past

        year? Yes/no  Has the odorous material been chemically identified?

        Yes/no  What is it?_____

          Not Applicable

III.1.Emissions (composition and flow).

Six copies provided
this section

Stream flow shown on block diagram by letter____B____.

1. Flow 10,000 SCFM Temperature 110°F  Pressure 25 PSIG .

| Component Name | Formula | State | Average amount or composition | Composition Range |
|---|---|---|---|---|
| Particulate | * | Solid | 150 lbs./hour | 100-200 lbs./hour |
| Nitrogen | $N_2$ | Gas | 83.8 Vol. % | 80-85% |
| Oxygen | $O_2$ | Gas | 1.4 " | 1-2% |
| Carbon Monoxide | CO | Gas | 4.1 " | 3-5% |
| Carbon Dioxide | $CO_2$ | Gas | 1.4 " | 1-2% |
| Hydrogen | $H_2$ | Gas | 2.1 " | 2-2.5% |
| Water | $H_2O$ | Vapor | 7.1 " | 6.5-7.5% |
| Various Amines | ** | Vapor | 0.1 " | 0.05-0.2% |
| Nitrogen Oxides | $NO_x$ | Gas | 300 VPPM | 200-500 VPPM |

* Particulate matter should be described as fully as possible. Catalyst Dust (composition is proprietary)

contains cobalt and chromium on alumina base. 100% less than 15 microns; 60% less than 10 microns; 20%

less than 5 microns; 5% less than 1 micron.

** Composition unknown - mixture of feed, products and other amines.

III. Continued    For stream flow shown on block diagram by letter____B____.

2. <u>Composition variation</u>.

During 2nd and 3rd quarter when plant is operated below capacity, nitrogen is at high end of range and all other materials near low end. During start-up or plant upset (average about 50 hours/year) nitrogen is near low end of range and all other materials near high end.

3. <u>Production rate during sampling</u>.

Average composition based on rated capacity.

4. <u>Method used to determine composition and flow</u>.

Engineering calculation and plant material balance (flow). Composition calculated on basis of stream "C" analysis and estimated amine losses prior to installation of scrubber.

III. Continued   For stream flow shown on block diagram by letter____B_____.

   5. Sampling procedure.

      Never sampled.

   6. Analytical procedure.

      Never Analyzed.

   7. Sampling frequency.

      See (5) above.

III. Continued  For stream flow shown on block diagram by letter_____B_____.

8. ‾Confidence level.

   ± 10%

9. Ease of sampling.

   No sample taps are available, but one could be easily installed

   in readily accessible location.  However, it would not be 8 pipe

   diameters from a disturbance.

10. Odor problem.  (Circle yes or no or mark "not applicable")

    Is the odor of this emission ever detectable at ground level

    on the plant property?  Yes/no  Off the plant property?  Yes/no

    If odors carry beyond the plant property are they detectable

    infrequently?  Yes/no Frequently?  Yes/no  Have you received a

    community odor complaint traceable to this source in the past

    year?  Yes/no  Has the odorous material been chemically identified?

    Yes/no  What is it?_____

         No applicable - this stream is no longer

         emitted to the atmosphere.

III.1.Emissions (composition and flow).

Stream flow shown on block diagram by letter____C____.

1.  Flow_10,000SCFM_Temperature___100°F___Pressure_0 PSIG___.

| Component Name | Formula | State | Average amount or composition | Composition Range |
|---|---|---|---|---|
| Particulate | * | Solid | 10 lbs./hour | 5-20 lbs./hour |
| Nitrogen | $N_2$ | Gas | 83.9 Vol. % | 80-85% |
| Oxygen | $O_2$ | Gas | 1.4 " | 1-2% |
| Carbon Monoxide | CO | Gas | 4.1 " | 3-5% |
| Carbon Dioxide | $CO_2$ | Gas | 1.4 " | 1-2% |
| Hydrogen | $H_2$ | Gas | 2.1 " | 2-2.5% |
| Water | $H_2O$ | Vapor | 7.1 " | 6.5-7.5% |
| Various Amine | ** | Vapor | 50 YPPMV | 30-100 PPMV |
| Nitrogen Oxides | $NO_x$ | Gas | 300 YPPMV | 200-500 PPMV |

* Particulate matter should be described as fully as possible. See "B". Size distribution 100% less than 5 microns; 60% less than 1 micron.

** See "B".

III.  Continued    For stream flow shown on block diagram by letter____C____.


2.  <u>Composition variation</u>.

See "B"


3.  <u>Production rate during sampling</u>.

See "B"


4.  <u>Method used to determine composition and flow</u>.

See "B" for flow.  Specific analysis methods are given in III-6(C)

III. Continued  For stream flow shown on block diagram by letter_____C_____.

5. Sampling procedure.

   a. Particulates and moisture collected in sampling train as detailed in Federal Register, Dec. 23, 1971 (Method 5).

   b. $NO_x$ sampled by EPA Method 7.

   c. Other constituents collected using grab sampling procedures for collection of gas. Sample size 10 liters in stainless steel tank.

6. Analytical procedure.

   a. Particulates and moisture determined gravimetrically as detailed in Federal Register, Dec. 23, 1971. (Method 5)

   b. $NO_x$ determined by EPA method 7.

   c. Hydrogen, oxygen, and nitrogen determined by mass spectrometer analysis at local university.

      Amine, CO and $CO_2$ determined by infra-red analysis.

7. Sampling frequency.

   Once, - one month after scrubber was put on stream.

III. Continued   For stream flow shown on block diagram by letter____C____.

8.  Confidence level.

Oxygen, $CO_2$, CO and H may be ± 10%.

Nitrogen would be better than this, perhaps ± 5%

Amines are near limit of detection - ± 50%.

9.  Ease of sampling.

Difficult - only sample tap is six feet above top of scrubber

tower - approximately 65 feet in air - reached by caged ladders.

10. Odor problem.   (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level

on the plant property? Yes/no  Off the plant property?  Yes/no

If odors carry beyond the plant property are they detectable

infrequently?  Yes/no Frequently?  Yes/no  Have you received a

community odor complaint traceable to this source in the past

year?  Yes/no  Has the odorous material been chemically identified?

Yes/no  What is it?____Amine compounds.____

III.1.Emissions (composition and flow).                                    Six copies provided
                                                                           this section


Stream flow shown on block diagram by letter____D_____.

1. Flow_300 GPH___ Temperature___300°F___ Pressure___10 PSIG__.

| Component Name | Formula | State | Average amount or composition | Composition Range |
|---|---|---|---|---|
| Particulate | * | Solid | Trace | |
| Heavy Amines | $(CH_x)_y NH_z$ | Liquid | 100% | |


* Particulate matter should be described as fully as possible. Very fine catalyst dust - never sampled

  or analyzed - estimated to be 1-5 lbs./hour.

III. Continued    For stream flow shown on block diagram by letter__D____.

    2. <u>Composition variation.</u>

       Not applicable - unknown - never analyzed.

    3. <u>Production rate during sampling</u>.

       See "B"

    4. <u>Method used to determine composition and flow.</u>

       Rotameter in liquid line for flow. Composition unknown.

III.  Continued  For stream flow shown on block diagram by letter____D____.

5.  <u>Sampling procedure</u>.

Not applicable.

6.  <u>Analytical procedure</u>.

Not applicable.

7.  <u>Sampling frequency</u>.

Not applicable.

III. Continued  For stream flow shown on block diagram by letter_____D_____.

8. Confidence level.

Not applicable.

9. Ease of sampling.

Liquid drain line is available at ground level.  Could be used

for sample tap.

10. Odor problem.  (Circle yes or no or mark "not applicable")

Is the odor of this emission ever detectable at ground level

on the plant property?  Yes/no  Off the plant property?  Yes/no

If odors carry beyond the plant property are they detectable

infrequently?  Yes/no Frequently?  Yes/no  Have you received a

community odor complaint traceable to this source in the past

year?  Yes/no  Has the odorous material been chemically identified?

Yes/no  What is it?_____

Not applicable - not an emitted stream.

III. 1 Emissions (composition and flow).                            Six copies provided
                                                                    this section


      Stream flow shown on block diagram by letter____E_____.

1.    Flow _10,000SCFM_ Temperature ___450°F___ Pressure _0 PSIG_____.


| Component Name | Formula | State | Average amount or composition | Composition Range |
|---|---|---|---|---|
| Particulate | * | Solid | Trace | |
| Nitrogen | $N_2$ | Gas | 77.0 Vol. % | 76.5-77.5% |
| Oxygen | $O_2$ | Gas | 9.2 Vol. % | 9-9.5% |
| Carbon Dioxide | $CO_2$ | Gas | 6.4 Vol. % | 6-7% |
| Water | $H_2O$ | Vapor | 7.4 Vol. % | 7-8% |
| Nitrogen Oxides | $NO_x$ | Gas | 150 VPPM | 100-300 VPPM |


* Particulate matter should be described as fully as possible.____See "D"_____

_____

_____

III. Continued    For stream flow shown on block diagram by letter____E____.

    2. <u>Composition variation.</u>

       Random variation depending on many variables such as production

       rate, ambient air temperature and humidity, catalyst age, etc.,

       all within limits shown.

    3. <u>Production rate during sampling.</u>

       See "B"

    4. <u>Method used to determine composition and flow.</u>

       Calculation based on incinerator vendor's specifications, guarantees

       and laboratory tests.

III. Continued  For stream flow shown on block diagram by letter_____E_____

    5. <u>Sampling procedure</u>.

       Never sampled.

    6. <u>Analytical procedure</u>.

       Never analyzed

    7. <u>Sampling frequency</u>.

       See (5) above

III.  Continued  For stream flow shown on block diagram by letter_____E_____.

    8.  <u>Confidence level</u>.

       ± 10%

    9.  <u>Ease of sampling</u>.

       No sample tap, very hot stream, no access ladders, minimal insulation.

   10.  <u>Odor problem</u>.  (Circle yes or no or mark "not applicable")

       Is the odor of this emission ever detectable at ground level

       on the plant property?  Yes/<u>no</u>  Off the plant property?  <u>Yes</u>/no

       If odors carry beyond the plant property are they detectable

       infrequently?*  <u>Yes</u>/no Frequently?  Yes/<u>no</u>  Have you received a

       community odor complaint traceable to this source in the past

       year?  Yes/<u>no</u>  Has the odorous material been chemically identified?

       <u>Yes</u>/no  What is it?____Amines_____

       * Only during start-up or upset of the incinerator and then only

         if atmospheric conditions are favorable for ground level detection.

## IV. Emission control device

For device shown on block diagram by number___101___.

### 1. Engineering description.
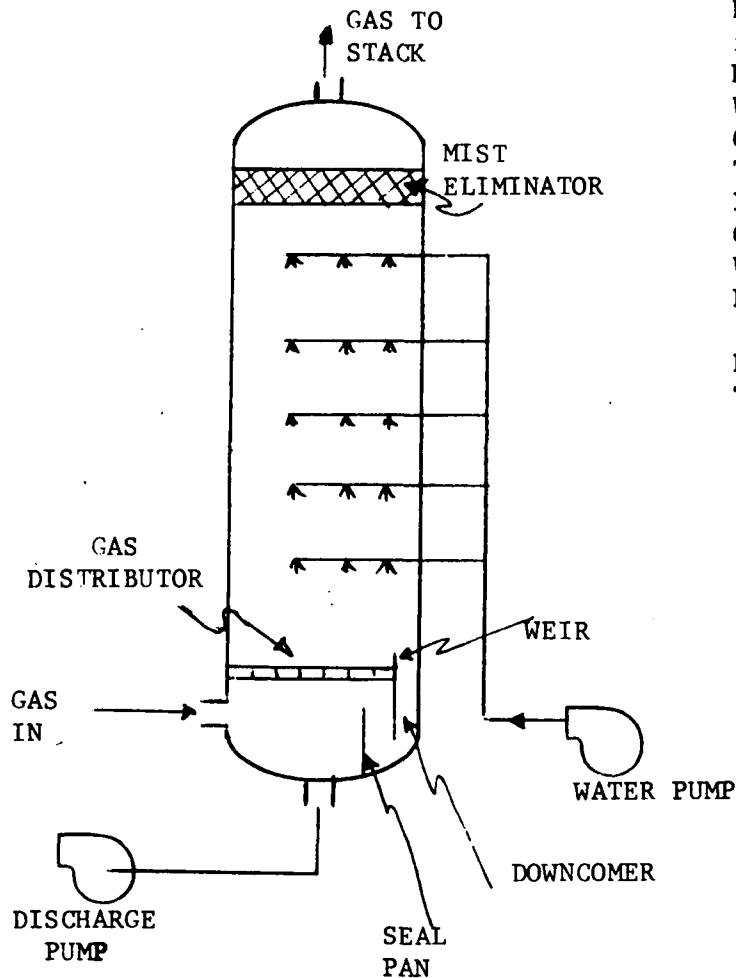


Multi-nozzle spray tower manu-
factured by Rebburcs Corp.
Model No. 10,000-W
Water rate:   100 GPM
Gas rate:     10,000 SCFM
Temperature: 100°F.
Pressure:  Atmospheric
Gas ΔP:      8 in, $H_2O$
Water Pump Head:   150 Ft.
Discharge Pump Head:   100 Ft.

Diameter of Tower:   6 Ft.
T-T Length:          60 Ft.

Utilities:

35 HP for Pumps

10,000,000 BTU/Hr.  Additional steam in product recovery section.

1500 GPM   Additional cooling water circulation in product recovery section.

IV. Continued  For device shown on block diagram by number_____101_____.

2. <u>Capital cost of emission control system.</u>

(a) Capital cost

Major equipment cost    $ 160,000_____

Total installed cost    $ 350,000_____

| Year | Cost |
|------|------|
| 1968 | $350,000 |
| | |
| | |

IV. Continued  For device shown on block diagram by number___101_____

(b) Check list.  Mark whether items listed are included in total

cost included in IV.2.a.  Do not give dollar value -

| Yes | No | Cost | Explanation |
|-----|----|------|-------------|
| X | | Site development | Additional foundation required for scrubber. |
| | X | Buildings | |
| | X | Laboratory equipment | |
| X | | Stack | |
| X | | Rigging etc. | |
| X | | Piping | |
| X | | Insulation | |
| X | | Instruments | |
| | X | Instrument panels | |
| X | | Electrical | |
| | X | Facilities outside battery limits* | |
| | X | Storage tanks, spheres drums, bins, silos | |
| | X | Catalysts | |
| | X | Spare parts and non-installed parts | |

*Such as - process pipe lines such as steam, condensate, water, gas, fuel,

air, fire, instrument and electric lines.

IV.  Continued  For device shown on block diagram by number __101__ .

| Yes | No | |
|---|---|---|
| X | | Was outside engineering contractor used? |
| X | | Was cost included in capital cost? |
| X | | Was in-house engineering used? |
| | X | Was cost included in capital cost? |
| | X | Was emission control equipment installed and constructed at the time plant (process) was constructed? |

3.  Operating costs of control system.

Give 1972 dollar values per year at capacity given in I.1.

(a)  Utilities                                                          $ 68,000

(b)  Chemicals *                                                        10,000

(c)  Labor  (No Additional Operators)                                  -

(d)  Maintenance (labor & materials)                                   14,000

(e)  Water treatment (cost of treating any waste
     water produced by this control system) **                        -

(f)  Solids remmoval (cost of removing any waste
     solids produced by this control system)                          20,000

(g)  Other disposal                                                    -

(h)  By-product or product recovery     CREDIT                        ($89,000 )

     Total operating costs                                            $ 23,000

\* Additional cooling water treatment included in utility costs -
this cost is for corrosion inhibition in scrubber.

\** Water waste is produced by process.  It is treated at cost of
$30,000/year.  This treatment was required before scrubber was
installed.

IV.  **Emission control device**

For device shown on block diagram by number____102____.

1.  **Engineering description.**
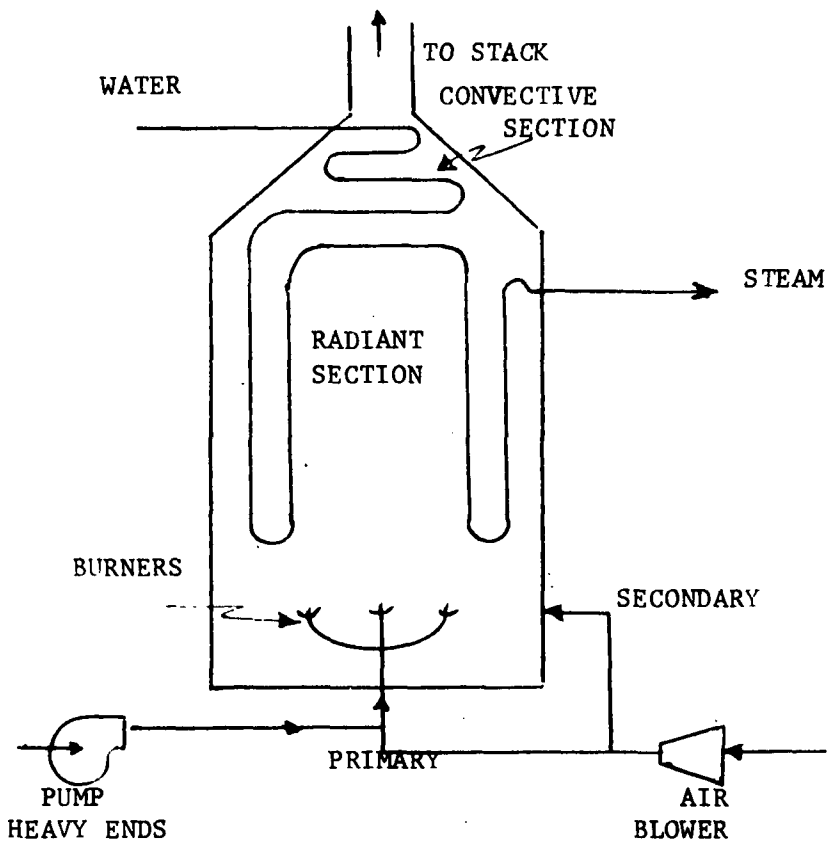


Steam Generator/Waste Incinerator

Manufactured by:  Xoberif Corp.
Model No.:  40-H
Heavy Ends Rate:  300 GPH
Air Rate:  9,500 SCFM
Steam Rate: 20,000 lbs./hour
Vessel Diameter:  15 Ft.
Height:  40 Ft.
Tube Diameter:  3 in. nominal
Tube Length:  (Material)
  Convective (mild steel): 6,000 Ft.
  Radiant (304 stainless): 2,000 Ft.

Utilities:

Heavy Ends Pump:  20 HP

Blower:  100 HP

IV. Continued  For device shown on block diagram by number_____102_____.

2. **Capital cost of emission control system.**

(a) Capital cost

Major equipment cost     $ 350,000_____

Total installed cost     $ 1,000,000_____

| Year | Cost |
|------|------|
| 1960 | $1,000,000 |
| _____ | _____ |
| _____ | _____ |

IV. Continued  For device shown on block diagram by number____101____.

(b) Check list.  Mark whether items listed are included in total

cost included in IV.2.a.  Do not give dollar value –

| Yes | No | Cost | Explanation |
|---|---|---|---|
| X | | Site development | Additional foundation required for scrubber. |
| | X | Buildings | |
| | X | Laboratory equipment | |
| X | | Stack | |
| X | | Rigging etc. | |
| X | | Piping | |
| X | | Insulation | |
| X | | Instruments | |
| | X | Instrument panels | |
| X | | Electrical | |
| | X | Facilities outside battery limits* | |
| | X | Storage tanks, spheres drums, bins, silos | |
| | X | Catalysts | |
| | X | Spare parts and non-installed parts | |

*Such as – process pipe lines such as steam, condensate, water, gas, fuel,

air, fire, instrument and electric lines.

IV. Continued  For device shown on block diagram by number __102__ .

| Yes | No | |
|-----|----|----|
| X | | Was outside engineering contractor used? |
| X | | Was cost included in capital cost? |
| | X | Was in-house engineering used? |
| X | | Was cost included in capital cost? |
| X | | Was emission control equipment installed and constructed at the time plant (process) was constructed? |

3. **Operating costs of control system.**

Give 1972 dollar values per year at capacity given in I.1.

(a) Utilities                                               $    5,000

(b) Chemicals                                                    -

(c) Labor ($\frac{1}{4}$ man per shift - excludes supervision & overhead)                                                    7,000

(d) Maintenance (labor & materials)                            40,000

(e) Water treatment (cost of treating any waste water produced by this control system)                    -

(f) Solids remmoval (cost of removing any waste solids produced by this control system)                    -

(g) Other disposal                                               -

(h) By-product or product recovery     CREDIT- STEAM      ($100,000)

   Total operating **credit**                               $   48,000

## V. Stack or vent description.

For stack or vent shown on block diagram by letter_____C_____.

    1. Stack height                                       100 ft

    2. Stack diameter                                  2 ft

    3. Gas temperature stack exit                      100 °F

    4. Stack flow   *                         SCFM(70°F & 1 Atm.)

For stack or vent shown on block diagram by letter_____E_____.

    1. Stack height                             60 Ft.

    2. Stack diameter                          3 Ft.

    3. Gas temperature stack exit            450°F

    4. Stack flow   *

For stack or vent shown on block diagram by letter_____.

    1. Stack height

    2. Stack diameter

    3. Gas temperature stack exit

    4. Stack flow   *

For stack or vent shown on block diagram by letter_____.

    1. Stack height

    2. Stack diameter

    3. Gas temperature stack exit

    4. Stack flow   *

* See instructions

VI. <u>Tankage</u>.

| No. of tanks | composition | temp. | capacity (each) | approximate turnovers per year | method of vapor conservation |
|---|---|---|---|---|---|
| 3 | Pyrrolidine $(CH_2)_4NH$ | Ambient | 100,000 gal.(ea) | 50 | None, vents to air |
| 4 | Pyrrole $(CH)_4NH$ | Ambient | 100,000 gal.(ea) | 25 | " |
| 1 | Pyrrolidone $(CH)_2CH_2CONH$ | Ambient | 100,000 gal.(ea) | 25 | " |

VII.   Fuels.

   800,000 gal./year fuel oil for fired air heater 3% sulfur.

VIII.   Other emissions.

   No other known emissions although minor leakages probably occur.

   Engineering estimate of average losses is 0.01% of throughput or 13,000 lbs./year of amines.

IX.   Future plans.

   1.  Current research on heavy amine stream indicates further processing will produce a marketable product - if so, incinerator will be shut down.

   2.  We are currently negotiating a long term contract to purchase 1% sulfur fuel oil from the Flused Oil Company.

# APPENDIX III

## FINAL QUESTIONNAIRE SUMMARY

| Chemical | Number of Questionnaires used as Basis for Report |
|---|---|
| Acetaldehyde via Ethylene | 1 |
| via Ethanol | 1 |
| Acetic Acid via Methanol | 2 |
| via Butane | 1 |
| via Acetaldehyde | 1 |
| Acetic Anhydride | 2 |
| Acrylonitrile | 4 |
| Adipic Acid | 4 |
| Adiponitrile via Butadiene | 1 |
| via Adipic Acid | 2 |
| Carbon Black | 7 |
| Carbon Disulfide | 4 |
| Cyclohexanone | 7 |
| Dimethyl Terephthalate (+TPA) | 6 |
| Ethylene | 13 |
| Ethylene Dichloride via Oxychlorination | 10 |
| via Direct Chlorination | 3 |
| Ethylene Oxide | 7 |
| Formaldehyde via Silver Catalyst | 12 |
| via Iron Oxide Catalyst | 6 |
| Glycerol | 2 |
| Hydrogen Cyanide | 1 |
| Isocyanates | 10 |
| Maleic Anhydride | 7 |
| Nylon 6 | 4 |
| Nylon 6,6 | 3 |
| Oxo Process | 6 |
| Phenol | 8 |
| Phthalic Anhydride via o-xylene | 5 |
| via naphthalene | 3 |
| Polyethylene (High Density) | 5 |
| Polyethylene (Low Density) | 7 |
| Polypropylene | 7 |
| Polystyrene | 4 |
| Polyvinyl Chloride | 8 |
| Styrene | 7 |
| Styrene - Butadiene Rubber | 6 |
| Vinyl Acetate via Acetylene | 3 |
| via Ethylene | 1 |
| Vinyl Chloride | 8 |

# INTRODUCTION TO APPENDIX IV AND V

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix IV discussion are:

1. Prediction of numbers of new plants.

2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix V discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

## Number of New Plants by 1980

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

Table 1. Number of New Plants by 1980

| Chemical | Process | Current Capacity | Marginal Capacity | Current Capacity on-stream in 1980 | Demand 1980 | Capacity 1980 | Capacity to be Added | Economic Plant Size | Number of New Units |
|---|---|---|---|---|---|---|---|---|---|
| Carbon Black | Furnace | 4,000 | 0 | 4,000 | 4,500 | 5,000 | 1,000 | 90 | 11 - 12 |
| | Channel | 100 | 0 | 100 | 100 | 100 | 0 | 30 | 0 |
| | Thermal | 200 | 0 | 200 | 400 | 500 | 300 | 150 | 2 |

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

IV-2

## Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation.
However, more important than format is a proposal for a weighting basis.
There is a wide divergence of opinion on which pollutants are more noxious
and even when agreement can be reached on an order of noxiousness, dis-
agreements remain as to relative magnitudes for tolerance factors.  In
general pollutants from the petrochemical industry can be broken down into
categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide,
and oxides of sulfur and nitrogen.  Of course, two of these can be further
broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons,
nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash,
catalyst, finely divided end products, etc.  It is felt that no useful
end is served by creating a large number of sub-groupings because it will
merely compound the problem of assigning a weighting factor.  Therefore,
it is proposed to classify all pollutants into one of five of the six
categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon
monoxide is the least noxious of the five and that $NO_x$ is somewhat more
noxious than $SO_x$.  However, there are widely divergent opinions concerning
hydrocarbons and particulates - probably due to the fact that these are
both widely divergent categories.  In recent years, at least two authors
have attempted to assign tolerance factors to these five categories.
Babcock (1), based his on the proposed 1969 California standards for
one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary
and secondary standards for a 24-hour period.  Both authors found it
necessary to extrapolate some of the basic standards to the chosen time
period.  Their rankings, on an effect factor basis with carbon monoxide
arbitrarily used as a reference are as follows:

|  | Babcock | Walther Primary | Walther Secondary |
|---|---|---|---|
| Hydrocarbons | 2.1 | 125 | 125 |
| Particulates | 107 | 21.5 | 37.3 |
| $NO_x$ | 77.9 | 22.4 | 22.4 |
| $SO_x$ | 28.1 | 15.3 | 21.5 |
| CO | 1 | 1 | 1 |

Recognizing that it is completely unscientific and potentially subject
to substantial criticism it is proposed to take arithmetic averages of the
above values and round them to the nearest multiple of ten to establish a
rating basis as follows:

|  | Average | Rounded |
|---|---|---|
| Hydrocarbons | 84.0 | 80 |
| Particulates | 55.3 | 60 |
| $NO_x$ | 40.9 | 40 |
| $SO_x$ | 21.6 | 20 |
| CO | 1 | 1 |

Table 2. Weighted Emission Rates

Chemical_____

Process_____

Increased Capacity_____

| Pollutant | Emissions, Lbs./Lb. | Increased Emissions Lbs./Year | Weighting Factors | Weighted Emissions Lbs./Year |
|---|---|---|---|---|
| Hydrocarbons | | | 80 | |
| Particulates | | | 60 | |
| $NO_x$ | | | 40 | |
| $SO_x$ | | | 20 | |
| CO | | | 1 | |

Total_____

## Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane will be included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. $NO_x$ should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. This determination is to be made on the basis of data reported on returned questionnaires.

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It is proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

## Increased Emissions (Weighted) by 1980 (continued)

(1)  Babcock, L. F., "A Combined Pollution Index for Measurement of Total
     Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2)  Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources
     by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

## Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it is proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It is recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it is recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

## Efficiency of Pollution Control Devices

### 1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of $NO_x$. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it is recommended that complete combustion be defined as the production of $N_2$, thus assuming that all $NO_x$ formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any $NO_x$ produced (regardless of its source) will be rated by the SERR as described below.

### 2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7O_2 \longrightarrow C + 2CO + 3CO_2 + 6H_2O$$
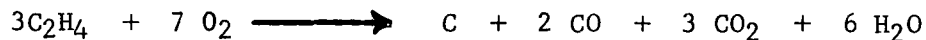
Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

## Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

| Pollutant | Weighting Factor | Pounds in | | Pounds out | |
|---|---|---|---|---|---|
| | | Actual | Weighted | Actual | Weighted |
| Hydrocarbons | 80 | 100 | 8000 | 0 | |
| Particulates | 60 | 0 | | 14.2 | 852 |
| $NO_x$ | 40 | 0 | | 1 | 40 |
| $SO_x$ | 20 | 0 | | 0 | |
| CO | 1 | 0 | | 66.5 | 66.5 |
| Total | | | 8000 | | 958.5 |

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2 \ CH_3Cl + 3 \ O_2 \longrightarrow 2 \ CO_2 + 2 \ H_2O + 2 \ HCl$$
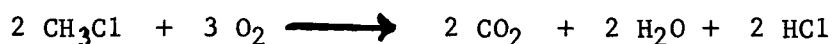
This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;
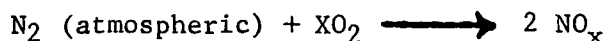
$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of $NO_x$ and the second is producing ten pounds of $NO_x$ in the same unit time. The assumed reactions are:

## Efficiency of Pollution Control Devices

2. ### Significance of Emission Reduction Rating (SERR) (continued)

$$4 \; HCN \; + \; 5 \; O_2 \; \longrightarrow \; 2 \; H_2O \; + \; 4 \; CO_2 \; + \; 2 \; N_2$$

$$N_2 \; (\text{atmospheric}) \; + \; XO_2 \; \longrightarrow \; 2 \; NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

However, $SERR_1 = \dfrac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \dfrac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

## Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the $SO_x$ and $NO_x$ which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it is suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \dfrac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

## Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent
contains 100 pounds of catalyst dust, 200 lbs. of
carbon monoxide and 10 pounds of sulfur oxides per unit
time. It is passed through a cyclone separator where
95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 95\%$$

and $SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1) \times 100}{(100 \times 60 + 10 \times 20 + 200 \times 1)}$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a
stream containing 50 pounds of $SO_2$ per unit time. All
but one pound of the $SO_2$ is removed but two pounds of
the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

and $SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document is one of a series of four volumes prepared for the Environmental Protection Agency (EPA) to assist it in determining the significance of air pollution from the petrochemical industry. A total of 33 distinctly different processes which are used to produce 27 petrochemicals have been surveyed, and the results are reported in four volumes numbered EPA-450/3-73-005-a, -b, -c, and -d.

This volume covers the following processes: Maleic Anhydride, Nylon 6, Nylon 66, Oxo Processes, Phenol, High-Density Polyethylene, and Low-Density Polyethylene. For each process the report includes a process description, a process emission inventory, a catalog of emission control equipment, a list of producers, and an evaluation of the significance of the air pollution from the process. Also included is a summary table of emissions to the atmosphere from all the processes studied.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
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