AP42 Section 6.10

Background Ref: 4

Title: Source Assessment: Maleic Anhydride Manufacture

US EPA

Dec 1978

Recd 12/27/78

December 1978

SOURCE ASSESSMENT: MALEIC ANHYDRIDE MANUFACTURE

by

W. A. Lewis, Jr., G. M. Rinaldi, and T. W. Hughes
Monsanto Research Corporation
Dayton, Ohio 45407

Contract No. 68-02-1874

Task Officer

Ronald J. Turner
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory-Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains an assessment of air emissions from the production of maleic anhydride. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division, Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for chemical and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

Monsanto Research Corporation (MRC) has contracted with EPA to investigate the environmental impact of various industries that represent sources of emissions in accordance with EPA's responsibility, as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program, entitled, "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer for this series. This study of maleic anhydride plants was initiated by IERL-Research Triangle Park, in September 1975; Mr. Edward J. Wooldridge served as EPA Task Officer. The project was transferred to the Industrial Pollution Control Division, IERL-Cincinnati in October 1976; Mr. Ronald J. Turner served as EPA Task Officer from that time through completion of the study.

Source Assessment Documents prepared in this program contain data on emissions from specific industries. Such data are gathered from the literature, government agencies and cooperating companies. Sampling and analysis are also performed by the contractor when the available information does not adequately characterize the source emissions.

ABSTRACT

This report describes a study of air emissions from maleic anhydride production. Maleic anhydride is manufactured primarily by the catalytic oxidation of benzene; some butane feedstock is also used domestically. Emission points in a maleic anhydride plant include the product recovery scrubber; the refining vacuum system; flaking, pelletizing, and packaging; aqueous waste storage; raw material and product storage tanks; and fugitive sources.

To assess the environmental impact of this industry, source severity was defined as the ratio of the time-averaged maximum ground level concentration of an emission to a potentially hazardous concentration from a given point. Source severities for a representative plant producing 23,900 metric tons/yr of product are 0.73 for carbon monoxide and up to 25.1 for hydrocarbons from various points. Severities for noncriteria pollutants were also calculated.

Maleic anhydride production contributes 0.15% of the total carbon monoxide emitted in the U.S. and 0.14% of the hydrocarbons.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 1975 to December 1978.

CONTENTS

FIGURES

TABLES

TABLES (continued).

ABBREVIATIONS AND SYMBOLS

A	--area affected by emission
A_R	--$Q/ac\pi u$
a,b, c,d,f	--constants (Appendix B)
B_R	-- $-H^2/2c^2$
C	--concentration
C'	--diameter factor
C_{AO}	--inlet concentration of pollutant A
C_i	--production capacity of plant i
Cap	--production capacity
D	--tank diameter
D_{P_i}	--county population density for plant i
$\overline{D}_P$	--capacity-weighted mean population density
E	--activation energy
E', E''	--emission factors
e	--2.72
exp	--natural log base e $\simeq$ 2.72
F	--hazard factor defined as primary ambient air quality standard for criteria pollutants and modified TLV (i.e., TLV • 8/24 • 1/100) for noncriteria pollutants
F'	--equivalent gasoline breathing loss
ΔF	--change in free energy due to reaction
F_i	--free energy of formation for component i
F_P	--paint factor
GC/MS	--gas chromatography/mass spectroscopy
H	--height of emission release
H'	--tank outage
K_P	--equilibrium constant
K_T	--turnover factor
k, k'	--rate constant

L --total petrochemical loss

L_l --petrochemical loss

L_g --equivalent gasoline loss

L_y --equivalent gasoline breathing loss

M --molecular weight

M_a --mass comcentration of compound "a"

MAN --maleic anhydride

N --number of turnovers per year

n --number

P --vapor pressure of material

P' --total affected population

P_f --final pressure

P_i --initial pressure

PPP --packed porous polymer

Q --mass emission rate

Q_a --quantity of compound "a" collected

R --gas constant

r --rate of oxidation

S --source severity

STP --standard temperature and pressure

T --absolute temperature

T_f --temperature of cylinder

THC --total hydrocarbon

TLV --threshold limit value

ΔT --average ambient temperature change

t --averaging time

t_o --instantaneous average time

u --wind speed

V --tank capacity

V_c --cylinder volume

V_s --sample volume

W --liquid density

X_A --fractional conversion

x --downwind dispersion distance from source of emission release

x_1, x_2 --roots of Equation B-73

y --horizontal distance from centerline of dispersion

ν_i --stoichiometric coefficient of component i

π --3.14

σ_y --standard deviation of horizontal dispersion

σ_z --standard deviation of vertical dispersion

χ --downwind ground level concentration at reference coordinate (x, y)

χ_{max} --maximum ground level concentration of species

$\overline{\chi}_{max}$ --time-averaged maximum ground level concentration of species

$\overline{\chi}(x)$ --mean ground level concentration at downwind distance x from source

CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	to	Multiply by
calorie	joule	0.239
degree Rankine	degree Fahrenheit	$t°_R = t°_F + 459.67$
degree Celsius	degree Fahrenheit	$t°_F = 1.8\ t°_C + 32$
joule (J)	British thermal unit	9.479×10^{-4}
kilogram (kg)	pound-mass (lb mass avoirdupois)	2.205
kilogram (kg)	ton (short, 2,000 lb)	1.102×10^{-3}
kilometer^2 (km^2)	mile^2	3.860×10^{-1}
meter (m)	foot	3.281
meter^3 (m^3)	barrel (42 gal)	6.293
meter^3 (m^3)	foot^3	3.531×10^{1}
meter^3 (m^3)	gallon (U.S. liquid)	2.642×10^{2}
meter^3 (m^3)	liters	1.000×10^{3}
metric ton	pound-mass	2.205×10^{3}
metric ton	ton (short, 2,000 lb mass)	1.102
pascal (Pa)	atmosphere	9.869×10^{-6}
pascal (Pa)	in. of Hg (60°F)	2.962×10^{-4}
pascal (Pa)	pound-force/inch^2 (psi)	1.450×10^{-4}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
M	mega	10^6	1 MJ = 1×10^6 joules
k	kilo	10^3	1 kPa = 1×10^3 pascals
m	milli	10^{-3}	1 mg = 1×10^{-3} gram
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

[a]Metric Practice Guide. ASTM Designation: E 380-74, American Society for Testing and Materials, Philadelphia, Pennsylvania, November 1974. 34 pp.

SECTION 1

INTRODUCTION

Maleic anhydride (MAN) is an important industrial chemical which is used in the manufacture of unsaturated polyester resins, fumaric acid, agricultural chemicals, alkyd resins, and a variety of miscellaneous products. Present production capacity in the United States is 233,600 metric tons/yr,[a] excluding recovery of maleic anhydride from phthalic anhydride production operations. Maleic anhydride is manufactured by the catalytic vapor phase oxidation of benzene, butane, and n-butenes. While 84% of the U.S. production is based on the oxidation of benzene, n-butane-based processes are being employed domestically, and n-butene-based processes are used outside of the U.S. Benzene-based plants employ fixed-bed reactors, but fluid-bed reactors have been used in European processes. This document presents a detailed study of the benzene-based maleic anhydride industry from the standpoint of its atmospheric emissions and their potential environmental impact. Available data on the use of other feedstocks is also provided.

The major results of this study, summarized in Section 2, include emission factors for each species emitted to the atmosphere from each emission point within a representative maleic anhydride plant. Also tabulated are several factors designed to measure the environmental hazard potential of maleic anhydride operations. These include source severities and the industry's contribution to total atmospheric emissions of criteria pollutants.

A detailed description of the maleic anhydride manufacturing process is given in Section 3. To reflect the predominant practice in the industry, discussion is based on the Scientific Design Co., Inc., process and its modifications. Descriptions of each major processing step, a flow diagram, the process chemistry, and material and energy balances are included.

Atmospheric emissions from maleic anhydride plants are discussed in Section 4. The species known to be emitted and/or produced by the process are identified, and each emission point

[a] 1 metric tons = 10^6 grams; conversion factors and metric-system prefixes are presented in the prefatory material.

within the plant is described. Health effects of selected pollutants from maleic anhydride manufacture are outlined. The compositions and flow rates of streams emitted to the atmosphere are provided. A representative maleic anhydride plant is defined, and emission factors are given for such a plant. These emission factors are then used to generate source severity factors, the industry contribution to total emissions of criteria pollutants, and the affected population.

Section 5 considers the present and future aspects of pollution control technology in the maleic anhydride industry. Economic and production trends in the maleic anhydride industry are covered in Section 6, which also analyzes the trends in each of the industries that are major consumers of maleic anhydride.

SECTION 2

SUMMARY

Maleic anhydride is manufactured in the U.S. by Scientific Design Co., Inc. process, the Lurgi process, and proprietary processes. The Scientific Design process predominates, accounting for nearly 90% of domestic benzene-based production. The nine U.S. maleic anhydride plants currently in operation have a combined production capacity of 233,600 metric tons per year. One U.S. phthalic anhydride plant recovers 4,500 metric tons per year of maleic anhydride as a byproduct.

Maleic anhydride is manufactured by the catalytic oxidation of benzene. In 1974, due to the rising cost of benzene, butane was selected for development as an alternate feedstock. Monsanto has shifted 20% of its 47,600-metric ton/yr production capacity to n-butane feedstock. n-Butane feedstock is also used in Amoco's 27,200-metric ton/yr plant.

In the Scientific Design process, maleic anhydride is produced by air oxidation of benzene in the presence of a catalyst. Vanadium pentoxide/molybdenum trioxide catalyst systems are used by manufacturers. Benzene is vaporized and mixed with preheated air, and the resulting mixture is fed to a molten-salt-cooled reactor. In the reactor, 90% to 97% of the benzene is converted to maleic anhydride, other organics, carbon oxides, and water. High-pressure steam is produced in a molten-salt cooling circuit. The gases leave the reactor and enter a crude product separator where 60% of the product is recovered; the remainder is converted to maleic acid in a product recovery scrubber. This latter portion of the product is recovered from maleic acid by azeotropic dehydration to remove the water, and vacuum distillation to remove impurities from the refined product. Both the crude and refined products are stored in tanks that are subject to working and breathing losses.

The refined maleic anhydride is shipped in molten form or flaked and bagged form, or pelletized into briquettes. The major end uses of maleic anhydride are unsaturated polyester resins (58%), fumaric acid (5%), agricultural pesticides (10%), and miscellaneous uses (27%).

Sources of atmospheric emissions within maleic anhydride plants include the product recovery scrubber; the refining vacuum system; flaking, pelletizing, and packaging; aqueous waste storage; raw material and product storage tanks; and fugitive sources.

The refining vacuum system vent exhausts the noncondensible gases from the dehydration and fractionation columns used in the maleic anhydride production process. An incinerator-scrubber combination may be used for liquid waste disposal, while emissions of particulate matter from flaking, pelletizing, and packaging are typically vented to a secondary scrubber. Fugitive emissions of volatile organic compounds from process pumps and valves are not controlled. Solid wastes, such as spent catalysts and tar deposits, are controlled by landfill operations or commercial removal contractors. However, two manufacturers send spent catalysts to a vanadium reclaimer for resource recovery processing.

Emission factors for a maleic anhydride plant employing the Scientific Design Co., Inc., process were computed from the most recent data available in the literature and from personal communications. The emission factors were used to generate a number of other factors designed to quantify the potential hazard from maleic anhydride production. The source severity was defined as the ratio of the time-averaged maximum ground level concentration (from Gaussian plume dispersion methodology) to a potentially hazardous concentration of a given pollutant from a given source. Source severities were calculated for a representative maleic anhydride plant having a production rate of 23,900 metric tons/yr. Results are summarized in Table 1. Also listed are the annual mass emissions from a 23,900-metric ton/yr plant and from the maleic anhydride industry, and the percentage contribution of the industry to the total mass emissions of two criteria pollutants (carbon monoxide [CO] and hydrocarbons) from all sources.

The average number of persons exposed to high contaminant levels from maleic anhydride production was estimated and designated as the "affected population." The calculation was made for each species emitted and for each emission point within a representative plant for which the source severity exceeds 1.0 and 0.1. Benzene emissions resulted in the largest affected populations for source severity greater than 1.0 and 0.1, and these values were 21,500 and 243,000 persons, respectively.

TABLE 1. SOURCE SEVERITIES AND INDUSTRY CONTRIBUTION TO TOTAL EMISSIONS FOR MALEIC ANHYDRIDE PRODUCTION

Material emitted	Emissions from all plants, metric tons/yr[c]	Emissions from representative plant,[a] including 95% confidence limits, metric tons/year[c]	Source severity	Industry contribution to total emissions,[b] % Nationwide	Illinois	Missouri	New Jersey	Pennsylvania	Texas	West Virginia
Criteria pollutants										
Carbon monoxide										
Product recovery scrubber	136,400	15,151 ± 21%	0.73	0.15	0.5	2.5	1.3	0.2	0.7	0.8
Hydrocarbons[d]										
Product recovery scrubber	22,590	2,510 ± 48%	25.1[f]	0.14	0.7	1.5	0.4	0.6	0.1	1.7
Vacuum system vent	20	2[e]	0.62[f]							
Secondary scrubber vent	40	5[e]	22.4[f]							
Storage tanks	310	34 ± 20%	3.19[f]							
Fugitive emissions	240	26[e]	14.1							
Chemical substances[g]										
Maleic anhydride										
Product recovery scrubber	670	74 ± 74%	25.1							
Vacuum system vent	20	2[e]	0.62							
Secondary scrubber vent	40	5[e]	22.4							
Storage tanks	20	2 ± 20%	1.68							
Fugitive emissions	85	9[e]	173							
Maleic acid										
Product recovery scrubber	670	74 ± 68%	25.1							
Storage tanks	2	0.2 ± 20%	0.14							
Benzene										
Product recovery scrubber	20,600	2,285 ± 58%	25.8							
Storage tanks	270	30 ± 20%	0.75							
Fugitive emissions	65	7[e]	4.34							
Formaldehyde										
Product recovery scrubber	1,460	163 ± 276%	18.3							
Formic acid										
Product recovery scrubber	450	50 ± 181%	1.89							
Xylene										
Product recovery scrubber	2,500	278[e]								
Storage tanks	20	2 ± 20%	0.003							
Fugitive emissions	65	7[e]	0.40							

[a] A representative plant is defined to be one having a production rate of 23,000 metric tons/yr.

[b] Industry and nationwide contribution calculated only for criteria pollutants.

[c] Values in this column may differ from actual values due to rounding errors.

[d] Include organic species emitted from all emission source points.

[e] Value taken from one source; hence, no confidence limit is computed.

[f] Severity factor computed by equation for individual species rather than general hydrocarbon equation.

[g] Sum of mass emissions of individual species does not equal total hydrocarbon mass emissions. Emission factors for individual species are based on data submitted by reporting plants.

SECTION 3

SOURCE DESCRIPTION

PROCESS DESCRIPTION

Maleic anhydride (MAN) is a white crystalline solid at 101.3 kPa (1 atm) and 25°C (room temperature), with a boiling point of 202°C and a melting point of 52.85°C. Maleic anhydride is produced by the vapor phase oxidation of C_6 and C_4 hydrocarbons such as benzene, n-butenes, and n-butane.

Historically, Weiss and Downs described in a 1919 U.S. patent the process by which maleic acid and maleic anhydride were produced (1). Maleic anhydride was first commercialized by National Aniline in 1933. Benzene and C_4 hydrocarbons (mainly n-butenes and n-butane) are the principal feedstocks of commercial importance in the manufacture of maleic anhydride with C_4 hydrocarbons selected in some European and Asian processes, while most of domestic plants use benzene. In the U.S., the 1977 maleic anhydride capacity was 196,900 metric tons/yr from benzene and 36,700 metric tons/yr from n-butane (2). The availability of competitively priced C_4 hydrocarbons supplied from large naphtha crackers in Europe and Asia offers a slight economic advantage over benzene for use as maleic anhydride feedstock in those areas (3). On the other hand, due to higher yields with benzene feedstock and the lack of inexpensive domestic C_4 hydrocarbons, all primary maleic anhydride (3) manufactured in the U.S. in 1974 was produced by vapor phase oxidation of benzene. Monsanto in 1974 and subsequently Amoco in 1976 started commercial maleic anhydride production based on n-butane feedstock (4).

Benzene-Based Process

Commercial production of maleic anhydride is conducted by seven U.S. manufacturers utilizing the Scientific Design Co., Inc.,

---

(1) Weiss, J. W., and C. R. Downs. Production of Quinone. U.S. Patent 1,318,631 (to Barrett Company), October 13, 1919.

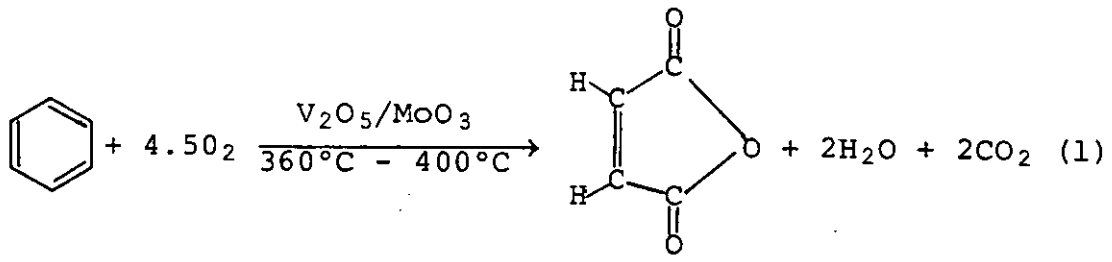
(2) Maleic Anhydride. Chemical Marketing Report, 213(7):9, 1978.

(3) Shio, S. Maleic Anhydride Produced from C_4 Hydrocarbons. Chemical Engineering, 78(21):107-109, 1971.

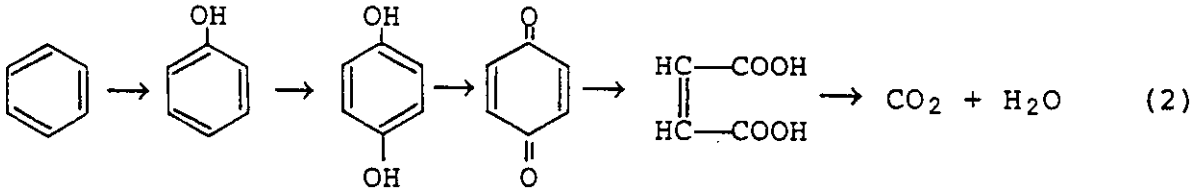
(4) Maleic Anhydride. Chemical Marketing Reporter, 207(11):9, 1975.

process, summarized by the flow diagram shown in Figure 1. The numbered streams in Figure 1 are identified in Table 2.

Chemistry--
The vapor phase oxidation of benzene to maleic anhydride on a vanadium oxide/molybdenum trioxide catalyst can be represented by the following equation:



The principal side reactions are formation of maleic acid and fumaric acid, and further oxidation to carbon oxides and water. The mechanism of these side reactions was studied by Battacharyya and Dixon, who suggested that the main sequence of reactions in the oxidation of benzene is as follows (5, 6):



Benzene Phenol Hydro-quinone Quinone Maleic acid

In their 1919 patent (1), Weiss and Downs noted that the reaction product maleic acid includes maleic anhydride. The exact mechanism for the oxidation of benzene to maleic anhydride is not

(5) Bhattacharyya, S. K., and N. Venkataraman. Catalytic Vapour-Phase Oxidation of Benzene to Maleic Acid. Journal of Applied Chemistry (London), 8(11):728-736, 1958.

(6) Nixon, J. K., and J. E. Longfield. Hydrocarbon Oxidation. In: Catalysis, Vol. VII, Oxidation, Hydration, Dehydration and Cracking Catalysts, P. H. Emmett, ed. Reinhold Publishing Corp., New York, New York, 1960. pp. 138-280.

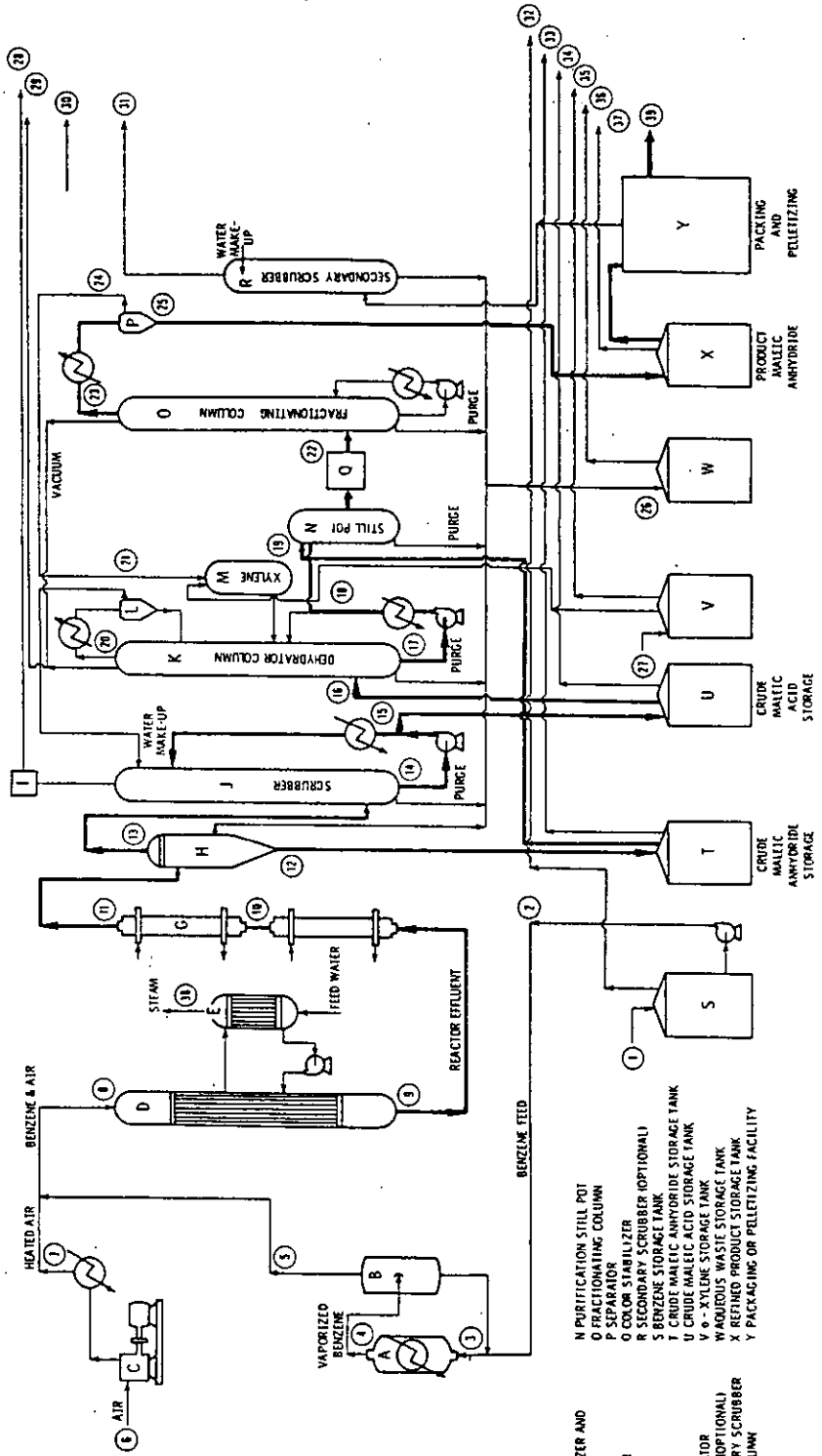


Figure 1. Maleic anhydride flow diagram.

TABLE 2. STREAM CODE FOR MALEIC ANHYDRIDE PROCESS ILLUSTRATED IN FIGURE 1

Stream	Identification
1	Benzene
2	Benzene feed
3	Total benzene feed to vaporizer
4	Vaporized benzene feed
5	Vaporized benzene feed from knockout drum
6	Air
7	Preheated air
8	Reactor feed
9	Reactor effluent
10	Primary condenser effluent
11	Product separator feed
12	Crude product
13	Separator off-gas
14	Scrubber bottoms liquor
15	Crude maleic acid
16	Dehydrator feed
17	Azeotropic bottom product
18	Purification still pot feed
19	Crude product feed
20	Dehydrator column overhead
21	Separated water
22	Purification column feed
23	Purification column overhead
24	Separated xylenes
25	Refined product
26	Aqueous waste and purge
27	Xylenes
28	Product recovery scrubber vent
29	Refining vacuum system vent
30	Fugitive emissions
31	Secondary scrubber vent
32	Benzene storage vent
33	Crude maleic anhydride storage vent
34	Crude maleic acid storage vent
35	Xylenes storage vent
36	Aqueous waste storage vent
37	Refined maleic anhydride storage vent
38	Generated steam
39	Transport loading facilities

known. Kinetic studies (7) reveal that the overall reaction sequence can be represented by two competitive pathways for benzene consumption: complete oxidation, and via maleic anhydride which can be further oxidized. The partial oxidation of benzene is accompanied by the formation of acetic anhydride, benzoic acid, ketones, and miscellaneous aldehydes (8).

Feed Materials--
Feed materials used in maleic anhydride production are benzene and air. The benzene feed (streams 1-5 in Figure 1) contains between 99% and 100% by weight benzene. Impurities in benzene are thiophene (5) and small amounts (less than 0.01 wet %) of mixed hydrocarbons. Thiophene in the benzene feed reacts to produce sulfur oxides, although the quantity generated is negligible, while mixed hydrocarbon impurities are responsible for the formation of color bodies in the crude product (8).

Compressed air (stream 7), which is preheated, is mixed with vaporized benzene. Excess air is necessary to keep the mixture outside explosive limits. The reactor feed (stream 8) enters the reactor at 206.9 kPa to 275.8 kPa and 350°C. A startup heater (electric or steam) is used to bring the reactor up to process temperature (300°C to 500°C).

Reactor--
The vapor mixture of 1.2 to 1.5 mole % benzene in air is fed downward through a catalyst bed maintained at 365°C. Catalyst systems with optimized geometry based on vanadium oxides (1) or vanadium-molybdenum oxide configuration (9), with a promoter (9, 10) and applied on a support, are used in commercial reactor designs. At present, catalyst beds cannot be regenerated and must be replaced upon degradation. It should be noted that catalyst technology (5, 11, 12) is changing; consequently, new

---

(7) Dmuchovsky, B., M. C. Freerks, E. O. Pierson, R. H. Munch, and F. B. Zienty. A Study of the Catalytic Oxidation of Benzene to Maleic Anhydride. Journal of Catalysis, 4(2): 291-300, 1965.

(8) Sherwood, P. W. The Technology of Maleic Anhydride Production. World Petroleum, 39:48-61, November 1968.

(9) Ryder, R. C. Maleic Anhydride Production and Catalyst Thereof. U.S. Patent 2,885,409 (to American Cyanamid Company), May 5, 1959.

(10) Robinson, W. D. Catalytic Production of Maleic and Phthalic Anhydride. U.S. Patent 3,105,569 (to Monsanto Chemical Company), October 8, 1963.

(11) Darby, J. R. Oxidation Catalyst. U.S. Patent 2,674,582 (to Monsanto Chemical Company), April 6, 1954.

(12) Di Cio´, A. and D. Zettel. How S.A.V.A. Makes Maleic. Hydrocarbon Processing, 50(9):167-169, 1971.

catalyst systems are being developed and tested. Commercial reactors operate at elevated temperatures (300°C to 500°C) while employing fixed-bed processes (9). Fluid-bed technology can be adapted to produce maleic anhydride (13, 14). A typical reactor consists of 12,000 to 13,000 catalyst-filled tubes which have an internal diameter less than 25.4 mm and may reach 4.7 m in length.

The benzene oxidation reaction is exothermic, releasing 25 MJ of heat per kilogram of benzene reacted (15). Consequently, a heat transfer medium (an inorganic salt liquid) is circulated through an annular space surrounding each catalyst-filled tube. The heat transfer fluid is circulated through a heat exchanger unit where high pressure steam is produced. The degree of benzene conversion in the reactor is between 90% and 97% with a maximum yield of 0.9 kg of maleic anhydride per kg of 99.9% benzene feed; the theoretical yield is 1.26 kg/kg of benzene (8). Hence, overall yield of maleic anhydride from benzene is 71% of theoretical. The reactor gases (steam 9) exit at 375°C and pass directly to two heat exchangers in series. The gases are cooled to 150°C by the heat exchangers, which generate high and low pressure steam.

Crude Product Separator--
The reaction gases enter the crude product separator (stream 11) and are condensed using water. The crude product separator is a partial surface condenser where the reaction mix is cooled to approximately 53°C, and liquid maleic anhydride is removed (16). Many patents have been issued on the recovery of maleic

(13) Rollman, W. F. Process for Controlled Catalytic Oxidation. U.S. Patent 2,526,689 (to Standard Oil Development Company), October 24, 1950.

(14) Burney, D. E., and Melvern C. Hoff. Production of Maleic and Phthalic Anhydride. U.S. Patent 2,954,385 (to The Standard Oil Company), September 27, 1960.

(15) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 12. John Wiley & Sons, Inc., New York, New York, 1967. pp. 819-837.

(16) Feder, J. B. Recovery of Maleic Anhydride. U.S. Patent 3,054,086 (to Scientific Design Company, Inc.), September 18, 1962.

anhydride (9, 16-20), and most reflect an effort to condense the anhydride by using a minimum amount of water in the recovery system. When effluent gas from a reactor is cooled to 132°C to 204°C, liquid droplets of tar form and are deposited on the tubular walls of the condenser (18). Scientific Design Co., Inc., reports 24.6 wt % tar deposit in condenser tubes that contain liquid maleic anhydride (19). The tar deposits are removed and may be passed to an incinerator along with liquid waste for disposal.

The liquid crude product (stream 12) passes to a storage tank, while the uncondensed gaseous mix (stream 13) exits the top of the separator and feeds into the bottom of a water scrubbing column.

Product Recovery Scrubber--
The separator exit gases are scrubbed with an aqueous solution of maleic acid (40 wt %) to recover the product they contain (40% of the maleic anhydride produced during reaction). The scrubbing solution is recycled, and its concentration is maintained by removing crude maleic acid for use in the dehydration column and adding make-up water from the top of the dehydration column. Another preferred scheme shunts a portion of the maleic acid wash stream to a surge tank, instead of directly to the dehydration column. It should be noted that adding the surge tank to the process introduces the tank vent as another emission point.

The gas enters the scrubber bottom and is scrubbed countercurrently by downward flowing maleic acid solution. Make-up water is added above the acid solution feed point. The scrubbed gas (stream 28) is released to the atmosphere at an average stack height 22.7 m above ground (shown later in Table 14).

---

(17) Cooper, W. M. Maleic Anhydride Recovery. U.S. Patent 2,951,555 (to Monsanto Chemical Company), September 6, 1960.

(18) Hoyte, W. N. Recovery of the Anhydride of Polycarboxylic Acids. U.S. Patent 3,040,059 (to Foster Wheeler Corporation), June 19, 1962.

(19) Feder, J. B., and J. L. Russell. Process for Cleaning Apparatus. U.S. Patent 3,024,251 (to Scientific Design Company, Inc.), March 6, 1962.

(20) Weyens, E. Continuous Process for the Preparation of Maleic Anhydride from an Aqueous Solution of Maleic Acid by Distillation. U.S. Patent 3,642,829 (to UCB), February 15, 1972.

The product recovery scrubber is the primary emission source in a maleic anhydride plant. This scrubber unit not only handles product recovery as a primary function, but in many facilities, streams from other process sections are routed to the scrubber.

Product Purification--
Dehydration--In the Scientific Design Co., Inc., process, the crude maleic acid solution, as bottoms from the product recovery scrubber (stream 15) or solution from the maleic acid surge tank (stream 16), is passed to a dehydration column. This solution could be dehydrated by heating above 138°C (boiling point of maleic acid), but formation of fumaric acid (isomer of maleic acid) would result. Also, decarboxylation of the maleic acid to acrylic acid, acrylic acid-maleic anhydride copolymers, and other decarboxylation products could be expected (8).

Maleic acid dehydration involves azeotropic distillation when using the Scientific Design Co., Inc., process (21). Table 3 compares the relative performance of the best known types of azeoptropic agents used in maleic acid dehydration (8). Distillation in the dehydration section is accomplished by a column equipped with a reboiler, head condenser and liquid/liquid separator (12). Xylene, an azeotropic agent, is pumped in at the center of the dehydration column (21). Column bottoms (stream 17), a mixture of maleic anhydride and xylene at 140°C to 160°C, are routed to a separation column while water and some xylene go overhead. The water condenses in the liquid/liquid separator and is sent to the product recovery scrubber, and the xylene is returned overhead.

TABLE 3. PERFORMANCE OF FIVE AZEOTROPIC AGENTS IN DEHYDRATION OF MALEIC ACID (8)

	Azeotropic agents				
Characteristic properties	Isoamyl butyrate	Di-isobutyl ketone	Anisole	Cumene	meta-Xylene
Boiling point, °C at 101 kPa pressure	178.5	169.3	153.8	152.4	139.0
Solvent content of azeotrope, solvent-H_2O mole %	6.1	10.5	19.7	17.0	23.4
Amount of solvent needed to entrain 1 mole H_2O, moles	0.065	0.12	0.24	0.20	0.30
Isomerized maleic acid, %	0.06	0 to 0.1	0.2 to 0.5	1	1 to 2
Maleic acid entrained in the azeotrope, %	0.3	0.2	0.65	8	3

(21) Jewett, J.E. Production of Maleic Anhydride. U.S. Patent 2,989,545 (to American Cyanamid Company), June 20, 1961.

Alternatively, a two-stage vacuum evaporation system is used in the Lurgi process to remove water and dehydrate the maleic acid to form maleic anhydride (22). In this case, the dehydration column is eliminated, and, since an azeotropic agent is not required, there will be no xylene emissions.

The dehydration of maleic acid to maleic anhydride is a delicate process, complicated by the presence of two types of impurities; the first type comes from the intermediate products of the oxidation of benzene to maleic anhydride, and the second is impurities, particularly fumaric acid, formed in the course of dehydration of the maleic acid solution.

Color stabilization--Color-forming bodies are produced in the reactor and remain in the maleic anhydride throughout the distillation steps. One removal approach attempts to promote polymerization of quinones and the copolymerization of quinones with maleic anhydride by introducing an aging or ripening period into the process. This involves retention times up to 10 hr at 150°C to 160°C. Heat aging alone is no longer preferred, however, due to the long retention times and the undesirable loss of products by isomerization of maleic to fumaric acid. A number of chemical condensation promoters have been proposed; among them are the use of sodium chloride together with boric acid prior to dehydration (23), and use of a 3-hr cook time at approximately 200°C in the presence of 0.5% to 1.0% manganese dioxide (24). The resulting tarry and carbonaceous products are removed by filtration, and the remaining impurities are separated from the maleic anhydride in the purification column by vacuum fractionation.

Purification column--Aged maleic anhydride (stream 22) is fed to the purification column where pure maleic anhydride vapors are condensed at 53°C under reduced pressure (approximately 4.0 kPa). A portion of the maleic anhydride is returned to the column as reflux; the remainder is heated to 93°C and recovered as refined product. The high boilers in the bottom, together with some maleic anhydride, are sent to waste disposal. Purification column bottoms discharge to a purge manifold and may subsequently be incinerated.

---

(22) Lawson, J. F. Trip report for visit to Reichhold Chemicals Inc., Morris, Illinois, July 28, 1977, under EPA Contract No. 68-02-2577.

(23) Kohn, G. K. Stabilization and Recovery of Dicarboxylic Acid Anhydrides in the Presence of Alkali Metal Cations, U.S. Patent 2,831,869 (to California Spray-Chemical), April 22, 1958.

(24) Cummings, H.D. Purification of Maleic Anhydride. U.S. Patent 2,806,861 (to Monsanto Chemical Company), September 17, 1957.

The refined product (stream 25) is sent to liquid storage. It may later be flaked, and then pelletized into briquettes and/or bagged. Domestic maleic anhydride producers normally pelletize less than 20 percent of the total amount of material processed (25). One foreign manufacturer (12) employs a special structure containing automatic pelletizing machines which function without human operators. The entire structure is held under a slight vacuum, and all intake air is washed in a column from which the water is returned to the product recovery scrubber.

Storage Tanks--
The feedstock, crude product, and refined product storage tank requirements for a 23,900-metric ton/yr benzene-based maleic anhydride plant are summarized in Table 4.

TABLE 4. SUMMARY OF TANKAGE REQUIREMENTS FOR A 23,900-METRIC TON/YR BENZENE-BASED MALEIC ANHYDRIDE PLANT

Tank no.[a]	Material stored	Capacity, m^3	Turnovers/yr	Vent height, m
1	Benzene	333	80	15.2
2	Benzene	2,460	20	15.2
3	Xylene	79	8	15.2
4	Xylene use	61	8	15.2
5	Crude maleic anhydride	91	52	15.2
6	Crude maleic anhydride	91	52	15.2
7	Crude maleic anhydride	95	80	15.2
8	Refined maleic anhydride	64	10	15.2
9	Refined maleic anhydride	79	90	15.2
10	Crude maleic acid	79	2	15.2

[a]Tank numbers correspond to those listed in Appendix A.

Benzene is stored at ambient temperature except during winter months, when tanks are heated to a temperature of approximately 7°C, just above the melting point. The benzene storage tanks may be blanketed with dry nitrogen to prevent the formation of an explosive mixture in the vapor space above the liquid benzene. Crude and refined maleic anhydride storage tanks are maintained at 60°C to 80°C, at which temperature the partial vapor pressure is 0.5 kPa to 1.5 kPa. The tanks are blanketed with dry nitrogen to prevent the entry of oxygen and water vapor. Oxygen can create a fire hazard, and water vapor promotes the hydrolysis of maleic anhydride to maleic acid. Xylene storage tanks are maintained at ambient temperature, at which xylene has a partial vapor pressure of 1.0 kPa.

(25) Letter, R. C. Weber, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, to D. Becker, U.S. Environmental Protection Agency, Cincinnati, Ohio, March 1, 1978.

Wastewater Streams--
The wastewater streams consist of the excess water withdrawn from the decanter and periodic washings from the dehydrator, purification, and product recovery scrubber columns. The stream composition includes maleic anhydride, maleic acid, fumaric acid, and tarry substances. Wash water from spill cleanup and from periodic storage tank washdowns would contribute to wastewater streams. Table 5 presents the waste water discharge composition from maleic anhydride production operations (26).

TABLE 5. MALEIC ANHYDRIDE WASTEWATER DISCHARGES (26)

Pollutant parameters	Effluent factor, g/kg of MAN produced	Concentration,[a] g/m³
Raw waste water	2,506.2	
Biological oxygen demand	117.7	47,000
Chemical oxygen demand	312.7	125,000
Total organic carbon	130.7	52,200
Total solids	275.0	110,000
Total suspended solids	5.9	2,400
Total dissolved solids	269.1	107,000
Oil and grease	4.2	1,700
Total nitrogen (as N)	0.1	40
Chromium	0.003	1
Phosphorus	1.0	400
Phenol	0.003	1
Zinc	0.04	16
Chloride	0.04	16
Iron	0.40	160
Copper	0.007	3
Cadmium	0.002	1

[a]Concentrations of components in waste water were calculated from effluent factors by multiplying by $10^6/2,506.2$; 2,506.2 is the raw waste water loading factor given in Reference 26; 10^6 converts grams of material discharged per kilogram of water to grams of material discharged per cubic meter.

(26) Capabilities and Costs of Technology for the Organic Chemicals Industry to Achieve the Effluent Limitations of P.L. 92-500. Report No. NCWQ-75/03, National Commission on Water Quality, Washington, D.C., June 1975. pp. 6-54, 6-55, and 10-12-1 to 10-12-15.

The aqueous wastes from some maleic anhydride plants are first neutralized with sodium hydroxide, then sent to municipal or industrial treatment plants where the neutralized solution is oxidized biologically. Alternatively, aqueous wastes may be treated by an optional incinerator-scrubber combination (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975). The waste stream is atomized and fed into the combustion chamber. Quench water is added at the exit end of the combustion chamber. The quenched and cooled gases are scrubbed in a trimmable venturi scrubber with sodium carbonate solution from a recirculating tank. The scrubbed gases are exhausted to the atmosphere through a mist eliminator section located in the stack. The removal efficiency of the incinerator-scrubber combination with respect to hydrocarbon emissions is reported to be 100%, although approximately 0.0001 g/kg of sodium carbonate is emitted as particulate.

Plant Shutdown, Turnaround and Startup--
Data on maleic anhydride plant shutdowns, turnarounds, and startups indicate that maleic anhydride plants are shut down an average of three times a year (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975). During shutdowns benzene feed is discontinued while process air purges the system at reduced flow.

Startup or other operating upsets can result in emissions of heat transfer fluid from heat transfer circuits. The emissions are in the form of an aerosol mist, which settles in the immediate vicinity of the emission point.

data on benzene conversion was deleted - why?

Catalyst--
Catalyst technology has provided numerous catalyst systems, and the search for optimum systems continues. However, in the oxidation of benzene, the predominant catalyst systems incorporate mixtures of molybdenum trioxide (MoO_3) and vanadium pentoxide (V_2O_5), generally with a promoter (10), and are supplied on a support. While the ratio of V_2O_5 to MoO_3 may vary over a wide range, in most instances the preferred weight ratio is 2.1: (27).

Few data have been published on catalyst life. It is known that the volatility of molbydenum has limited the maximum temperature allowable for many catalyst systems. In the patent literature (9) it has been reported that a reactor with a V_2O_5/MoO_3 catalyst system and a bath temperature of 500°C experienced a 50% loss of

(27) Dreibelbis, J. A. Preparation of Maleic Anhydride and Catalysts Thereof. U.S. Patent 3,005,831 (to Pittsburgh Chemical Company), October 24, 1961.

molybdenum oxide in 6 months of operation. In practice, as the temperature of the catalyst is increased to compensate for catalyst aging and loss of activity, a limit is reached that forces catalyst replacement (maleic anhydride plants to not regenerate catalyst beds). An optimum temperature range for vanadium-molybdenum catalyst is 400°C to 430°C (9).

Considerable work has been directed toward use of promoters and modifiers. Addition of phosphorous pentoxide to a molybdenum-vanadium oxide system is of value in butene oxidation to increase catalyst life (28, 29). Similarly, in benzene oxidation, addition of phosphorus to vanadium-molybdenum catalyst reduces the required reaction temperature and therefore lengthens catalyst life.

Reactor System Heat Balance--Oxidation of benzene is an exothermic chemical reaction. The standard heats of reaction for the main reaction and principal alternate reactions are calculated on the basis that all of the compounds involved are in the vapor state, and the results are listed in Table 6. The heat released in a commercial reactor is approximately 25 MJ/kg maleic anhydride formed (8).

The heat of reaction is used to generate steam in the molten salt heat exchanger. Part of this steam is used to satisfy process requirements and the remainder is available for export. An energy balance for a representative maleic anhydride plant is given in Table 7.

n-Butane-Based Process

Although domestic maleic anhydride processes are based on the catalytic oxidation of benzene, one-third of the carbon in benzene is not utilized in the reaction. Consequently, U.S. maleic anhydride producers have developed 4-carbon-atom based processes, namely n-butane, n-butene, and butadiene. Only the n-butane process has reached commercialization in the U.S. (4).

Due to the proprietary nature of the n-butane-based process, published literature on commercial designs is unavailable. Nevertheless, the reaction sequence is similar to that of benzene-based process, which indicates that its reaction products are similar (6). It also indicates that the product purification

(28) Becker, M., and R. S. Barker. Preparation of Maleic Anhydride and Catalyst Thereof. U.S. Patent 2,967,185 (to Scientific Design Company, Inc.), January 3, 1961.

(29) Kerr, R. O. Catalytic Oxidation of Hydrocarbons. U.S. Patent 3,484,384 (to Petro-Tex Chemical Company), December 16, 1969.

TABLE 6. HEATS OF REACTION FOR THE OXIDATION OF BENZENE

Equation No.	Reaction	Heat of reaction, MJ/kg of benzene	Heat of reaction, MJ/kg-mole of benzene
3	Benzene + $4.5O_2$ → maleic anhydride + $2CO_2$ + $2H_2O$	22.36	1,746
4	Benzene + $4O_2$ → maleic anhydride + CO_2 + CO + $2H_2O$	18.75	1,465
5	Benzene + $5O_2$ → CO_2 + 5CO + $3H_2O$	22.06	1,723

TABLE 7. REACTOR SYSTEM HEAT BALANCE FOR PRODUCTION OF MALEIC ANHYDRIDE FROM BENZENE
(MJ/kg MAN)

Heat in	
Exothermic heat of reaction[a]	41.92
Benzene vaporizer and superheater	0.58
Air preheat[b]	0.16
TOTAL	42.66
Heat out	
Steam generation reactor internal cooling	24.98
Differential enthalpy[c]	17.47
Reactor heat loss	0.21
TOTAL	42.66

[a]Derived using Reference 15 based on yields given in Reference 8. For an average reaction heat of 27.95 MJ/kg benzene consumed at 2/3 of theoretical, 41.92 MJ/kg (maleic anhydride produced) is produced.

[b]Air is compressed at 21.1°C, 0 kPa gage, and heated to 185°C, 275 kPa gage.

[c]Reactor effluent enthalpy minus reactor feed enthalpy.

schemes for commercial n-butane processes would employ product recovery and refining techniques as varied as those of the benzene-based processes.

MATERIAL FLOW

The flow diagram for the maleic anhydride process is given in Figure 1. Table 8 contains a material balance for a typical 23,900-metric ton/yr plant (personal communication between T.W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975).

Sources of atmospheric emissions from the maleic anhydride process are: product recovery scrubber vent (stream 28); refining vacuum system vent (stream 29); secondary scrubber vent (stream 31) for those plants employing this scheme to control emissions from falking, pelletizing, and/or packaging operations; benzene storage vent (stream 32); crude maleic anhydride storage vent (stream 33); crude maleic acid storage vent (stream 34); *o*-xylene storage vent (stream 35); aqueous waste storage vent (stream 36); refined maleic anhydride storage vent (stream 37); and fugitive emissions (stream 30). It should be noted that major emissions result from the product recovery scrubber vent. Further, solid waste (tarry substances, spent catalyst, etc.) may generate odor pollution from landfill disposal.

GEOGRAPHICAL DISTRIBUTION

There are currently eight companies manufacturing maleic anhydride from benzene or n-butane at nine locations within the continental U.S. Table 9 lists the manufacturers, 1977 plant capacities, and feedstocks (2), and Figure 2 shows their plant distribution, keyed to plant numbers in the table. The population densities of the counties in which the plants are located range from 23 to 3,847 persons/km^2. The total U.S. production capacity in 1977 was 233,600 metric tons/yr. In addition to this total are 4,500 metric tons of maleic anhydride per year which are recovered as a byproduct of phthalic anhydride manufacture by Koppers Company, Inc., in Cicero, Illinois (personal communication between G. M. Rinaldi, Monsanto Research Corporation, Dayton, Ohio, and J. Anderson, Koppers Company, Inc., Pittsburgh, Pennsylvania, August 11, 1977).

TABLE 8. MATERIAL BALANCE FOR A 23,900-METRIC TON/YR MALEIC ANHYDRIDE PLANT

Stream number	1	2	3	4	5	6	7	8	9	10	11
Description	Benzene	Benzene feed	Total benzene feed to vaporizer	Vaporized benzene feed	Vaporized benzene feed from knockout	Air	Preheated air	Reactor feed	Reactor product	Primary condenser effluent	Product separator feed
Temperature, °C	38	38	[a]	[a]	586	38	103	[a]	400	[a]	[a]
Gage pressure, kPa	0	[a]	[a]	[a]	586	0	[a]	[a]	[a]	[a]	[a]
Component	Flow rate, kg/hr										
Particulates	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Oxygen	[b]	[b]	[b]	[b]	[b]	19,700	19,700	19,700	12,400	12,400	12,400
Nitrogen	[b]	[b]	[b]	[b]	[b]	65,700	65,700	65,700	65,700	65,700	65,700
Carbon dioxide	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	3,000	3,000	3,000
Carbon monoxide	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	1,600	1,600	1,600
Water	[b]	[b]	[b]	[b]	[b]	[c]	[b]	[b]	2,800	2,800	2,800
Maleic anhydride	[b]	[b]	[b]	[b]	[b]	[c]	[b]	[b]	3,000	3,000	3,000
Maleic acid	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Benzene	3,300	3,300	3,300	3,300	3,300	[b]	[b]	3,300	230	230	230
Formaldehyde	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Formic acid	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[c]	[c]	[c]
Xylenes	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Polymers (tar, fumaric acid, etc.)	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[c]	[c]	[c]
TOTAL	3,300	3,300	3,300	3,300	3,300	85,400	85,400	88,700	88,700	88,700	88,700

[a] Unknown.

[b] Component not present or present in negligible amounts in the stream shown.

[c] Trace.

(continued)

TABLE 8 (continued)

Stream number	12	13	14	15	16	17	18	19	20	21
Description	Crude product	Separator off-gas	Scrubber bottom liquor	Crude maleic acid	Dehydrator feed	Azeotropic bottom product	Purification still pot feed	Crude product feed	Dehydrator column overhead	Separated water
Temperature, °C	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]
Gage pressure, kPa	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]
Component	Flow rate, kg/hr									
Particulates	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Oxygen	_[b]	12,400	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Nitrogen	_[b]	65,700	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Carbon dioxide	_[b]	3,000	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Carbon monoxide	_[b]	1,600	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Water	_[b]	2,800	62,700	2,500	2,600	_[b]	_[b]	_[b]	2,300	2,200
Maleic anhydride	1,300	1,700	_[b]	_[b]	_[b]	_[b]	_[b]	2,500	_[b]	_[b]
Maleic acid	_[b]	_[b]	55,300	2,200	2,500	2,000	1,600	_[b]	490	_[b]
Benzene	_[b]	230	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Formaldehyde	_[b]	_[c]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Formic acid	_[b]	_[c]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Xylenes	_[b]	_[b]	_[b]	_[b]	_[b]	250	210	_[b]	_[b]	_[b]
Polymers (tar, fumaric acid, etc.)	_[c]	_[c]	_[b]	_[c]	_[c]	120	_[c]	_[c]	_[b]	_[b]
TOTAL	1,300	87,400	118,000	4,700	5,100	2,400	1,810	2,500	2,800	2,200

[a] Unknown.

[b] Component not present or present in negligible amounts in the stream shown.

[c] Trace.

(continued)

TABLE 8 (continued)

Stream number	22	23	24	25	26	27	28	29	30
Description	Purification column feed	Purification column overhead	Separated xylene	Refined product	Aqueous waste and purge	Xylenes	Product recovery scrubber vent	Refining vacuum system vent	Fugitive emissions
Temperature, °C	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]
Gage pressure, kPa	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]
Component	Flow rate, kg/hr								
Particulates	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Oxygen	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	12,400	9	_[b]
Nitrogen	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	65,700	27	_[b]
Carbon dioxide	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	3,000	2	_[b]
Carbon monoxide	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	1,600	_[b]	_[b]
Water	_[b]	_[b]	_[b]	_[b]	7,600	_[b]	3,000	_[b]	_[b]
Maleic anhydride	2,800	2,700	_[b]	2,700	18	_[b]	7	0.3	_[b]
Maleic acid	37	_[b]	_[b]	_[b]	37	_[b]	7	_[b]	_[b]
Benzene	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	230	_[b]	3
Formaldehyde	_[b]	_[b]	_[b]	_[b]	_[b]	_[c]	17	_[b]	_[b]
Formic acid	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	5	_[b]	_[b]
Xylenes	250	250	250	_[b]	_[c]	370	28	_[b]	_[b]
Polymers (tar, fumaric acid, etc.)	_[c]	_[b]	_[b]	_[b]	98	_[b]	_[b]	_[b]	_[b]
TOTAL	3,100	3,000	250	2,700	7,800	370	86,000	38	26

[a] Unknown.

[b] Component not present or present in negligible amounts in the stream shown.

[c] Trace.

(continued)

TABLE 8 (continued)

Stream number	31	32	33	34	35	36	37	38	39
Description	Secondary scrubber vent	Benzene storage vent	Crude product storage vent	Crude maleic acid storage vent	o-Xylene storage vent	Aqueous waste storage vent	Refined maleic anhydride storage vent	Generated steam	Transport loading facilities
Temperature, °C	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]
Gage pressure, kPa	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	_[a]	2,069	_[a]
Component	Flow rate, kg/hr								
Particulates	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Oxygen	1,500	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Nitrogen	4,900	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Carbon dioxide	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Carbon monoxide	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Water	120	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	11,900	_[b]
Maleic anhydride	0.6	_[b]	0.2	_[b]	_[b]	_[a]	0.04	_[b]	_[b]
Maleic acid	_[b]	_[b]	_[b]	0.02	_[b]	_[a]	_[b]	_[b]	_[b]
Benzene	_[b]	4	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Formaldehyde	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Formic acid	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
Xylenes	_[b]	_[b]	_[b]	_[b]	0.1	_[a]	_[b]	_[b]	_[b]
Polymers (tar, fumaric acid, etc.)	_[b]	_[b]	_[b]	_[b]	_[b]	_[a]	_[b]	_[b]	_[b]
TOTAL	6,500	4	0.2	0.02	0.1	_[a]	0.04	11,900	_[b]

[a] Unknown.

[b] Component not present or present in negligible amounts in the stream shown.

[c] Trace.

TABLE 9. MALEIC ANHYDRIDE PRODUCTION PLANTS (2, 30, 31)

Number[a]	Company	Capacity, metric tons/yr	Location	County population density, persons/km^2	Raw material	Process
1	Amoco Chemicals Corp.	27,200	Joliet, IL	112	n-Butane	(Proprietary)
2	Ashland Oil, Inc.	27,200	Neal, WV	28	Benzene	Scientific Design Co., Inc. (30)
3	Denka Chemical Corp.[b]	22,700	Houston, TX	386	Benzene	Scientific Design Co., Inc. (31)
4	Koppers Company, Inc.[c]	15,400	Bridgeville, PA	842	Benzene	Scientific Design Co., Inc.
5	Monsanto Co.[d]	38,100 9,500	St. Louis, MO	3,847	Benzene n-Butane	Scientific Design Co., Inc. (Proprietary)
6	Reichhold Chemicals, Inc.	18,100	Elizabeth, NJ	2,021	Benzene	Scientific Design Co., Inc.
7	Reichhold Chemicals, Inc.	27,200	Morris, IL	23	Benzene	Lurgi (22)
8	Tenneco, Inc.	11,800	Fords, NJ	714	Benzene	Scientific Design co., Inc.
9	United States Steel Corp.	36,400	Neville Island, PA	842	Benzene	Scientific Design Co., Inc.

wrong numbers !

[a] Shown in Figure 2.

[b] Denka Chemical Corporation purchased its maleic anhydride production plant at Houston, Texas, from Petro-Tex Chemical Corporation, effective July 1, 1977 (personal communication between G. M. Rinaldi, Monsanto Research Corporation, Dayton, Ohio, and R. D. Pruessner, Petro-Tex Chemical Corporation, Houston, Texas, July 29, 1977).

[c] Koppers Company, Inc., in Cicero, Illinois recovers maleic anhydride as a byproduct of phthalic anhydride manufacture (personal communication between G. M. Rinaldi, Monsanto Research Corporation, Dayton, Ohio, and J. Anderson, Koppers Company, Inc., Pittsburgh, Pennsylvania, August 11, 1977). Air emissions from this plant were studied by MRC in two previous efforts (32, 33).

[d] Monsanto Company's plant in St. Louis, Missouri has two production trains, one with a capacity of 38,100 metric tons/yr of maleic anhydride from benzene, and the other with a capacity of 9,500 metric tons/yr using butane as the raw material (2).

(30) Letter, R. C. Sterrett, Ashland Chemical Company, Columbus, Ohio, to D. R. Patrick, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 21, 1978.

(31) Maxwell, W. H., and G. W. Scheil. Stationary Source Testing of a Maleic Anhydride Plant at the Denka Chemical Corporation, Houston, Texas. Contract No. 68-02-2814, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1978.

(32) Chi, C. T., and T. W. Hughes. Phthalic Anhydride Plant Air Pollution Control. Contract No. 68-02-1320, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (Preliminary document submitted to the EPA by Monsanto Research Corporation, July 1977.) 104 pp.

(33) Serth, R. W., and T. W. Hughes. Source Assessment: Phthalic Anhydride (Air Emissions). EPA-600/2-76-032d, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1976. 145 pp.

NUMBERS CORRESPOND TO PLANTS LISTED IN TABLE 9

Figure 2. Maleic anhydride plant locations.

SECTION 4

EMISSIONS

SELECTED POLLUTANTS

Benzene-Based Process

A complete list of the possible reaction products from the oxidation of benzene is unavailable in the published literature. However, investigators (1, 6) studying the oxidation of benzene to various intermediates or byproducts have reported numerous reaction products. In addition to these compounds, emissions from benzene-based maleic anhydride plants contain particulates. A compilation of possible reaction products from the oxidation of benzene is presented in Table 10. The following materials are either known to be or suspected of being emitted from maleic anhydride plants: benzene, maleic anhydride, maleic acid, acrolein, carbon monoxide, formaldehyde, formic acid, quinone, benzoic acid, ethylbenzene, fumaric acid, and xylenes. These compounds were therefore selected for study.

Selected Pollutants and Their Characteristics

The process mechanism and the formation of emissions from maleic anhydride manufacture have been described in Section 3. Based on that description, the atmospheric emissions are hydrocarbons from raw materials, byproducts, and intermediates; and carbon monoxide from incomplete oxidation of benzene. Table 11 (34-36) lists these potential pollutants with their respective toxicities (expressed as TLV®) and health effects. In addition

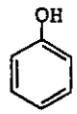
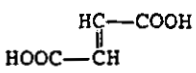
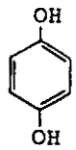
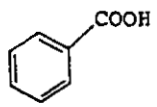
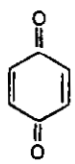
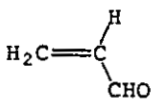
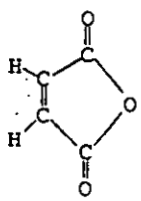
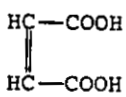
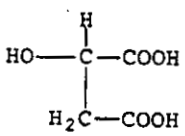
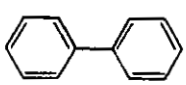
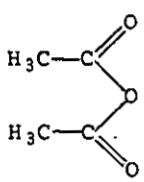
---

(34) Sax, N. I. Dangerous Properties of Industrial Materials, Third Edition. Reinhold Publishing Corp., New York, New York, 1968. 1,251 pp.

(35) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

(36) Registry of Toxic Effects of Chemical Substances, 1975 Edition. H. E. Christensen and T. T. Luginbyhl, eds. U.S. Department of Health, Education, and Welfare, Rockville, Maryland, June 1975. p. 687.

TABLE 10. POSSIBLE REACTION PRODUCTS FROM THE OXIDATION OF BENZENE

Compound	Structure/formula	Compound	Structure/formula
Phenol		Fumaric acid	
Hydroquinone		Benzoic acid	
		Carbon oxides and water	CO, CO_2, H_2O
Quinone		Acrolein	
Maleic anhydride		Formaldehyde	HCHO
		Acetaldehyde	CH_3CHO
Maleic acid		Formic acid	HCOOH
Malic acid		Acetic acid	CH_3COOH
Biphenyl		Acetic anhydride	
Propionaldehyde	CH_3CH_2CHO		

Minor constituents: Ethylene, ethane, propylene, propane, butene, butane, ethylene oxide, propylene oxide.

to being recognized as highly toxic, maleic anhydride has been designated as carcinogenic (36). Air pollution literature from the USSR indicates a TLV of 80 $\mu g/m^3$ for maleic anhydride on the basis of a toxicity study (37).

TABLE 11. CHARACTERISTICS OF EMISSIONS FROM MALEIC ANHYDRIDE PRODUCTION PLANTS (34-36)

Compound emitted	TLV, mg/m^3	Health effects
Acrolein	0.25	Highly toxic; affects the membranes of the eyes and respiratory tract
Benzene	30	Moderately toxic; strong irritating effect producing erythema and burning; suspected leukemic agent
Benzoic acid	-[a]	Slightly toxic; may cause nausea
Carbon monoxide	55	Highly toxic by inhalation; high affinity for hemoglobin
Ethylbenzene	435	Moderately toxic; liquid form is an irritant to skin and mucuous membrane
Formaldehyde	3	Highly toxic; inhalation can cause vomiting and diarrhea
Formic acid	9	Moderately toxic; strong irritant to tissue
Fumaric acid[b]	1	Slightly irritating
Maleic acid	1	Moderately toxic; strong irritant to tissue
Maleic anhydride	1	Highly toxic
Quinone	0.4	Highly toxic; strong irritant to skin and mucuous membrane
Xylenes	435	Moderately toxic

[a] Not available.

[b] Commonly used as food additive and under normal use is not toxic as defined in Reference 34.

Industry's reaction to the designation of maleic anhydride as a suspected carcinogen is illustrated by the following Monsanto Company statement (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and M. Pierle, Monsanto Co., St. Louis, Missouri, October 1976):

(37) Nuttonson, M. Y. AICE Survey of USSR Air Pollution Literature. American Institute of Crop Ecology, Silver Springs, Maryland, July 1971. pp. 30-43.

"Monsanto recognizes that the 1975 edition of the Department of Health, Education, and Welfare's 'Registry of Toxic Effects of Chemical Substances' lists one reference which indicates that maleic anhydride exhibits carcinogenic effects. However, the Registry is a compendium of all known health effects references and contains the following caution or disclaimer as to the accuracy of the individual references, 'No attempt has been made to resolve any questions about data that have been published.'

"Monsanto has reviewed this reference (Dickens and Jones, British J. Cancer 17:100-108, 1963) and feels the available report deals with a very small and inadequately controlled study of the effects of subcutaneous injection of maleic anhydride. Three rats were injected twice per week, with 1 mg maleic anhydride in arachis oil, for 61 weeks. Fibroblastic changes, reported to be fibrosarcomas, were found at the site of injection in two rats. No evidence of metastasis of these lesions was found in any animals injected with maleic anhydride. Changes such as these observed following the subcutaneous injection of maleic anhydride are produced by the repeated injection of a wide variety of substances. Among the materials that induce similar changes are hypertonic solutions of simple salts, weakly acidic or weakly alkaline solutions and the simple implantation of inert substances that result in local physical irritation. As a result, the report by Dickens and Jones is not evidence of the carcinogenicity of maleic anhydride."

The species listed in Table 11 have been listed at times in published emission surveys as lumped components; e.g., maleic anhydride and maleic acid listed as one compound. With this in mind, all aldehydes are listed as formaldehydes in Table 11.

LOCATION AND DESCRIPTION

Sources of atmospheric emissions within a maleic anhydride plant include the product recovery scrubber, refining vacuum system, secondary scrubber (since plants which flake or pelletize maleic anhydride typically employ this emission control system), aqueous waste storage, raw material and product storage tanks, and fugitive emissions from process pumps and valves. Several of these sources are discussed below.

Product Recovery Scrubber

The product recovery scrubber vent gas (stream 28 in Figure 1) is a continuous source of emissions, consisting of scrubbed off-gas from the crude product separator. Gaseous emissions from the dehydration and purification sections may also be vented to the product recovery scrubber. Typical components and average flow rates for the product recovery scrubber vent gas are listed in Table 12.

TABLE 12. TYPICAL PRODUCT RECOVERY SCRUBBER VENT GAS COMPONENTS AND AVERAGE FLOW RATES FOR BENZENE-BASED PROCESS

Production rate: 23,900 metric tons/yr Temperature: 37°C Gage pressure: 0 kPa	
Component	Average flow rate, kg/hr
Oxygen	12,400[a]
Nitrogen	65,700[a]
Carbon dioxide	3,000[a]
Carbon monoxide	1,600[a]
Water	3,000[a]
Maleic acid	7[a]
Maleic anhydride	7[a]
Formaldehyde	17[a]
Benzene	230[a]
Formic acid	5[a]
Xylenes	28[a]
Toluene	-[b]
Acetaldehyde	-[b]
Quinone	-[b]
Cresols	-[b]
Biphenyl	-[b]
Dimethylphenol	-[b]
Dimethyl/ethylnaphthalene	-[b]
C_3/C_4 Naphthalene	-[b]
C_6-Alkanes	-[b]
C_7-Alkanes	-[b]
C_3/C_4 Alcohols	-[b]
C_{12}-C_{17} Hydrocarbons	-[b]
Methylnaphthalene	-[b]

why are these numbers different from previous editions?

[a] Based on personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

[b] Components identified in gas chromatography/mass spectroscopy analyses of samples obtained through product recovery scrubber vent gas presurvey sampling.

Secondary Scrubber

The secondary scrubber stack gas (stream 31 in Figure 1) is an intermittent source of emissions. The secondary scrubber[a] is used to control vented emissions of maleic anhydride particles from flaking, pelletizing, and packaging operations. Emissions from the secondary scrubber consist mainly of nitrogen, oxygen, water, and small quantities of maleic anhydride. The scrubbing efficiency of the secondary scrubber is reported to be approximately 98%. Two maleic anhydride plants report complete removal of maleic anhydride from the secondary scrubber vent (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975).

Aqueous Waste Storage

The aqueous waste storage vent (stream 36 in Figure 1) is also an intermittent source of emissions. An incinerator may be used to burn the liquid purge from the dehydration column and the various units involved in product purification. Two plants employ such an incinerator device (22, 38). The organic compounds in the waste stream are combusted in the incinerator, and any particulates formed may be removed by a scrubber (22). The efficiency of the combined system is approximately 100%. However, the plant that scrubs the incinerator off-gases reports that some sodium carbonate is emitted as particulate (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975).

Storage Tank Vents

The emissions from feedstock, crude product, and refined product storage tank vents (streams 32, 33, 34, 35, 36, and 37 in Figure 1) for a 23,900-metric ton/yr production rate have been estimated and are presented in Table 13. These estimates were obtained using the data in Table 4 together with the empirical correlations for petrochemical losses by the American Petroleum

---

[a]An industry term used to describe a device for controlling emissions from solids handling; the secondary scrubber is not a piece of equipment added on after a primary control device.

---

(38) Lawson, J. F. Trip report for visit to Amoco Chemicals Corporation, Chicago, Illinois, January 24, 1978, under EPA Contract No. 68-02-2577.

Institute (39-43). The correlations give uncontrolled emission rates; the controlled emission rates listed in Table 13 are based on control efficiency for hydrocarbons of 99%, assumed to be accomplished by manifolding tank vents to a vapor recovery system. The estimated accuracy of the empirical correlations is ±10% (39-43). Details of the calculations are given in Appendix A.

TABLE 13. STORAGE TANK WORKING AND BREATHING LOSSES FOR A 23,900-METRIC TON/YR MALEIC ANHYDRIDE PLANT USING BENZENE RAW MATERIAL

Species	Uncontrolled emission rate, kg/hr	Uncontrolled emission factor, g/kg	Controlled emission rate, kg/hr	Controlled emission factor, g/kg	Control efficiency, %
Benzene	3.38	1.24	0.03	0.012	99
Maleic anhydride (crude)	0.22	0.081	0.002	0.0008	99
Maleic anhydride (refined)	0.04	0.014	0.0004	0.0001	99
Maleic acid (crude)	0.02	0.009	0.0002	<0.0001	99
Xylenes	0.05	0.018	0.0005	0.0004	99

(39) Evaporation Loss from Fixed Roof Tanks. API Bulletin 2518, American Petroleum Institute, New York, New York, 1962. 38 pp.

(40) Use of Variable Vapor Space Systems to Reduce Evaporation Loss. API Bulletin 2520, American Petroleum Institute, New York, New York, 1964. 14 pp.

(41) Petrochemical Evaporation Loss from Storage Tanks. API Bulletin 2523, American Petroleum Institute, New York, New York, 1969. 14 pp.

(42) Evaporation Loss from Floating Roof Tanks. API Bulletin 2517, American Petroleum Institute, New York, New York, 1962. 13 pp.

(43) Evaporation Loss in the Petroleum Industry - Causes and Control. API Bulletin 2513, American Petroleum Institute, New York, New York, 1959. 57 pp.

Fugitive Emissions

Fugitive emissions from maleic anhydride manufacture originate from a number of sources: pump seals, flanges, valves, and compressor seals, as well as flaking, bagging, and pelletizing operations. Fugitive emissions of volatile organic compounds from process pumps and valves amount to approximately 1.1 g/kg of maleic anhydride produced (44). Benzene was reported (44) to account for 0.3 g/kg of this amount, and the remainder was assumed to consist of equal parts of xylene and maleic anhydride for the purposes of this report. In addition to the losses that occur under normal operating conditions, operating upsets can result in emissions of fluid from heat transfer circuits associated with the process reactor. Emissions that result from flaking and bagging operations are maleic anhydride particles, and these amount to 8.81 g/kg of maleic anhydride produced (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975). However, five of the nine plants use scrubbers for approximately 98% control of these emissions.

ENVIRONMENTAL EFFECTS

Definition of a Representative Source

For the purpose of assessing the source severity, a representative benzene-based maleic anhydride plant is defined as one having a production rate of 23,900 metric tons/yr and using the modified Scientific Design Co., Inc. process (Figure 1). This process is specified because it is the predominant engineering design used, accounting for about 90% of benzene-based U.S. production. The eight benzene-based plants operating in the United States range in capacity from 11,800 to 38,100 metric tons/yr.

Environmental impact is assessed on the basis that all storage tanks as well as transport loading facility vents are controlled. In addition, the bagger or pelletizer vent is assumed to be vented to a secondary scrubber. Data used to determine a representative source, including capacity (2), are presented in Table 14.

---

(44) Lawson, J. F. Maleic Anhydride - Draft Product Report. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1978.

TABLE 14. PLANT PARAMETERS USED IN DETERMINING THE REPRESENTATIVE MALEIC ANHYDRIDE SOURCE

Plant parameter	Plant number 1	2	3	4	5	6	7	8	9	Selected Parameter or mean value	Standard deviation	Percent relative uncertainty[a]	Relative uncertainty
Technology	[b]	[c]	[c]	[c]	[c]	[c]	[d]	[c]	[c]	[c]	[e]	[e]	[e]
Capacity, metric tons/yr	27,200	27,200	22,700	15,400	47,600	18,100	27,200	11,800	36,400	26,000[f]	10,990	±32.5	8,448
Product recovery scrubber height, m	[g]	[g]	19.8	22.6	[g]	17.3	27.4	22.0	27.1	22.7	4.0	±18.4	4.2
Secondary scrubber height, m	[g]	[g]	[g]	[g]	3.0	9.1	6.1	[g]	[g]	6.1	3.1	+124.2 −100.0	7.6
Refining vacuum system vent height, m	[g]	[g]	[g]	[g]	[g]	[g]	25.9	[g]	[g]	25.9	[e]	[e]	[e]

[a] Percent relative uncertainty = $100(n)^{-1/2}(\bar{x})^{-1}(s_x)(t)$, where n = number of observations, $\bar{x}$ = observed mean, s_x = standard deviation, and t = value from student's t-distribution tables for the 95% confidence level.

[b] Plant technology proprietary or unknown.

[c] Scientific Design Co., Inc. process.

[d] Lurgi process.

[e] Not applicable.

[f] This capacity figure was multiplied by an assumed load factor of 0.92 to obtain the representative production rate of 23,900 metric tons/yr mentioned in the text.

[g] Not reported.

Emission Factors

The emission factors for the maleic anhydride manufacture by emission point are given in Table 15. These emission factors are used in the calculations of source severity, mass emissions, and affected population presented below.

Source Severity

In order to obtain a quantitative measure of the hazard potential of emissions from maleic anhydride production, a source severity, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} \qquad (6)$$

where $\bar{\chi}_{max}$ is the time-averaged maximum ground level concentration of each species emitted from a representative plant, and F, a hazard factor, is defined as a primary ambient air quality standard for criteria pollutants (i.e., carbon monoxide and hydrocarbons[a]), while for noncriteria pollutants,

$$F \equiv TLV \bullet 8/24 \bullet 0.01 \ (g/m^3)$$

[a] There is no standard for hydrocarbons. It is a recommended guideline for meeting the oxidants standard.

TABLE 15. EMISSION FACTORS FOR MALEIC ANHYDRIDE MANUFACTURE BY EMISSION POINT (g/kg)

Material emitted	Emission point														
					Tanks										
	Product recovery scrubber	Secondary scrubber	Refining vacuum system vent	Fugitive emissions	Benzene storage tank	Benzene storage tank	Xylene storage tank	Xylene use tank	Crude maleic anhydride storage tank	Crude maleic anhydride storage tank	Crude maleic anhydride storage tank	Refined maleic anhydride storage tank	Refined maleic anhydride storage tank	Crude maleic acid storage tank	Total[a]
Criteria pollutants															
Carbon monoxides	633.3 ± 21%	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	633.3
Hydrocarbons	104.9[c] ± 48%	0.2	0.1	1.1	0.218 ± 20%	1.023 ± 20%	0.01 ± 20%	0.065 ± 20%	0.034 ± 20%	0.034 ± 20%	0.012 ± 20%	0.003 ± 20%	0.011 ± 20%	0.008 ± 20%	107.7
Particulates	[d]	[b]	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	0.1[e]
Chemical substances															
Toluene	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Benzene	95.5[f] ± 58%	[b]	[b]	0.3	0.218 ± 20%	1.023 ± 20%	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	97.0
Acetaldehyde	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Formaldehyde	6.8 ± 100%	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	6.8
Formic acid	2.1 ± 100%	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	2.1
Maleic acid	3.1 ± 68%	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	0.008 ± 20%	3.1
Maleic anhydride	3.1 ± 74%	0.2	0.1	0.4	[b]	[b]	[b]	[b]	0.034 ± 20%	0.034 ± 20%	0.012 ± 20%	0.003 ± 20%	0.011 ± 20%	[b]	3.9
Quinone	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Cresol(s)	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Xylenes	11.6[g]	[b]	[b]	0.4	[b]	[b]	0.01 ± 20%	0.065 ± 20%	[b]	[b]	[b]	[b]	[b]	[b]	12.1
Biphenyl	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Dimethylphenol(s)	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Methylnaphthalene(s)	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Dimethyl/ethylnaphthalene(s)	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_3/C_4 Naphthalenes	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_6 Alkanes	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_7 Alkanes	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_3/C_4 Alcohols	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_{12}-C_{17} Hydrocarbons	[d]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]

[a] Data used for product recovery scrubber in calculating total emission factors were obtained in personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

[b] Assumed to be negligible.

[c] Total hydrocarbon emission factor does not equal the sum of emission factors for individual hydrocarbons. Value represents mean value emission factor for total hydrocarbons from plants reported in personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

[d] Not reported.

[e] Engineering estimates of the emission factors for particulates indicate that the value will be no greater than 1.0 and no less than 0.01, estimate based on plant material balance. Included are uncontrolled particulate maleic anhydride emissions resulting from flaking, pelletizing, and packaging operations.

[f] Value does not include 3.3 g/kg emission factor for one plant employing benzene recovery unit in conjunction with product scrubber.

[g] Engineering estimates of the emission factors for xylene indicate the value should not exceed 23.2 with a mean value of 11.6; estimate based on storage tank data obtained in personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

The factor 8/24 adjusts the TLV for continuous rather than work-day exposure, and the factor of 0.01 accounts for the fact that the general population is a higher risk group than healthy workers (34).

Thus, the source severity represents the ratio of the time-averaged maximum ground level exposure to the hazard level of exposure for a given pollutant.

The maximum ground level concentration, χ_{max}, was estimated using Gaussian plume dispersion theory. Detailed derivations of all source severity equations are given in Appendix B. χ_{max} values were calculated using the formula:

$$\chi_{max} = \frac{2\,Q}{\pi H^2 e u} \qquad (7)$$

where Q = mass emission rate, g/s
u = wind speed, m/s
H = height of emission release, m
e = 2.72
π = 3.14

Equation 4 yields a value for a short-term averaging time during which the Gaussian plume dispersion equation is valid. The short-term averaging time was found to be 3 minutes in a study of published data on lateral and vertical diffusion (45). For a continuously emitting source, the time-averaged maximum ground level concentration for time intervals between 3 minutes and 24 hours can be estimated from the relation:

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t}\right)^{0.17} \qquad (8)$$

where t = averaging time
t_o = "instantaneous" average time (i.e., 3 min)

(45) Nonhebel, G. Recommendations on Heights for New Industrial Chimneys. Journal of the Institute of Fuel, 33:479-511, July 1960.

For noncriteria pollutants, the averaging time, t, is 24 hours. For criteria pollutants, the averaging times are those used in the definition of the primary ambient air quality standards.

Insertion of the national average wind speed of 4.5 m/s into the above equations leads to the severity equations listed in Table 16. The emission heights which were used in the calculations are given in Table 17. The height for the fugitive emissions was estimated; the others were obtained during personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975. The resulting source severity factors are presented in Table 18. In these calculations, intermittent sources such as fugitive emissions and storage tank vents were treated as continuous sources with their respective annual emission rates. In addition, it was assumed that Gaussian plume dispersion theory is equally valid for all emissions, regardless of their chemical, physical, or topological characteristics.

TABLE 16. SOURCE SEVERITY EQUATIONS

Pollutant	S	Equation No.	Equation No. in Appendix B
Hydrocarbons	$S = 162.5\ QH^{-2}$	9	B-50
CO	$S = 0.78\ QH^{-2}$	10	B-44
All others	$S = 5.5\ QH^{-2}\ (TLV)^{-1}$	11	B-36

Q = mass emission rate, g/s
H = height of emission release, m
TLV = threshold limit value, g/m^3

TABLE 17. EMISSION HEIGHTS FOR REPRESENTATIVE SOURCE (2)

Source of emissions	Emission height, m
Product recovery scrubber	22.7
Secondary scrubber	6.1
Storage tanks	15.2
Fugitive emissions	3.1
Refining vacuum system vent	25.9

TABLE 18. SEVERITY FACTORS FOR BENZENE-BASED MALEIC ANHYDRIDE MANUFACTURE BY EMISSION POINT

Material emitted	Emission point													
			Refining	Tanks										
	Product recovery scrubber	Secondary scrubber	vacuum system vent	Benzene storage tank	Benzene storage tank	Xylene storage tank	Xylene use tank	Crude maleic anhydride storage tank	Crude maleic anhydride storage tank	Crude maleic anhydride storage tank	Refined maleic anhydride storage tank	Refined maleic anhydride storage tank	Crude maleic acid storage tank	Fugitive emissions
Criteria pollutants														
Carbon monoxides	0.73	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Hydrocarbons	25.1	22.4	0.62	0.13	0.62	0.0004	0.003	0.61	0.61	0.21	0.054	0.20	0.14	14.1
Chemical substances														
Toluene	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Benzene	25.8	[b]	[b]	0.13	0.62	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	4.34
Acetaldehyde	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Formaldehyde	18.3	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Formic acid	1.89	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Maleic acid	25.1	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Maleic anhydride	25.1	22.4	0.62	[b]	[b]	[b]	[b]	0.61	0.61	0.21	0.054	0.20	0.14	17.3
Quinone	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Cresol(s)	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Xylenes	0.22	[b]	[b]	[b]	[b]	0.0004	0.003	[b]	[b]	[b]	[b]	[b]	[b]	0.40
Biphenyl	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Dimethylphenol(s)	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Methylnaphthalene(s)	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Dimethyl/ethylnaphthalene	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_3/C_4 Naphthalenes	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_6 Alkanes	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_7 Alkanes	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_3/C_4 Alcohols	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
C_{12}-C_{17} Hydrocarbons	[c]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]

[a] All severity factors computed in this table are based on the emission factors in Table 15.

[b] Assumed to be negligible.

[c] Severity not calculated owing to lack of emission-factor data.

Industry Contribution to Total Atmospheric Emissions

The mass emissions of criteria pollutants (carbon monoxide and hydrocarbons) resulting from maleic anhydride production were calculated using the emission factors from Table 15 and the production capacity data from Table 9. The appropriate emission factor was multiplied by the production capacity nationwide and for each state in which maleic anhydride plants are located. The total mass emissions from all sources nationwide and for each state were obtained (46) and the percent contributions to the total emissions resulting from benzene-based maleic anhydride production were computed using these values. The results are presented in Table 19 for nationwide emissions and Table 20 for individual state emissions.

TABLE 19. CONTRIBUTION OF THE MALEIC ANHYDRIDE INDUSTRY TO NATIONAL EMISSIONS OF CRITERIA POLLUTANTS

Material emitted	National emissions, (39) metric tons/yr[a]	Maleic anhydride emissions, metric tons/yr[b]	Maleic anhydride contribution, %
Carbon monoxide	8.813×10^7	136,400	0.15
Hydrocarbons	1.658×10^7	23,100	0.14

[a] National emissions for stationary sources only.

[b] Emission rate = 0.92 x (total industry capacity) x (emission factor). Table 15 lists the emission factors for maleic anhydride manufacture.

[c] Assumed to be negligible.

Affected Population

A measure of the population which is exposed to a high contaminant concentration due to a representative maleic anhydride plant can be obtained as follows. The values of x, the downwind distance from the source, for which

$$\frac{\bar{\chi}(x)}{F} \geq 0.1 \text{ or } \geq 1.0 \qquad (12)$$

(46) Eimutis, E. C., and R. P. Quill. Source Assessment: State-by-State Listing of Criteria Pollutant Emissions. EPA-600/2-76-032, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1977. p. 6.

TABLE 20. EMISSIONS OF CRITERIA POLLUTANTS FROM THE MALEIC ANHYDRIDE INDUSTRY BY STATE

Material emitted	State	Total emissions, (39) metric tons/yr[a]	Emissions from maleic anhydride plants, metric tons/yr[b]	Maleic anhydride contribution, %
Carbon monoxide	Illinois	6.401×10^6	32,400	0.5
	Missouri	1.134×10^5	28,400	2.5
	New Jersey	1.158×10^5	15,100	1.3
	Pennsylvania	1.794×10^7	30,800	0.2
	Texas	1.913×10^6	13,500	0.7
	West Virginia	2.092×10^6	16,200	0.8
Hydrocarbons	Illinois	8.286×10^5	5,500	0.7
	Missouri	3.099×10^5	4,800	1.5
	New Jersey	6.341×10^5	2,600	0.4
	Pennsylvania	9.022×10^5	5,200	0.6
	Texas	2.184×10^6	2,300	0.1
	West Virginia	1.623×10^5	2,700	1.7

[a] Total emissions are from stationary sources only.

[b] Emission rate = 0.92 x (total industry capacity) x (emission factor). Table 15 lists the emission factors for maleic anhydride manufacture.

are determined by iteration. The value of $\bar{\chi}(x)$, the mean ground level concentration, is computed from the following equation:

$$\bar{\chi}(x) = \frac{2.03\ Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \quad (13)$$

where

$$\sigma_z = 0.113\ x^{0.911},\ m \quad (14)$$

for atmospheric stability class C (neutral conditions) (47). The affected area is then computed as

$$A = \pi(x_2^2 - x_1^2),\ km^2 \quad (15)$$

where x_1 and x_2 are the two roots of Equation 12.

The capacity-weighted mean population density, $\bar{D}_p$, is calculated as follows:

$$\bar{D}_p = \frac{\sum_i C_i D_{p_i}}{\sum_i C_i},\ persons/km^2 \quad (16)$$

where C_i = production capacity of plant i, metric tons/yr

D_{p_i} = county population density for plant i, persons/km^2

The product $A \cdot \bar{D}_p$ is designated the "affected population."

The affected population was computed for each compound and each source for which the severity factor, S, exceeds 0.1 and/or exceeds 1.0. The mean population density for benzene emissions from maleic anhydride plants is 1,204 persons/km^2. Further, the total number of people affected by benzene emissions from a representative maleic anhydride plant based on a severity factor greater than or equal to 1.0 is 21,500 persons, and that based on a severity factor greater than or equal to 0.1 is 243,000 persons.

---

(47) Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

SECTION 5

CONTROL TECHNOLOGY

INSTALLED CONTROLS

The maleic anhydride industry in the United States currently employs four types of air pollution control techniques: 1) scrubbing, 2) adsorption, 3) incineration, and 4) controlled venting of storage tanks. Available information on the application of specific control devices at nine maleic anhydride plants is summarized in Table 21.

The product recovery scrubber serves as process equipment rather than as an air pollution control device since it is used to recover maleic acid. Atmospheric emissions of benzene from this unit have the largest source severity (i.e., S = 25.8) of all point sources in a representative maleic anhydride plant. Two plants control these benzene emissions by adsorption on activated carbon with a design recovery efficiency of 98% (22). Other control devices in use are wet scrubbers and catalytic or thermal incinerators. By using the exhaust gas from the product recovery scrubber (stream 28 in Figure 1), as the feed for an incincerator, the fuel value of the large carbon monoxide content of the gas can be reclaimed.

Control devices presently used on storage tanks include conservation vents, floating roofs, and carbon adsorbers for benzene emissions, and return vents and scrubbers for maleic anhydride emissions. Conservation vents can also be used to minimize breathing losses from crude and refined maleic anhydride storage tanks. However, emissions from some storage tanks are vented directly to the atmosphere.

Emissions of maleic anhydride particles from flaking, pelletizing, and packaging operations are typically controlled by venting to a secondary scrubber. Other possibilities for controlling emissions from packaging operations are the use of cyclones or baghouses.

INCINERATOR

TABLE 21. CONTROL DEVICES CURRENTLY USED BY THE MALEIC ANHYDRIDE INDUSTRY IN THE U.S.

Company	Emission point					
	Flaking, pelletizing, and packaging	Product recovery scrubber	Secondary scrubber	Aqueous waste storage	Vacuum system vent	Storage tank vents
Amoco Chemicals Corp.	N.R.[a]	N.R.	N.R.	Incinerator	N.R.	N.R.
Ashland Oil, Inc.[b]	_c	Scrubber	_d	_c	N.R.	Floating roof tanks
Denka Chemical Corp.[e]	Scrubber	Incinerator	_d	_c	Scrubber	Floating roof tanks
Koppers Company, Inc.[f]	Scrubber	Incinerator	_d	_c	N.R.	Return vents, carbon adsorber
Monsanto Co.[g]	Scrubber	_h	_d	_c	_c	Scrubber
Reichhold Chemicals, Inc.[i] (Elizabeth, New Jersey)	Scrubber	Carbon adsorber	N.R.	_c	N.R.	Conservation vents
Reichhold Chemicals, Inc.[j] (Morris, Illinois)	_c,k	Carbon adsorber	N.R.	Incinerator - scrubber	_h	Scrubber, conservation vents
Tenneco, Inc.[l]	_h	_h	_c	_c	N.R.	Scrubber, conservation vents
United States Steel Corp.[m]	Scrubber	Catalytic incinerator	N.R.	_c	N.R.	Floating roof tanks

[a] Not reported.

[b] Personal communication from W. Clift, Ashland Chemical Co., Neal, West Virginia, to G. M. Rinaldi, Monsanto Research Corporation, August 10, 1977.

[c] Plant does not have this emission point.

[d] No control because emission point is a control device.

[e] Personal communication from R. Hinkson, Denka Chemical Corp., Houston, Texas, to G. M. Rinaldi, August 11, 1977.

[f] Personal communication from R. C. Ryder, Koppers Company, Inc., Bridgeville, Pennsylvania, to G. M. Rinaldi, August 1, 1977.

[g] Personal communication from M. Pierle, Monsanto Co., St. Louis, Missouri, to T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, November 1976.

[h] No control.

[i] Personal communication from G. P. Baier, Reichhold Chemicals, Inc., Elizabeth, New Jersey, to G. M. Rinaldi, August 10, 1977.

[j] Personal communication from D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, to T. W. Hughes, June 12, 1975.

[k] Personal communication from R. E. White, Hydroscience Environmental Systems, Inc., Knoxville, Tennessee, to T. W. Hughes, November 23, 1977.

[l] Personal communication from S. J. Jelich, Tenneco Chemicals, Inc., Fords, New Jersey, to G. M. Rinaldi, August 10, 1977.

[m] Personal communication from P. Serokis, USS Chemicals, Neville Island, Pennsylvania, to G. M. Rinaldi, August 10, 1977.

ASSESSMENT OF AIR POLLUTION CONTROL METHODS

Methods for controlling air emissions from maleic anhydride (MAN) manufacture include the following:

- Direct thermal incineration with heat recovery
- Direct catalytic incineration
- Carbon adsorption with vapor recovery
- Wet scrubbing with waste disposal

When direct thermal incineration or direct catalytic incineration is applied, the cleaned gases are directed to a stack after waste heat recovery. The carbon adsorption/vapor recovery method consists of collecting organic vapors and returning them in concentrated form to the appropriate process stream. In the case of wet scrubbing, pollutants are absorbed into water, and the contaminated purge liquor is further treated by incineration (32).

The individual processes involved in the above control methods are described in the following subsections. Also included is a technical evaluation of each control method in relation to (a) its ability to reduce air emissions; (b) process and operating parameters that will affect emissions from the control device; (c) changes in process or operating parameters that will affect control efficiency; (d) the operating or maintenance requirements of the processes involved; and (e) technical advantages and disadvantages.

Thermal Incineration

System Description--

Thermal incinerators are used to control the release of hydrocarbon fumes from industrial processes. Inside the incinerator, the hydrocarbon pollutants are oxidized to form carbon dioxide and water. The incinerator consists of a refractory-lined combustion chamber with a raw gas burner fired at one end to supply heat. Since a large amount of fuel is needed to heat the total volume of waste gas, and because the price of fuel is high, some form of heat recovery is practiced to make use of the heat energy contained in the flue gases discharged from the incinerator (32).

Figure 3 shows the steps required for successful incineration of pollutants in a dilute stream. First, the supplemental fuel is burned by utilizing part of the oxygen contained in the dilute fume stream to produce high temperature combustion products (>1200°C). At the same time, the rest of the cold fume bypasses the flame and is mixed with the combustion products in the second step. The mixing gives a nearly uniform temperature to all fumes flowing through the incinerator. This is done as

rapidly as possible without causing flame quenching so that sufficient residence time can be provided at the required temperature in the third step for the oxidation of pollutants contained in the bypassed fume. Residence time is governed by the size of the combustion chamber. Mixing (turbulence) is caused by baffles or by tangential entry of either the dilute fume or the combustion products from the incinerator burner (32).

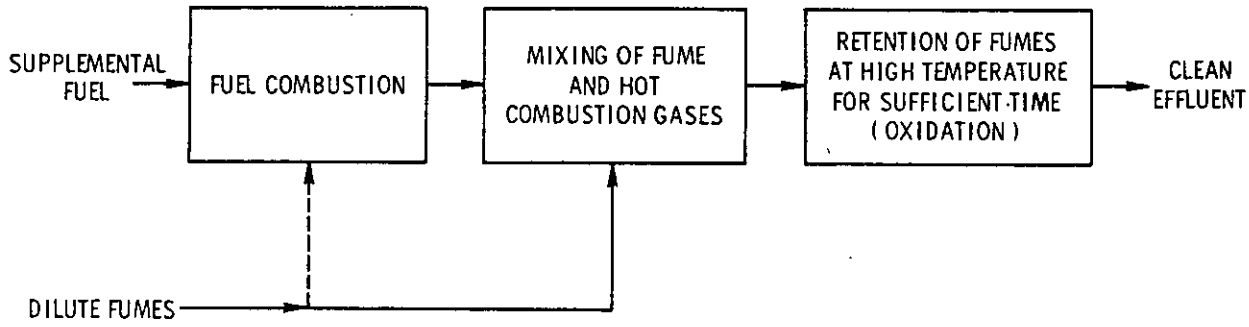


Figure 3. Steps required for successful incineration of dilute fumes (32).

Technical Evaluation--
Thermodynamic considerations--Calculations have been performed (32) to determine whether there is a thermodynamic limitation on the efficiency of incineration of maleic anhydride from the product recovery scrubber vent gas.

The oxidation of maleic anhydride can be expressed as follows:

$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O$$

maleic anhydride

The first step in determining the equilibrium conversion efficiency is to calculate the equilibrium constant for the above reaction according to the following equation:

$$K_p = \exp(-\Delta F/RT) \qquad (17)$$

where $\Delta F = \sum_i \nu_i F_i$ products $- \sum_i \nu_i F_i$ reactants = change in free energy due to reaction
F_i = free energy of formation for component i
ν_i = stoichiometric coefficient of component i
K_p = equilibrium constant at constant pressure
R = gas constant
T = absolute temperature

To obtain the equilibrium constant as functions of temperature, the free energies of formation for H_2O, CO_2, and maleic anhydride in the temperature range of interest are needed (O_2 has a free energy of formation of zero).

The free energy data for CO_2 and H_2 are available for a wide range of temperatures. Unfortunately, similar data for maleic anhydride at incineration temperatures are not available. However, the available data for some hydrocarbons and oxygenated hydrocarbons indicate that the free energy of formation at temperatures around 1,000°K ranges from -20 to 40 kcal/mole (48). The values for H_2O and CO_2 at that temperature are -46.0 and -94.6 kcal/mole, respectively (48). For a worst case estimate, assume that the free energy of formation for maleic anhydride is -20 kcal/mole. The resulting K_p, calculated from Equation 17 for maleic anhydride, is an infinite value.

The above calculations show that there is no theoretical limitation on the conversion efficiencies for maleic anhydride in the incinerator. One hundred percent control efficiency for maleic anhydride removal can be achieved under equilibrium conditions.

Kinetic considerations--Oxidation involves bimolecular reactions between the combustible compound and the oxidizer. The rate at which oxidation proceeds, r, can be approximately represented by the overall expression:

$$r = k(C_{O_2})(C_{combustible}) \qquad (18)$$

where k is the rate constant and C is the concentration. The rate constant, k, is an exponential function of temperature in the following form:

$$k = A \cdot \exp(-E/RT) \qquad (19)$$

with the activation energy, E, typically in the range of 10 to 60 kcal/mole for this overall rate constant (49). For an activation energy of 30 kcal/mole, the reaction rate will double for an increase of temperature from 700°C to 750°C.

---

(48) JANAF Thermochemical Tables, Second Edition. NSRDS-NBS 37, U.S. Department of Commerce, Washington, D.C., June 1971. 1141 pp.

(49) Rolke, R. W., R. D. Hawthorne, C. R. Garbett. E. R. Slater, and T. T. Phillips. Afterburner Systems Study. EPA-R2-72-062, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1972. 512 pp.

In the product recovery scrubber vent gas, the concentrations of combustible materials (including maleic anhydride, benzene, and carbon monoxide) are very small compared to that of O_2. Therefore, the concentration of O_2 in the post-flame area in the incinerator is almost constant despite the consumption due to the oxidation of pollutants. Equation 18 can thus be rewritten as:

$$r = C_{AO} \frac{dX_A}{dt} = k' C_{AO} (1 - X_A) \qquad (20)$$

where C_{AO} = the inlet concentration of pollutant A
X_A = the fractional conversion

Integration of Equation 20 over time, t, gives:

$$-\ln (1 - X_A) = k't = A't \cdot \exp(-E/RT) \qquad (21)$$

This equation shows the fractional conversion as a function of residence time, t, and temperature, T. It should be noted that in deriving Equation 21, it is assumed that perfect mixing (uniform temperature) in the combustion chamber is attained. Figure 4 schematically indicates the general effects of temperature and residence time on the fractional conversion of combustibles in an incinerator (32).

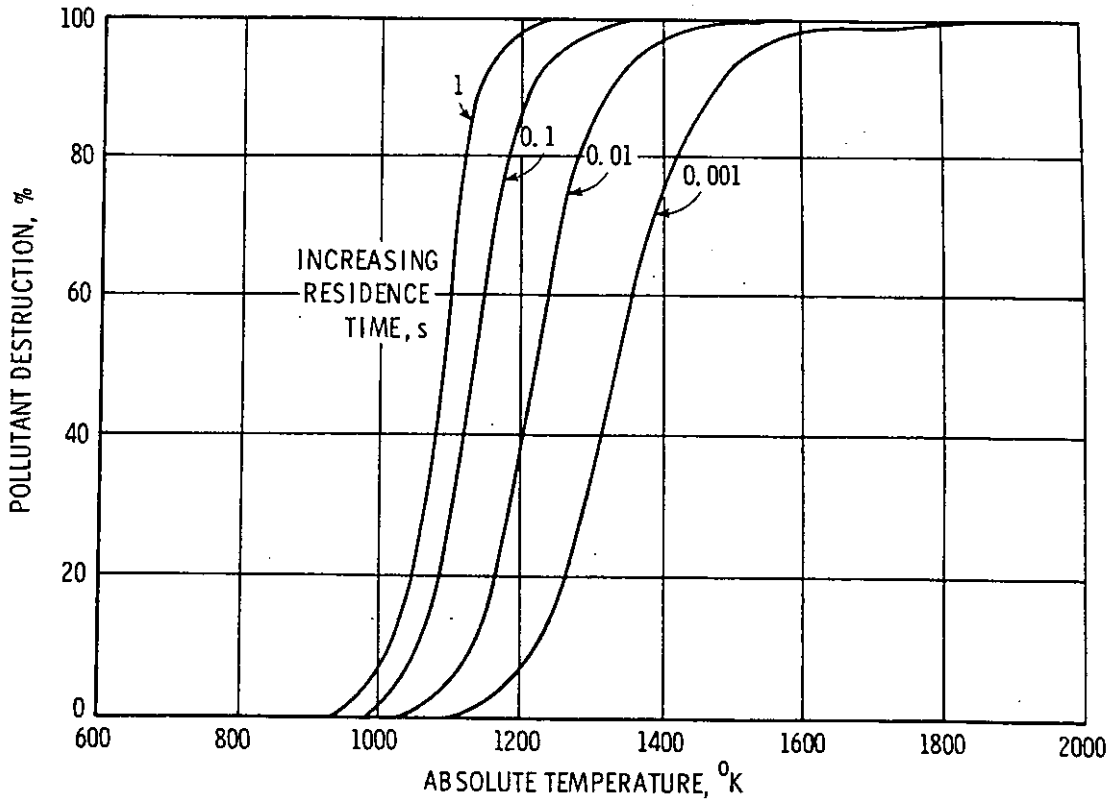


Figure 4. Coupled effects of temperature and time on rate of pollutant oxidation (32).

Past experiences in the incineration of other organic pollutants indicate that the destruction of most hydrocarbons occurs very rapidly at temperatures in excess of 590°C to 650°C (49). Possible exceptions - methane, cellosolve, and benzene derivatives, like toluene - are stable molecules and require a higher temperature (∿760°C) for complete oxidation to occur in a few tenths of a second (49). Since maleic anhydride is an oxygenated hydrocarbon and is an intermediate in the oxidation of hydrocarbons, it is expected that the destruction of this compound would not be more difficult than that of toluene.

Experimental data on the conversion efficiency of benzene and three other hydrocarbons are shown in Figure 5 (49, 50). The curves show that the rate of hydrocarbon disappearance was first order with respect to hydrocarbon concentrations. With a residence time of 0.35 s in an experimental plug-flow reactor, a 99.9% destruction of benzene is possible at 766°C. The initial benzene concentration used to generate the curve in Figure 5 was 1000 ppm on a mole basis (50).

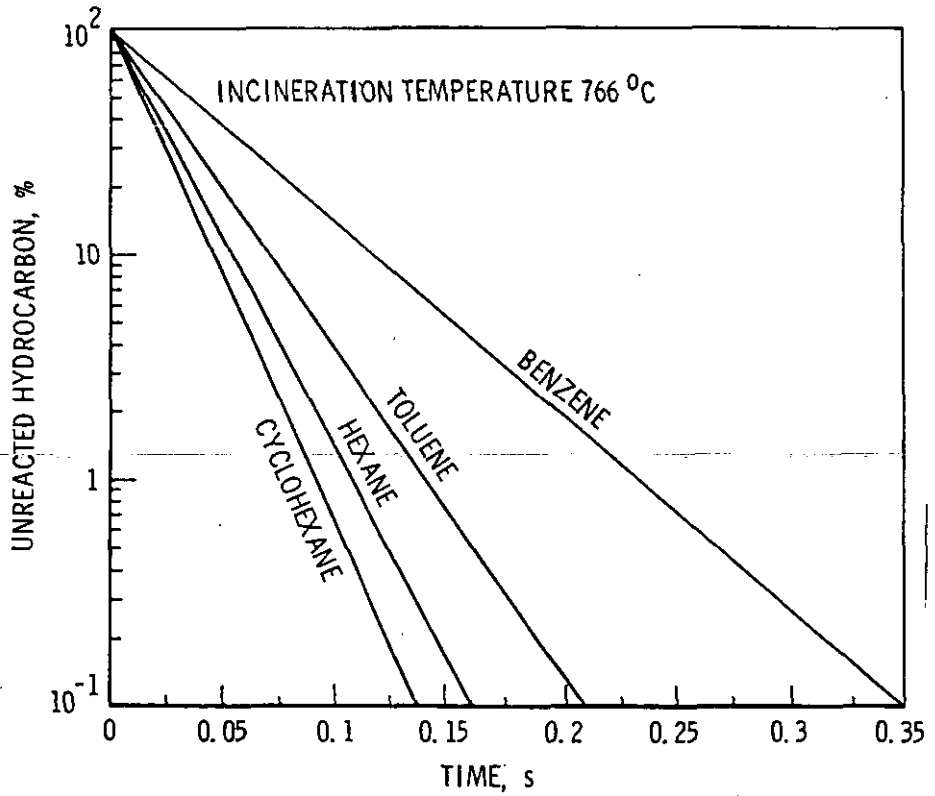


Figure 5. Hydrocarbon oxidation rates in absence of flame (49, 50).

(50) Lee, K. C., H. J. Jahnes, and D. C. Macauley. Thermal Oxidation Kinetics of Selected Organic Compounds. (Presented at the 71st Annual Meeting of the Air Pollution Control Association. Houston. June 25-20, 1978). 16 p.

It is indicated in a systems study that temperatures of 760°C to 816°C are sufficient to obtain nearly complete conversion of most substances in 0.1 s to 0.3 s (42). However, incinerators are usually designed to have total residence times of 0.3 s to 1 s. Even with so much excessive residence time, some of the units still have poor conversion efficiency because time is required for the mixing step and many designs fail to complete the mixing in the distance (time) available. The greatest variation among different incinerator (afterburner) designs is in how well they achieve the goal of raising all of the fume to the required temperature for the required time (42). Most cases of poor performance are due to nonuniform temperatures and flows which allow some of the combustible pollutants to escape without treatment.

NO_x Formation--There are no nitrogen-containing compounds in the product recovery scrubber vent gas. The formation of nitrogen oxides (NO_x) in an incinerator results from the fixation of N_2 and O_2 which are present in the waste gas. Substantially all of the NO_x is formed in the high temperature region (>1150°C) of the burner flame. At the temperature of the main combustion chamber (700°C to 900°C), the overall rate of reaction of nitrogen with oxygen is too slow for significant formation of NO_x (49).

When the combustion chamber temperature is raised to achieve a better control efficiency, the increased supplemental fuel injection into the burner will result in a larger flame size and thus a longer residence time in the high temperature region to form NO_x. It has been estimated that an increase of the incinerator operating temperature from 650°C to 815°C will result in a gain of NO_x emissions from 18 ppm to 22 ppm (49).

Heat Recovery--
When an incinerator is used to control maleic anhydride and other combustible materials in the product recovery scrubber vent gas, large amounts of fuel are needed to heat the large volume of waste gas to the required temperature. Both the high cost and inadequate supply of fuel become problems in operating the incinerator. As a result, some form of heat recovery becomes necessary (32).

Two types of heat recovery equipment are considered in this study. One is the waste heat boiler and the other is the feed-effluent heat exchanger, shown in Figures 6 and 7, respectively.

In the thermal incinerator/waste heat boiler system, the feed gas to the incinerator is not preheated. This permits maximum steam generation but substantially increases the fuel requirements. Since most of the required heat is supplied by supplemental fuel, it is relatively easy to sustain combustion. The major drawback of the system is that steam consumers must be found (32).

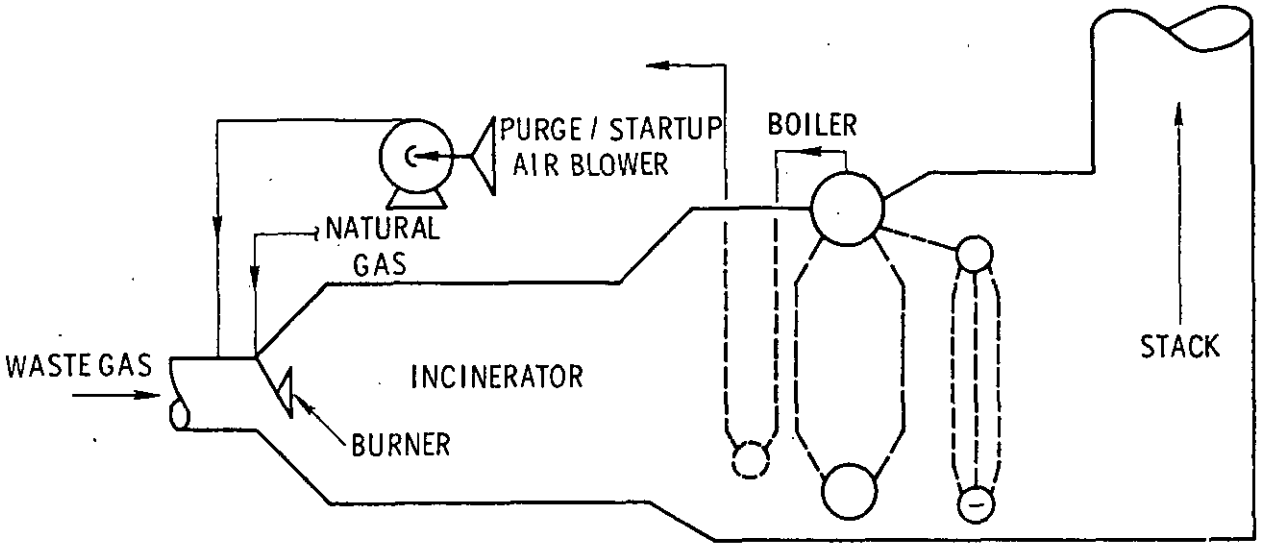


Figure 6. Thermal incinerator with waste heat boiler (32).

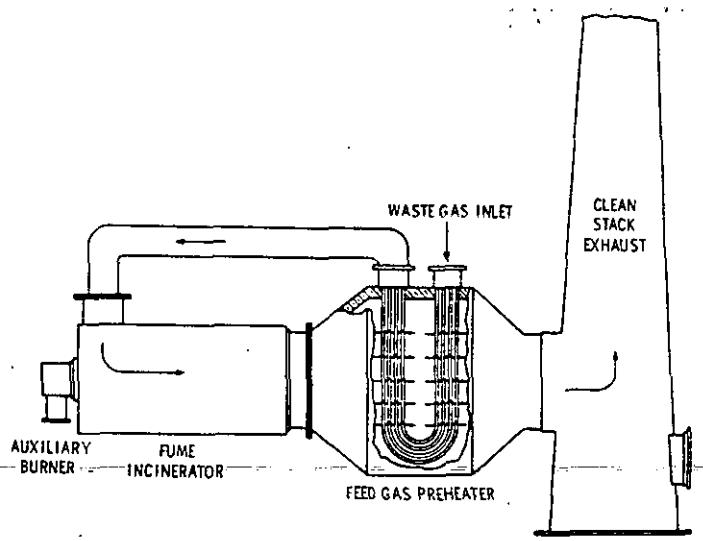


Figure 7. Thermal incinerator with feed gas preheater (1).

In the thermal incinerator/feed-effluent heat exchanger system, the product recovery scrubber vent gas is preheated by the effluent gas from the incinerator; this reduces the fuel requirement for heating the feed gas to the incineration temperature. A problem associated with this system is that preheating of the incinerator feed stream will reduce the amount of burner flame present and thus reduce the radicals generated by the flame for effective destruction of combustible pollutants (42).

---

(51) Ross, R. D. Pollution Abatement: Incineration of Solvent-Air Mixtures. Chemical Engineering Progress, 68(8):59-64, 1972.

Applications in the Maleic Anhydride Industry--
An existing system for the control of emissions from maleic anhydride manufacture uses the exhaust gases from the product recovery scrubber as part of the combustion air stream for a natural-gas-fired incinerator. Such a unit is illustrated in Figure 8, which is based on information obtained by personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

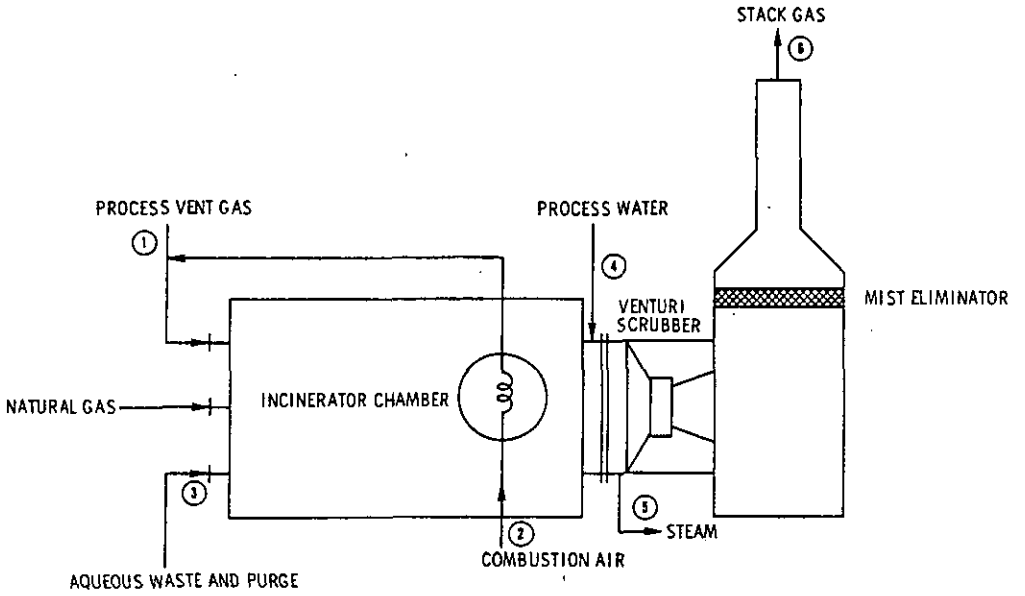


Figure 8. Thermal incinerator-scrubber control system.

A material balance based on the product recovery scrubber vent gas composition (stream 28) of Table 8 is given in Table 22. Oxidation of greater than 99 percent of all combustible species is reported when the scrubber off-gas is burned with air at 1090°C (personal communication between A. W. Lawrence, Koppers Company, Inc., Bridgeville, Pennsylvania, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 28, 1978). The only supplemental fuel required is natural gas for the incinerator pilot. It should be noted that aqueous waste disposal occurs simultaneously. Furthermore, a venturi scrubber is provided to remove any combustion products remaining in the incinerator flue gas before it is released to the atmosphere. One maleic anhydride manufacturer that utilizes process vent gases as the primary air supply for an incinerator-boiler unit reports 95% to 99% removal of carbon monoxide by this system (personal communication from R. C. Ryder, Koppers Company, Inc., Bridgeville, Pennsylvania, to G. M. Rinaldi, Monsanto Research Corporation, Dayton, Ohio, August 9, 1977. Data supplied are the result of testing performed by Dr. J. O. Frohlinger and Dr. D. J. Penkala, University of Pittsburgh, Pittsburgh, Pennsylvania, for Koppers Company, Inc., Bridgeville, Pennsylvania, on January 22-24, 1973).

TABLE 22. MATERIAL BALANCE FOR A THERMAL INCINERATOR-SCRUBBER CONTROL SYSTEM

Stream No.	1	2	3	4	5	6
Description	Process vent gas	Combustion air	Aqueous waste and purge	Process water	Steam	Stack gas
Temperature, °C	38	27	[a]	[a]	[a]	88
Gage Pressure, kPa	0	[a]	[a]	[a]	[a]	0
Component			Flow rate, kg/hr			
Particulates	[b]	[b]	[b]	[b]	[b]	0.2
Oxygen	12,400	3,700	[b]	[b]	[b]	4,900
Nitrogen	65,700	12,700	[b]	[b]	[b]	78,400
Carbon dioxide	3,000	[b]	[b]	[b]	[b]	4,900
Carbon monoxide	1,600	[b]	[b]	[b]	[b]	[b]
Water	3,000	[b]	7,600	3,700	3,700	22,100
Maleic anhydride	7	[b]	18	[b]	[b]	[b]
Maleic acid	7	[b]	37	[b]	[b]	[b]
Benzene	230	[b]	[b]	[b]	[b]	[b]
Formaldehyde	17	[b]	[c]	[b]	[b]	[b]
Formic acid	5	[b]	[b]	[b]	[b]	[b]
Xylenes	28	[b]	[c]	[b]	[b]	[b]
Polymers	[b]	[b]	98	[b]	[b]	[b]
Sulfur oxides	[c]	[b]	[b]	[b]	[b]	[b]
TOTAL	86,000	16,400	7,800	3,700	3,700	110,000

[a] Unknown.

[b] Assumed to be negligible.

[c] Trace.

Another maleic anhydride plant uses thermal incineration to burn 100,000 kg/hr of waste gases containing 0.25 wt % hydrocarbons and 1.8 wt % carbon monoxide (52). The corrosive waste gas stream is fed to a stainless steel incinerator which was designed to operate at 760°C with a residence time of 0.7 s (52). The residence time is longer, and the control efficiency below is less, than that indicated by Figure 5 because backmixing which occurs in a commercial-scale incinerator downgrades performance relative to that observed during experimentation due to dilution and "short-circuiting" effects (50). The natural gas requirement for this unit is about 2,300 m^3/hr (at 16°C and 101.3 kPa), and the heat recovery system generates 32,000 kg/hr of steam at 5.2 MPa (52). The control efficiencies of the above incinerator for a maleic anhydride production plant are greater than 98% for hydrocarbons and approximately 50% for carbon monoxide, as determined from the data of Table 23 (31).

TABLE 23. SUMMARY OF SOURCE TESTING OF A THERMAL INCINERATOR AT A MALEIC ANHYDRIDE PRODUCTION PLANT (31)

	Pollutant concentration, ppm			
	Benzene		Carbon monoxide	
Run No.	Incinerator inlet	Incinerator outlet	Incinerator inlet	Incinerator outlet
1	780	11.1	>2,000	>1,060
2	820	11.8	>2,130	>1,070
3	940	14.4	>1,990	>950

Catalytic Incineration

System Description--

A catalytic incinerator is an alternative to a thermal incinerator as a means of oxidizing gaseous hydrocarbons (including oxygenated hydrocarbons) to carbon dioxide and water. Contact of a waste stream with a catalyst bed allows the oxidation reaction to occur rapidly at a lower temperature than that required in a thermal incinerator and decreases fuel consumption (32).

(52) Preussner, R. D., and L. D. Broz. Air Pollution Control: Hydrocarbon Emission Reduction Systems. Chemical Enginering Progress, 73(8):69-73, 1977.

The solid-catalyzed vapor-phase reaction has five steps:

- Diffusion of the reactants through the stagnant fluid around the surface of the catalyst
- Adsorption of the reactants on the catalyst surface
- Reaction of the adsorbed reactants to form products
- Desorption of the products from the catalytic surface
- Diffusion of the products through the pores and surface film to the bulk vapor phase outside the catalyst.

The various noble metals such as platinum, palladium, rhodium, etc., in varying concentrations, cause different reaction rates for each specific hydrocarbon. However, in air pollution control, it is not practical to undertake a research program to develop a specific catalyst for each problem. Therefore, commercial catalyst manufacturers have attempted to make available a universal catalyst which is effective in oxidizing the entire range of organic materials over an extended period of exposure time with minimum maintenance and replacement (32).

Technical Evaluation--
Reduced catalyst life due to possible fouling or poisoning is a problem with catalytic incinerators. Maleic anhydride may polymerize with organic material in the product recovery scrubber vent gases and deposit coke over the active sites of the catalyst (32).

Past experience in the use of catalytic incinerators for other air pollution sources indicates that removal efficiencies of 90% to 95% can be achieved (32). However, the catalyst volume required for very high conversions (e.g., >98%) generally makes these units uneconomical, or the unit must be operated at temperatures close to that required for thermal incineration (49).

Applications in the Maleic Anhydride Industry--
Only one maleic anhydride plant currently has a low-temperature catalytic incinerator for controlling hydrocarbon emissions from the product recovery scrubber (personal communication between G. M. Rinaldi, Monsanto Research Corporation, Dayton, Ohio, and P. Serokis, USS Chemicals, Neville Island, Pennsylvania, August 10, 1977). This unit is designed to reduce benzene emissions by greater than 85% and carbon monoxide emissions by greater than 95% (53).

---

(53) Mackay, J. S. Statement to the National Air Pollution Control Techniques Advisory Committee on EPA's Proposed Standard for Benzene Emissions from Maleic Anhydride Plants. August 22-23, 1978.

Carbon Adsorption

The degree of benzene conversion to maleic anhydride decreases as the catalyst degenerates. Benzene recovery from the product recovery scrubber vent gas would reduce operating costs and eliminate benzene as an atmospheric emissions; it can be achieved by absorption onto activated carbon.

System Description--
Adsorption is the process for removing molecules from a fluid by contacting them with a solid. The important characteristics of activated carbon as an adsorbent are its large surface-to-volume ratio and preferential affinity for organic materials (54). Adsorption is a three-step process. First the adsorbent contacts the fluid, and adsorption results. Then the unadsorbed portion of the fluid is separated from the adsorbent. For gases, this operation is completed when the gases leave the adsorbent bed. Third, the adsorbent is regenerated by removal of the adsorbate (benzene). Low-pressure steam is used for the regenerate, and the condensed vapors are separated from the water by decantation, distillation, or both (54).

Activated carbon is capable of adsorbing 95% to 98% of the organic vapor from air at ambient temperature in the presence of water in the gas stream (55). When an organic vapor-in-air mixture starts to pass over activated carbon, complete adsorption of the organic vapor takes place. As the retentive capacity of the activated carbon is approached, traces of vapor appear in the exit air, indicating that the activated carbon has reached its breakpoint.

Figure 9 illustrates this change in operating characteristics of the carbon bed while removing a single organic compound (56). As the flow of contaminated gas is continued, additional amounts of organic material are adsorbed, but the concentration of the organic compound in the outlet increases and eventually equals that in the inlet. At this stage, the carbon is saturated at the operating temperature and pressure of the adsorption system.

---

(54) Hughes, T. W., D. A. Horn, C. W. Sandy, and R. W. Serth. Source Assessment: Prioritization of Air Pollution from Industrial Surface Coating Operations. EPA-650/2-75-019a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1975. 303 pp.

(55) Hydrocarbon Pollutant Systems Study, Vol. L. Stationary Sources, Effects, and Control. MSA Research Corporation, Evans City, Pennsylvania. Report No. APTD-1499, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1972. 377 pp.

(56) Air Pollution Engineering Manual, Second Edition. J.A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

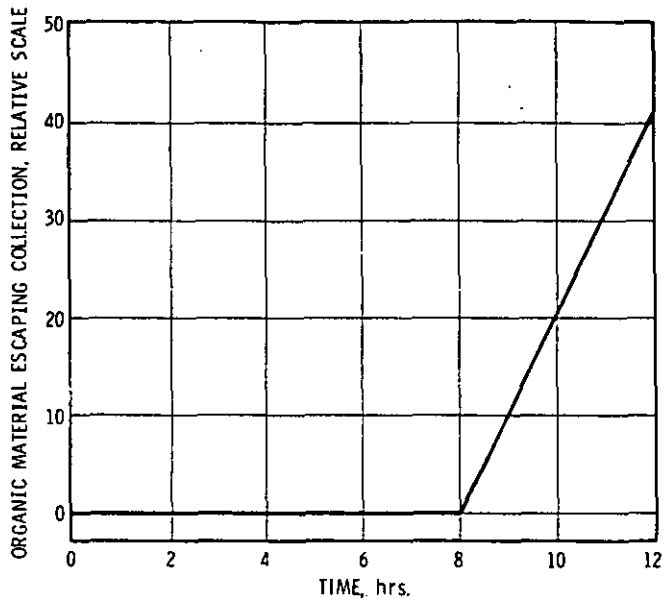


Figure 9. Adsorption efficiency of a carbon bed for a single organic compound (56).

The adsorption of a mixture of organic vapors in air is not uniform; the more easily adsorbed components are those with the higher boiling points. When air containing a mixture of organic vapors is passed over activated carbon, the vapors are equally adsorbed at the start. However, as the amount of the higher boiling component in the adsorbent increases, the more volatile component revaporizes. The exit vapor consists primarily of the more volatile component after the breakpoint has been reached. This process continues for each organic mixture component, as shown in Figure 10, until the highest boiling component is present in the exit gas. In the control of organic vapor mixtures, the adsorption cycle should be stopped when the first breakpoint occurs as determined by detection of vapors in the exit gas (56).

After the breakpoint of the activated carbon adsorbent has been reached, the bed is regenerated by heating it with low-pressure saturated steam until adosrbed materials revaporize. Superheated steam at temperatures greater than 300°C may be necessary to drive off high-boiling organic compounds (56).

Steam requirements for regeneration are a function of external heat losses and the nature of the organic adsorbates. The amount of steam required per kilogram of adsorbate, as a function of elapsed time, passes through a minimum. The carbon should be regenerated for this length of time to permit the minimum use of steam (56). After regeneration, the hot, water-saturated carbon is cooled and dried by blowing organic-free air through the carbon bed. Evaporation of the water aids cooling of the carbon. If high temperature steam has been used, other means of cooling the carbon are required.

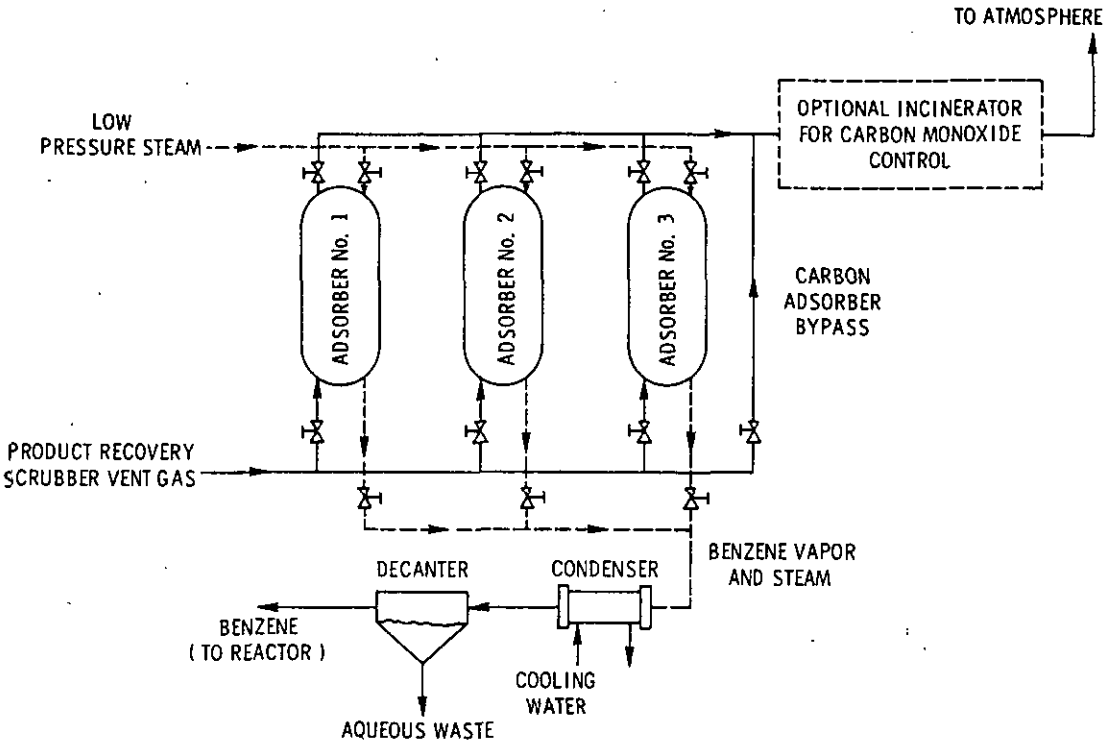


Figure 11. Carbon adsorption system for emissions from maleic anhydride production.

Technical Evaluation--
From the mass balance for a similar source, phthalic anhydride manufacture, the concentration of organic compounds in the exit gases from a regenerating carbon adsorber may be more than 20 times that in the contaminated inlet stream (32). When controlling emissions from the product recovery scrubber at a maleic anhydride plant, the exit gases will contain a large fraction of benzene, an expensive raw material whose recovery is economically desirable.

From the theory of carbon adsorption described above, this control method can achieve nearly 100% reduction of hydrocarbon emissions. However, it is difficult to estimate the service life of an adsorber bed for use at a maleic anhydride plant without laboratory tests to determine the retentivity of benzene and other organics on the carbon bed under specific operating conditions. The possibility of polymeric materials forming on the activated carbon surface when high-temperature steam is used for regeneration should be considered (32).

Since maleic acid, formic acid, fumaric acid, and other organic acids are present in the product recovery scrubber vent gas, and high-temperature steam may be used to regenerate the adsorber beds, the materials of construction are potentially subject to corrosion. Stainless steel vessels, stainless steel pipes, and corrosion-resistant valves are necessary (32).

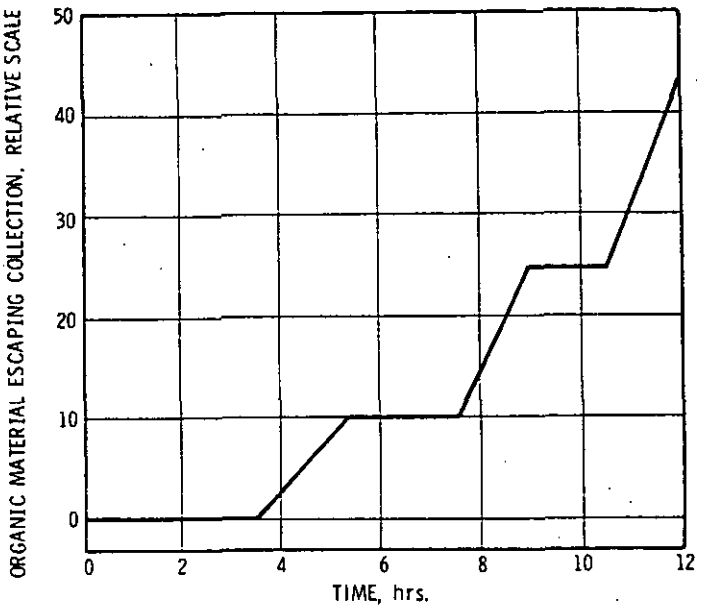


Figure 10. Adsorption efficiency of a carbon bed for a three-component mixture (56).

The equipment used for control of organic vapors by carbon adsorption consists of vessels which hold the solid adsorbent and auxiliary equipment for regeneration of the adsorbent and recovery or disposal of the adsorbate. The simplest adsorber design of this type is a two-bed system where one carbon bed is being regenerated as the other is adsorbing organic vapors. In a three-bed arrangement (Figure 11), a greater quantity of material can be adsorbed per unit of carbon because the effluent passes through two beds in series while the third bed is being regenerated. This permits the activated carbon to be used after breakthrough since the second bed in the series removes organic vapors in the exit gas from the first bed. When the first bed is saturated, it is removed from the stream for regeneration; the bed which was used to remove the final traces of organic vapors from the effluent then becomes the new first bed; and the bed which has been regenerated becomes the new second bed (54).

The off-gases from a carbon adsorber that is being regenerated are passed on to a condenser and then to a decanter. In the case of maleic anhydride operations, the organic layer will consist of benzene, which can be recycled to the reactor. The aqueous waste layer is pumped to an incinerator-scrubber for disposal (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and R. E. White, Hydroscience Environmental Systems, Inc., Knoxville, Tennessee, November 13, 1977).

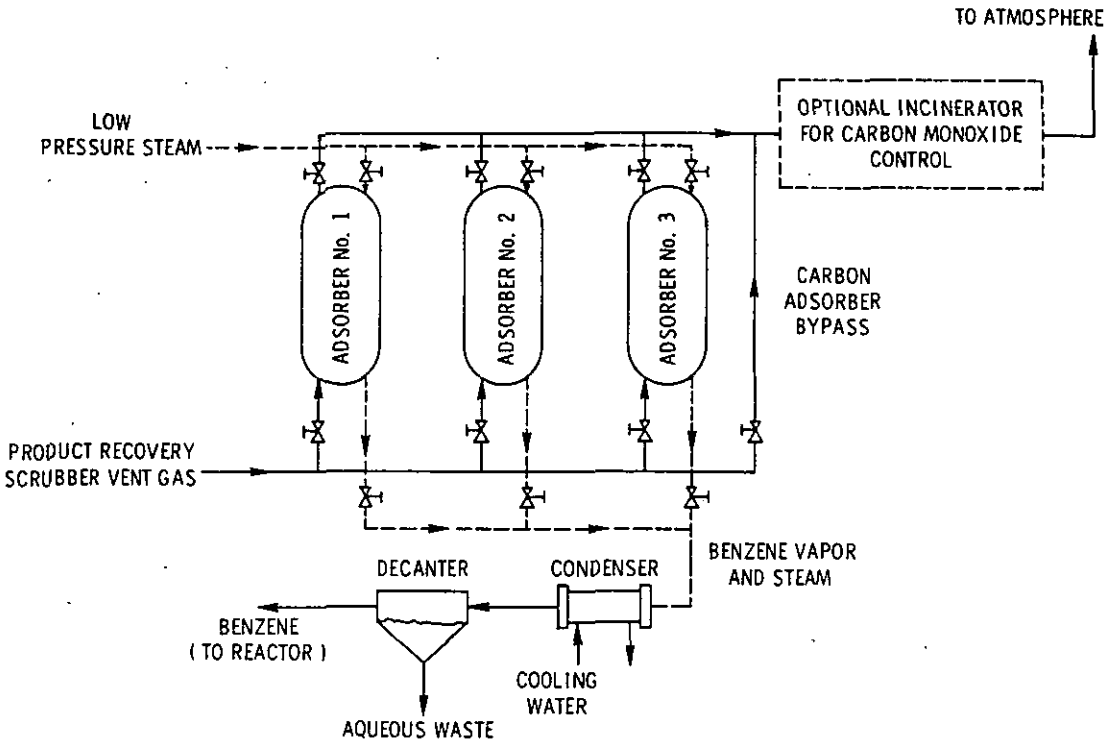


Figure 11. Carbon adsorption system for emissions from maleic anhydride production.

Technical Evaluation--
From the mass balance for a similar source, phthalic anhydride manufacture, the concentration of organic compounds in the exit gases from a regenerating carbon adsorber may be more than 20 times that in the contaminated inlet stream (32). When controlling emissions from the product recovery scrubber at a maleic anhydride plant, the exit gases will contain a large fraction of benzene, an expensive raw material whose recovery is economically desirable.

From the theory of carbon adsorption described above, this control method can achieve nearly 100% reduction of hydrocarbon emissions. However, it is difficult to estimate the service life of an adsorber bed for use at a maleic anhydride plant without laboratory tests to determine the retentivity of benzene and other organics on the carbon bed under specific operating conditions. The possibility of polymeric materials forming on the activated carbon surface when high-temperature steam is used for regeneration should be considered (32).

Since maleic acid, formic acid, fumaric acid, and other organic acids are present in the product recovery scrubber vent gas, and high-temperature steam may be used to regenerate the adsorber beds, the materials of construction are potentially subject to corrosion. Stainless steel vessels, stainless steel pipes, and corrosion-resistant valves are necessary (32).

Application in the Maleic Anhydride Industry--
Two maleic anhydride plants use the carbon adsorption method to control hydrocarbon emissions from the product recovery scrubber. A third plant uses a carbon adsorber to collect ventings from benzene storage tanks when recycle to the reactor feed stream is not possible (personal communication between G. M. Rinaldi, Monsanto Research Corporation, Dayton, Ohio, and R. G. Ryder, Koppers Company, Inc., Bridgeville, Pennsylvania, August 1, 1977).

Figure 12 was prepared from operating data for a carbon adsorption system used to control benzene emissions from the product recovery scrubber (personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and R. E. White, Hydroscience Environmental Systems, Inc., Knoxville, Tennessee, November 23, 1977). The gas stream vented to the three-bed adsorber arrangement contained an average of 3,314 ppm of benzene, and the flow rate of contaminated air was approximately

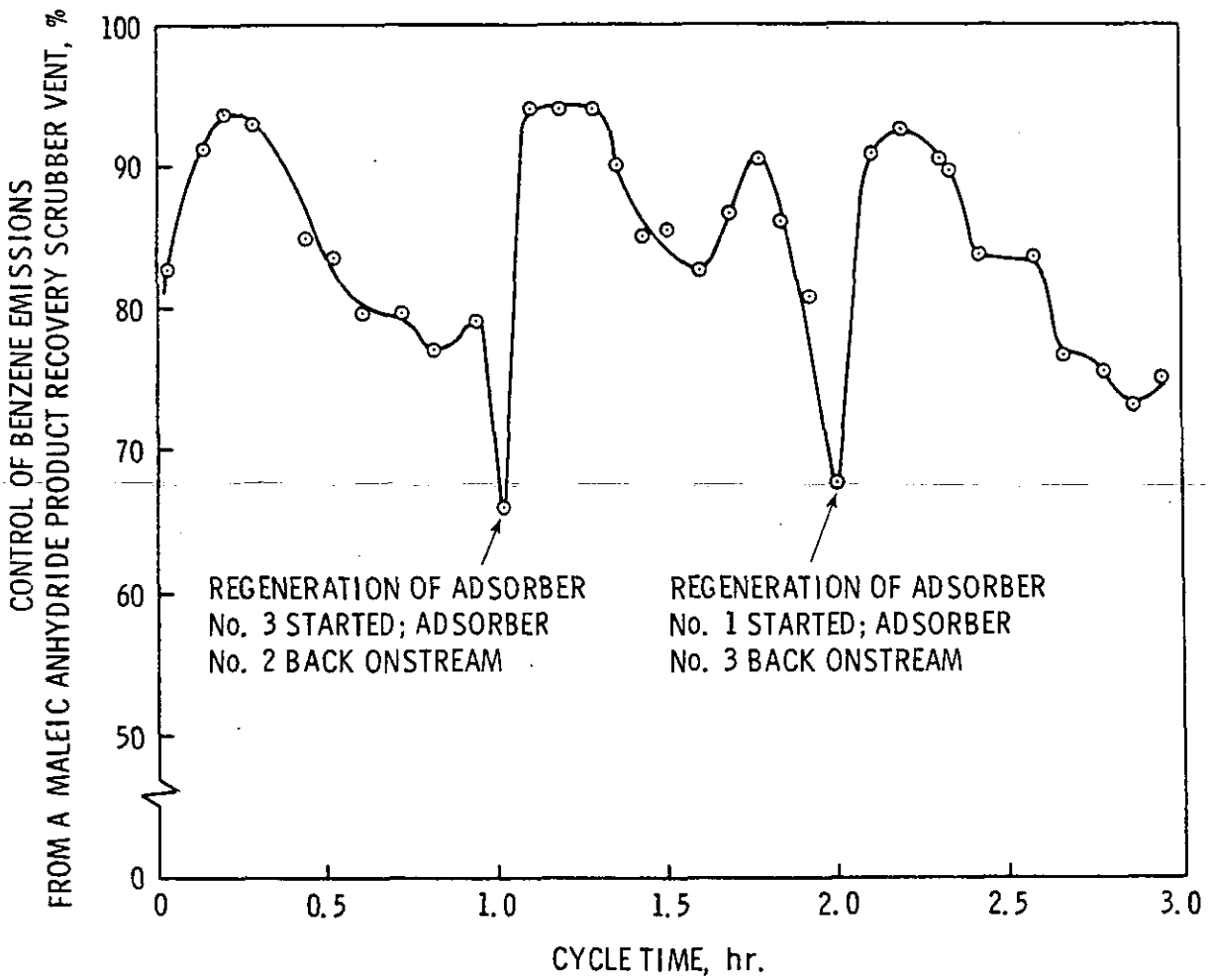


Figure 12. Control of benzene emissions from maleic anhydride production by three-bed carbon adsorption.

70,800 kg/hr. Benzene emissions were reduced by 66% and 94% with a design control efficiency of 98% (22). There are several possible reasons why the operating efficiency of this adsorber is less than the design value. The moisture content of the contaminated inlet stream is high, and breakthrough may occur before switching to another bed is accomplished. Organic-free gas is not used to cool the adsorber beds after steam regeneration, thus accounting for the drop in control efficiency after regeneration. For a very brief period, only one carbon bed is actually adsorbing benzene from the contaminated vent gases, as opposed to the two beds operating in series under normal conditions. In addition, polymerization of organic acids and aldehydes on the surface of the activated carbon granules can adversely affect control efficiency.

Wet Scrubbing

System Description--

Scrubbers can be used to control both vapor-phase pollutants and particulates emitted from faliing, pelletizing, and packaging operations at maleic anhydride production plants. A schematic diagram for a wet scrubber system is presented in Figure 13. Note that waste disposal is included in the system. This is necessary because wet scrubbing produces a secondary pollution problem caused by the discharge of the purge liquor. If this liquid discharge is not properly handled, an air pollution problem is traded for a water pollution problem.

Maleic anhydride would be hydrolyzed to maleic acid on adsorption into the scrubbing liquor. To concentrate the purge liquor for easier disposal (by minimizing the volume of the effluent stream), a certain degree of scrubbing liquor recycling is necessary. The means of purge liquor disposal considered here is incineration. This process is described in Section 5, following the technical evaluation of wet scrubbing.

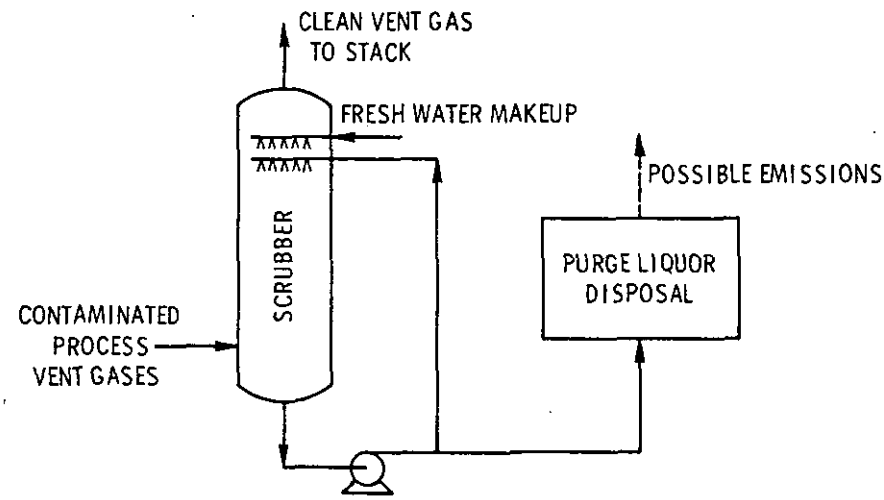


Figure 13. Wet scrubber/waste disposal system (32).

A new wet scrubber design (57) for treating process vent gases from maleic anhydride production is illustrated in Figure 14. The unit consists of two stages, each of which contains a conventiontal fluid-bed packing on a supporting grid. The two stages are separated by a cone-shaped deflector plate and collection tray. The unit is designed to operate between 35°C and 40°C with an organic removal efficiency of 98% and 99%. This high efficiency is possible because most of the organics are solids at the scrubber operating conditions.

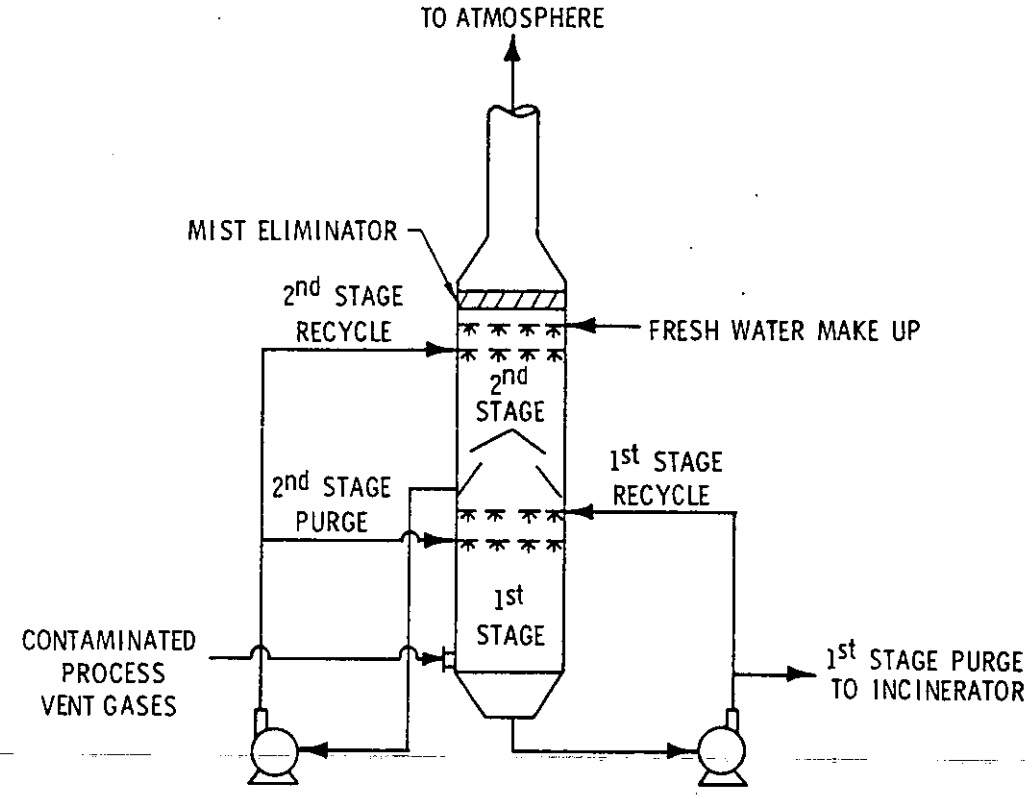


Figure 14. Schematic diagram of scrubber for emissions from maleic anhydride production (58).

The scrubbing liquor for the first stage consists of the purge from the second stage and the first stage recycle stream. The liquor is a slurry, containing 10% to 12% by weight of organic solids. The concentration of organic compounds, both dissolved and in the form of slurry solids, ranges from 10% to 50% by

(57) Ferrari, D. C., and C. G. Bertram. Method and Apparatus for Removal of Organics from Chemical Waste Gases. U.S. Patent 3,624,984 (to Badger Company), December 7, 1971.

(58) Yevzel'man, I. B., and G. D. Kharlampovish. Neutrailization of Exhaust Gas from Phthalic Anhydride Production. Khimicheskaya Promyschlennost (Moscow), 49(6):379-380, 1983.

weight, depending on the composition of the gas being treated. A portion of the recycle stream is continously purged and sent to a waste disposal process.

In the second stage, the gas is scrubbed with a dilute solution (0.5% to 3% by weight) of organic pollutants (chiefly maleic acid). Fresh water is added to the second state at a rate sufficient to replace the water removed from the scrubber in the two exit streams. The makeup water combines with the second stage recycle stream to form the second stage scrubbing liquor. The scrubbed gas stream passes through a mist eliminator and is then vented to the atmosphere.

Technical Evaluation--
In order to obtain a given overall removal efficiency for maleic anhydride, the wet scrubber would be able to remove this pollutant from a gas stream with a higher efficiency. This is due to the possibility of air emissions from the waste disposal area which should be accounted for as emissions from the control system.

In this particular case, the removal of maleic anhydride by the scrubber is achieved by two distinct mechanisms. The first is the removal of solid particles by scrubbing. The second is absorption of maleic anhydride vapor into the scrubbing liquid.

The operating temperature of the scrubber shown in Figure 14 can be maintained at approximately 38°C (32). At this temperature, maleic anhydride is soluble in amounts up to 40 wt % of maleic acid (57).

From data obtained from a Russian article (58), the Henry's law constant for maleic anhydride at the scrubber temperature was estimated to be 1.55×10^{-5}. This constant defines the vapor content of a particular component in a gas mixture which is in equilibrium with a dilute solution of the said component. This small value of the Henry's law constant, together with the high solubility of maleic anhydride in water, indicates that even if the scrubbing liquid is recycled to provide concentrated purge liquior (and hence reduce the volume of the liquid efficient), the resulting maleic anhydride vapor in the gas phase is still very low. For example, supposing the purge liquor has a concentration of 20% maleic acid, under equilibrium conditions, the concentration of maleic anhydride in the gas phase will be 6.99×10^{-5} volume percent (32).

Liquid Waste Disposal--
The liquid purge discharged from the multistage wet scrubber, described in Section 5, will contain relatively high concentraions of organic chemicals, such as maleic acid, which can be disposed of in a thermal incinerator (Figure 15). The liquid purge stream is atomized immediately before entering the combustion area of the incinerator by either steam or an air stream.

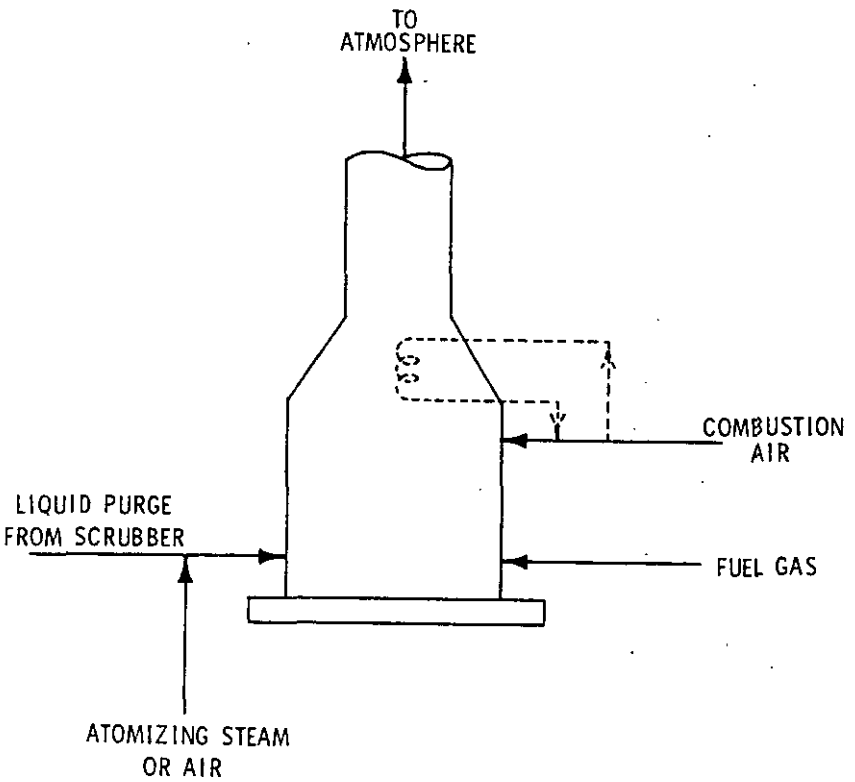


Figure 15. Schematic diagram of thermal incinerator for scrubber purge liquor (57).

Fuel gas (e.g., methane) and combustion air (25% in excess of the stoichiometric amount) are introduced into the incinerator in a conventional manner to provide an operating temperature of 760°C to 870°C (32). Heat recovery can be achieved by means of a coil which can be used either to preheat the combustion air (as shown in Figure 15) or to generate steam.

The incinerator reportedly attains an efficiency of 99.9% conversion of organic materials (57). This high combustion efficiency becomes possible due to the smaller size of this incinerator (as compared with the direct thermal incinerator mentioned in Section 5) which permits better mixing in the combustion chamber. The liquid waste (which contains solid particles) is first evaporated and then burned in the main combustion chamber of the incinerator.

SECTION 6

GROWTH AND NATURE OF THE INDUSTRY

PRESENT TECHNOLOGY

Maleic anhydride is currently produced in the U.S. via the fixed-bed benzene oxidation process, from n-butane employing multiple-stage reactors, and as a byproduct of phthalic anhydride manufacture. Over the years, benzene has been valued as a feedstock because of its high yields, low cost, availability, and the lower capital cost required to process it. However, the need for low-lead and no-lead motor fuels has resulted in an increase in the value of benzene as a blending component of high-octane fuels. Hence, the price of benzene feedstock has increased. In Europe and Asia, C_4 hydrocarbons, especially n-butenes and BB fractions (containing n-butene and butadienes), have become available from large naphtha crackers in ever-increasing, low-cost quantities, and they are being selected over benzene as the feedstock in those areas.

A few years ago, in anticipation of the rising cost of benzene, maleic anhydride manufacturers began research and development programs on the use of an alternate feedstock. Two U.S. maleic anhydride manufacturers (Monsanto and Amoco), have recently converted a portion of existing capacity and brought new capacity onstream, respectively, to produce maleic anhydride using n-butane as a feedstock.

EMERGING TECHNOLOGY

The increased cost of benzene has recently intensified interest in converting n-butane to maleic anhydride. Commercial production of maleic anhydride from n-butane was made feasible by a breakthrough in catalyst technology that increased yields and selectivity. In U.S. Patent 3,864, 280, Chevron employs a vanadium/phosphorus system that yields 62 mole % and has a selectivity of 69.2 mole % at space velicity of 1,000 hr^{-1} (59).

---

(59) Schneider, R. A. Catalyst for a n-Butane Oxidation to Maleic Anhydride. U.S. Patent 3,864,280 (to Chevron Research Company), February 4, 1975.

Monsanto, in U.S. Patent 3,832,359, employs a vanadium/phosphorus/iron catalyst system which yields 29.2 mole % and has a selectivity of 52 mole % at space velocity of 1,366 hr^{-1} (60). Other patents have been issued, in this country and abroad, for maleic anhydride from n-butane, and, if economics remain favorable, n-butane is likely to be selected over benzene as the feedstock in new maleic anhydride plants.

The stoichiometric equations for the oxidation of n-butane to maleic anhydride and carbon oxides are:

$$C_4H_{10} + 7/2O_2 \rightarrow C_4H_2O_3 + 4H_2O \qquad (22)$$

n-Butane — Maleic anhydride

and

$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O \qquad (23)$$

Maleic anhydride

The high temperatures needed for n-butane conversion cause a high maleic anhydride decomposition rate (61). Commercial processes based on n-butane employ a multistage reactor system (typically two stages), with maleic anhydride being removed from the gas stream between stages. This technique solves the decomposition problem, but adds to initial capital investment requirements.

MARKETING STRENGTHS AND WEAKNESSES

Figure 16 is a schematic diagram of maleic anhydride uses in the U.S. (62). The largest use is in the manufacture of unsaturated

---

(60) Freerks, M. C., and M. Juda. Production of Maleic Anhydride by Catalytic Oxidation of Saturated Aliphatic Hydrocarbons. U.S. Patent 3,832,359 (to Monsanto Company), August 27, 1974.

(61) Bissot, T. C., and K. A. Benson. Oxidation of Butane to Maleic Anhydride. Industrial and Engineering Chemistry, Product Research and Development, 2(1):57-60, 1963.

(62) Chemical Origins and Markets, Fifth Edition. Stanford Research Institute, Menlo Park, California, 1967. 99 pp.

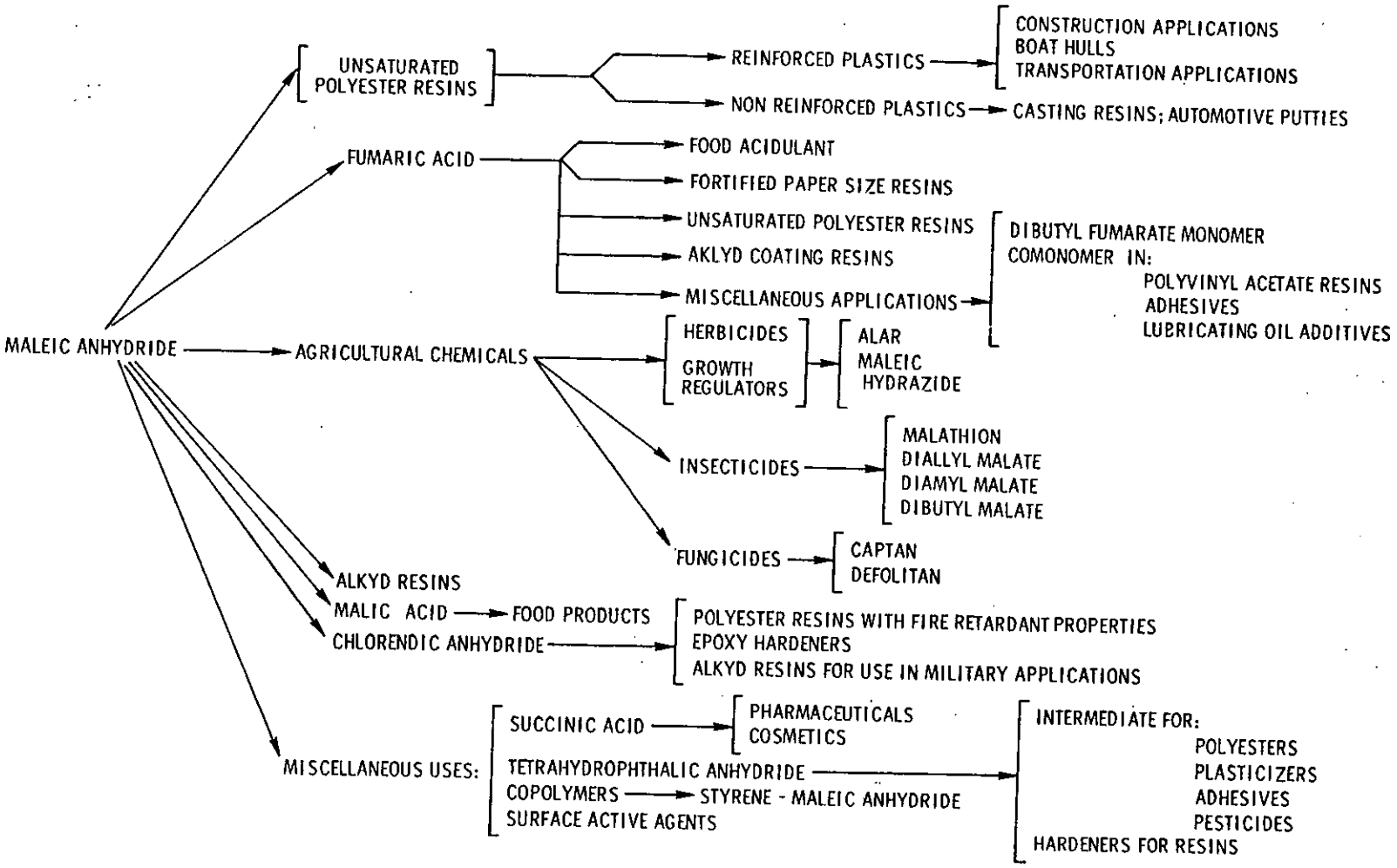
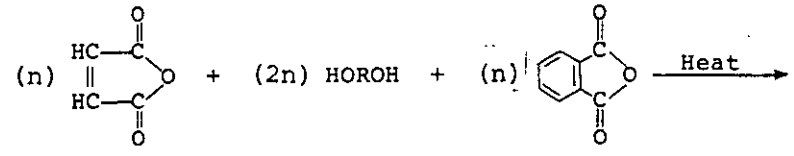


Figure 16. Uses of maleic anhydride (62).

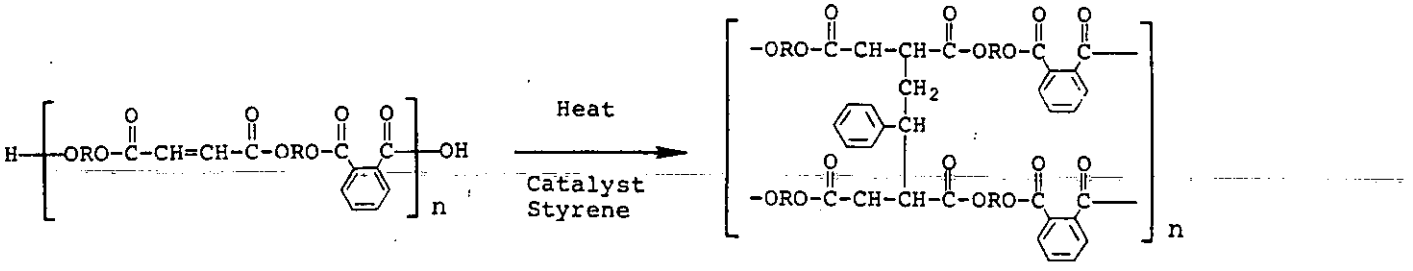
Reproduced with permission of Chemical Origins and Markets, Fifth Edition, Stanford Research Institute, Menlo Park, California.

polyester resins, which accounts for 58% of domestic maleic anhydride production (2). Unsaturated polyesters are made from unsaturated organic acid anhydrides and glycols, crosslinked with monomers such as styrene, vinyltoluene, and diallyl phthalate. A typical reaction involving maleic and phthalic anhydride is shown in Equation 24. In 1973, 78% of unsaturated polyester resins were used for the production of glass fiber reinforced plastics (FRP) and the remainder for nonreinforced applications (63).

The average annual growth of unsaturated polyester resin production from 1968 to 1973 was 15% (64). After a slight decline in 1970, growth in the 1971-1973 period averaged 25% (65, 66). These large increases in polyester resin consumption were the result of a large increase in the pleasure boat business, the large-scale use of synthetic marble and FRP tub/shower units in construction, and the first large-scale applications of low-profile, low-shrink resins in the transportation and equipment markets.



Maleic anhydride Glycol Phthalic anhydride



Prepolymer

Unsaturated polyester resin

(24)

(63) 1972 Annual Statistical Report. The Society of the Plastics Industry, New York, New York, November 16, 1973.

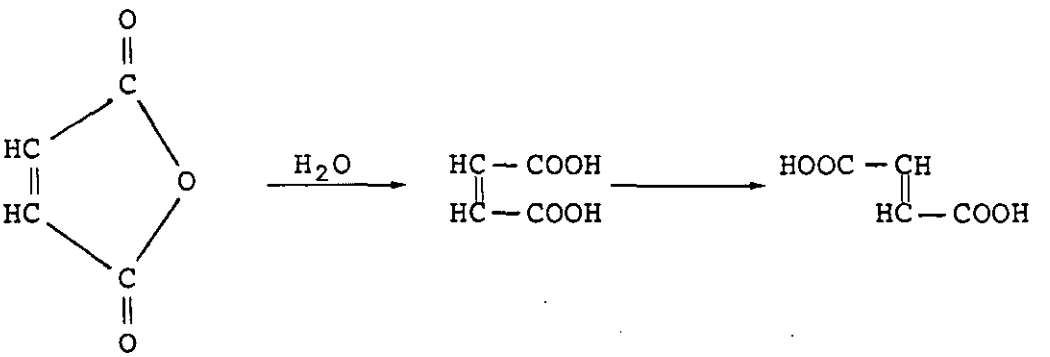
(64) Anderson, E. V. Growth Slows in Top 50 Chemicals' Output. Chemical and Engineering News, 52(18):10-13, 1974.

(65) Anderson, E. V. Recession Stifles Output of Top 50 Chemicals. Chemical and Engineering News, 53(18):30-33, 1975.

(66) Fumaric Acid. Chemical Marketing Report, 208(16):9, 1975.

The years 1973 and 1974, especially the latter, were characterized by widespread shortages of raw materials, including styrene, maleic anhydride, and most glycols. By late 1974, raw material availability was generally adequate, although some glycols were still in short supply. As a result of the severe raw material shortages in the first nine months of 1974, reported unsaturated polyester resin production for this period was down by 10% compared to the same period in 1973 (59).

Another major use of maleic anhydride is in the manufacture of fumaric acid, which acounts for 5% of domestic maleic anhydride production (2). Fumaric acid is produced by isomerization of maleic acid, which is obtained either directly from benzene oxidation or from maleic anhydride. It can be produced from maleic anhydride by the following reactions:



(25)

Maleic anhydride Maleic acid Fumaric acid

The major market for fumaric acid, as a fortifier in paper size resins, accounted for 33% of domestic production in 1975. Unsaturated polyesters and alkyl surface coating resins accounted for 20% and 11% respectively, and plasticizers and other miscellaneous applications consumed the remainder (66).

REFERENCES

1. Weiss, J. W., and C. R. Downs. Production of Quinone. U.S. Patent 1,318,631 (to Barrett Company), October 13, 1919.

2. Maleic Anhydride. Chemical Marketing Report, 213(7):9, 1978.

3. Ushio, S. Maleic Anhydride Produced from C_4 Hydrocarbons. Chemical Engineering, 78(21):107-109, 1971.

4. Maleic Anhydride. Chemical Marketing Report, 207(11):9, 1975.

5. Bhattacharyya, S. K., and N. Venkataraman. Catalytic Vapour-Phase Oxidation of Benzene to Maleic Acid. Journal of Applied Chemistry (London0, 8(11):728-736, 1958.

6. Nixon, J. K., and J. E. Longfield. Hydrocarbon Oxidation. In: Catalysis, Vol. VII, Oxidation, Hydration, Dehydration and Cracking Catalysts. P. H. Emmett, ed. Reinhold Publishing Corp., New York, New York, 1960. pp. 183-280.

7. Dmuchovsky, B., M. C. Freerks, E. O. Pierson, R. H. Munch, and F. B. Zienty. A Study of the Catalytic Oxidation of Benzene to Maleic Anhyride. Journal of Catalysis, 4(2):291-300, 1965.

8. Sherwood, P. W. The Technology of Maleic Anhydride Production. World Petroleum, 39:48-61, November 1968.

9. Ryder, R. C. Maleic Anhydride Production and Catalyst Thereof. U.S. Patent 2,885,409 (to American Cyanamid Company), May 5, 1959.

10. Robinson, W. D. Catalytic Production of Maleic and Phthalic Anhydride. U.S. Patent 3,106,569 (to Monsanto Chemical Company), October 8, 1963.

11. Darby, J. R. Oxidation Catalyst. U.S. Patent 2,674,582 (to Monsanto Chemical Company), April 6, 1954.

12. Di Ció, A. and D. Zettel. How S.A.V.A. Makes Maleic. Hydrocarbon Processing, 50(9):167-169, 1971.

13. Rollman, W. F. Process for Controlled Catalytic Oxidation. U.S. Patent 2,526,689 (to Standard Oil Development Company), October 24, 1950.

14. Burney, D. E., and Melvern C. Hoff. Production of Maleic and Phthalic Anhydride. U.S. Patent 2,954,385 (to The Standard Oil Company), September 27, 1960.

15. Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 12. John Wiley & Sons, Inc., New York, New York, 1967. pp. 819-837.

16. Feder, J. B. Recovery of Maleic Anhydride. U.S. Patent 3,054,086 (to Scientific Design Company, Inc.), September 18, 1960.

17. Cooper, W. M. Maleic Anhydride Recovery. U.S. Patent 2,951,555 (to Monsanto Chemical Company), September 6, 1960.

18. Hoyte, W. N. Recovery of the Anhydride of Polycarboxylic Acids. U.S. Patent 3,040,059 (to Foster Wheel Corporation), June 19, 1962.

19. Feder, J. B., and J. L. Russell. Process for Cleaning Apparatus. U.S. Patent 3,024,251 (to Scientific Design Company, Inc.), March 6, 1962.

20. Weyens, E. Continuous Process for the Preparation of Maleic Anhydride from an Aqueous Solution of Maleic Acid by Distillation. U.S. Patent 3,642,829 (to UCB), February 15, 1972.

21. Jewett, J. E. Production of Maleic Anhydride. U.S. Patent 2,989,545 (to American Cyanamid Company), June 20, 1961.

22. Lawson, J. F. Trip report for visit to Reichhold Chemicals, Inc., Morris, Illinois, July 28, 1977, under EPA Contract No. 68-02-2577.

23. Kohn, G. K. Stabilization and Recovery of Dicarboxylic Acid Anhydrides in the Presence of Alkali Metal Cations. U.S. Patent 2,831,869 (to California Spray-Chemical), April 22, 1958.

24. Cummings, H. D. Purification of Maleic Anhydride. U.S. Patent 2,806,861 (to Monsanto Chemical Company), September 17, 1957.

25. Letter, R. C. Weber, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, to D. Becker, U.S. Environmental Protection Agency, Cincinnati, Ohio, March 1, 1978.

26. Capabilities and Costs of Technology for the Organic Chemicals Industry to Achieve the Effluent Limitations of P.L. 92-500. Report No. NCWQ-75/03, National Commission on Water Quality, Washington, D.C., June 1975. pp. 6-58, 6-59, and 10-1-1 to 10-1-16.

27. Dreibelbis, J. A. Preparation of Maleic Anhydride and Catalysts Thereof. U.S. Patent 3,005,831 (to Pittsburgh Chemical Company), October 24, 1961.

28. Becker, M., and R. S. Barker. Preparation of Maleic Anhydride and Catalyst Thereof. U.S. Patent 2,967,185 (to Scientific Design Company, Inc.), January 3, 1961.

29. Kerr, R. O. Catalytic Oxidation of Hydrocarbons. U.S. Patent 3,484,384 (to Petro-Tex Chemical Company), December 16, 1969.

30. Letter, R. C. Sterett,Ashland Chemical Company, Columbus, Ohio, to D. R. Patrick, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 21, 1978.

31. Maxwell, W. H., and G. W. Scheil. Stationary Source Testing of a Maleic Anhydride Plant at the Denka Chemical Corporation, Houston, Texas. Contract No. 68-02-2814, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1978. 74 pp.

32. Chi, C. T., and T. W. Hughes. Phthalic Anhydride Plant Air Pollution Control. Contract 68-02-1320, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (Preliminary document submitted to the EPA by Monsanto Research Corporation, July 1977.) 104 pp.

33. Serth, R. W., and T. W. Hughes. Source Assessment: Phthalic Anhydride (Air Emissions). EPA-600/2-76-032d, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1976. 145 pp.

34. Sax, N. I. Dangerous Properties of Industrial Materials, Third Edition. Reinhold Publishing Corp., New York, New York, 1968. 1251 pp.

35. TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

36. Registry of Toxic Effects of Chemical Substances, 1975 Edition. H. E. Christensen and T. T. Luginbyhl, eds. U.S. Department of Health, Education, and Welfare, Rockville, Maryland, June 1975. p. 687.

37. Nuttonson, M. Y. AICE Survey of USSR Air Pollution Literature. American Institute of Crop Ecology, Silver Springs, Maryland, July 1971. pp. 30-43.

38. Lawson, J. F. Trip report for visit to Amoco Chemicals Corporation, Chicago, Illinois, January 24, 1978, under EPA Contract No. 68-02-2577.

39. Evaporation Loss from Fixed Roof Tanks. API Bulletin 2518, American Petroleum Institute, New York, New York, 1962. 38 pp.

40. Use of Variable Vapor Space Systems to Reduce Evaporation Loss. API Bulletin 2520, American Petroleum Institute, New York, New York, 1964. 14 pp.

41. Petrochemical Evaporation Loss from Storage Tanks. API Bulletin 2523, American Petroleum Institute, New York, New York, 1969. 14 pp.

42. Evaporation Loss from Floating Roof Tanks. API Bulletin 2517, American Petroleum Institute, New York, New York, 1962. 13 pp.

43. Evaporation Loss in the Petroleum Industry - Causes and Control. API Bulletin 2513, American Petroleum Institute, New York, New York, 1959. 57 pp.

44. Lawson, J. F. Maleic Anhydride - Draft Product Report. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1978.

45. Nonhebel, G. Recommendations on Heights for New Industrial Chimneys. Journal of the Institute of Fuel, 33:479-511, July 1960.

46. Eimutis, E. C., and R. P. Quill. Source Assessment: State-by-State Listing of Criteria Pollutant Emissions. EPA-600/2-76-032, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1977. p. 6.

47. Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

48. JANAF Thermochemical Tables, Second Edition. NSRDS-NBS 37, U.S. Department of Commerce, Washington, D.C., June 1971. 1141 pp.

49. Rolke, R. W., R. D. Hawthorne, C. R. Garbett. E. R. Slater, and T. T. Phillips. Afterburner Systems Study. EPA-R2-72-062, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1972. 512 pp.

50. Lee, K. C., H. J. Jahnes, and D. C. Macauley. Thermal Oxidation Kinetics of Selected Organic Compounds. (Presented at the 71st Annual Meeting of the Air Pollution Control Association. Houston, Texas. June 25-30, 1978.) 16 pp.

51. Ross, R. D. Pollution Abatement: Incineration of Solvent-Air Mixtures. Chemical Engineering Progress, 68(8):59-64, 1972.

52. Pruessner, R. D., and L. D. Broz. Air Pollution Control: Hydrocarbon Emission Reduction Systems. Chemical Engineering Progress, 73(8):69-73, 1977.

53. Mackay, J. S. Statement to the National Air Pollution Control Techniques Advisory Committee on EPA's Proposed Standard for Benzene Emissions from Maleic Anhydride Plants. August 22-23, 1978.

54. Hughes, T. W., D. A. Horn, C. W. Sandy, and R. W. Serth. Source Assessment: Prioritization of Air Pollution from Industrial Surface Coating Operations. EPA-650/2-75-019a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1975. 303 pp.

55. Hydrocarbon Pollutant Systems Study, Vol. 1. Stationary Sources, Effects, and Control. MSA Research Corporation, Evans City, Pennsylvania. Report No. APTD-1499, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1972. 377 pp.

56. Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

57. Ferrari, D. C., and C. G. Bertram. Method and Apparatus for Removal of Organics from Chemical Waste Gases. U.S. Patent 3,624,984 (to Badger Company), December 7, 1971.

58. Yevzel'man, I. B., and G. D. Kharlampovish. Neutralization of Exhaust Gas from Phthalic Anhydride Production. Khimicheskaya Promyscholennost (Moscow), 49(6):379-380, 1973.

59. Schneider, R. A. Catalyst for a n-Butane Oxidation to Maleic Anhydride. U.S. Patent 3,864,280 (to Chevron Research Company), February 4, 1975.

60. Freerks, M. C., and M. Juda. Production of Maleic Anhydride by Catalytic Oxidation of Saturated Aliphatic Hydrocarbons. U.S. Patent 3,832,359 (to Monsanto Company), August 27, 1974.

61. Bissot, T. C., and K. A. Benson. Oxidation of Butane to Maleic Anhydride. Industrial and Engineering Chemistry, Product Research and Development, 2(1):57-60, 1963.

62. Chemical Origins and Markets, Fifth Edition. Stanford Research Institute, Menlo Park, California, 1967. 99 pp.

63. 1972 Annual Statistical Report. The Society of the Plastics Industry, New York, New York, November 16, 1973.

64. Anderson, E. V. Growth Slows in Top 50 Chemicals' Output. Chemical and Engineering News, 52(18):10-13, 1974.

65. Anderson, E. V. Recession Stifles Output of Top 50 Chemicals. Chemical and Engineering News, 53(18):30-33, 1975.

66. Fumaric Acid. Chemical Marketing Reporter, 208(16):9, 1975.

67. Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

68. Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

69. Tadmor, J., and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment, 3(6):688-689, 1969.

70. Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

71. Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

72. Schwartz, W. A., et al. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume I: Carbon Black Manufacturing by the Furnace Process. EPA-450/3-73-006-a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 116 pp.

APPENDIX A

STORAGE TANK CALCULATIONS[a]

The procedure for calculating the emissions from storage tanks is outlined below. The equations given were derived in References 39-43.

Step 1. Calculate the equivalent gasoline breathing loss:

$$Ly = \frac{24}{1000}\left(\frac{P}{14.7 - P}\right)^{0.68} D^{1.73}(H')^{0.51}(\Delta T)^{0.50} F_P C' \qquad (A\text{-}1)$$

where Ly = equivalent gasoline breathing loss, bbl/yr
P = vapor pressure of material stored at bulk temperature, psia
D = tank diameter, ft
H' = tank outage, ft
ΔT = average ambient temperature change, °F
F_P = paint factor
C' = diameter factor

The bulk temperatures of the material stored were taken to be 140°F for maleic anhydride tanks, and 74°F for benzene tanks. The benzene temperature was obtained by adding 5°F to the ambient temperature, as recommended in References 39-43 for tanks held at ambient temperature. The latter was assumed to be 69°F, the national mean ambient temperature. Tank diameters were computed by assuming a height of 50 ft for all tanks. The tank outage, i.e., freeboard, was taken as one-half the tank height, or 25 ft.

The average ambient temperature change, ΔT, was taken as 20°F, which is the national average value. The paint factor, F_P, was assumed equal to unity, the value for white paint in good condition. This factor can be as high as 1.46 for gray surfaces. The diameter factor, C', is equal to unity for tanks 30 ft or larger in diameter. For smaller tanks the value is obtained from a graph given in Reference 39, and is between 0.25 and 1.0.

Step 2. Calculate the equivalent gasoline working loss:

---

[a]Nonmetric units are shown in this appendix because they correspond to the actual units used in performing the calculations. Final results were converted to metric form for use in the report.

$$F' = \left(\frac{3}{10,000}\right) PVNK_T \qquad (A\text{-}2)$$

where F' = equivalent gasoline breathing loss, bbl/yr
V = tank capacity, bbl
N = number of turnovers per year
K_T = turnover factor = 1.0 for $N \leq 36$

$$= \frac{180 + N}{6N} \text{ for } N > 36$$

Step 3. Compute total equivalent gasoline loss, Lg:

$$Lg = Ly + F' \qquad (A\text{-}3)$$

Step 4. Compute petrochemical losses:

$$L = 0.08 \left(\frac{M}{W}\right) Lg \qquad (A\text{-}4)$$

where L = total petrochemical loss, bbl/yr
M = molecular weight of chemical stored
W = liquid density of chemical stored, lb/gal

Step 5. Calculate emission factor:

$$L_1 = L\ (42)\ (W) \qquad (A\text{-}5)$$

$$E' = \frac{L_1}{Cap} \qquad (A\text{-}6)$$

$$E'' = \frac{E'}{2} \qquad (A\text{-}7)$$

where L_1 = petrochemical loss, lb/yr
Cap = production capacity, ton/yr
E' = emission factor, lb/ton
E'' = emission factor, g/kg

The necessary input data for the above calculations are given in Table A-1 and the results are summarized in Table A-2. The tank numbers in these tables correspond to those in Table 4 for benzene-based plants.

TABLE A-1. STORAGE TANK INPUT DATA FOR BENZENE-BASED PLANT[a]

	Tank number								
	1	2	3	4	5 & 6	7	8	9	10
Average ambient temp., °F	69	69	69	69	69	69	69	69	69
Average ambient temp. change, °F	20	20	20	20	20	20	20	20	20
Material molecular weight	78.11	78.11	106.16	106.16	98.06	98.06	98.06	98.06	116.1
Liquid density, lb/gal	7.34	7.34	7.3	7.3	12.51	12.51	12.51	12.51	13.26
Vapor pressure at bulk temp., psia	1.20	1.20	0.14	0.14	0.39	0.39	0.1	0.1	0.01
Bulk temp., °F	69	69	69	69	200	140	140	140	140
Tank diameter, ft	17.3	47.0	19.2	17.5	20	20.4	11.3	16.9	19.2
Tank outage, ft	25	25	5	4	5	5	4	5	5
Paint factor	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Diameter factor	0.6	1.0	0.7	0.6	0.7	0.7	0.6	0.7	0.7
Turnover factor	0.54	1.0	1.0	1.0	0.74	0.54	1.0	0.5	1.0
No. turnovers per year	80	20	8	8	52	80	10	90	2
Tank capacity, bbl	2,095	15,476	500	381	571	595	405	500	500

[a]Personal connumication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

TABLE A-2. STORAGE TANK CALCULATION SUMMARY FOR BENZENE-BASED PLANT[a]

Tank No.	Material stored	Capacity, gal	Losses		Emission factor, g/kg
			gal/yr	lb/yr	
1	Benzene	88,000	1,483	10,800	0.218
2	Benzene	650,000	6,969	51,160	1.023
3	Xylenes	21,000	67.1	489.6	0.010
4	Xylenes use	16,000	44.6	325.6	0.065
5	Crude maleic anhydride	24,000	136.9	1,712	0.034
6	Crude maleic anhydride	24,000	136.9	1,712	0.034
7	Crude maleic anhydride	25,000	48.3	604.0	0.012
8	Refined maleic anhydride	17,000	11.3	141.2	0.003
9	Refined maleic anhydride	21,000	42.5	531.3	0.011
10	Crude maleic acid	21,000	28.3	377.1	0.008

[a]Personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

APPENDIX B

DERIVATION OF SOURCE SEVERITY EQUATIONS[a]

SUMMARY OF MAXIMUM SEVERITY EQUATIONS

The maximum severity of pollutants may be calculated using the mass emission rate, Q, the height of the emissions, H, and the ambient air quality standard or modified TLV. The equations summarized in Table B-1 are developed in detail in this appendix.

TABLE B-1. POLLUTANT SEVERITY EQUATIONS FOR ELEVATED POINT SOURCES

Pollutant	Severity equation
Particulates	$S = \frac{70\ Q}{H^2}$
SO_x	$S = \frac{50\ Q}{H^2}$
NO_x	$S = \frac{315\ Q}{H^{2.1}}$
Hydrocarbons	$S = \frac{162\ Q}{H^2}$
Carbon monoxide	$S = \frac{0.78\ Q}{H^2}$
Others	$S = \frac{5.5\ Q}{TLV \cdot H^2}$

[a]This Appendix was originally prepared by T. R. Blackwood and E. C. Eimutis, Monsanto Research Corporation, Dayton, Ohio.

(67) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

DERIVATION OF χ_{max} FOR USE WITH U.S. AVERAGE CONDITIONS

The most widely accepted formula for predicting downwind ground level concentrations from a point source is (58):

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(B-1)}$$

where χ = downwind ground level concentration at reference coordinate x and y with emission height of H, g/m^3

Q = mass emission rate, g/s

σ_y = standard deviation of horizontal dispersion, m

σ_z = standard deviation of vertical dispersion, m

u = wind speed, m/s

y = horizontal distance from centerline of dispersion, m

H = height of emission release, m

x = downwind dispersion distance from source of emission release, m

π = 3.1416

We assume that χ_{max} occurs when $x >> 0$ and $y = 0$. For a given stability class, standard deviations of horizontal and vertical dispersion have often been expressed as a function of downwind distance by power law relationships as follows (68):

$$\sigma_y = ax^b \qquad \text{(B-2)}$$

$$\sigma_z = cx^d + f \qquad \text{(B-3)}$$

Values for a, b, c, d, and f are given in Tables B-2 (40) and B-3. Substituting these general equations into Equation B-1 yields:

---

(68) Martin, D.)., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

TABLE B-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a] (47)

Stability class	a
A	0.3658
B	0.2751
C	0.2089
D	0.1471
E	0.1046
F	0.0722

[a]For the equation

$$\sigma_y = ax^b$$

where x = downwind distance
b = 0.9031 (from Reference 69)

TABLE B-3. VALUES OF THE CONSTANTS USED TO ESTIMATE VERTICAL DISPERSION[a] (68)

Usable range, m	Stability class	Coefficient		
		c_1	d_1	f_1
>1,000	A	0.00024	2.094	-9.6
	B	0.055	1.098	2.0
	C	0.113	0.911	0.0
	D	1.26	0.516	-13
	E	6.73	0.305	-34
	F	18.05	0.18	-48.6
		c_2	d_2	f_2
100 to 1,000	A	0.0015	1.941	9.27
	B	0.028	1.149	3.3
	C	0.113	0.911	0.0
	D	0.222	0.725	-1.7
	E	0.211	0.678	-1.3
	F	0.086	0.74	-0.35
		c_3	d_3	
<100	A	0.192	0.936	
	B	0.156	0.922	
	C	0.116	0.905	
	D	0.079	0.881	
	E	0.063	0.871	
	F	0.053	0.814	

[a]For the equation

$$\sigma_z = cx^d + f$$

(69) Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11): 859-863, 1972.

$$\chi = \frac{Q}{ac\pi ux^{b+d} + a\pi ufx^{b}} \exp\left[-\frac{H^2}{2(cx^{d} + f)^2}\right] \qquad \text{(B-4)}$$

Assuming that χ_{max} ocurs at x<100 m or the stability class is C, then f = 0 and Equation B-4 becomes:

$$\chi = \frac{Q}{ac\pi ux^{b+d}} \exp\left[\frac{-H^2}{2c^2x^{2d}}\right] \qquad \text{(B-5)}$$

For convenience, let:

$$A_R = \frac{Q}{ac\pi u} \text{ and } B_R = \frac{-H^2}{2c^2}$$

so that Equation B-5 reduces to:

$$\chi = A_R x^{-(b+d)} \exp\left[\frac{B_R}{x^{2d}}\right] \qquad \text{(B-6)}$$

Taking the first derivative of Equation B-6

$$\frac{d\chi}{dx} = A_R \left\{x^{-b-d}\left(\exp\left[B_R x^{-2d}\right]\right)\left(-2dB_R x^{-2d-1}\right) + \exp\left[B_R x^{-2d}\right]\left(-b-d\right)x^{-b-d-1}\right\} \qquad \text{(B-7)}$$

and setting this equal to zero (to determine the roots which give the minimum and maximum conditions of χ with respect to x) yields:

$$\frac{d\chi}{dx} = 0 = A_R x^{-b-d-1}\left(\exp\left[B_R x^{-2d}\right]\right)\left[-2dB_R x^{-2d} - b - d\right] \qquad \text{(B-8)}$$

Since we define that $x \neq 0$ or ∞ at χ_{max}, the following expression must be equal to 0:

$$-2dB_R x^{-2d} - d - b = 0 \qquad \text{(B-9)}$$

or

$$(b+d)x^{2d} = -2dB_R \qquad \text{(B-10)}$$

or

$$x^{2d} = \frac{-2dB_R}{b+d} = \frac{2d\ H^2}{2c^2(b+d)} \qquad \text{(B-11)}$$

or

$$x^{2d} = \frac{d\ H^2}{c^2(b+d)} \tag{B-12}$$

or

$$x = \left(\frac{d\ H^2}{c^2(b+d)}\right)^{1/2d} \text{ at } \chi_{max} \tag{B-13}$$

Thus Equations B-2 and B-3 (at f = 0) become:

$$\sigma_y = a\left(\frac{d\ H^2}{c^2(d+b)}\right)^{b/2d} \tag{B-14}$$

$$\sigma_z = c\left(\frac{d\ H^2}{c^2(b+d)}\right)^{d/2d} = \left(\frac{d\ H^2}{b+d}\right)^{1/2} \tag{B-15}$$

The maximum will be determined for U.S. average conditions of stability. According to Gifford (70), this is when $\sigma_y = \sigma_z$. Since b = 0.9031, and upon inspection of Table B-2 under U.S. average conditions, $\sigma_y = \sigma_z$, it can be seen that $0.881 \leq d \leq 0.905$ (class C stability[a]). Thus, it can be assumed that b is nearly equal to d in Equations B-14 and B-15 or:

$$\sigma_z = \frac{H}{\sqrt{2}} \tag{B-16}$$

and

$$\sigma_y = \frac{aH}{c\sqrt{2}} \tag{B-17}$$

Under U.S. average conditions, $\sigma_y = \sigma_z$ and $a \cong c$ if $b \cong d$ and f = 0 (between class C and D, but closer to belonging in class C).

---

[a]The values given in Table B-3 are mean values for stability class. Class C stability describes these coefficients and exponents, only within about a factor of two (67).

- - - - - - - - - - -

(70) Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

Then

$$\sigma_y = \frac{H}{\sqrt{2}} \tag{B-18}$$

Substituting for σ_y and σ_z into Equation B-1 and letting y = 0:

$$\chi_{max} = \frac{2\ Q}{\pi u H^2} \exp\left[-\frac{1}{2}\left(\frac{H\sqrt{2}}{H}\right)^2\right] \tag{B-19}$$

or

$$\chi_{max} = \frac{2\ Q}{\pi e u H^2} \tag{B-20}$$

For U.S. average conditions u = 4.47 m/s so that Equation B-20 reduces to:

$$\chi_{max} = \frac{0.0524\ Q}{H^2} \tag{B-21}$$

DEVELOPMENT OF SOURCE SEVERITY EQUATIONS

The general source severity, S, relationship has been defined as follows:

$$S = \frac{\bar{\chi}_{max}}{F} \tag{B-22}$$

where $\bar{\chi}_{max}$ = time-averaged maximum ground level concentration

F = hazard factor defined as the ambient air quality standard for criteria pollutants and a modified TLV (i.e., TLV • 8/24 • 1/100) for noncriteria pollutants

Noncriteria Emissions

The value of $\bar{\chi}_{max}$ may be derived from χ_{max}, an undefined "short-term" (t_o) concentration. An approximation for longer term (t) concentration may be made as follows (67):

For a 24-hr time period,

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t}\right)^{0.17} \tag{B-23}$$

or

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3\ min}{1{,}440\ min}\right)^{0.17} \tag{B-24}$$

$$\bar{\chi}_{max} = \chi_{max}\ (0.35) \tag{B-25}$$

Since the hazard factor is defined and derived from TLV values as follows:

$$F = (TLV)\left(\frac{8}{24}\right)\left(\frac{1}{100}\right) \tag{B-26}$$

$$F = (3.33 \times 10^{-3})\ TLV \tag{B-27}$$

then the severity factor, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.35)\chi_{max}}{(3.33 \times 10^{-3})\ TLV} \tag{B-28}$$

$$S = \frac{105\ \chi_{max}}{TLV} \tag{B-29}$$

If a weekly averaging period is used, then:

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3}{10,080}\right)^{0.17} \tag{B-30}$$

or

$$\bar{\chi}_{max} = (0.25)\chi_{max} \tag{B-31}$$

and

$$F = (TLV)\left(\frac{40}{168}\right)\left(\frac{1}{100}\right) \tag{B-32}$$

$$F = (2.38 \times 10^{-3})TLV \tag{B-33}$$

and the severity factor, S, is:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.25)\chi_{max}}{(2.38 \times 10^{-3})TLV} \tag{B-34}$$

or

$$S = \frac{105\chi_{max}}{TLV} \tag{B-35}$$

which is entirely consistent, since the TLV is being corrected for a different exposure period.

Therefore, the severity can be derived from χ_{max} directly without regard to averaging time for noncriteria emissions. Thus, combining Equations B-35 and B-21, for elevated sources, gives:

$$S = \frac{5.5\ Q}{TLV \cdot H^2} \qquad \text{(B-36)}$$

Criteria Emissions

For the criteria pollutants, established standards may be used as F values in Equation B-22. These are given in Table B-4. However, Equation B-23 must be used to give the appropriate averaging period. These equations are developed for elevated sources using Equation B-21.

TABLE B-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS (71)

Pollutant	Averaging time	Primary standards	Secondary standards
Particulate matter	Annual (geometric mean)	75 $\mu g/m^3$	60[a] $\mu g/m^3$
	24-hour[b]	260 $\mu g/m^3$	160 $\mu g/m^3$
SO_x	Annual (arithmetic mean)	80 $\mu g/m^3$	60 $\mu g/m^3$
	24-hour[b]	365 $\mu g/m^3$	260[c] $\mu g/m^3$
	3-hour[b]	-	1,300 $\mu g/m^3$
Carbon monoxide	8-hour[b]	10,000 $\mu g/m^3$	
	1-hour[b]	40,000 $\mu g/m^3$	(Same as primary)
Nitrogen dioxide	Annual (arithmetic mean)	100 $\mu g/m^3$	(Same as primary)
Photochemical oxidants	1-hour[b]	160 $\mu g/m^3$	(Same as primary)
Hydrocarbons (nonmethane)	3-hour (6 a.m. to 9 a.m.)	160 $\mu g/m^3$[d]	(Same as primary)

[a] The secondary annual standard (60 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the 24-hour secondary standard.

[b] Not to be exceeded more than once per year.

[c] The secondary annual standard (260 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the annual standard.

[d] There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons in this report is an EPA recommended guideline for meeting the primary ambient air quality standard for oxidants.

(71) Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

Carbon Monoxide Severity--
The primary standard for CO is reported for a 1-hr averaging time. Therefore,

$$t = 60 \text{ min}$$

$$t_o = 3 \text{ min}$$

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3}{60}\right)^{0.17} \quad \text{(B-37)}$$

$$= \frac{2\,Q}{\pi e u H^2}\left(\frac{3}{60}\right)^{0.17} \quad \text{(B-38)}$$

$$= \frac{2\,Q}{(3.14)(2.72)(4.5)H^2}(0.6) \quad \text{(B-39)}$$

$$= \frac{0.052\,Q}{H^2}(0.6) \quad \text{(B-40)}$$

$$\bar{\chi}_{max} = \frac{(3.12 \times 10^{-2})Q}{H^2} \quad \text{(B-41)}$$

$$\text{Severity (S)} = \frac{\bar{\chi}_{max}}{F} \quad \text{(B-42)}$$

Setting F equal to the primary standard for CO, i.e., 0.04 g/m^3, yields:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(3.12 \times 10^{-2})Q}{0.04\,H^2} \quad \text{(B-43)}$$

or

$$S_{CO} = \frac{0.78\,Q}{H^2} \quad \text{(B-44)}$$

Hydrocarbon Severity--
The primary standard for hydrocarbon is reported for a 3-hr averaging time.

$$t = 180 \text{ min}$$

$$t_{max} = 3 \text{ min}$$

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{180}\right)^{0.17} \quad \text{(B-45)}$$

$$= 0.5\chi_{max} \quad \text{(B-46)}$$

$$= \frac{(0.5)(0.052)\ Q}{H^2} \quad \text{(B-47)}$$

$$\bar{\chi}_{max} = \frac{0.026\ Q}{H^2} \quad \text{(B-48)}$$

For hydrocarbons, the concentration of 1.6×10^{-4} g/m^3 has been issued as a guideline for achieving oxidant standards. Therefore,

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.026\ Q}{1.6 \times 10^{-4}\ H^2} \quad \text{(B-49)}$$

or

$$S_{HC} = \frac{162.5\ Q}{H^2} \quad \text{(B-50)}$$

Particulate Severity--
The primary standard for particulate is reported for a 24-hr averaging time.

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{1,440}\right)^{0.17} \quad \text{(B-51)}$$

$$= \frac{(0.052)\ Q\ (0.35)}{H^2} \quad \text{(B-52)}$$

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \quad \text{(B-53)}$$

For particulates, F = 2.6×10^{-4} g/m^3, and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \quad \text{(B-54)}$$

$$S_P = \frac{70\ Q}{H^2} \tag{B-55}$$

SO_x Severity--
The primary standard for SO_x is reported for a 24-hr averaging time. Using t = 1,440 minutes and proceeding as before:

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \tag{B-56}$$

The primary standard is 3.65×10^{-4} g/m^3. Therefore,

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.0182)Q}{3.65 \times 10^{-4}\ H^2} \tag{B-57}$$

or

$$S_{SO_x} = \frac{50\ Q}{H^2} \tag{B-58}$$

NO_x Severity--
Since NO_x has a primary standard with a 1-yr averaging time, the χ_{max} correction equation cannot be used. As an alternative, the following equation is used:

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \tag{B-59}$$

A difficulty arises, however, because a distance x, from emission point to receptor, is included; hence, the following rationale is used:

Equation B-20 is valid for neutral conditions or when $\sigma_z \cong \sigma_y$. This maximum occurs when

$$H \cong \sqrt{2}\sigma_z$$

and since, under these conditions,

$$\sigma_z = ax^b$$

then the distance, x_{max}, where the maximum concentration occurs is:

$$x_{max} = \left(\frac{H}{\sqrt{2a}}\right)^{\frac{1}{b}}$$

For class C conditions,

$$a = 0.113$$

$$b = 0.911$$

Simplifying Equation B-59,

$$\sigma_z = 0.113\ x_{max}^{0.911}$$

and

$$u = 4.5\ m/s$$

Letting $x = x_{max}$ in Equation B-59,

$$\bar{\chi}_{max} = \frac{4\ Q}{x_{max}^{1.911}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (B\text{-}60)$$

where

$$x_{max} = \left(\frac{H}{0.16}\right)^{1.098} \qquad (B\text{-}61)$$

$$x_{max} = 7.5\ H^{1.098} \qquad (B\text{-}62)$$

and

$$\frac{4\ Q}{x_{max}^{1.911}} = \frac{4\ Q}{(7.5\ H^{1.098})^{1.911}} \qquad (B\text{-}63)$$

Therefore,

$$\bar{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (B\text{-}64)$$

As noted above,

$$\sigma_z = 0.113x^{0.911} \qquad (B\text{-}65)$$

$$\sigma_z = 0.113\ (7.5\ H^{1.1})^{0.911} \qquad (B\text{-}66)$$

or

$$\sigma_z = 0.71\ H \qquad (B\text{-}67)$$

Therefore,

$$\bar{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{0.71\ H}\right)^2\right] \quad \text{(B-68)}$$

$$= \frac{0.085\ Q}{H^{2.1}} (0.371) \quad \text{(B-69)}$$

$$\bar{\chi}_{max} = \frac{3.15 \times 10^{-2}\ Q}{H^{2.1}} \quad \text{(B-70)}$$

Since the NO_x standard is 1.0×10^{-4} g/m^3, the NO_x severity equation is:

$$S_{NO_x} = \frac{(3.15 \times 10^{-2})\ Q}{1 \times 10^{-4}\ H^{2.1}} \quad \text{(B-71)}$$

$$S_{NO_x} = \frac{315\ Q}{H^{2.1}} \quad \text{(B-72)}$$

AFFECTED POPULATION CALCULATION

Another form of the plume dispersion equation is needed to calculate the affected population since the population is assumed to be distributed uniformly around the source. If the wind directions are taken to 16 points and it is assumed that the wind directions within each sector are distributed randomly over a period of a month or a season, it can be assumed that the effluent is uniformly distributed in the horizontal within the sector. The appropriate equation for average concentration, $\bar{\chi}$, in g/m^3 is then (for 100 m $\leq x \leq$ 1,000 m and stability class C) (72):

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \quad \text{(B-59)}$$

To find the distance at which $\bar{\chi}/F = 1.0$, roots are determined for the following equation:

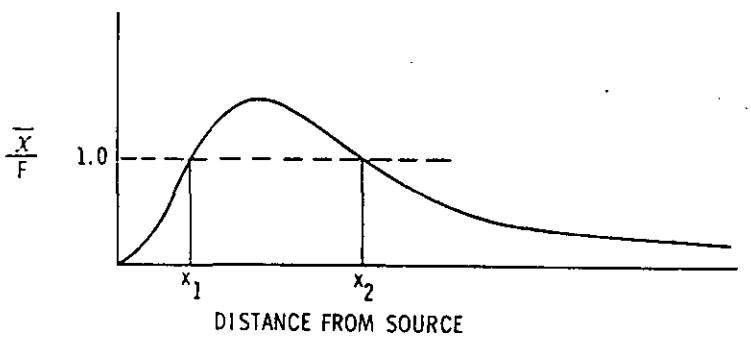
(72) Schwartz, W. A., et al. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume I: Carbon Black Manufacturing by the Furnace Process. EPA-450/3-73-006-a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 116 pp.

$$1 = \frac{2.03\ Q}{F\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(B-73)}$$

keeping in mind that:

$$\sigma_z = cx^d + f$$

where c, d, and f are functions of atmospheric stability and are assumed to be selected for stability class C. Since Equation B-73 is a transcendental equation, the roots are found by an iterative technique using the computer. For a specified emission from a typical source, χ/F as a function of distance might look as follows:



The affected population is contained in the area

$$A = \pi(x_2^2 - x_1^2) \qquad \text{(B-74)}$$

If the affected population density is D_p, the total affected population, P', is:

$$P' = D_p A \text{ (persons)} \qquad \text{(B-75)}$$

APPENDIX C

MALEIC ANHYDRIDE PLANT EMISSION FACTORS OBTAINED FROM INDUSTRY

TABLE C-1. MALEIC ANHYDRIDE PRODUCT RECOVERY SCRUBBER EMISSION FACTORS[a] (g/kg of product maleic anhydride)

Material emitted	Plant number						
	18-1	18-2	18-3	18-4	18-5	18-6	18-7
Inert materials							
Nitrogen	26,328	26,782	22,823	32,181[b]	24,266	19,725	19,042
Oxygen	6,128	5,673	6,930	NR	4,955	3,990	2,459
Carbon Dioxide	1,842	1,280	848	NR	1,313	1,036	1,078
Water Vapor	2,235	873	393	1,514	1,364	1,222	654
Criteria pollutants							
Carbon monoxide	867	611	684	671	443	470	686
Hydrocarbons	NR	NR	NR	NR	NR	NR	NR
Chemical substances							
Benzene	62.4	3.3[c]	100.8	61.6	62.7	87.9	198
Maleic anhydride	NR	2.7	2	5.9	NR	4.7	NR
Formaldehyde	15.4	NR	NR	NR	NR	NR	NR
Formic acid	1.2	NR	NR	NR	NR	NR	NR
Xylenes	NR	NR	11.6	NR	NR	NR	NR
Maleic acid	4	NR	NR	NR	11.5	NR	NR

[a] Personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio, and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

[b] Not reported.

[c] An activated carbon bed is used to recover benzene from the product recovery scrubber.

TABLE C-2. MALEIC ANHYDRIDE SECONDARY SCRUBBER VENT EMISSION FACTORS

(g/kg of product maleic anhydride)

Material emitted	Plant number 18-2	18-7
Nitrogen	1,835	6,623
Oxygen	560	1,891
Water vapor	49.9	232
Maleic anhydride	0.2	NR[b]

[a]Personal communication between T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio and D. R. Goodwin, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 12, 1975.

[b]Not reported.

APPENDIX D

PRE-SURVEY SAMPLING AND ANALYSIS RESULTS FOR A MALEIC ANHYDRIDE PLANT PRODUCT RECOVERY SCRUBBER

INTRODUCTION

Emissions from a maleic anhydride product recovery scrubber exhaust stack were sampled. This appendix contains a summary of the results, sampling results, analysis results, sample calculations, a discussion of sampling procedures, and a discussion of analysis procedures.

Atmospheric emissions from the main product recovery scrubber were sampled and analyzed. Grab flasks, solid sorbent sampling tubes, and a wet chemical procedure were used to collect samples of carbon monoxide, total hydrocarbons, and miscellaneous chemical substances. Analysis of the various samples was made by gas chromatography/infrared absorption, gas chromatography/mass spectroscopy, and gas chromatography/flame ionization. Concentrations of the emissions are presented in Table D-1. The highest concentration listed in Table D-1 is CO at 14,400,000 $\mu g/m^3$ (1.15% by volume).

TABLE D-1. COMPOSITION OF VENT GAS LEAVING THE MALEIC ANHYDRIDE PRODUCT RECOVERY SCRUBBER

Component	Concentration µg/m³	Concentration ppm by volume
Criteria pollutants		
Carbon monoxide	14,400,000	11,500
Hydrocarbons (as CH_4)	552,000	773
Chemical substances		
Benzene	31,200	8.96
Toluene	37	0.01
Xylenes	8,200	1.73
Quinone	88	0.02
Cresols	51	0.01
Dimethylphenol	470	0.09
Dimethylnaphthalene	4,600	0.66
C_3/C_4 naphthalene	44	0.01
C_{12}-C_{17} hydrocarbons	7,700	1.01
Acetaldehyde	1,400	0.71
Formaldehyde	4,500	2.29
Hexanes	320	0.24
Heptanes	140	0.04
C_3/C_4 alcohols	2,400	0.54
Biphenyl	390	0.05
Methylnaphthalene	490	0.08
Maleic anhydride	<7	<0.002
Maleic acid	<7	<0.002
Phenol	<7	<0.002
Benzoic acid	<7	<0.002
Benzaldehyde	<7	<0.002
Formic acid	<7	<0.002
Acetic anhydride	<7	<0.002
Fumaric acid	<7	<0.002
Malic acid	<7	<0.002

SAMPLING DATA

The field sampling results for the maleic anhydride product recovery scrubber exhaust stack are presented in Table D-2. Non-metric units are shown in this appendix since they correspond to the actual units used to acquiring the sampling data. Results were finally converted to metric form for use in the report.

TABLE D-2. FIELD SAMPLING DATA

Run number	Type of sampling procedure	Run time, min	Cylinder pressure, in. Hg initial	Cylinder pressure, in. Hg final	Cylinder temperature, °F initial	Cylinder temperature, °F final	Porous polymer tube number Tenax	Porous polymer tube number Chromosorb 105	Cylinder volume, scf	Sampling rate, acf/hr	Volume of gas sampled,[a] scf
G-2	Grab flask	0.25	2.95	29.41	72	72			0.07		
G-3	Grab flask	0.25	2.95	29.41	72	72			0.07		
P-1	Porous polymer	5.0	28.4	23.8	72	72	110	86	0.425	3.0	0.065
P-2	Porous polymer	5.0	23.8	20.4	72	72	107	87	0.425	1.0	0.048
P-3	Porous polymer	15.0	28.3	17.4	71	72	65	88	0.425	2.0	0.17
W-1	Wet chemical	6.0	17.4	5.5	72	72			0.425	2.0	0.168
W-2	Wet chemical	6.0	20.5	8.0	69	72			0.425	2.0	
W-3	Wet chemical	6.0	8.0	0.0	69	72			0.425	2.0	0.113

[a] Calculated values

NOTE: Blanks indicate information not applicable.

ANALYSIS DATA

The results of GC/MS analysis of the packed porous polymer (PPP) tubes are presented in Table D-3. Compounds expected to be found, but not identified during analysis, are listed in the table as less than 7 $\mu g/m^3$. The reason some compounds were not identified may be due to poor collection efficiency of the collection media for those species.

TABLE D-3. ANALYSIS OF POROUS POLYMER TUBE FOR EMISSIONS FROM THE MALEIC ANHYDRIDE PRODUCT RECOVERY SCRUBBER

Compound	Quantity collected, µg[a]	Concentration, $\mu g/m^3$[b]
Benzene	42.4	31,200
Toluene	0.05	37
Xylenes	11.1	8,200
Quinone	0.12	88
Cresols	0.07	51
Dimethylphenol	0.64	470
Dimethylnaphthalene	6.28	4,600
C_3/C_4 naphthalene	0.06	44
C_{12}-C_{17} hydrocarbons	10.5	7,700
Acetaldehyde	1.87	1,400
Formaldehyde	6.08	4,500
Hexanes	0.43	320
Heptanes	0.19	140
C_3/C_4 alcohols	3.20	2,400
Biphenyl	0.53	390
Methylnaphthalene	0.66	490
Maleic anhydride	<0.01	<7
Maleic acid	<0.01	<7
Phenol	<0.01	<7
Benzoic acid	<0.01	<7
Benzaldehyde	<0.01	<7
Formic acid	<0.01	<7
Acetic anhydride	<0.01	<7
Fumaric acid	<0.01	<7
Malic acid	<0.01	<7

[a] The porous polymer tubes used were numbers 107 (Tenax) in series with 87 (Chromosorb 105)

[b] The volume sampled was 0.0481 ft^3 at standard conditions. (STP = 70°F, 14.7 psia). (0.0481 ft^3 = 0.00136 m^3)

The grab flasks were submitted to gas chromatographic analysis, and the results are presented in Table D-4. The method of component quantification employed in the analysis was peak area comparison.

TABLE D-4. MALEIC ANHYDRIDE PRODUCT RECOVERY SCRUBBER EFFLUENT ANALYSIS (GRAB FLASKS)

Sample, flask no.	Total hydrocarbon THC, ppm[a]	Methane CH_4, ppm	Carbon monoxide CO, ppm	Background concentration, ppm
2	328	N/D[b]	12,000	15
3	773	N/D	11,000	25

[a] THC expressed as CH_4 equivalents.

[b] Not detected, <50 ppm

SAMPLE CALCULATIONS

The volume of gas sampled at standard conditions (530°R; 29.92 in. Hg) may be calculated as follows:

$$V_s = 17.71 \times V_c \times \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) \qquad \text{(D-1)}$$

where V_s = sample volume, ft^3

V_c = cylinder volume, ft^3

P_f = final pressure (barometric-cylinder), in. Hg

T_f = temperature of cylinder, °R

P_i = initial pressure (barometric-cylinder), in. Hg

17.71 = conversion factor

Using the values recorded on the data sheet for run #2 (included in Appendix A), we have

$$V_s = 17.71 \times 0.425\ ft^3 \left(\frac{9.11}{532} - \frac{5.61}{532}\right)$$

$$V_s = 0.048\ ft^3$$

or

$$V_s = 1.36\ \ell$$

The mass concentration of those compounds identified by GC/MS may be calculated as follows:

$$M_a = 0.353\ Q_a/V_s \qquad (D\text{-}2)$$

where M_a = mass concentration of compound "a", mg/m^3
Q_a = quantity of compound "a" collected, µg
V_s = sample volume, ft^3
0.035 = conversion factor

For example, the mass concentration of benzene may be computed simply as,

$$M_{benzene} = 0.035\ Q_{benzene}/V_s$$
$$= 0.035 \times 42.4/0.048$$
$$M_{benzene} = 31.2\ mg/m^3$$

SAMPLING PROCEDURES

Maleic Anhydride/Maleic Acid

A sampling tain, Figure D-1, was assembled which consisted of a glass probe; 2 midget impingers in series containing 15×10^{-6} m^3 each of isopropyl alcohol maintained at 0°C by an ice bath; a calcium chloride tube containing drierite; and a gas moving system comprised of a flow meter and an evacuated cylinder with a vacuum gauge and a thermometer.

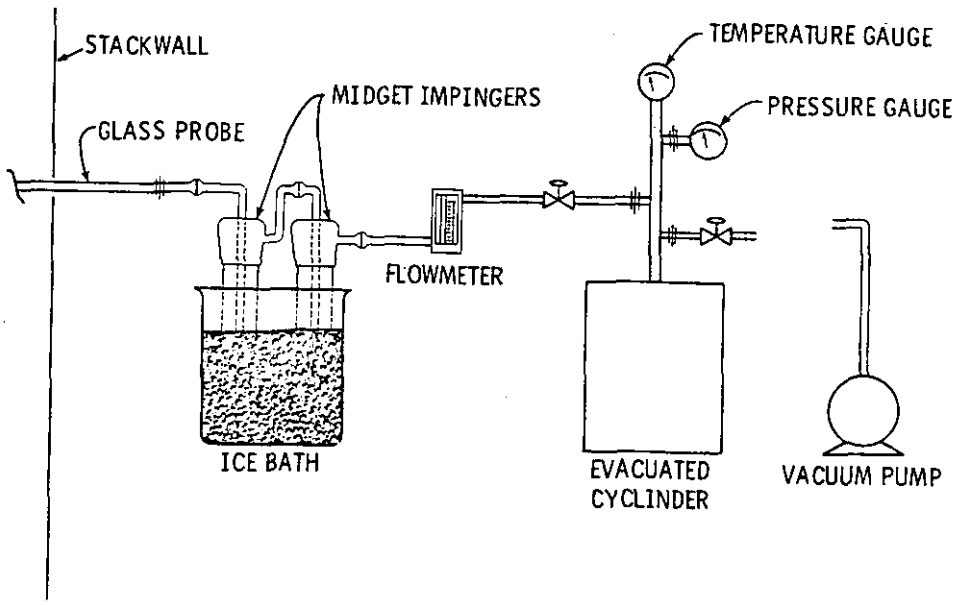


Figure D-1. Maleic anhydride/maleic acid wet chemical sampling train.

Prior to sampling, the initial pressure and temperature of the tank were recorded on a data sheet. The valve on the cylinder was opened and the flow meter was adjusted to maintain a 1 ℓ (actual/min flow rate. The sampling period was 6 min after which the flow was stopped, the train allowed to equilibrate, and the final temperature and pressure recorded. The samples were transferred to a brown glass sample bottle, sealed and transported to Dayton Laboratory for analysis.

Grab Flasks

A nitrogen-conditioned 2-ℓ glass flask was evacuated to approximately 75 mm of Hg absolute pressure. A glass probe and suitable glass valving were attached to the evacuated flask. The probe was inserted into the sampling port, and the value was slowly opened to allow flow into the flask. The stack gas entered the flask until pressures were equal. The valve was closed, after which the flask was disconnected from the sampling train, placed in a shipping case, and transported to Dayton Laboratory for analysis.

Porous Polymer Tubes

The sampling train (Figure D-2) was comprised of a stainless steel probe; a one quarter inch stainless steel tube packed with Tenax in series with a one quarter inch stainless steel tube paced with Chromosorb 105 and a gas moving system consisting of a flow meter and an evacuated cylinder equipped with a thermometer and a vacuum gauge. Prior to sampling, the initial temperature and pressure of the cylinder were recorded on a data sheet along with other data such as tube and run numbers, cylinder volume, etc.; the probe was inserted into the sampling port, valve opened, and flow meter adjusted to maintain 2 acf/hr flow rate. At the end of the prescribed run period, the flowmeter was shut off, the sampling train allowed to equilibrate (approximately 15 s), and the final cylinder temperature and pressure recorded on the data sheet. The packed porous polymer tubes were removed from the sampling train, individually sealed with stainless steel caps, placed in plastic bags which were also sealed and stored at 0°C, and transported to the Dayton analytical laboratory for analysis.

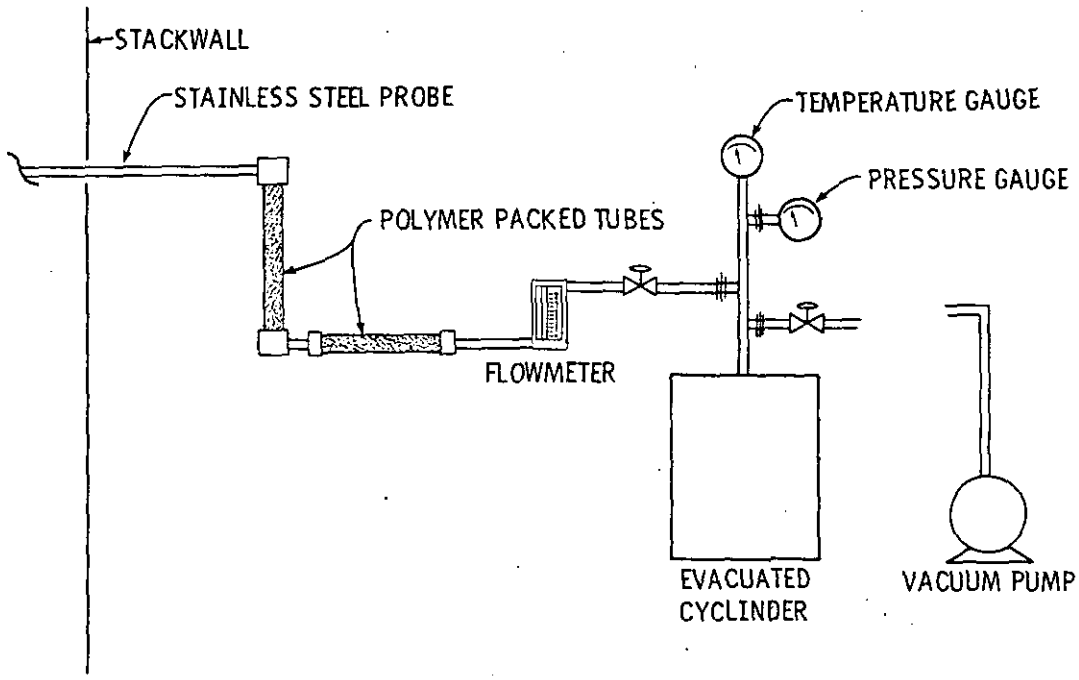


Figure D-2. Porous polymer collector tube sampling train.

ANALYTICAL PROCEDURES

Maleic Anhydride/Maleic Acid

The samples collected by the wet chemical procedure were submitted for gas chromatographic (GC) analysis. The gas chromatographic technique employed to measure maleic anhydride/maleic acid used the following: H.P. 402 Gas Chromatograph equipped with flame ionization detector and on-column injection; column: F & M, 6 ft x 1/8 in. with Se-30 on 80-100 mesh support.

Grab Flasks

The samples collected by grab flasks were submitted to gas chromatograph (GC) analysis to determine total hydrocarbon (THC), methane (CH_4), and carbon monoxide (CO) concentrations.

The method used to measure THC, CH_4 and CO was based on a standard EPA procedure described in Federal Register Vol. 36, No. 228, 25 November 1971. The technique used a gas chromatographic system equipped with a flame ionization detector. Measured volumes of gas samples were delivered directly (no analytical column) to the flame ionization detector to measure THC content. An aliquot of the same gas sample was introduced into a stripper column which removes water, carbon dioxide, and hydrocarbons other than methane. Methane and carbon monoxide were passed quantitatively to a gas chromatographic column where they were separated. The methane was eluted first and passed unchanged

through a catalytic (nickel) reduction tube into the flame ionization detector. The carbon monoxide eluted into the catalytic reduction tube where it was reduced to methane before passing through the flame ionization detector.

The system was calibrated with standard gas mixtures of CH_4 and CO in synthetic air prepared by Scott Research Labs. The standard EPA procedure for reporting THC was based on using CH_4 equivalents.

Packed Porous Polymer Tubes

The samples collected by packed porous polymer (PPP) tubes were submitted to gas chromatograph and mass spectral (GC/MS) analysis. The tubes were thermally desorbed as a helium flow was passed through the tubes in a reverse direction to which the samples were taken. The desorbed samples were passed through a heated line into a Hewlett-Packard (HP) GC/MS system. The GC/MS system was comprised of the following components:

- HP 5982A Mass Spectrometer - dodecapole with vacuum system and control unit, GC/MS membrane interface, and heated expansion volume inlet
- Chemical ionization source and gas manifold system
- Direct introduction probe
- HP 5780A Gas Chromatograph, with digital oven programmer for subambient operation with nitrogen (N_2), and heated gas sampling valve
- HP 5933A Data System - 8K computer, with dual disk memory (capacity for 0.5 million spectra per disk), Aldermaston spectra library (12,800 spectra), complete software package of HP mass and standard computer programs
- High speed plotter, CRT graphic display, and hard copier

The classes of compounds present were identified by their mass spectra and quantified by ratioing intensity-areas of the main ion peaks for the compounds to the response for a benzene standard, also thermally desorbed from a Tenax tube.

GLOSSARY

affected population: Number of nonplant persons living in the area around a representative plant where the ratio of the ground level concentration of airborne materials to the hazard factor is greater than 1.0 or 0.1, as specified.

criteria pollutant: Emission species for which ambient air quality standards have been established; these include particulates, sulfur oxides, nitrogen oxides, carbon monoxide, and nonmethane hydrocarbons.

emission factor: Quantity of a species that is emitted per unit weight of final product.

fugitive emissions: Gaseous and particulate emissions that result from industrial related operations or sources, such as seals, flanges and valves, but which are not emitted through a primary exhaust system, such as a stack, flue, or control system.

hazard factor: Value equal to the primary ambient air quality standard in the case of criteria pollutants or to a reduced TLV (i.e., TLV • 8/24 • 1/100) for noncriteria pollutants.

incinerator-scrubber: System which includes a thermal oxidizer to reduce organic emissions and a scrubber to remove the products of combustion from the incinerator flue gas.

noncriteria pollutant: Emission species for which no ambient air quality standards have been established.

representative plant: Plant defined for the purpose of establishing a base on which to determine the emissions and severity of a source.

Scientific Design process: Process for the production of maleic anhydride based on air oxidation of benzene in the presence of a catalyst.

source severity: Ratio of the time-averaged maximum ground level concentration of an emission species to the hazard factor for the species.

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE SOURCE ASSESSMENT: MALEIC ANHYDRIDE MANUFACTURE		5. REPORT DATE December 1978 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. A. Lewis, Jr., G. M. Rinaldi, and T. W. Hughes		8. PERFORMING ORGANIZATION REPORT NO. MRC-DA-719
9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation 1515 Nicholas Road Dayton, Ohio 45407		10. PROGRAM ELEMENT NO. 1AB604 11. CONTRACT/GRANT NO. 68-02-1874
12. SPONSORING AGENCY NAME AND ADDRESS Office of Research and Development Industrial Environmental Research Laboratory U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Task Final 9/75 - 12/78 14. SPONSORING AGENCY CODE 600/12
15. SUPPLEMENTARY NOTES IERL-Ci task officer for this report is R. J. Turner, 513/684-4481		

16. ABSTRACT

This report summarizes data on air emissions from maleic anhydride manufacture. Maleic anhydride is manufactured primarily by the catalytic oxidation of benzene; butane feedstock is also used domestically. Emission points in a maleic anhydride plant include the product recovery scrubber, secondary scrubber, vacuum system vent, incinerator-scrubber vent, and storage tanks. To assess the environmental impact of this industry, source severity was defined as the ratio of the time-averaged maximum ground level concentration of an emission to a potentially hazardous concentration from a given point. Source severities are 0.04 and 3,820 for particulate from the incinerator-scrubber vent and fugitive emissions, respectively; 0.47 for nitrogen oxides; 0.73 for carbon monoxide; and 0.6 to 25.1 for hydrocarbons from various emissions points. Severities for noncriteria pollutants were also calculated. Assuming the same level of control in 1979 as existed in 1974, emissions from this industry will increase by 34% over that period.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Assessments Maleic anhydride	Air Pollution Control Source Assessment	13B
18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES 120 22. PRICE

EPA Form 2220-1 (9-73)