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ASSESSMENT OF MALEIC ANHYDRIDE AS A POTENTIAL AIR POLLUTION PROBLEM

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by

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ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

Volume I	Acetylene
Volume II	Methyl Alcohol
Volume III	Ethylene Dichloride
Volume IV	Benzene
Volume V	Acetone
Volume VI	Acrylonitrile
Volume VII	Cyclohexanone
Volume VIII	Formaldehyde
Volume IX	Methyl Methacrylate
Volume X	Ortho-Xylene
Volume XI	Maleic Anhydride
Volume XII	Dimethyl Terephthalate
Volume XIII	Adipic Acid
Volume XIV	Phthalic Anhydride.

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SECTION I

SUMMARY AND CONCLUSIONS

Maleic anhydride is a white, crystalline solid with a sharp, irritating odor. The primary method of manufacture is based on the reaction between benzene vapor and air in the presence of a vanadium catalyst; and it is used to manufacture phthalic anhydride, esters, polyester resins, dye intermediates, pharmaceuticals, agricultural chemicals, and fumaric acid.

Maleic anhydride dust or vapor is an acute skin, eye, and respiratory tract irritant at concentrations of about 2 ppm. Sensitization is possible, so that much lower concentrations will be irritating to sensitized persons. The U.S. occupational standard for exposure to maleic anhydride is 1 mg/m^3 (0.25 ppm) for an 8-hour time weighted average, based on skin, eye, and upper respiratory tract irritation data.

Simple, worst case diffusion modeling estimates place the likely maximum 1-hour average ambient concentration at about 0.79 mg/m^3 (0.20 ppm). The maximum 24-hour average ambient concentration might be expected to be about 0.44 mg/m^3 (0.10 ppm).

About 283 million pounds of maleic anhydride were produced at seven plants in 1974, with 50 percent of this being used in the manufacture of polyester resins. Total production is expected to increase at 10 percent per year for the next several years. The primary emission sources in descending order are phthalic anhydride production, maleic anhydride production, end product manufacture, and packaging losses. Total emissions are estimated to have been 4.72 million pounds in 1974.

Control of maleic anhydride emissions can be effected by scrubbing the uncondensed portion of the reactor effluent after it passes through a partial condenser. This is done principally to recover maleic anhydride. Scrubbing is also used to control particulate emissions from flaking, tableting, and packaging operations with efficiencies of at least 98 percent. A number of other techniques are under development for controlling maleic anhydride emissions.

Based on the results of the health effects research presented in this report, and the ambient concentration estimates, it is possible that maleic anhydride as an air pollutant might pose a threat to the health of the general population. However, the concentration estimates are extremely conservative and the individual sources and ambient concentrations should be investigated further before any regulatory action is contemplated.

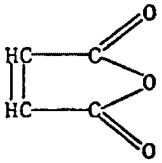
SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Maleic anhydride is a white crystalline solid with a sharp irritating odor. The main method of manufacture is the reaction between benzene vapor and air in the presence of a vanadium catalyst. It is used in the production of esters, polyester resins, dye intermediates, pharmaceuticals, agricultural chemicals, and fumaric acid. Significant properties are given in Table 1.

Table 1. SIGNIFICANT PROPERTIES OF MALEIC ANHYDRIDE

Synonyms:	cis-buternedioic anhydride, 2,5-furandione, maleic acid anhydride, toxilic anhydride
Chemical formula	
Molecular weight	98.06
Boiling point	200-202°C at 760 mm Hg
Melting point	52-53°C
Specific gravity	0.934 (20°/4°C)
Vapor density	3.4 (air 1)
Vapor pressure	1.9 mm Hg at 50°C 0.10 mm Hg at 25°C
Solubility	Soluble in water, but hydrolyzes slowly. Also soluble in acetone, ethyl acetate, chloroform, and benzene.
At 25°C and 760 mm Hg	1 ppm vapor 4.01 mg/m^3 1 mg/m^3 vapor 0.25 ppm

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Maleic anhydride dust or vapor is an acute skin, eye, and respiratory tract irritant. Human sensory response data are presented in Table 2.[1,2] The Russian literature[1] gives the threshold of irritative action as 1 mg/m^3 (0.25 ppm vapor), and the odor threshold as 1.3 mg/m^3 (0.33 ppm vapor). Persons not accustomed to handling maleic anhydride showed nasal and upper respiratory tract irritation within 1 minute at 6.0 - 8.0 mg/m^3 (1.5 2.0 ppm.) Eye irritation followed within 15 to 20 minutes.[1] However, maleic anhydride is a respiratory tract sensitizer and any concentration may initiate a reaction in highly sensitized persons. Concentrations above 10.0 mg/m^3 (2.5 ppm) vapor are immediately irritating to man. Chronic ulceration and congestion of the nasal mucous membranes may occur from severe exposures. No deaths have been reported in the literature.

Table 2. HUMAN SENSORY RESPONSE TO MALEIC ANHYDRIDE[1,2]

Exposure		Time	Response
mg/m^3	ppm vapor		
1.0	0.25		Threshold or irritative action[1]
1.0	0.25		May cause eye discomfort[1]
1.3	0.33		Smell threshold for sensitive people[1]
2.0	0.50	2-3 hours	Faint odor; no nose, throat, eye, or skin irritation[2]
6.0 - 8.0	1.5 - 2.0	1 minute	Upper respiratory irritation; nasal irritation[2]
6.0 - 8.0	1.5 - 2.0	15-20 minutes	Eye irritation[2]
10.0	2.5	Immediate	Extreme, acute irritation[2]

Contact of maleic anhydride and its dust with moist skin will cause an immediate burning sensation.[1] If the skin is dry there may be no burning. Continued skin contact will cause reddening, burning, and blistering. Maleic anhydride is a skin sensitizer, and contact dermatitis may result from repeated and prolonged contact. It is readily absorbed through skin despite the burning.

Eye irritation at 1 mg/m^3 (0.25 ppm) has been observed.[1] Marked irritation of the conjunctiva and corneal swelling can be caused by exposure to vapor above 6.0 8.0 mg/m^3 (1.5 - 2.0 ppm.) Double vision and intolerance to light may result, but the effects are usually temporary. Severe exposure will cause corneal burns.[3]

The U.S. occupational standard for exposure to maleic anhydride is 1 mg/m^3 (0.25 ppm) for an 8-hour time weighted average.[4] This standard is based on human skin, eye, and upper respiratory tract irritation data.

Chronic Poisoning Maleic anhydride vapors or dust mainly act as acute irritants. However, repeated exposure to concentrations above 5 mg/m^3 (1.25 ppm) has caused an asthmatic response in workers,[1] which can persist after the removal of the vapor.[5] An allergy can develop such that lower concentrations can no longer be tolerated. There is an increased incidence of chronic bronchitis. Repeated exposures may cause dermatitis.[1]

Effects on Animals

Acute Poisoning Maleic anhydride dust or vapor acts as an acute irritant on the eyes, skin, and upper respiratory tract of animals. As in man, any concentration of dust or vapor in air may initiate a reaction in sensitized animals.

Direct contact with the powder or solution can produce severe eye burns. The conjunctival sac of rabbits was filled with 1 percent and 5 percent maleic anhydride solutions and drained after 2 minutes.[6] Membrane irritation and cloudiness of the cornea lasted 1 day after administration of the 5 percent solution. A minute amount of powder placed in the eyes of rabbits was allowed to be washed away by tears. The cornea immediately clouded, with the animal in obvious pain. After 24 hours severe inflammation persisted, and edema and corneal ulcers had developed. Seven weeks after treatment the rabbit corneas were white, opaque, and well vascularized with obvious impairment of vision.

Maleic anhydride is a skin sensitizing agent in animals,[7] and direct contact with the powder or liquid can cause severe burns. The skin LD_{50} in guinea pigs was greater than 20 mg/kg body weight.[8]

The oral LD_{50} in rats for a single administration is in the range of 400-800 mg/kg.[8] The single dose oral LD_{50} for the guinea pig is 390 mg/kg, 465 mg/kg for the white mouse, 850 mg/kg for the white rat, and 875 mg/kg for the rabbit.[9]

Chronic Poisoning Maleic anhydride acts primarily as an acute irritant. However, as in man, chronic vapor exposure at any level will cause respiratory discomfort to sensitized animals.

Oral administration of 85 mg/kg (0.1 LD_{50})[9] in the white rat for 20 days caused no cumulative toxic effects. One mg of maleic anhydride dissolved in oil was subcutaneously injected twice weekly for 61 weeks into 100-gram rats.[10] The total dose corresponded to 122 mg/kg body weight, with tumors developing 80 weeks after the first dose.

Effects on Vegetation

The effects of maleic anhydride on vegetation have not been documented in the literature.

Effects on Materials

Above 150°C maleic anhydride decomposes in the presence of alkali metals and amines. Its vapors and dust are flammable.

AMBIENT CONCENTRATIONS AND MEASUREMENTS

Ambient Concentration Estimates

The largest emission source of maleic anhydride is a production facility for phthalic anhydride with a capacity of 130 million pounds per year. This facility is located near Chicago, which has a population of over 3 million. The emission factor for phthalic anhydride is 0.0015, and emissions of maleic anhydride are estimated to be 1.9 times those of phthalic anhydride.

Hence, the emission rate is

$$\frac{(1.9)\ (0.0015\ \text{emission factor})\ (130 \times 10^{6}\ \text{lb/yr})\ (453.6\ \text{g/lb})}{3.1536 \times 10^{7}\ \text{sec/yr}}$$

$$= 5.3\ \text{g/sec of maleic anhydride.}$$

Some assumptions must be made regarding this chemical release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant where maleic anhydride leaks to the atmosphere. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed.

Ground level concentrations can then be estimated at locations downwind of the facility.[11] To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100\text{m}/4.3 = 23.3\text{m}$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z}\, e^{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2}$$

or

$$\chi = \frac{5.3}{(2)\ \pi\ (36)\ (18.5)}\, e^{-\frac{1}{2}\left(\frac{10}{18.5}\right)^2}$$

$$= 1.09 \times 10^{-3}\ \text{g/m}^3$$

for a 10-minute average concentration. Over a period of an hour this becomes 1.09×10^{-3} (0.72) = 0.79 mg/m^3 (or 0.20 ppm vapor) 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 0.44 mg/m^3 (0.11 ppm vapor).

Maleic Anhydride Measurement Techniques

Very limited data exist in the literature for the determination of maleic anhydride in air. A polarographic method[12] has been modified for analysis of airborne maleic anhydride by utilizing a midget impinger containing 10 ml of 1.0 N potassium hydroxide. However, no information is available concerning its lower detection limit or its accuracy.

Other methods for the determination of maleic anhydride are infrared and mass spectrometry and gas chromatography.[12,13] All of these methods are capable of detecting maleic anhydride in the parts per million range, and if a flame ionization detector is used with the gas chromatograph, concentrations as low as 1 ppb can be detected.

SOURCES OF MALEIC ANHYDRIDE EMISSIONS

Maleic Anhydride Production and Consumption

The production of maleic anhydride in 1974 was 283 million pounds[14] and is expected to increase at 10 percent per year for the next several years. Its major use, accounting for about 50 percent of total production, is in the formulation of polyester resins. An additional 25 percent is used as an intermediate in the production of fumaric acid and agricultural pesticides. Alkyd resins and other miscellaneous uses account for the remaining 25 percent of production. Presently six companies at seven locations are manufacturing maleic anhydride, as listed in Appendix A. Consumption for final products and the expected growth rates for each sector of the market are presented in Table 3.

Maleic Anhydride Sources and Emission Estimates

Primary sources of emissions of maleic anhydride result from the production of phthalic anhydride, the production of maleic anhydride, material handling and packaging losses, and from the manufacturing of end products. Total emissions from all categories are estimated to be 4.72 million pounds, representing 1.7 percent of total production. See Table 4.

The major source of maleic anhydride emissions results from the manufacturing of phthalic anhydride. Maleic anhydride is formed as a side reaction during the manufacturing process and is primarily emitted from the main process vent gas stream. It is estimated, based upon recently

Table 3. ESTIMATED MALEIC ANHYDRIDE CONSUMPTION 1974[15]

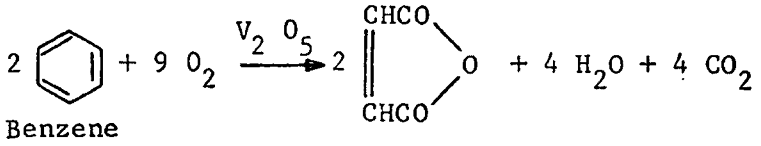
Product	Million pounds	% annual growth
Unsaturated polyester resins	141	13
Fumaric acid	25	0
Lubricating additives	22	10
Reactive plasticizers	15	10
Copolymers	16	10
Maleic acid	13	10
Malathion	12	6
Chlorendic anhydride	10	20
Alkyd resins	5	2
Maleic hydrazide	4	5
Captan	4	1
Surface-active agents	2	5
Other	14	5
Total	283	10

Table 4. SOURCES AND EMISSION ESTIMATES OF MALEIC ANHYDRIDE - 1974

Source	Emissions, million pounds
Phthalic anhydride production	2.96
Maleic anhydride production	0.85
Packaging losses	0.06
End product manufacturing	0.85
Total	4.72

published data,[16] that emissions of maleic anhydride are approximately 1.9 times greater than the emissions of phthalic anhydride. Since emissions of phthalic anhydride from the manufacturing process have been estimated at 1.56 million pounds,[17] it is estimated that maleic anhydride emissions from the manufacturing of phthalic anhydride are approximately 2.96 million pounds.

The second major source of emissions results from the manufacturing of maleic anhydride. Maleic anhydride is manufactured primarily from benzene, which is converted to maleic anhydride by catalytically oxidizing it in the vapor-phase. The reaction is presented below.



Losses from this manufacturing process are reported[18] to be approximately 0.3 percent with the scrubber exhaust from the product recovery vent being the prime contributor (90 percent). Using this emission factor and the total production (283 million pounds) results in approximately 0.85 million pounds being emitted. Since there are no data available concerning emission rates for end product manufacturing it is assumed that the 0.3 percent factor will also apply to the manufacturing of all end products. Therefore, this will also result in 0.85 million pounds of maleic anhydride emissions.

The last major source of emissions results from product handling and packaging. It has been reported that 0.0002 pounds of maleic anhydride is emitted from product flaking, pelleting, packaging and storage per pound of maleic anhydride produced.[18] This factor applied to the most recent production figure results in approximately 0.06 million pounds of material lost.

MALEIC ANHYDRIDE EMISSION CONTROL METHODS

Most plants currently scrub the uncondensed portion of the reactor effluent after it passes through a partial condenser. This is done principally to recover maleic anhydride. Many plants do utilize this same control device to scrub vent gases from various other areas of the plant. However, CO and hydrocarbon emissions (benzene, maleic anhydride and formic acid) are quite high. Appreciably better control could be achieved by combining the product scrubber with a combustion type device. One plant is currently planning such an installation with a reported total cost of \$1,000,000.[18]

Several plants utilize separate scrubbers to control emissions of maleic anhydride particulates from their flaking, tableting, and packaging operations. Expected scrubbing efficiencies are 98 percent and higher.

Developmental work in reducing emissions has been suggested for the following areas. It is not currently known if any or all of these practices have or will be studied.

1. Substitution of oxygen for air.
2. Fluidized bed development for reduction of air/benzene.
3. Development of a more selective catalyst.
4. Better utilization and design of current control equipment.
5. Use of recycled air to improve yield and reduce emissions.

SECTION III

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APPENDIX A

MALEIC ANHYDRIDE MANUFACTURERS[19]

		Annual capacity,* million pounds
Koppers Co.	Bridgeville, Pennsylvania	34
Monsanto	St. Louis, Missouri	105
Petro-Tex Chemical	Houston, Texas	50
Reichold Chemicals	Elizabeth, New Jersey	30
Reichold Chemicals	Morris, Illinois	60
Tenneco Chemicals	Fords, New Jersey	26
U.S. Steel Corp.	Neville Island, Pennsylvania	40
	Total	345

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*As of March 1975.