

# MALEIC ANHYDRIDE

B. C. Trivedi and B. M. Culbertson

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# PREFACE

In just fifty years maleic anhydride has evolved from a little-known, little-used compound to a truly high-volume chemical. Between 1940 and 1978 its production has increased seventy-fivefold. The fact that more than half of all maleic anhydride produced in the United States is consumed in a single application tends to obscure the great versatility of this intermediate. Because this relatively simple molecule plays a key role in numerous chemical reactions, it finds applications in such diverse areas as adhesives, elastomers, plastics, coatings, fibers, lubricants, fuels, detergents, agricultural chemicals, pharmaceuticals, and surfactants, to name only a few.

The chemistry of the maleic anhydride molecule seems to be uniquely suited to illuminate many facets of organic chemistry. In addition to its important role in functional-group chemistry, study of maleic anhydride lends itself to analysis of such diverse processes as ionic, radical, and cycloaddition reactions. Similarly, polymer chemistry is exemplified in a variety of ways by reactions of maleic anhydride, including its role in charge-transfer, addition, and condensation polymerizations.

Although some aspects of the maleic anhydride molecule are well understood, others need extensive research and elucidation. Further, the development over the last twenty years of new processes utilizing maleic anhydride, such as photochemistry, homopolymerization, and charge-transfer polymerization, suggests that the potential of this intermediate is far from exhausted. Herein, we believe, lies a challenge for chemists and technologists.

The existence of extensive archival, trade, and patent literature and a large market notwithstanding, no comprehensive, hardbound, technical reference work on maleic anhydride has so far been available. This book attempts to correct that situation and provides, for the first time, a single reference source of scientific background information and state-of-the-art technical data on this unique chemical. *Maleic Anhydride* collates the interesting chemistry of maleic anhydride that was until now scattered over 30,000 references, including patents, giving equal emphasis to fundamental and applied chemistry, while at the same time directing the reader's attention to sources for reaction recipes.

In keeping with the authors' intent to furnish chemists, chemical engineers, and others interested in maleic anhydride with an accurate and practical reference source, the book provides not only a review and discussion of key raw materials, production procedures, and the economics of maleic anhydride, but also delves into the multifaceted chemistry and polymerization

reactions of the monomer. Uses, both known and potential, are surveyed and discussed, and attention is also paid to health and safety factors.

It is the authors' hope that the breadth of the material and the thoroughness of presentation will make *Maleic Anhydride* of value to both technologist and scientist as well as to those concerned with the production and marketing of the raw material and its derivatives.

Columbus, Ohio  
1981

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# INTRODUCTION

## 1.1. INTRODUCTION

Maleic anhydride (MA)\* was first produced some 150 years ago by dehydration of maleic acid. Today, it is a chemical of considerable commercial importance. Next to acetic and phthalic anhydride, it is the second most important anhydride in commercial use.

From only 4.5 million lbs produced in 1940,<sup>(1,2)</sup> MA has gained impressively, with a production of 341 million lbs in 1978.<sup>(3)</sup> MA has seen some impressive growth periods in the past as is evident in Fig. 1-1. The effect of the oil embargo of 1974 is also evident.<sup>(2)</sup> Japan saw an average 27% increase in MA consumption during the period 1971-1973.<sup>(2,4)</sup>

Table 1.1. Maleic Anhydride Production Capacity<sup>(5)</sup>

Producer	Raw material <sup>a</sup>	Capacity, million lb/year
Amoco Joliet, Illinois	Butane	60
Ashland Chemical Neil, West Virginia	Benzene	60
Denka Houston, Texas	Benzene	50
Koppers Company <sup>b</sup> Cicero, Illinois	By-product from PA	10
Monsanto <sup>d</sup> St. Louis, Missouri		115
Reichhold Chemical <sup>c</sup> Morris, Illinois	Benzene	44
Tenneco Fords, New Jersey	Benzene	26
USS Chemical Neville Island, Pennsylvania	Benzene	80

<sup>a</sup> New EPA regulation requiring 100% control of benzene (no detectable benzene emissions) for new plants may favor butane-based plants in the future (Federal Register, April 18, 1980).

<sup>b</sup> Koppers shut down a benzene-based facility.<sup>(7)</sup>

<sup>c</sup> Reichhold closed a benzene-based plant (60 million lb/year) in October 1979.

<sup>d</sup> Monsanto reportedly uses butane feed stock for about 20% of its capacity. Also, it has announced plans for additional 130 million lb/year capacity of butane-based MA.<sup>(8)</sup> The plant is scheduled to be on stream in early 1983.

\* Sometimes in the literature acronyms MAN and MAH are used. For this work, MA will be used.

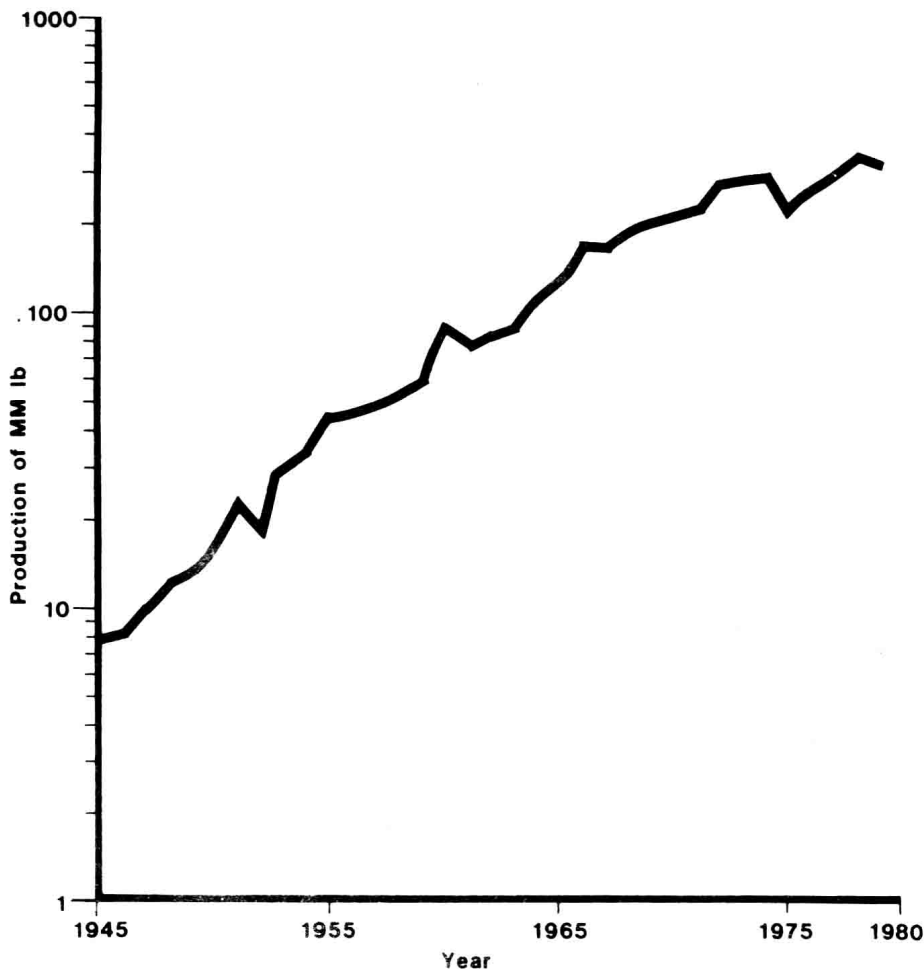


Fig. 1-1. U.S. production of MA.

In the United States there are currently eight major producers of MA. Table 1.1 gives a list of producers along with their location and production capacities; the raw material used by each is also indicated.

## 1.2. PROPERTIES AND STRUCTURE OF MA

Maleic anhydride (MA) is chemically 2,5-furandione,\* or *cis*-butene-dioic anhydride. It is also known by other names such as toxilic anhydride, maleic

\* CAS Registry No. 108-31-6.



Table 1.2. Physical Properties of MA<sup>(9,40,58)</sup>

Crystalline forms	Needles, rhombic
Flash point	Open cup 110°C (230°F) Closed cup 102°C (215°F)
Flammable limits (by volume)	Lower 1.4%, Upper 7.1%
Autoignition temperature	477°C (890°F)
Boiling point at 760 mm Hg	202°C (395°F)
Color	Colorless crystals
Corrosivity	Not corrosive to metals except in the presence of water
Deliquescence	Slight
Density (water = 1.00)	Molten 1.3 g/cm <sup>3</sup> at 70°C. Solid 1.48 g/cm <sup>3</sup>
Heat of combustion	333.9 kcal/mole (332.29 kcal/mole) <sup>(75)</sup>
Heat of evaporation	13.1 kcal/mole
Heat of fusion	3.26 kcal/mole (2.929 kcal/mole) <sup>(62)</sup>
Light sensitivity	None
Melting point (freezing point)	52.8°C (127°F) (However, see Ref. 58)
Odor	Acrid
Solubility in water	Hydrolyzes slowly
Specific heat	0.285 (solid), 0.396 (liquid)
Vapor density (air = 1)	3.38
Dipole moment (benzene, 25°C)	3.92–3.95 D <sup>(73)</sup>
Viscosity (absolute)	15 millipoises at 70°C (158°F)
Threshold limit value (OSHA)	0.25 ppm or 1 mg/M <sup>3</sup>

acid anhydride, or malic acid anhydride. It is a white hygroscopic solid and forms orthorhombic crystalline needles. In Table 1.2 physical properties of MA are given.<sup>(9)</sup> Data on vapor pressure of MA are given in Fig. 1-2.<sup>(9,10)</sup> Note that even as a solid it has a significant vapor pressure and this should be kept in mind while handling it.<sup>(11)</sup> Commercially, it is available from producers either as a molten liquid or as briquettes.

Recently, Vykhest *et al.*<sup>(82)\*</sup> have examined the temperature dependency of the viscosity, electrical conductivity, and density of MA, thus providing data of considerable importance in handling MA.

MA, being an anhydride, is subject to hydrolysis to the acid on storage. Thus, to obtain a pure sample of MA, purification is necessary. It is purified commercially by distillation. In small-scale laboratory-type uses, MA can be purified by sublimation or crystallization. Its solubility in various solvents is given in Table 1.3.<sup>(12)</sup> Chloroform or aromatic solvents such as benzene, toluene, and xylene are adequate as crystallizing solvents. Larger batches may

\* In this reference viscosity and conductivity seem to have been measured at 50°C. This is strange considering the melting point of MA is 53°C (Table 1.2).