

AP42 Section 6.10

Background Report: AP42 Background Documentation for  
Maleic Anhydride, Section 5.26

@1980. This is the only background documentation

AP-42 BACKGROUND DOCUMENTATION

FOR

MALEIC ANHYDRIDE

Section 5.26

The principal document used to derive the emission factors was the Maleic Anhydride - Product Report by J. F. Lawson.<sup>1</sup> The four sources of emissions are product recovery absorber and refining vacuum system combined vent, storage and handling, fugitive, and secondary.

It is uncertain exactly how the uncontrolled emission factors for the product recovery absorber and refining vacuum system combined vent were arrived at in the Hydrosience report. J. F. Lawson, the original author of the report, is no longer with Hydrosience. The man currently in charge of this report is Ralph White. The explanation he gave was that a weighted average of site visits and factors from Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume III<sup>2</sup> were used to derive factors which were then adjusted for the model plant. Mr. White could not give me any details on how the emission factors were derived because the information was not readily available. If the EPA desired the details they would need to sign a voucher because Mr. White believed it would take a couple of hours to derive that number and the EPA has no contract with Hydrosience at the present. The model MA plant has a capacity of 22,700 MT of MA/year. One year is equivalent to 8000 hours. Mr. White said that they are currently revising this report such that one year will be equivalent to:

$$8760 \text{ hours} \left( 1 \text{ year} \times \frac{365 \text{ days}}{1 \text{ year}} \times \frac{24 \text{ hours}}{1 \text{ day}} = 8760 \text{ hours} \right)$$

He said a change in the efficiency of the thermal oxidizer from 99.5 percent to 99 percent for secondary emission are also in order for the revision. The change in the number of hours per year would not change the emission per metric ton of maleic anhydride produced. Any questions in regard to these emissions factors are referred to Ralph White of Hydrosience, Inc., Knoxville, TN at (615) 690-3211.

In the section I say that the conversion of benzene to MA is 94.5 percent. No mention of the conversion rate is given in the Hydrosience product report. I got the number from the BID report on benzene emissions from the MA industry<sup>3</sup> developed by ESED. The Hydrosience product report was written for ESED in preparation for the BID. In the BID they use the same uncontrolled emissions as the Hydrosience product report but they also give a 94.5 percent conversion rate. I don't know why they used that number or how with that number one can arrive at the given emission factors.

A possible approach on how the uncontrolled benzene emissions were derived is as follow:

1. Three to ten percent of total benzene feed will be unreacted.<sup>4</sup>  
Or, an average of 6.5 percent will be unreacted.

2. 93.5 percent of the benzene feed will be converted into MA and other organic materials that occur from side reactions.

$$3. \frac{22700 \text{ MT of MA produced}}{1 \text{ year}} \times \frac{1 \text{ year}}{8000 \text{ hours}} \times$$

$$\frac{1000 \text{ kg}}{1 \text{ MT}} = \frac{2837.5 \text{ kg of MA produced}}{1 \text{ hr}}$$

4. If T = total kg of benzene fed per hour  
and  $T(0.935) = 2837.5 \text{ kg of MA produced}$

then

$$T = 3034.759\dots$$

Therefore

$$(3034.76)(0.065) = 197.26 \text{ kg of benzene unreacted/hr}$$

The equation  $T(0.935) = 2837.5$  is not exactly true. Because  $T(0.935)$  equals the amount of MA and other organic materials formed in the reactor, not just MA, and 2837.5 is the amount that is finally produced. If we knew exactly how much MA was produced in the reactor we would not necessarily get that same quantity in the end product. Some MA may change into another chemical form or escape into the atmosphere further on in the process. Taking the average of the percent of the total benzene feed may not be an accurate procedure. If we were to use 3 percent instead of 6.5 percent we would have 87.76 kg of benzene unreacted/hr. If we were to use 10 percent we would have 315.28 kg of benzene unreacted/hr.

It is not known how Monsanto arrived at the fact that three to ten percent of the total benzene feed will be unreacted. Now assuming the uncontrolled emissions in the Hydrosience report are correct the controlled emission can be calculated.

Both the carbon adsorbtion and the incineration control system<sup>CAN</sup> have an efficiency of 99.5 percent according to Lawson's report. So for benzene,  $67 \text{ kg/MT} \times 0.005 = 0.335 \text{ kg/MT}$ . For total VOC it is 0.335 kg/MT also because in order to use the carbon adsorption, the exhaust gas stream must be scrubbed with caustic to remove organic acids and water-soluble organics. Benzene is likely the only VOC remaining. For incineration, the emissions are  $67 \text{ kg/MT} \times 0.005 = 0.335 \text{ kg/MT}$  and  $86 \text{ kg/MT} \times 0.005 = 0.43 \text{ kg/MT}$ .

Emissions can result from the storage and handling of benzene, xylene, and maleic anhydride. It was decided not to use the storage and handling emissions as given in the Hydroscience product report for two reasons. First, I could not reproduce the emission factors they had and second, it was felt that the reader could figure out more accurately the emission factors from the other section since he would know the storage and handling parameters of the MA plant in question.

Fugitive emissions can result from process pumps and valves. For the same two reasons I gave for storage and handling emissions, I decided not to use the emission factors for fugitive emissions as given in the Hydroscience product report.

The four potential sources of secondary emissions are spent reactor catalyst, aqueous effluent from the dehydration column, aqueous effluent from the refining vacuum system, and residue stream from the fractionation column. I didn't use the emission factors from the Hydroscience product report because I was informed by Bob Weber on April 22, 1980 that these emission factors are engineering estimates and not from real tests. Bob Weber recommended that I not use those numbers.

People who reviewed my work and would be of help if there are any questions in regard to MA are:

John Warren - Research Triangle Institute, 919 541-6478  
Bob Weber - EPA, (FTS) 684-4481 Cincinnati  
Rick Coyler and David Patrick - EPA, ESED, (FTS) 541-5477

#### References

1. J. F. Lawson, Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry: Maleic Anhydride - Product Report EPA Contract Number 68-02-2577, Hydroscience, Inc., Knoxville, TN, March 1978.
2. J. W. Pervier, et. al, Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume III, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1974.
3. Benzene Emissions from Maleic Anhydride Industry - Background Information for Proposed Standards, EPA-450/3-80-001a, U. S. Environmental Protection Agency, Research Triangle Park, NC, February 1980.
4. W. A. Lewis, G. M. Rinaldi, and T. W. Hughes, Source Assessment: Maleic Anhydride Manufacture, EPA Contract Number 68-02-1874, Monsanto Research Corporation, Cincinnati, OH, December 1978, p. 3.

Andrew M. Smith  
Andrew M. Smith