13799.000

REF #1

5.13 Plastics

Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va Prepared for National Air Pollution Control Administration, Durham, N.C., Contract Number CPA-22-69-119. April 1970.

This document is in two parts: The main volume (April 1970) and a Supplement dated August 1970.

# AIR POLLUTANT
# EMISSION FACTORS

April 1970

Prepared for

Department of Health, Education and Welfare
Public Health Service
Environmental Health Service
National Air Pollution Control Administration
Washington, D. C.

TRW
SYSTEMS GROUP OF TRW INC.

# 1. INTRODUCTION

This report represents a compilation of the latest atmospheric emission data available for a wide variety of selected processes. One-half of the 40 processes discussed in this report involve an updating or review of existing emission factors presented in Public Health Service Publication 999-AP-42, "A Compilation of Air Pollutant Emission Factors" by R.L. Duprey. The remaining factors represent new processes for which emission factors were not previously reported. All emission factors refer to uncontrolled processes unless otherwise stated.

Information for emission factors was gathered primarily from the technical literature up to November 1969, state and local air pollution control agencies, trade and professional associations, releasable portions of data obtained by TRW in various past studies, and individual companies and persons within the various industries under study. In all cases, attempts were made to obtain some idea of the validity of the information obtained, and thus place each bit of data relative to other data in the same area. Greatest weight was given to actual measured emission data, i.e., source tests, especially when the measuring technique was known. Estimates of emissions were also made when feasible by making material balances and process loss or yield calculations.

In general, it was found that except for the combustion and incineration fields, very little new emission factor data has been made public since Duprey's work in 1967. In the metallurgical and mineral industries, additional emission data has been obtained by various companies and control equipment manufacturers. This information has not been made public, however. Some emission data was available for most of the new factors developed in this report. Frequently, however, these data were in the form of concentrations only, not quantitative emission rates. Process weight rates were also frequently not given or reported. Considerable engineering calculations were thus required in order to put these data into a form usable for emission factors. These calculations, based on material balances, combustion reactions, humidity balances, and comparisons with similar processes with available emission data, allowed one to relate the reported data with process throughputs and develop a factor which is usable until better data are made available.

Detailed information used to obtain the emission factors is generally presented in an appendix to each section. Selection of a final emission factor depended on the amount and range of data available. Where considerable data existed a direct arithmetic average was used. Values on order of magnitude greater or less than the bulk of the data were not considered in determining the arithmetic average. Where limited data were available (1 to 5 values) and the values covered a wide range, the selected factor was based on our best judgment considering the factors affecting emissions. Whenever possible, the range or variation in emission factors was reported and shown in parenthesis following the factor. This range represents the range of values used in obtaining the factor and represents the expected variation in emissions. A lack of information sometimes prevented the reporting of a reasonable factor range.

Standard statistical deviations of the emission factors were not generally reported since insufficient or only widely scattered data were available and a significant deviation could not be calculated.

All emission factors in this report were ranked according to the available data upon which they were based. A system which weighted various information categories was used to rank the final factors. These categories were: measured emission data with a total possible weight of 20, process data with a weight of 10, and engineering analysis with a weight of 10. The highest possible score for any factor was thus 40. Any factor ranking less than 20 was considered questionable and those ranked 20 or greater were considered reliable.

The emission data category rated the amount of measured emission data, i.e., stack test data available with which to develop an emission factor.

The process data category included such factors as the variability of the process and its effect on emissions, and available data on the variables. The engineering analysis category included the data available upon which a material balance or related emission calculation could be based.

The range of values for many emission factors is large. However, when the factors are applied to a large number of sources, the calculated overall emissions should approximate the true value. When applied to a single isolated source, an emission factor may yield emissions that differ considerably from the true value. Measured emission data should therefore be used, if possible, for single sources.

# 4. CHEMICAL MANUFACTURING INDUSTRIES

This section deals with the emissions from the manufacture and/or use of chemicals or chemical products. Potential emissions from many of these processes are high, but due to the nature of these compounds, they are, in general, recovered as an economic necessity to the profitable operation of the process. In still other cases, the manufacturing operation is run as a closed system allowing little or no escape to the atmosphere of any of the reactants or by-products.

In general, the emission which can reach the atmosphere from these processes is primarily gaseous and is controlled by incineration, adsorption, or absorption. In some cases, however, particulate emissions are also a problem from the manufacturing processes. When these occur, they are generally particles of extremely small size and require very efficient treatment for removal.

In a few cases, such as carbon black, charcoal, and rayon manufacture, emission of various noxious gases is a major problem which could be controlled, but control is apparently not economically attractive.

For many chemical processes emission data is extremely sparse, or non existent. Emissions were therefore frequently estimated based on material balances, yields, or similar processes. These factors are,of course,not as reliable as measured emission data.

Since the major emissions from the processes presented in this section are gases, no particle size summary is presented.

## 4.7 PLASTICS

### Process Description

The manufacture of most resins or plastics begins with the polymerization or linking of the basic compound (monomer) usually a gas or liquid, into high molecular weight non-crystalline solids. The manufacture of the basic monomer is not considered part of the plastics industry and is usually accomplished at a chemical or petrochemical plant.

The three largest selling plastics are currently polyethylene, polystyrene, and polyvinyl chloride. Consumption of some of the major plastics in 1967 were:[1]

| | |
|---|---|
| Polyethylene | 3632 million lbs/year |
| Polyvinyl Chloride | 2167 |
| Polystyrene | 2110 |
| Phenolics | 800 |
| Polypropylene | 641 |

Plastic manufacture of most compounds involves an enclosed reaction or polymerization step in the presence of a catalyst, a drying step, and a final treating and forming step. Two principal types of polymerization reactions occur in the manufacture of resins or plastics, namely, condensation and addition reactions. Condensation polymerization occurs when single molecules or monomers combine to form larger functional groups with a resulting loss of simple molecules such as water or alcohol. Addition reactions involve the joining of bonds between like molecules without the formation of any side products.

Phenolic and polyester resins such as phenol-formaldehyde are made via condensation reactions while polyolefins such as polyethylene, polyvinyl chlorides, and polystyrene are made by addition reactions.

Most plastics are polymerized or otherwise reacted in stainless steel or glass-lined vessels, which are completely enclosed, equipped with a stirring mechanism, and generally contain an integral reflux condenser. Since most of the reactions are exothermic, cooling coils are usually required. Some resins, especially those formed by condensation reactions, require that the kettle be under vacuum during part of the cycle. This can be supplied either by a vacuum pump or by a steam or water jet ejector. Alternatively, the addition reactions usually occur at elevated temperatures and pressures.

The following process description for polyvinyl chloride (PVC) also shown in Figure 4.7-1, will illustrate the steps involved in making many types of plastics.[2,3]

> The vinyl chloride monomer is purified by scrubbing and distillation, (the monomer is shipped with an inhibitor such as phenol to prevent polymerization). The purified monomer is then stored at 60°F at 50 psig before charging to the reactor. The polymerization addition reaction is carried out in a 3000 - 4000 gallon batch reaction at a temperature of 100 - 160°F and a pressure of 80 - 180 psig in the presence of organic peroxide, persulfate, or metallic chloride catalysts. Reaction time varies from 12 to 72 hours depending on the reaction conditions, desired product, and yield. The reactor contents are then stripped of unreacted monomer by applying a vacuum, and the polymerized slurry is dried in a spray dryer or dewatered and dried in a rotary dryer. Unreacted monomer is recycled. Particle size of the finished product varies from 0.1 to 1 micron and is further processed by adding plasticizers, stabilizers, etc.

Treatment of the resin after polymerization varies with the proposed use. Resins for moldings are dried and crushed or ground into molding powder. Resins, such as the alkyd resins, to be used for protective coatings are normally transferred to an agitated thinning tank, where they are thinned with some type of solvent and then stored in large steel tanks equipped with water-cooled condensers to prevent loss of solvent to the atmosphere. Still other resins are stored in latex form as they come from the kettle.

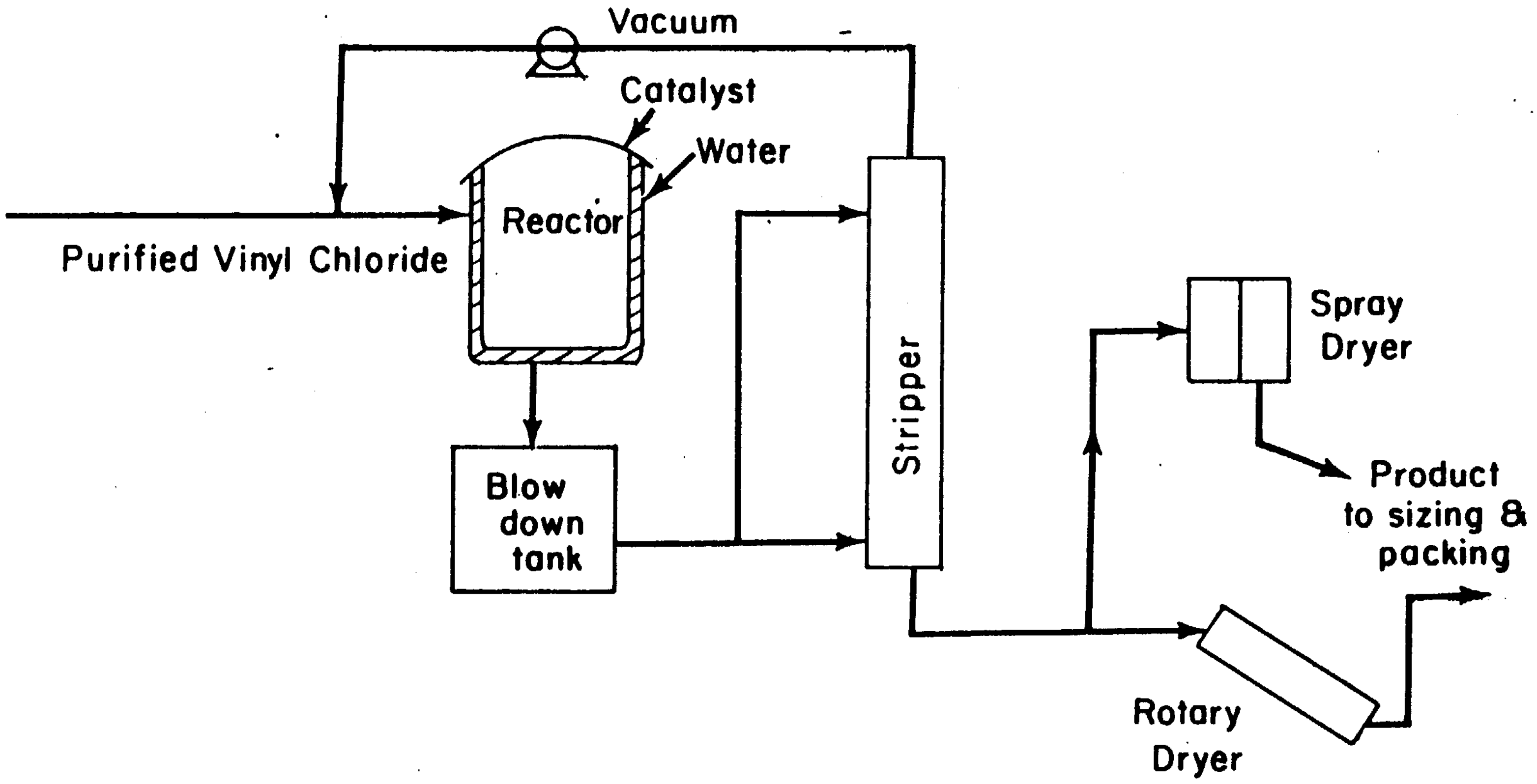

Figure 4.7-1. Typical Flow Diagram for Polyvinyl Chloride Manufacture

Because of the many types of raw materials, ranging from gases to solids, storage facilities vary accordingly. Ethylene is handled under pressure; vinyl chloride, a gas at standard conditions, is liquefied easily under pressure and is stored as a liquid in a pressurized vessel. Most of the other liquid monomers do not present any particular storage problems. Some, such as styrene, must be stored under an inert atmosphere to prevent premature polymerization. Some of the more volatile materials are stored in cooled tanks to prevent excessive vapor loss. Some of the materials have strong odors, and care must be taken to prevent emission odors to the atmosphere. Solids, such as phthalic anhydride, are usually packaged and stored in bags or fiber drums.

The major sources of possible air contamination in plastic manufacturing are the emissions of raw materials or monomer to the atmosphere, emissions of solvent or other volatile liquids during the reaction, emissions of sublimed solids such as phthalic anhydride in alykd production, emissions of solvents during storage and handling of thinned resins. Table 4.7-1 lists the most probable types and sources of air contaminants from various plastic manufacturing operations.

Table 4.7-1. Plastic Manufacturing Emissions and Sources[4]

| Plastic | Emission | Source |
|---|---|---|
| Phenolic Resins | Aldehydes | Storage, leaks, condenser outlets |
| Amino Resins | Aldehydes | Storage and leaks |
| Polyesters | Oil cooking odors, phthalic anhydride, solvents | Cooker discharge, condenser discharge |
| Polyvinyl Acetate | Odors, solvents | Storage, condenser outlets |
| Polyvinyl Chloride | Odors | Leaks |
| Polystyrene | Odors | Leaks |
| Polyurethane | Toluene, Odor | Product |

Much of the emission control equipment used in this industry is really a basic part of the system and serves to recover a reactant or product. These controls include: floating roof tanks or vapor recovery systems on volatile material storage units, vapor recovery systems (adsorption or condensers), purge lines and relief valves which vent to a flare system; and recovery systems on vacuum exhaust lines.

## Factors Affecting Emissions

The major factor affecting atmospheric emissions is the basic design of the plant, its maintenance, and the amount of control equipment included in the basic plant. Greater emissions may be expected from those processes operating at atmospheric pressure since condensers then vent directly to the atmosphere, and care in sealing the reactor is not generally as great.

## Emissions

Quantitative emission data from plastics manufacturing are not readily available. In the manufacture of ethylene gas (a high pressure process) hydrocarbon emissions amounted to 0.21% (4.2 lbs/ton) of the feed.[5] Other reported data, from manufacturing plant estimates based largely on material balance estimates, are shown in Table 4.7-2.[6,7]

Table 4.7-2. Estimated Emissions From Plastics Manufacturing, lbs/ton

| Plastic | Gases[b] | Particulate |
|---|---|---|
| Polyvinyl Chloride | 17 | 35[a] |
| Polypropylene | 0.7 | 3 |
| General | 5 to 10 | - |

a) Usually controlled with a fabric filter, efficiency of 98-99%.
b) Reported as the monomer (vinyl chloride, or propylene, etc.).

This wide range in emission data is due to the difficulty in accurately performing material balance estimates, and to actual emission differences.

Based on the reported emissions from ethylene manufacture and the two estimates in Table 4.7-2, a general gaseous emission factor of about 5 - 10 lbs/ton of feed may be used until better data are available.

## Reliability of Emission Factor

Due to the limited data available and the wide variation in processing methods and products, the emission factor for plastics manufacturing must be classified as questionable. Table 4.7-3 presents the factor ranking.

Table 4.7-3. Emission Factor Ranking

| Emission Data 0-20 | Process Data 0-10 | Engineering Analysis 0-10 | Total |
|---|---|---|---|
| 5 | 2 | 2 | 9 |

## REFERENCES 4.7

1. Modern Plastics Encyclopedia. 1968-1969, p. 46-47.
2. Shreve, R.N. (ed.). Chemical Process Industries. New York, McGraw-Hill Book Company, 1967. p. 660-673.
3. Anon. Drying Tricks Tailor Resin Properties. Chem. Eng. 66:166-169, November 16, 1959.
4. Chatfield, H.E. Resin Kettles, In: Air Pollution Engineering Manual, Danielson, J.A. (ed.). National Air Pollution Control Administration, Raleigh, North Carolina, Public Health Service Publication 999-AP-40, 1967. p. 687.
5. Mencher, S.K. Change Your Process to Alleviate Your Pollution Problems. Petro/Chem Eng. 39:(6): 21-24, May 1967.
6. Communication with M. McGraw. National Air Pollution Control Administration, Division of Air Quality and Emission Data. December 1969.
7. Communication with Maryland State Department of Health, November 1969.

## GENERAL REFERENCES

Sittig, M. Organic Chemical Process Encyclopedia. Park Ridge, New Jersey, Noyes Development Corporation, 1969. p. 545-569.

Parker, C. H. Plastics and Air Pollution. SPE Journal. p. 26-30. December 1967.