

**Emission Factor Documentation for AP-42  
Section 4.12**

**Manufacture of Rubber Products**

**Final Report**

**For U.S. Environmental Protection Agency  
Office of Air Quality Planning and Standards  
Measurement Policy Group**

**November 2008**

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**EMISSION FACTOR BACKGROUND REPORT FOR AP-42 Section 4.12**  
**Manufacture of Rubber Products**

**1. Introduction**

**1.1 Program Overview And Objectives**

The Clean Air Act Amendments (CAAA) of 1990 contain a variety of new programs and approaches designed to reduce emissions of hazardous air pollutants (HAPs), improve urban air quality and to control the precursors of acid rain. The Environmental Protection Agency (EPA) and the state/local air agencies now have at their disposal an expanded authority base to meet the CAAA objectives including an expanded array of enforcement tools. As the CAAA implementation moves forward, industry will be faced with numerous complex and burdensome air compliance issues.

On July 21, 1992, EPA promulgated the Operating Permit Rule, which represents an expanded and very different approach to permitting air emission sources. The operating permit program commonly referred to as *Title V* is a national program which is now being implemented on a state by state (and in the case of California, county by county) basis. In other words, each state has been charged with developing and implementing its own federally enforceable operating permit program which meets or exceeds the CAAA requirements.

Title V now requires each facility which exceeds a major source threshold to secure a facility wide permit. The Title V program defines major source applicability on the basis of potential to emit. All facilities which have the potential to emit more than any of the following must secure a facility operating permit:

- 100 tons/year of a criteria pollutant except in certain urban areas (non attainment areas) where the threshold can be as low as 10 tons/year
- 10 tons/year of a single HAP or 25 tons/year in aggregate of any listed HAPs.

Title V requirements represent a significant departure from past state permitting programs which addressed some but not all sources at a facility on a process by process basis. Before the federal 1990 CAAA, fewer than 20 pollutants were federally regulated. Now there are in excess of 200 regulated pollutants without taking into account additional air toxics requirements that may exist in some states.

To prepare a facility Title V permit, there are several tasks which must be completed. One such activity is the development of the plant emissions inventory which is the largest part of the permitting effort and also one of the areas where accuracy is critical. An inaccurate inventory can result in future compliance problems.

Producing an accurate inventory is contingent upon the availability of sound emissions data or emission factors for each process in a facility. These factors coupled with commonly archived process and production data are used to calculate emissions and produce the inventory.

Unfortunately, emission factors have not been established by EPA or the states for many industrial processes, including the rubber manufacturing industry. In the absence of established emissions

factors or readily available emissions data, EPA and the states have typically adopted the fallback position of requiring emissions testing for each significant process within a facility, an endeavor which is expensive in addition to being very complex.

As a result of the lack of documented emissions factors for the industry, the Rubber Manufacturers Association (RMA), on behalf of its membership, embarked on a large project to address the emission factor issue. Specifically, the objectives of the project were as follows:

- Develop emission factors for the commonly used rubber manufacturing processes;
- Develop a consistent applications approach for developing plant-wide emissions inventories;
- Develop a standard protocol for estimating emissions related to future process changes;
- Provide background information for addressing Title V record keeping and compliance demonstration requirements;
- Provide support for addressing future enhanced monitoring requirements; and
- Provide information sufficient to address equipment scale differences.

An intense testing-based project was conducted which resulted in emission factors for the commonly used rubber compounds and processes. The results of the project and the emission factors now available are discussed below:

## **1.2 Emission Factor Project Definitions**

The following is a brief list of key definitions which define pollutant categories measured in the test program, as well as terminologies which will assist the reader in interpreting the emission factor data provided in this volume.

- (1) *Total Speciated Volatiles*: The sum of the target volatile organic compounds as well as those compounds tentatively identified during a mass spectral library search.
- (2) *Total Speciated Semivolatiles*: The sum of the target semivolatile organic compounds as well as those compounds tentatively identified during a mass spectral library search.
- (3) *TVOC*: Total volatile organic compounds measured as total hydrocarbons (THC) calibrated to a methane standard. Measurements were made on a continuous basis using a THC analyzer in accordance with EPA Reference Method 25A.
- (4) *Total Metals*: The sum of the target analytes detected. The target analytes are were cadmium, chromium, copper, lead, magnesium, nickel and zinc.
- (5) *Total Sulfur*: The sum of the target sulfur compounds detected during sample analysis using gas chromatography/flame photometric detection (GC/FPD).
- (6) *Total Speciated Organics*, as used in the summary and speciation tables: The total speciated organic compounds measured in the test program, is the sum of the semivolatile and volatile emissions for a given rubber compound minus any duplicate compounds. Where the same compound may have been measured by two different test methods, the higher value was used

to present a conservative emissions total. The other value was ignored and not included in the total.

- (7) *Speciation Factors*: These are the fraction by weight, of a particular compound to the total for a specific pollutant category. For example, a speciation factor for benzene is determined by dividing the measured benzene emissions by the Total Speciated Organic compound emissions (Total Speciated Organics is defined above).
- (8) *Volatile Organic Compounds (VOCs)* as defined for permitting requirements is based on the EPA definition cited in 40 CFR 52.21:

*Volatile Organic Compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate which participates in atmospheric photochemical reactions. This includes any organic compound other than the following which have been determined to have negligible photochemical reactivity:*

- (a) Methane (CAS 74-82-8);
- (b) Ethane (CAS 74-84-0);
- (c) 1,1,1-Trichloroethane (CAS 71-55-6);
- (d) Methylene Chloride (CAS 75-09-2);
- (e) Trichlorofluoromethane (CAS 75-69-4);
- (f) Dichlorodifluoromethane (CAS 75-71-8);
- (g) Chlorodifluoromethane (CAS 75-45-6);
- (h) Trifluoromethane (CAS 75-46-7);
- (i) Trichlorotrifluoroethane (CAS 76-13-1);
- (j) Dichlorotetrafluoroethane (CAS 76-14-2);
- (k) Chloropentafluoroethane (CAS 76-15-3);
- (l) Dichlorotrifluoroethane (CAS 306-83-2);
- (m) Tetrafluoroethane (CAS 811-97-2);
- (n) Dichlorofluoroethane (CAS 1717-00-6);
- (o) Chlorodifluoroethane (CAS 75-68-3);
- (p) Chlorotetrafluoroethane (CAS 2837-89-0);
- (q) Pentafluoroethane (CAS 354-33-6);
- (r) Tetrafluoroethane (CAS 359-35-3);
- (s) Trifluoroethane (CAS 420-46-2);
- (t) Difluoroethane (CAS 75-37-6);
- (u) Perchloroethylene (CAS 127-18-4); and,
- (v) the following four classes of perfluorocarbon compounds:
  - (1) Cyclic, branched, or linear, completely fluorinated alkanes;
  - (2) Cyclic, branched, or linear, completely fluorinated ethers with no unsaturation;
  - (3) Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturation; and
  - (4) Sulfur-containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

### 1.3 Emission Factor Summary

Standardized rubber formulations based on published industry references such as The Vanderbilt Rubber Handbook, 13th Edition were used as the test compounds for the internal mixing/milling, platen press curing, extruder, autoclave, hot air curing, and milling tests. Data for the calendaring, grinding, and tire curing processes were generated in actual manufacturing settings. For tire curing, actual tires from several of the participating companies were used to collect test data.

#### REFERENCES FOR SECTION 1

1. The Vanderbilt Rubber Handbook, by Robert F. Ohm, Thirteenth Edition. R. T. Vanderbilt Company, Inc., New York. 1978.

## 2. Emissions Factor Development Approach

### 2.1 Selection of Compounds and Target Pollutants

The initial step necessary in developing emission factors is to identify which pollutants are emitted to the atmosphere from the process. Previous investigations into the emissions from rubber manufacturing showed that the predominant emissions are low molecular weight organic compounds (C<sub>6</sub>-C<sub>8</sub>). However, the potential for heavier, less volatile organic compound emissions also exists due to the chemistry and the elevated temperatures of many of the processes. Particulate matter emissions can also be significant, especially during the mixing process when carbon black is added to the mix.

Title III of the 1990 CAAA lists 189 HAPs (since the original publication of the HAP list, caprolactam has been dropped.). Many of these are applicable to the rubber manufacturing industry. In addition, many states where rubber manufacturing facilities operate have developed their own air toxic lists. Since the Title V operating program will be administered by the individual states, there exists the possibility that facilities will need to conduct emission inventories for all of the HAPs in Title III as well as on the state compounds. A comprehensive target test list was developed using all the chemicals from Title III, selected state air toxics compounds, as well as the SARA 313 toxic chemicals. Information presented in the tables includes only HAPs data.

The emissions from each process may vary depending upon the type of rubber used (natural or synthetic), the specific additives (metal oxides, accelerators, retardants, antioxidants, softeners, fillers, and vulcanizing agents) in the mix, the physical characteristics of the processes, and the reaction chemistry of the processes.

The tire manufacturing industry principally uses natural rubber, styrene-butadiene (SBR) rubber, and polybutadiene rubber. Polybutadiene is often mixed with SBR to improve the abrasion and cracking resistance of the tire. For nontire rubber goods where oil resistance is a priority, rubbers such as polyacrylates, nitrile, neoprene, polyurethanes, epichlorohydrins, chlorosulfonated polyethylene, chlorinated polyethylene, and fluoroelastomers are used. Potential emissions from rubber consists of breakdown compounds such as the monomers used to create the rubber.

Accelerators initiate the vulcanization process. Typical accelerators are metal oxides (zinc oxide, lead oxide, and magnesium oxide) and a large variety of organic accelerators. These organic accelerators are typically from the following classes of organic compounds: benzothiazoles, benzothiazolesulfonamides, dithiocarbamates, dithiophosphates, guanidines, thioureas, and thiram.

Antioxidants help to prevent oxidation (aging) of the vulcanized product. Antioxidants are usually high molecular weight amine compounds such as dioctylated diphenylamine.

Retarders are used to prevent the premature vulcanization (scorching) of the rubber during processing. Retarders currently in use consist mainly of organic acids (salicylic and benzoic acids),

phthalic anhydride, and N-(cyclohexylthio)phthalimide. The potential emissions consist of the retarders themselves along with their thermal breakdown components.

Softeners are used to increase the workability of the mix for lubrication during extrusion and molding, and, to aid in the dispersion of fillers. The predominant softener used in the rubber industry is petroleum oil. The potential emission compounds from petroleum oil are extensive. The majority of the compounds would most likely be aromatic hydrocarbons of various sizes and types.

Fillers are added to the rubber mix for several reasons. They provide color but are mainly used to reinforce the final product. Fillers are fine particles which increase the abrasion resistance and tensile strength of the product. Carbon black is used as the primary filler in tire manufacturing. Rubber goods requiring a color other than black use numerous types of inorganic fillers. Due to the fine particle size of fillers, rubber mixers are typically equipped with particulate emission control equipment.

Sulfur compounds comprise the vast majority of vulcanizing agents currently used. Sulfur can be added as elemental sulfur or within inorganic or organic sulfur compounds. The presence of sulfur and the high temperatures involved in the processes results in the possible emission of sulfur compounds such as carbon disulfide that can be emitted.

Twenty three rubber compounds/mixtures were studied in this program.

## **2.2 Description of Sampling / Analytical Regimes**

The ten processes tested were: tire press, oven curing of tire cuts, autoclave, extruder, internal mixers, grinding, platen press, calender, warmup mill, and oven curing of engineered products. Nine of the processes were tested for total volatile organic compounds, speciated volatiles, volatile ozone precursors, sulfur compounds, and semivolatile organic compounds. Two processes (tire press and autoclave) were tested for amines. Four processes (tire press, oven curing of tire cuts, extruder, and some grinding processes) were tested by Fourier transform infrared spectroscopy (FTIR). Three processes (extruder, internal mixers, and grinding) were tested for particulate matter and metals.

To quantify the emissions from each process accurately, the emissions tests were conducted using enclosure methodologies to ensure that all emissions were captured. The design of each enclosure was based upon the criteria in EPA Method 204 for a total enclosure. The objective in using the enclosure approach was to collect and "concentrate" non-point source emissions from the individual process in a way that enclosure exhaust could be sampled.

A highly ventilated enclosure with rapid air turnover would not allow for adequate detection limits of the target parameters. EPA's criteria for enclosures were followed, as guidance. However, air velocities were varied to allow for optimal sampling conditions within the exhaust duct. Specific enclosure construction and exhaust details vary with the process, fugitive release rate, and target sampling parameters.

During each test run for all processes, all pertinent operating parameters were recorded. These parameters consisted of the quantity and types of materials being processed, processing and/or production rate, process temperature, and process pressure. These data were recorded at the start of each test run and at 15 minute intervals thereafter until the completion of the test run.

The emissions test data, process data, and laboratory data acquired from the sampling program were compiled and evaluated for each test run. Mass emission rates from each rubber type and each pollutant were calculated from the laboratory results and field test data. The mass emission rates were calculated utilizing the measured exhaust air flow rate and concentration of each target pollutant in the sample vent for each individual test run. All emission calculations were performed in accordance with the specific sampling methodologies utilized for this program.

In addition to the sampling conducted at each process emission vent, numerous sampling runs were conducted to quantify background concentrations of target pollutants present in the atmosphere where the sampling was conducted. These background tests were conducted since most of the emissions testing was performed in process areas containing several air pollutant emitting processes. The necessity of background emissions testing was determined by the team leader for each test program based upon field observations. These field observations included assessing the presence of visible emissions, odors, and plant activities which could bias the test data, such as maintenance painting. Quantifiable background concentrations were subtracted from the sample concentrations for that day to provide more accurate emission results from the processes.

Laboratory and field blank samples were also collected for each sampling method to recognize and quantify contamination of any sampling media. The results of these blank sample runs were compared with the process sample runs to identify emission results which might have been biased. If quantifiable pollutant concentrations were found in the sample blanks, these concentrations were subtracted from the specific test results associated with the blank sample. Sample results which were found to have values less than or equal to background or blank sample concentrations were assumed to be equal to zero.

The emission sampling results and the process data were then correlated to quantify emissions on a basis of pounds of pollutant emitted per pound of rubber processed. For three of the grinding operations (sidewall grinding, carcass grinding, and belt grinding), emissions were quantified on a pound of pollutant emitted per pound of rubber removed basis. For batch operations such as internal mixing and autoclave curing, this was done by determining the total pounds of pollutant emitted and dividing by the total pounds of rubber processed. For continuous operations such as the extruder and calendering, this was performed by dividing the average hourly mass emission rate by the average hourly rubber processing rate. Results for tire curing were developed on both a lb/lb tire and lb/lb rubber basis to account for the non-rubber components of the tires such as fabric and steel cords, wire beads, and belts.

In addition to the results of the compound specific sampling methods data, total organic compound emissions were determined using the data collected during the Method 25A continuous process monitoring. Average total organic concentrations were recorded for each one minute interval for each test run. An average value was then determined from the average of all of the one minute data points collected over the duration of each test. Background concentrations were quantified at the beginning of each test run to correct the final result. Mass emissions of total organics were then quantified for each run.

Concentration data were provided for every target analyte and every tentatively identified compound. In each case where a particular compound was not detected, the detection limit was provided.

For sampling methods having more than one target pollutant, the pollutant emissions were aggregated to provide total emissions by pollutant category. Total emissions were developed in this manner for metals, organics (including volatiles, ozone precursors, and semivolatiles), sulfur compounds, and in some cases, amines. Many of the target pollutants in these sampling methods were not present in the sample at quantifiable concentrations. Mass emission rates of these pollutants were calculated based upon their detection limit, as stated in the laboratory results, and their values were denoted with a "<" symbol prior to their stated emission value in the results tables. Emissions totals for detected compounds include emissions of all compounds which were detected in the sample by chemical analysis.

## 2.3 Development of Final Factors

The results of the data analysis were assembled to develop pollutant and rubber type specific emission factors for each process. This effort involved collecting and collating the results of several emission tests performed on similar processes at different facilities. Emission factors are reported as point estimates. The emission factors were developed based upon the aggregate emission totals in the data analysis discussed above.

For calculation of emission factors, emissions of all organic compounds were computed as the sum of ozone precursors, volatile organic compounds, and semivolatile organic compounds. For organic compounds which were detected by more than one method, the higher concentration value was used.

Target analytes which were not detected in any runs for a particular process or compound were not included in the tables. The assumption is that if a target analyte was not detected in any runs, there is a high probability that even if it were present, the low detection limits indicate its overall contribution is insignificant. Target analytes detected in one or more runs were averaged together. If an analyte was not detected in all runs, then those runs in which it was not detected were counted at one-half of the analytical detection level for averaging purposes. If an analyte was not detected in any run, then the average was designated in the emissions factors tables as "ND". The tables are available in spreadsheets on the CHIEF web site at <http://www.epa.gov/ttn/chief/ap42/ch04/>.

Four emissions tests provide data for the emissions factors. TRC's May 1995 report, which contains most of the VOC, PM, metals, amines, sulfur compounds, ozone precursors, and speciated volatiles, has a data quality rating of D, since only summary data are provided. Envisage's September 1987 report on opacity and PM emissions from the retread process has a data quality rating of B. Trigon Engineering's January 1999 report on total gaseous organics, toluene, and methylene chloride from the tire carcass grinding process has a data quality rating of B. Trigon Engineering's July 1999 report on hexachlorobenzene and total gaseous emissions from Compound #3 has a data quality rating of B. Each emissions factor has a rating of E, since the majority of test results represent averages of just 3 runs (one total gaseous emissions series relies on 4 runs) for just one compound or process.

## 2.4 Update to Factors in 1999

The draft section was originally released for review and comment in 1998. The following changes were made to the emissions factors following the review in 1999:

- The interpolated compound 3 emission factor for hexachlorobenzene (HCB) in tables for calendering, extruding, and mixing, has been updated from the original based on mixing emission testing performed by the Rubber Manufacturers Association (RMA) in July 1999. RMA conducted testing to confirm that HCB is not present in tire manufacturing. This result was formalized in the Federal Register on August 3, by removing tire manufacturing from the list of sources of HCB in the CAA 112(c)(6) inventory (65 FR 47725). The updated factor was submitted to EPA as an update to the AP-42. The factors for Total Speciated Organics, Total Organic HAPs and Total HAPs have also been updated to reflect this update.
- Toluene and methylene chloride factors in the table for carcass grinding were updated from the original by testing performed by Michelin North America in January 1999. The updated factors were submitted to EPA for inclusion in the AP-42. The revisions for toluene and methylene

chloride are also reflected in the factors for Total HAPs, Total Organic HAPs and Total Speciated Organics.

## REFERENCES FOR SECTION 2

1. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 1: Emission Factor Program Results. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
2. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 2: Project Data. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
3. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 3: Test program Protocol. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
4. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 4: Emission Factor Application Manual. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
5. Stationary Source Sampling Report for Michelin North America, Inc., Duncan, South Carolina by Trigon Engineering Consultants, Inc., Charlotte, NC, January 1999.
6. Stationary Source Sampling Report for Farrel Process Laboratory, prepared for the Rubber Manufacturers Association (RMA) by Trigon Engineering Consultants, Inc., Charlotte, NC, July 1999.
7. Section 112(c)(6) Source Category List: Tire Production, Federal Register. 40 CFR Part 63. Vol. 65, No. 150. August 3, 2000. pp. 47725.
8. National Emission Standards for Hazardous Air Pollutants: Rubber Tire Manufacturing, Federal Register. 40 CFR Part 63. Vol. 65, No. 202. October 18, 2000. pp. 62414.
9. National Emission Standards for Hazardous Air Pollutants: Rubber Tire Manufacturing - Final Rule, Federal Register. 40 CFR Part 63. Vol. 67, No. 161. July 9, 2002. pp. 45588.
10. National Emission Standards for Hazardous Air Pollutants: Rubber Tire Manufacturing - Final Rule, technical correction, Federal Register. Vol. 68, No. 48. March 11, 2003. pp. 11745

### 3. Description of Test Facilities

#### 3.1 Processes Employing Generic Rubber Compounds

The following descriptions provide detail of the specific operations that were tested at specific locations.

##### 3.1.1 Internal Mixing and Milling

Emissions during rubber mixing were evaluated from four internal mixers at three facilities during this the test program. For this report series, the mixers are designated as:

Large Banbury Mixer (F-80)	Large Mixer No. 1
Small Banbury Mixer (BR-1600)	Small Mixer No. 1
Small Banbury Mixer (BR-1600)	Small Mixer No. 2
Large Banbury Mixer / Control Device	Mixer Control Device

Emissions from Large Mixer No. 1 occurred at two points in the process, during charging / mixing, and during drop milling. Batch sizes of 125 to 140 pounds per drop were mixed during the testing. Temperatures of the nonproductive runs were approximately 335°F. The productive run temperatures were typically 220°F (240°F for EPDM 2). The configuration of the unit tested allowed for sampling of the fume collector and duct system. The charging / mixing zone was serviced by an 18-inch exhaust duct leading to a baghouse for control of emissions. Sampling was conducted in the round duct in an area with a suitable length of straight run. Emissions from the drop milling zone were handled similarly, being routed to a collector duct via a long rectangular duct.

The small internal mixers were similar in design and capacity. Emissions were sampled from a section of duct installed in a flexible exhaust hose. Sampling took place during charging and mixing. Batch sizes were typically 2 to 3 pounds for each drop with a fill of approximately 65 percent. Mixing temperatures were the same as with the larger units, and consistent with the recipes (335°F for the non-productive and 220°F for the productive drops). At the completion of mixing, the rubber dropped into a tray drawer for transfer to the adjacent milling unit.

The milling units used with the small internal mixers were enclosed to contain pollutants released during operation. The enclosures were equipped with an outlet exhaust duct to facilitate sampling. Monitoring / sampling continued once the mixed rubber was placed inside the enclosures and continued throughout the milling process.

Control efficiencies of emissions from the control device serving the large “Banbury” mixer were determined through the simultaneous sampling of inlet and outlet ducts of a fabric filter control device. The sampling was conducted during two modes of operation: charging / mixing and drop milling. Batch sizes of approximately 465 pounds per drop were mixed during the testing. Temperatures of these master batch nonproductive runs ranged from 315° to 330°F.

### 3.1.2 Extrusion

Evaluation of emissions during the rubber extrusion process was conducted on a 3.5-inch extruder. Two pallets each of tread (Compound No. 6), sidewall (Compound No. 4), emulsion SBR (Compound No. 22), and peroxide-cure EPDM (Compound No. 9) rubber were provided. Optimum target melt temperatures were provided for each compound. These were as follows:

Tread -	255° - 275°F
Sidewall -	230° - 260°F
SBR 1502 -	255° - 275°F
EPDM 2 -	250° - 280°F.

The extruder consisted of a power-driven screw within a stationary cylinder. A die with a 1/8 x 3-inch extrusion slot was attached to the head of the screw to produce the desired cross section of the extruded rubber. During the testing, it became necessary to install additional screens behind the die plate to increase rubber back pressure and temperature. The rubber strips were fed manually into the hopper rollers.

Two zones were sampled during operation of the extruder process. The extruder outlet, or head, was enclosed to permit capture of emissions throughout operation. The enclosure was equipped with an outlet exhaust duct from which sampling was conducted. After extrusion, the product entered the cool-down zone, which was also enclosed to allow for sampling of pollutant emissions. Rubber temperatures were measured at the die head and at two points of the cool-down zone.

### 3.1.3 Autoclave Curing

Autoclave curing utilizes saturated steam at an elevated pressure to cure the rubber mix and is the predominant curing method in nontire (commonly referred to as “engineered products”) rubber manufacturing facilities. The eleven rubber compounds selected for testing included compounds used primarily for engineered products, but also included compounds used in tire manufacturing. These compounds were provided by several manufacturers. The compounds selected and their designated compound numbers were as follows:

- |   |                                      |
|---|--------------------------------------|
| - Tire Base/Sidewall (#4)                 | - CRW Neoprene (#11)                 |
| - Tire Apex (#5)                          | - Hypalon (#15)                      |
| - Tire Tread (#6)                         | - HNBR Hydrogenated Nitrile (#18)    |
| - EPDM 1 (sulfur-cured) (#8)              | - CPE Chlorinated Polyethylene (#21) |
| - EPDM 2 (unextruded peroxide-cured) (#9) | - Emulsion SBR (SBR 1502) (#22)      |
| - EPDM 2 (extruded peroxide-cured) (#9).  |                                      |

The curing tests were conducted using a steam-contact autoclave setup. A rack loaded with the desired quantity of rubber strips was loaded by electric winch into the autoclave chamber. Three batches of approximately 50 pounds each were loaded and cured for each rubber type. The autoclave was operated at 340°F and approximately 110 psig during each curing run.

Sampling of the autoclave emissions was conducted throughout the three basic phases of operation. Sampling was initiated during the curing phase with sampling of the water trap effluent, conducted during the blowdown phase, and continued through the cool-down phase.

The approach was to set up a total capture method whereby all steam and pollutant releases were sampled. The autoclave curing entailed sampling of the water trap condensate (during curing), the blowdown steam, and cool-down air emissions. All steam releases were vented through the 1-inch water trap or blowdown pipe into a series of condensing impingers and sorbent tubes kept under negative pressure by a metering pump. During curing, the water trap condensate was directed into sample containers and large impingers for volume determination. The blowdown pipe was connected to the condensing coils and the first of a series of large impingers. Steam and entrained pollutants were directed into the impingers for condensing and pollutant scrubbing through impingement. Remaining gaseous or entrained pollutants then passed through the sorbent traps for the collection of organic species. A control valve was installed on the blowdown system to control the rate of steam release during the blowdown cycle.

Following completion of each autoclave run, the rack containing the cured rubber products was removed from the autoclave but kept within the temporary enclosure for sampling during the cool-down period.

### **3.1.4 Platen Press Curing**

The platen press curing process is a general approach to pressure curing engineered products in molds. Specific molds are used to form the desired engineered product at set pressures and curing temperatures. Most emissions occur during mold release, at the end of the curing cycle.

During this program, seventeen rubber compounds were cured at temperatures between 340° and 350°F and pressures of 30 tons for the first three minutes and 20 tons for the second three minutes. The rubber compounds were from batches mixed during testing of Small Mixer No. 2. The compounds cured and their designated numbers were as follows:

- Tire Inner Liner (#1)
- Tire Ply Coat (#2)
- Tire Belt Coat (#3)
- Tire Apex (#5)
- Tire Curing Bladder (#7)
- EPDM 2 (unextruded peroxide-cured) (#9)
- EPDM 3 (non-black sulfur-cured) (#10)
- CRW Neoprene (#11)
- CRG Neoprene (#12).
- Paracryl OZO (#13)
- Paracryl BLT (#14)
- Fluoroelastomer (#16)
- AEM (#17)
- Silicone (#19)
- Acrylate Rubber (#20)
- Emulsion SBR (SBR 1502) (#22)
- Epichlorohydrin (#23)

Nine samples of approximately 50 grams each were cured for each rubber type. Each 50-gram tab of rubber was placed directly onto the lower plate and pressed into a "pancake" of approximately 185-mm diameter and 1-mm thickness. The cool-down period lasted for 6 minutes when the cured samples were removed from the press and left inside the enclosure. Emissions were contained by an exhaust hood and flexible Tyvek sheeting, and exhausted by a single 5-inch duct and blower.

### **3.1.5 Hot Air Curing**

Hot air curing of engineered rubber products is used for final curing of preformed products. Three rubber compounds were evaluated. One compound used in tire manufacturing (Tire Apex, Compound #5) and two compounds typical of engineered products manufacturing (sulfur-cured EPDM 1, Compound #8; and Emulsion SBR 1502, Compound #22) were tested. To simulate the process for this program, a lab-scale system with enclosure was designed and set up to evaluate the emissions during curing and cool-down. The rubber compound samples were placed in the oven and allowed to reach the curing temperature of 400°F for a period of 5 to 8 minutes. Each sample weighed approximately 100 grams. After completion of curing, each rubber sample was removed and allowed to cool down in the enclosure and another sample of the same compound was placed in the oven and brought up to temperature.

The oven was set up with a preheated sweep gas inlet and an exhaust gas outlet. A temporary enclosure was erected around the oven to contain emissions during the curing and cool-down and when the door was opened. An exhaust duct similar to that used for the platen press was constructed to vent the enclosure and to provide the sampling locations.

## **3.2 Tire Curing**

### **3.2.1 Full-Scale Tire Curing**

Evaluation of tire curing press emissions was conducted on a full-scale tire press equipped with a single mold set and an integral cool-down rack. A total of nine tire types / brands were press-cured, representing two tire sizes from seven manufacturers. The tires were received uncured and varied in size, weight, and type. Multiple tires for each type were cured during each test run to allow for adequate sampling times. The two sizes tested were 195/75 and 205/70. A generic mold for each tire size was used for the curing. The different types received were: original equipment (OEM), replacement, and high-performance.

Mold temperatures ranged from 330°F to 355°F and steam pressures ranged from 200 to 300 psig. Each tire was cured for a period of 10 to 15 minutes. There were two emission zones sampled on the tire press: the press itself and the tire cool-down zone. An enclosure was set up on the tire press to collect fugitive emissions during the press curing of green tires. The enclosure was equipped with an outlet exhaust duct in which sampling was conducted for the target parameters. A similar enclosure was erected around the integral cool-down rack where the tire cools after completion of press curing.

## **3.3 Other Rubber Processing**

### **3.3.1 Milling**

Milling is utilized by the industry as a preparation / warmup step for feeding rubber to calenders and extruders or to warm the rubber to prepare it for subsequent processing. A warmup mill is similar or identical to a drop mill in that it has a series of rollers, some toothed, to increase the shearing of the compound. The mill can be batch or continuously fed, depending on the production need.

Evaluations of milling emissions were conducted at two facilities during this program. Emissions from both were captured using a temporary enclosure and exhaust duct system. Emissions from a lab-scale warmup mill were tested during the milling of the following three compounds:

- Tire Ply Coat (#2)
- Tire Belt Coat (#3)
- Tire Base/Sidewall (#4).

Multiple batches were made for each test run. One test run was conducted per compound. Each drop was approximately 2.5 pounds of rubber, which represents a fill of approximately 65 percent.

A second warmup milling test was conducted at an engineered products manufacturing facility. This was a production facility that operated a warmup mill in a batch mode for the test. The facility ran a Neoprene compound in the warmup mill for the three test runs. The mill roll temperature was approximately 90°F. The rubber was milled to a thickness of 0.3 inches and a temperature of approximately 175°F.

### **3.3.2 Calendering**

The calendering process is used to bond a continuous textile or metal mesh web to one or two layers of rubber for use in building tires and other engineered rubber products. The web passes through a series of rollers through which one or two rubber strips also passes. Under pressure and elevated temperatures induced by the rollers, the rubber is bonded to the web. The nip of the rollers can be adjusted to vary the thickness of the calendered product. The calendered material is then cooled and cut to the proper dimensions.

During this program, emissions from the calendering process were tested at two facilities. The first was a continuous production process where the rubber was continuously fed from a warmup mill. A tire ply coat rubber compound was being run on the test days. Three test runs were conducted from an exhaust collector system outlet stack.

The second process tested involved a batch- or "pig-"fed calender during calendering of a neoprene compound at an engineered rubber products manufacturing facility. The calender itself had 54-inch wide rolls and ran approximately 1100 linear yards of a neoprene compound during each of the three test runs. The emissions from this system were measured using a temporary enclosure and exhaust duct configuration.

### **3.4 Tire Grinding Processes**

The grinding processes used in tire manufacturing are specific to each application. Four types were identified for this program: retread buffing, carcass grinding, whitewall (sidewall) grinding, and truing (force) or uniformity grinding. The grinding processes, in general, generate quantities of rubber dust and particles, and may generate HAP emissions, depending on the rubber formulation and the amount of heat generated during grinding. To control these emissions, cyclones, baghouses, and electrostatic precipitators (ESPs) are used either alone or in combination.

Grinding operations are typically conducted in a collector hood with an exhaust duct leading to the control device(s). Emissions sampling was conducted in the hood's exhaust duct (control device

inlet). Simultaneous sampling was also conducted at the outlet duct of each downstream control device to determine control efficiency and the final pollutant emissions rate.

The processes described below, although typical of industry operations, represent the specific machinery tested, and may not represent the description of all such units in the industry.

### **3.4.1 Force/Balance Grinding**

A screening evaluation of emissions from a force or uniformity grinder was conducted at a full-scale tire manufacturing facility using FTIR and total hydrocarbon analyzers. The force grinder is used to buff areas of a tire that are out of specification when the tire is put under load. Observations of the force grinder showed that only a small percentage of tires are force ground, and the quantity of rubber removed is very low, resulting in insignificant or no emissions. See Section 4.1.6 for details.

### **3.4.2 Sidewall/Whitewall Grinding**

Another surface grinding process, sidewall/whitewall grinding, was also evaluated. The grinder tested consisted of two stones set in a wheel which rotated at high speed over the whitewall area of the tire, to remove a thin coat of black rubber which overlaid the whitewall section. The grinder was set into a frame equipped with four powered exhaust ducts. Emissions from the grinding operation were carried via flexible hose to overhead ductwork. Emissions were ducted to a cyclone for removal of rubber dust and pieces ground from the tires. The exhaust air passed through the cyclone and was exhausted to the atmosphere. Approximate grinding time per tire was 20 seconds. Testing was conducted during normal operations, and emission factors were based on pounds emitted per pound of rubber removed, as measured by the quantity of rubber dust and particles collected in the cyclone hopper.

### **3.4.3 Retread Buffing**

Retread buffing was also studied as a surface grinding operation in this program. At the testing facility, the surface of the back of the tread was buffed to prepare it to receive adhesive before application to a tire carcass. The retread buffer consists of an edger and four inline buffing wheels with hasps around the circumference of each wheel. Each wheel was covered by a hood exhausted through a flexible duct. The four exhaust ducts entered a common header duct.

A tread section approximately 37 feet long was fed to the edger where the edge was squared. The tread was then fed to the first wheel of the inline buffer which caught and drew the tread into the line. As the tread passed each succeeding wheel, the wheel came down onto the surface. A predetermined pressure is applied to the buffing wheels to remove the required layer of rubber. As the hasps dull, greater pressure on the surface is required to remove the same amount of material. The emissions consisted of solid rubber particles and volatile and semivolatile organic compounds. It took approximately 40 seconds to buff a tread with approximately five seconds between tread sections. Sampling was conducted in the 20-inch inlet duct to the cyclone, in the 20-inch baghouse outlet duct prior to the I.D. fan, and in the 22-inch stack after the I.D. fan. Emission factors were presented as pounds emitted per pound of rubber processed.

### 3.4.4 Tire Carcass Grinding

Tire carcass grinding is used for gross rubber removal (tread section) and for preparation of the resulting tire carcass for retreading. This operation consists of two phases, a coarse grind module and a fine grind module. The tire is first ground to a predetermined depth with a coarse grind hasp to prepare it for the fine grind operation. The fine grind operation completely removes the old tread and prepares the carcass surface to receive the new tread. The tire carcass to be ground is placed on a shaft and rotated at a predetermined speed. The carcass is then placed against a rotating fine-toothed hasp at a desired pressure. The hasp moves across the surface of the carcass in a predetermined pattern.

The fine grinding operation was selected for the study because the grinding period is longer, the pressure of the hasp on the wheel is greater than the coarse grind, and the temperature of the carcass surface is higher than for the coarse grinding operation. The grinding time for the coarse grind operation is one to two minutes, while the grinding time for the fine grind operation is four minutes. Approximately 10 to 12 tires are ground per hour.

The fine grind module consists of the rotating shaft on which the carcass is placed and a rotating fine-tooth hasp which is covered by a hood. At the facility tested, a flexible exhaust duct connects the hood to an elevated horizontal duct which leads to a cyclone. The exhaust from the cyclone passes through a horizontal centrifugal fan to an outlet stack on the roof. The entire module was enclosed with Tedlar sheeting to enhance the capture of volatiles, semivolatiles, and particulate matter by the hasp hood. Sampling was conducted in the 10-inch horizontal cyclone inlet duct and in the 16-inch outlet stack. Emissions are presented as pounds emitted per pound of rubber removed, measured by the quantity of rubber dust and rubber particles collected in the cyclone hopper.

### 3.5 Engineered Products Grinding - Drive Belts

The belt grinding operation selected for this study was located at an engineered rubber products manufacturing facility. The selected process line was deemed to be representative of surface grinding operations. This particular line was used for V-belt grinding and consists of eight grinders. Each grinder is enclosed within a close-fitting hood. An exhaust duct exited from each hood and entered an overhead exhaust manifold. The combined exhaust streams entered the 16-inch diameter central cyclone inlet duct which led to a cyclone. An 18-inch duct exited from the top of the cyclone and enters a dual three-stage electrostatic precipitator (ESP). The effluent streams exiting the ESP were combined into a single 14-inch duct which exited the roof through an I.D. fan. During the grinding operation the belts were cooled with a localized water spray located within each grinder hood. Sampling was conducted in the cyclone inlet duct, cyclone exit duct, and ESP exit duct. Emissions are presented as pounds per hour and as pounds emitted per pound of rubber removed, as measured by initial and final weights of the belt batches for each test run.

#### REFERENCES FOR SECTION 3

1. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 1: Emission Factor Program Results. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.

2. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 2: Project Data. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
3. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 3: Test program Protocol. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
4. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 4: Emission Factor Application Manual. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.

## **4. Data Analysis, and Discussion of Results, and Use of the Emission Factors**

This section provides estimates of emission factors for the following individual compounds and elements:

- speciated organic compounds (including volatile compounds, volatile ozone precursors, and semivolatile compounds)
- sulfur compounds
- amines
- metals
- particulate matter.

Process and rubber mix/formulation specific emission factors are provided in the following sections.

### **4.1 Processes Employing Generic Materials**

Twenty-three rubber formulations / products were tested to determine emission factors for internal mixing and milling, extrusion, autoclave curing, and platen press curing. Emissions tests for the mixers were performed on three different size systems: Two 2-pound laboratory mixers, a 200-pound pilot scale system, and a 500-pound production mixer. Emissions did not appear to be dependent on mixer size, based on the emission factors of pounds of pollutant emitted per pound of rubber mixed.

#### **4.1.1 Internal Mixing / Drop Mill**

All 23 formulations were tested once on Small Mixer No. 2.

During the earlier stages of the project, data collected on Small Mixer No. 1 and Large Mixer No. 1 were compared for scale differences. Emission factors were calculated for Compounds #4, #6, #9, and #22. Results for these two mixers were found to be consistent based on emission rate categories. Emissions for the large and the small mixers did not appear to be dependent on mixer size. Mixers did show variability for total metals. This was likely the result of greater losses into the ventilation system when charging the larger equipment versus smaller scale equipment.

Means, maxima, and standard deviations were determined for tire compounds (1-7) and engineered product compounds (18-23). Pollutant emission factors include organic compounds, metals, sulfur compounds, and particulate matter.

In using these factors to estimate emissions from sources, the following guidelines should be used:

- Internal mixing in rubber production facilities are referred to as “non-productive” and “productive.” The former encompasses mixing of rubber from its main components - oils, carbon black, sulfur, and a variety of other additives. “Productive” rubber is frequently made from “non-productive” rubber plus additional materials. In some facilities, a mixer may be dedicated to mixing either non-productive or productive batches. In other facilities, however, a single mixer may be used for both non-productive and productive batches. It is conceivable

that a batch of mixed rubber that is ready for use in succeeding manufacturing steps could have passed through a mixing operation more than once. The mixing factors, however, are based on the weight of “productive” rubber.

- If in a specific application it is necessary to separate the fractions of emissions between “non-productive” and “productive” mixers, 90% of the emissions factors (in terms of unit weight of emissions per unit weight of rubber mixed) should be assigned to “non-productive” mixers and 10% of the factor should be applied to “productive” mixers.
- The emission factors consider the number of passes through the mixer necessary for a compound to be mixed. Therefore, it is not necessary to multiply by the number of passes.
- The emission factors encompass emissions from certain rubber processing equipment that may be directly associated with the mixer itself, such as “drop mills” or roller die extruders. However, if mills or extruders in a specific facility are clearly distinct and separate from a mixer, then it may be appropriate to calculate emissions separately for those mills or extruders, using emissions factors developed for those units of equipment.
- Emissions capture and control device efficiencies should be applied as appropriate to the factors. For example, particulate matter emission reductions should be based on the efficiency of the specific control devices being used in specific facilities, as compared to the efficiency of a generic fabric filter control device.
- No VOC or gaseous pollutant reductions were assumed through fabric filter control devices.
- Since metallic compounds in rubber mixing are in the form of particulate matter, reductions in emissions of metallic compounds through air pollution control devices can be assumed to be similar to reductions in particulate matter emissions.

#### **4.1.2 Milling**

Warmup mills are utilized by the industry for further mixing of rubber compounds following each drop from an internal mixer, or to warm the rubber to prepare it for subsequent processing (*e.g.*, calendaring). A warmup mill is similar or identical to a drop mill in that it has a series of rollers, some toothed, to increase the shearing of the compound. The mill can be batch or continuously fed, depending on the production need.

In using these factors to estimate emissions from sources, the following guideline should be observed:

- The emission factor assumes rubber arrives at the mill after having received one pass through a “warmup mill”. Beyond this, where multiple mills are used, emissions from each mill should be counted separately.

#### **4.1.3 Extruder**

In using these factors to estimate emissions from sources, the following should be observed:

- The emission factor encompasses all emissions from a cold-feed extruder, including the die head and cooling conveyor, and

- For a hot-feed extruder, it is necessary to calculate and add separately the emissions from the mill(s) that may precede the extruder.

#### **4.1.4 Calender**

The calendering process is used to bond a continuous textile or metal mesh web to one or two layers of rubber for use in building tires or engineered products. The textile passes through a series of rollers through which one or two rubber strips also passes. Under pressure and elevated temperatures induced by the rollers, the rubber is bonded to the web. The nip of the rollers can be adjusted to vary the thickness of the calendered product. The calendered material is then cooled and cut to the proper dimensions.

In using these factors to estimate emissions from sources, the following should be observed:

- The emission factor does not include emissions from mill(s) that may precede the calender.

#### **4.1.5 Curing**

##### **4.1.5.1 General Information**

In using these factors to estimate emissions from sources, the following should be observed:

- The emission factor includes emissions from vulcanizing, opening of the curing device, and cooling of the cured product.

##### **4.1.5.2 Autoclave Curing**

Autoclave curing is a process which can utilize either a steam contact or non-contact system. During this program, air emissions and water discharges were evaluated from a steam contact system. Emission factors were calculated using ten of the generic rubber mixtures tested in Small Mixer No. 2. One rubber compound, EPDM 2, was also tested using extruded and unextruded rubber to determine what, if any, differences result in curing emissions if the rubber was previously extruded. Based on the limited amount of data available, there were no substantial differences between extruded and unextruded EPDM.

In this steam contact autoclave system, uncured rubber loaded into the pressurization chamber is in full contact with the steam, resulting in both waterborne and airborne pollutants. The steam condensate from this type of system is discharged during blowdown at the end of the curing cycle and, often, from the water trap during the curing cycle.

In the non-contact system, the uncured rubber is enclosed in a bladder within the pressurization chamber and does not come into contact with the steam. Therefore, pollutants are not discharged with the steam condensate as occurs with the steam contact system, but are emitted as airborne pollutants upon opening of the autoclave chamber.

In evaluating pollutant discharges from the steam contact type of system, samples were collected and analyzed from two aqueous (water trap and blowdown condensate) and one gaseous (cool-down air) matrices. The total emissions for the autoclave system were obtained by combining the emission and discharge rates (lbs/hr and lbs/lb rubber) for volatiles, semivolatiles, and sulfur compounds. This total is most representative of a non-contact system where all pollutants are discharged as air contaminants and should be considered in an emissions inventory. To enable a comparison of a steam contact system with a non-contact system, the waterborne pollutants from a steam contact system could be considered separately, possibly as a discharge under a NPDES permit, and not as an air emission. Please see the related discussion below. However, there is a possibility of downstream fugitive emissions from this aqueous discharge.

In using these factors to estimate emissions from sources, the following should be observed:

- The emission factor is based on the use of “non-contact” steam. In other curing applications where steam contacts the product being cured, the test program determined that 17% of each component condenses out with the steam rather than being emitted into air.
- The emission factor does not encompass emissions of mold release agents that may be used in specific facilities.

Certain classes of pollutants exhibit higher condensibility or solubility properties and a higher percentage of removal in the aqueous discharge streams. As much as 100 percent of sulfur emissions are removed in the aqueous streams, and need not be included in air emissions inventories when steam contact autoclaves are in use. Similarly, up to 95 percent of semivolatile organic emissions are removed in aqueous streams. Predictably, volatile organics exhibited a much lower removal rate, with a maximum of 36 percent removal in the aqueous streams.

Removal percentages vary not only by pollutant class, but also by rubber compound. Individual chemical speciation was not determined, but could be obtained through further detailed review of the speciated data. The autoclave data are presented in an Excel spreadsheet on the CHIEF web site with section 4.12 at <http://www.epa.gov/ttn/chief/ap42/ch04/>.

#### **4.1.5.3 Platen Press Curing**

The platen press curing process is a general approach to pressure curing engineered rubber products in molds. Specific molds are used to form the desired engineered product at set pressures and curing temperatures.

In using these factors to estimate emissions from sources, the following should be observed:

- The emission factor includes emissions from curing and cooling of the cured rubber article.
- The emission factor does not encompass emissions of mold release agents that may be used in specific facilities.

- Emissions of methylene chloride were found in the test program, but are suspected of being laboratory anomalies. Therefore, methylene chloride, if reported at all, should be calculated using the detection level of the test.

#### **4.1.5.4 Hot Air Curing**

In using these factors to estimate emissions from sources, the following should be observed:

- Emissions of methylene chloride were found in the test program, but are suspected of being laboratory anomalies. Therefore, methylene chloride, if reported at all, should be calculated using the detection level of the test.
- The emission factor does not encompass emissions of mold release agents that may be used in specific facilities.

#### **4.1.6 Grinding Operations**

In using these factors to estimate emissions from sources, the following should be observed:

- For the specific application of “force grinding” in tire manufacture, the emission factor for white sidewall grinding may be used. However, the weight of rubber ground from each tire can vary from manufacturer to manufacturer.
- For white sidewall grinding, it may be assumed that 0.061 pound of rubber is removed on average from every tire that is ground.
- For V-belt grinding, the compound tested was approximated closely by Compound #12 (see Table 4.12-2 in the AP-42 section 4.12).

### **4.2 Effects of Temperature**

Specific tests were not conducted to determine the effects of elevated temperatures on any compound. However, several compounds were subjected to temperatures varying from 200°F to 400°F, as a result of the tests conducted for each process. No compounds were tested at multiple temperatures on any process.

These data should be used as a guide for making decisions in plant-specific situations. The test program was conducted using analytical methods and rubber compounds that were common in 1994 and 1995. In specific situations, significantly different compounds or processing temperatures may require specific emission factors to be developed.

#### REFERENCES FOR SECTION 4

1. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 1: Emission Factor Program Results. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
2. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 2: Project Data. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.
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4. *Development of Emission Factors for the Rubber Manufacturing Industry, Volume 4: Emission Factor Application Manual. Final Report*, prepared for the Rubber Manufacturers Association (RMA) by TRC Environmental Corporation, Lowell, MA, May 1995.