# SUPPLEMENT NO. 13 FOR

# COMPILATION OF AIR POLLUTANT EMISSION FACTORS, THIRD EDITION (INCLUDING SUPPLEMENTS 1-7)

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

# SUPPLEMENT NO. 13 **FOR**

# **COMPILATION OF AIR POLLUTANT EMISSION FACTORS,** THIRD EDITION (INCLUDING SUPPLEMENTS 1-7)

Environmental Protection Agency

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U.S. ENVIRONMENTAL PROTECTION AGENCY Office of Air, Noise and Radiation Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711

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U.S. Environmental Protection Agency

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Pages iii through v replace same. New Contents.

Add page ix. New Publications in Series.

Pages 1 and 2 replace pp. 1 through 3. New Introduction.

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#### COMPILATION OF AIR POLLUTANT EMISSION FACTORS

#### INTRODUCTION

Emission factors are very useful tools for estimating air pollutant emissions from sources. An emission factor relates the quantity of a pollutant released to the atmosphere to an activity associated with release of that pollutant, and it is usually expressed as weight of pollutant divided by unit weight, volume, distance or time of that activity (e.g., kg particulate emitted per Mg coal combusted). In most cases, these factors are simply averages of all available data of acceptable quality, without regard to the influence of process parameters such as temperature, reactant concentrations, etc. However, for a few cases, such as in the estimation of volatile organic emissions from petroleum storage tanks, empirical formulae have been developed which relate emissions to such variables as tank diameter, liquid temperature and wind velocity. Emission factors which are correlated with such variables tend to yield more precise emission estimates than do factors derived from broader statistical averages.

Because emission factors are averages obtained from data of wide range and varying degrees of accuracy, emissions calculated from such factors for a given facility are likely to be different from that facility's actual emissions. Only an onsite source test can accurately determine actual emissions from a source, under the conditions existing at the time of the test. Factors are more appropriately used to estimate collectively the emissions of a number of sources, such as is done in emission inventory work.

If factors are used to predict emissions from new or proposed sources, the user should review the latest literature and technology to determine if such sources are likely to exhibit emission characteristics different from those of typical existing sources.

In a few AP-42 Sections, emission factors are presented for facilities with air pollution control equipment in place. These factors generally are not intended to represent best available or state of the art control technology, rather they relate to the level of control commonly found on existing facilities. The reliability of this information should be considered carefully in light of rapid changes in air pollution control technology. The user should consider the age, level of maintenance, and other aspects which may influence equipment efficacy.

Calculating carbon monoxide (CO) emissions from distillate oil combustion serves as an example of the simplest use of emission factors. Consider an industrial boiler which burns 90,000 liters of distillate oil per day. In Table 1.3-1 of AP-42, the CO emission factor for industrial boilers burning distillate oil is  $0.63 \text{ kg CO per } 10^3 \text{ liters of oil burned.}$  Then,

kg CO emissions/day

- = CO emission factor  $\times 10^3$  1 distillate oil burned/day
- $= 0.63 \times 90$
- = 56.7

In some instances, the factors may reflect more complex relationships between process characteristics and emissions, as with fuel ash in coal combustion, where emissions involve rate of combustion and ash content.

In a somewhat more complex case, suppose a sulfuric acid  $(H_2SO_4)$  plant produces 200 Mg of 100%  $H_2SO_4$  per day by converting sulfur dioxide  $(SO_2)$  to sulfur trioxide  $(SO_3)$  at 97.5% efficiency. In Table 5.17-1, the  $SO_2$  emission factors are listed according to  $SO_2$  to  $SO_3$  conversion efficiencies, in whole numbers. The reader is directed to Footnote b, an interpolation formula which may be used to obtain the emission factor for 97.5%  $SO_2$  to  $SO_3$  conversion:

Emission factor, kg SO<sub>2</sub>/Mg 100% H<sub>2</sub>SO<sub>4</sub>

```
= 682 - [(6.82)(\% SO_2 \text{ to } SO_3 \text{ conversion})]
```

= 682 - [(6.82)(97.5)]

= 682 - 665

= 17

For production of 200 Mg of 100%  $\rm H_2SO_4/day$ ,  $\rm SO_2$  emissions are calculated as kg  $\rm SO_2$  emissions/day

= 17 kg  $SO_2$  emissions/Mg 100%  $H_2SO_4$  x 200 Mg 100%  $H_2SO_4$ /day

= 3400

To help users understand the reliability and accuracy of AP-42 emission factors, each table (and sometimes individual factors in a table) is subjectively assigned a rating (ranging from A through E) which reflects the quality and the amount of data on which the factors are based. In general, factors based on many observations are assigned higher rankings, as are factors based on more widely accepted test procedures. For instance, an emission factor based on ten or more source tests on different plants would likely get an A rating, if all tests were conducted under a single reference measurement technique or equivalent techniques. Conversely, a factor based on a single observation of questionable quality or extrapolated from another factor for a similar process would probably be labeled D or E. Several subjective schemes have been used in the past, and continue to be used, to assign these ratings, depending upon data availability, source characteristics, etc. Because these ratings are subjective and take no account of the inherent scatter among the data used to calculate factors, they should be used only as approximations, to infer error bounds or confidence intervals about each emission factor. At most, a rating should be considered an indicator of the accuracy and precision of a given factor used to estimate emissions from a large number of sources. And this indicator will largely reflect the professional judgment of an AP-42 Section's author and reviewers of the reliability of any estimates derived with the factor.

#### 1. EXTERNAL COMBUSTION SOURCES

External combustion sources include steam/electric generating plants, industrial boilers, and commercial and domestic combustion units. Coal, fuel oil and natural gas are the major fossil fuels used by these sources. Other fuels, used in relatively small quantities, are liquefied petroleum gas, wood, coke, refinery gas, blast furnace gas and other waste or byproduct fuels. Coal, oil and natural gas currently supply about 95 percent of the total thermal energy consumed in the United States. 1980 saw nationwide consumption of over 530 x  $10^6$  megagrams (585 million tons) of bituminous coal, nearly 3.6 x  $10^6$  megagrams (4 million tons) of anthracite coal, 91 x  $10^9$  liters (24 billion gallons) of distillate oil,  $114 \times 10^9$  liters (37 billion gallons) of residual oil, and 57 x  $10^{12}$  cubic meters (20 trillion cubic feet) of natural gas.

Power generation, process heating and space heating are some of the largest fuel combustion sources of sulfur oxides, nitrogen oxides and particulate emissions. The following Sections present emission factor data on the major fossil fuels - coal, fuel oil and natural gas - and for other fuels as well.

<sup>&</sup>lt;sup>1</sup>1980 National Emissions Data System (NEDS) Fuel Use Report, EPA-450/4-82-011, U. S. Environmental Protection Agency, Research Triangle Park, NC, August 1982.

#### 1.1. BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION

#### 1.1.1 General<sup>1</sup>

Coal is a complex combination of organic matter and inorganic ash formed over eons from successive layers of fallen vegetation. Coal types are broadly classified as anthracite, bituminous, subbituminous or lignite, and classification is made by heating values and amounts of fixed carbon, volatile matter, ash, sulfur and moisture. Formulas for differentiating coals based on these properties are given in Reference 1. See Sections 1.2 and 1.7 for discussions of anthracite and lignite, respectively.

There are two major coal combustion techniques, suspension firing and grate firing. Suspension firing is the primary combustion mechanism in pulverized coal and cyclone systems. Grate firing is the primary mechanism in underfeed and overfeed stokers. Both mechanisms are employed in spreader stokers.

Pulverized coal furnaces are used primarily in utility and large industrial boilers. In these systems, the coal is pulverized in a mill to the consistency of talcum powder (i.e., at least 70 percent of the particles will pass through a 200 mesh sieve). The pulverized coal is generally entrained in primary air before being fed through the burners to the combustion chamber, where it is fired in suspension. Pulverized coal furnaces are classified as either dry or wet bottom, depending on the ash removal technique. Dry bottom furnaces fire coals with high ash fusion temperatures, and dry ash removal techniques are used. In wet bottom (slag tap) furnaces, coals with low ash fusion temperatures are used, and molten ash is drained from the bottom of the furnace. Pulverized coal furnaces are further classified by the firing position of the burners, i.e., single (front or rear) wall, horizontally opposed, vertical, tangential (corner fired), turbo or arch fired.

Cyclone furnaces burn low ash fusion temperature coal crushed to a 4 mesh size. The coal is fed tangentially, with primary air, to a horizontal cylindrical combustion chamber. In this chamber, small coal particles are burned in suspension, while the larger particles are forced against the outer wall. Because of the high temperatures developed in the relatively small furnace volume, and because of the low fusion temperature of the coal ash, much of the ash forms a liquid slag which is drained from the bottom of the furnace through a slag tap opening. Cyclone furnaces are used mostly in utility and large industrial applications.

In spreader stokers, a flipping mechanism throws the coal into the furnace and onto a moving fuel bed. Combustion occurs partly in suspension and partly on the grate. Because of significant carbon in the particulate.

flyash reinjection from mechanical collectors is commonly employed to improve boiler efficiency. Ash residue in the fuel bed is deposited in a receiving pit at the end of the grate.

In overfeed stokers, coal is fed onto a traveling or vibrating grate, and it burns on the fuel bed as it progresses through the furnace. Ash particles fall into an ash pit at the rear of the stoker. The term "overfeed" applies because the coal is fed onto the moving grate under an adjustable gate. Conversely, in "underfeed" stokers, coal is fed into the firing zone from underneath by mechanical rams or screw conveyers. The coal moves in a channel, known as a retort, from which it is forced upward, spilling over the top of each side to form and to feed the fuel bed. Combustion is completed by the time the bed reaches the side dump grates from which the ash is discharged to shallow pits. Underfeed stokers include single retort units and multiple retort units, the latter having several retorts side by side.

#### 1.1.2 Emissions and Controls

The major pollutants of concern from external coal combustion are particulate, sulfur oxides and nitrogen oxides. Some unburnt combustibles, including numerous organic compounds and carbon monoxide, are generally emitted even under proper boiler operating conditions.

Particulate<sup>2-4</sup> - Particulate composition and emission levels are a complex function of firing configuration, boiler operation and coal properties. In pulverized coal systems, combustion is almost complete, and thus particulate is largely comprised of inorganic ash residue. In wet bottom pulverized coal units and cyclones, the quantity of ash leaving the boiler is less than in dry bottom units, since some of the ash liquifies, collects on the furnace walls, and drains from the furnace bottom as molten slag. In an effort to increase the fraction of ash drawn off as wet slag and thus to reduce the flyash disposal problem, flyash is sometimes reinjected from collection equipment into slag tap systems. Ash from dry bottom units may also be reinjected into wet bottom boilers for this same purpose.

Because a mixture of fine and coarse coal particles is fired in spreader stokers, significant unburnt carbon can be present in the particulate. To improve boiler efficiency, flyash from collection devices (typically multiple cyclones) is sometimes reinjected into spreader stoker furnaces. This practice can dramatically increase the particulate loading at the boiler outlet and, to a lesser extent, at the mechanical collector outlet. Flyash can also be reinjected from the boiler, air heater and economizer dust hoppers. Flyash reinjection from these hoppers does not increase particulate loadings nearly so much as from multiple cyclones. <sup>5</sup>

Particulate emissions from uncontrolled overfeed and underfeed stokers are considerably lower than from pulverized coal units and spreader stokers, since combustion takes place in a relatively quiescent fuel bed. Flyash reinjection is not practiced in these kinds of stokers.

Other variables than firing configuration and flyash reinjection can affect emissions from stokers. Particulate loadings will often increase as

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load increases (especially as full load is approached) and with sudden load changes. Similarly, particulate can increase as the ash and fines contents increase. ("Fines" are defined in this context as coal particles smaller than one sixteenth inch, or about 1.6 millimeters, in diameter.) Conversely, particulate can be reduced significantly when overfire air pressures are increased.<sup>5</sup>

The primary kinds of particulate control devices used for coal combustion include multiple cyclones, electrostatic precipitators, fabric filters (baghouses) and scrubbers. Some measure of control will even result due to ash settling in boiler/air heater/economizer dust hoppers, large breeches and chimney bases. To the extent possible from the existing data base, the effects of such settling are reflected in the emission factors in Table 1.1-1.

Electrostatic precipitators (ESP) are the most common high efficiency control device used on pulverized coal and cyclone units, and they are being used increasingly on stokers. Generally, ESP collection efficiencies are a function of collection plate area per volumetric flow rate of flue gas through the device. Particulate control efficiencies of 99.9 weight percent are obtainable with ESPs. Fabric filters have recently seen increased use in both utility and industrial applications, generally effecting about 99.8 percent efficiency. An advantage of fabric filters is that they are unaffected by high flyash resistivities associated with low sulfur coals. ESPs located after air preheaters (i.e., cold side precipitators) may operate at significantly reduced efficiencies when low sulfur coal is fired. Scrubbers are also used to control particulate, although their primary use is to control sulfur oxides. One drawback of scrubbers is the high energy requirement to achieve control efficiencies comparable to those of ESPs and baghouses.<sup>2</sup>

Mechanical collectors, generally multiple cyclones, are the primary means of control on many stokers and are sometimes installed upstream of high efficiency control devices in order to reduce the ash collection burden. Depending on application and design, multiple cyclone efficiencies can vary tremendously. Where cyclone design flow rates are not attained (which is common with underfeed and overfeed stokers), these devices may be only marginally effective and may prove little better in reducing particulate than large breeching. Conversely, well designed multiple cyclones, operating at the required flow rates, can achieve collection efficiencies on spreader stokers and overfeed stokers of 90 to 95 percent. Even higher collection efficiencies are obtainable on spreader stokers with reinjected flyash because of the larger particle sizes and increased particulate loadings reaching the controls. 5-6

Sulfur Oxides  $^{7-9}$  - Gaseous sulfur oxides from external coal combustion are largely sulfur dioxide (SO<sub>2</sub>) and much lesser quantities of sulfur trioxide (SO<sub>3</sub>) and gaseous sulfates. These compounds form as the organic and pyritic sulfur in the coal is oxidized during the combustion process. On average, 98 percent of the sulfur present in bituminous coal will be emitted as gaseous sulfur oxides, whereas somewhat less will be emitted when subbituminous coal is fired. The more alkaline nature of the ash in some subbituminous coals causes some of the sulfur to react to form various sulfate

EMISSION FACTORS FOR EXTERNAL BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION<sup>a</sup> TABLE 1.1-1.

|  | Partie            | Particulateb    | Sulfur Oxides         | des       | Nitrogen Oxides                            | bxides <sup>d</sup> | Carbon Monoxide | noxide | Nonmethane VOCe, f | , 200v s | Meth         | Methane    |
|--|-------------------|-----------------|-----------------------|-----------|--|---------------------|-----------------|--------|--------------------|----------|--------------|------------|
| Firing Contiguration   | kg/Mg             | kg/Mg lb/ton    | kg/Mg                 | 1b/ton    | kg/Mg                                      | 1b/ton              | kg/Mg           | 1b/ton | kg/Mg              | 1b/ton   | kg/Mg lb/ton | 1b/ton     |
| Pulverized coal fired<br>Dry bottom                                  | <b>5A</b>         | 10A             | 19.58(17.58)          | 398 (358) | 10.5(7.5) <sup>8</sup> 21(15) <sup>8</sup> | 21(15)8             | 0.3             | 9.0    | 0.04               | 0.07     | 0.015        | 0.015 0.03 |
| Wet bottom   | 3.5A <sup>h</sup> |                 | 19.58(17.58)          | 398 (358) | 17   | 34                  | 0.3             | 9.0    | 0.04               | 0.07     | 0.015        | 0.03       |
| Cyclone furnace  | 14 <sup>h</sup>   | $^{2A}$         | 19.58(17.58)          | 398 (358) | 18.5                                       | 37                  | 0.3             | 9.0    | 0.04               | 0.0      | 0.015        | 0.03       |
| Spreader stoker<br>Uncontrolled                                      | 301               | <sup>‡</sup> 09 | 19.55(17.58) 395(358) | 398 (358) | 7  | 14                  | 2.5             | 5      | 0.04               | 0.07     | 0.015        | 0.03       |
| After multiple cyclone With flyash reinjection from multiple cyclone | 8.5               | 17              | 19.58(17.58)          | 398 (358) | 7  | 14                  | 2.5             | \$     | 0.04               | 0.07     | 0.015        | 0.03       |
| No flyash reinjection from multiple cyclone                          | 9                 | 12              | 19.58(17.58) 398(358) | 398 (358) | 7  | 14                  | 2.5             | 5      | 0.04               | 0.07     | 0.015        | 0.63       |
| Overfeed stoker <sup>j</sup><br>Uncontrolled                         | *8 <sub>6</sub>   | 16 <sup>k</sup> | 19.58(17.58)          | 398 (358) | 3.25                                       | 7.5                 | e               | •      | 0.04               | 0.07     | 0.015        | 0.03       |
| After multiple cyclone   | 4.5               | 6               | 19.58(17.58)          | 398 (358) | 3.25                                       | 7.5                 | 3               | 9      | 0.04               | 0.07     | 0.015        | 0.03       |
| Underfeed stoker<br>Uncontrolled                                     | 7.5               | 151             | 15.58                 | 318       | 4.75                                       | 5.6                 | 5.5             | п      | 0.65               | 1.3      | 7.0          | 8.0        |
| After multiple cyclone   | 5.5               | 11              | 15.58                 | 318       | 4.75                                       | 9.5                 | 5.5             | 11     | 0.65               | 1.3      | 9.0          | 8.0        |
| Handfired units  | 7.5               | 15              | 15.58                 | 318       | 1.5  | 3                   | 45              | 06     | 5                  | 10       | 4            | 89         |
|  |                   |                 |                       |           |  |                     |                 |        |                    |          |              |            |

Pactors represent uncontrolled emissions unless otherwise specified and should be applied to coal consumption as fired.

catch for pulverized coal Where particulate is expressed in terms of the coal ash content (A), the and cyclone furnaces; about 10% for spreader stokers; about 15% for other stokers; and about 50% for handfired units (References 6, 19, and 49). factor is determined by multiplying the weight % ash content of the coal (as fired) by the numerical value preceding the "A". For example coal having 8% ash is fired in a dry bottom unit, the particulate emission factor would be 5 x 8 or 40 kg/Mg (80 lb/ton). On average, the densible" material collected in the back half catch of EPA Method 5 is less than 5% of the front half, or "filterable", catch for pulveri based on EPA Method 5 (front half catch) as described in Reference 12.

bottom ash. With subbituminous coal, generally about 10% more fuel sulfur is retained in the bottom ash and particulate, because of the more alkaline Expressed as SO2, including SO2, SO3 and gaseous sulfates. The factors in parentheses should be used to estimate gaseous sulfur oxide emissions for On average equally small percent of the fuel sulfur is emitted as particulate sulfate (References 9, 13). Small quantities of sulfur are also retained in the for bituminous coal, 97% of the fuel sulfur is emitted as 502, whereas only about 0.7% of the fuel sulfur is emitted as S03 and gaseous sulfate. subbituminous coal. In all cases, "S" is the weight % sulfur content of the coal as fired. See Footnote b for an example calculation. nature of the coal ash. Conversion to gaseous sulfate appears to be about the same as for bituminous coal.

dexpressed an NO2. Generally, 95 - 99 volume % of the nitrogen oxides present in combustion exhaust will be in the form of NO, the rest being (Reference 11). To express these factors as NO, multiply by a factor of 0.66. All factors represent emissions at baseline operation (i.e., 60 - 1102 load and no NO<sub>x</sub> control measures, as discussed in the text).

Nonmethane volatile organic compounds (VOC), expressed as C<sub>2</sub> to C<sub>16</sub> n-alkane equivalents (Reference 58). Because limited data on NAVOC were available to distinguish the effects of firing configuration, all data were averaged collectively to develop a single average for pulverized coal units, cyclones, spreader and overfeed stokers. Rominal values achieveable under normal operating conditions. Values one or two orders of magnitude higher can occur when combustion is not complete.

Bparenthetic value is for tangentially fired boilers.

<sup>t</sup>bucontrolled particulate emissions, when no flyash reinjection is employed. When a control device is installed, and collected flyash is reinjected to the boiler, particulate from the boiler reaching the control equipment can increase by up to a factor of two.

the boller heater or at t Accounts for flyash settling in an economizer, air heater or breeching upstream of a control device or stack. (Particulate directly outlet typically will be twice this level.) This factor should be applied even when flyash is reinjected to the holler from boller,

Includes traveling grate, vibrating grate and chain grate stokers.

AND REFERENCES FOR BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION \*EMISSION FACTOR RATINGS TABLE 1.1-2.

| Distance Configuration  | Part     | Particulate           | Sulfur   | Sulfur Oxides                           | Nitro    | Nitrogen Oxides          | Carbon | Carbon Monoxide          | Nonmeth  | Nonmethane VOC | Met      | Methane |
|---|----------|-----------------------|----------|---|----------|--------------------------|--------|--------------------------|----------|----------------|----------|---------|
| riting whitegraph   | Rating   | Ref.                  | Rating   | Ref.                                    | Rating   | Ref.                     | Rating | Ref.                     | Rating   | Ref.           | Rating   | Ref.    |
| Pulverized coal fired<br>Dry bottom                               | ∢        | 14-25                 | ∢        | 9,16-19,21,<br>31-37,39,<br>41-46,51-55 | ∢        | 11,14,16-17,<br>21,46,56 | ∢      | 16,18–19,21<br>47,57     | ∢        | 55,58          | ∢        | 58      |
| Wet bottom  | Ω        | 14,16,26              | ∢        | :                                       | ပ        | 14,16                    | ∢      | =                        | <b>⋖</b> | 58             | ∢        | =       |
| Cyclone furnace   | Q        | 14,19,22,<br>27-29    | ∢        | Ξ                                       | æ        | 11                       | ¥      | :                        | <b>∢</b> | =              | ∢        | =       |
| Spreader stoker<br>Uncontrolled                                   | Ø        | 17,30-35              | <b>∢</b> | =                                       | ∢        | 11,17,31-37<br>39-40,46  | ∢      | 17,19,31-34,<br>36,47,51 | ∢        | E              | <b>∀</b> | =       |
| After multiple cyclone<br>With flyash reinjection<br>from cyclone | æ        | 14,32,36-38           | ∢        | Ē                                       | <        | =                        | ∢      | =                        | ∢        | =              | ∢        | z       |
| No flyash reinjection<br>from cyclone                             | <b>∢</b> | 17,31-35,<br>39,40,59 | <b>∀</b> | =                                       | <b>⋖</b> | :                        | ∢      | :                        | ∢        | =              | <b>⋖</b> | =       |
| Overfeed stoker<br>Uncontrolled                                   | æ        | 6,17,41-43,<br>45-47  | ∢        | =                                       | <b>⋖</b> | 11,17,19,<br>41-45       | æ      | 17,41–42,45,<br>47,51    | ∢        | =              | <b>⋖</b> | =       |
| After multiple cyclone  | æ        | 6,41,44-45            | ∢        | =                                       | ∢        | =                        | μA     | z                        | ∢        | ŧ              | 4        | =       |
| Underfeed stoker<br>Uncontrolled                                  | æ        | 6,19,47-48            | æ        | 19,48                                   | ø        | 19,47-48                 | æ      | 19,47-48                 | ∢        | 47,58          | 4        | 47,58   |
| After multiple cyclone  | ပ        | 9                     | æ        | =                                       | ø        | =                        | m      | =                        | <        | =              | 4        | =       |
| Handfired units   | ۵        | 49-50                 | a        | =                                       | Q        | 50                       | Ω      | 50                       | Q        | 50,58          | Q        | 50,58   |
|   |          |                       |          |   |          |                          |        |                          |          |                |          |         |

These ratings, in the context of this Section, refer to the number of test data on which each emission factor is based. An "A" rating means the factor is based on tests at ten or more boilers, a "B" rating on six to nine test data, and a "C" rating on test data for two to five boilers.

A "D" rating indicates the factor is based on only a single datum or extrapolated from a secondary reference. These ratings are not a measure of the scatter in the underlying test data. However, a higher rating will generally increase confidence that a given factor will better approximate the average emissions for a particular boiler category.

salts that are retained in the boiler or in the flyash. Generally, boiler size, firing configuration and boiler operation have little impact on the percent conversion of fuel sulfur to sulfur oxides.

Several techniques are used to reduce sulfur oxides from coal combustion. One way is to switch to lower sulfur coals, since sulfur oxide emissions are proportional to the sulfur content of the coal. This alternative may not be possible where lower sulfur coal is not readily available or where a different grade of coal cannot be satisfactorily fired. In some cases, various cleaning processes may be employed to reduce the fuel sulfur content. Physical coal cleaning removes mineral sulfur such as pyrite but is not effective in removing organic sulfur. Chemical cleaning and solvent refining processes are being developed to remove organic sulfur.

Many flue gas desulfurization techniques can remove sulfur oxides formed during combustion. Flue gases can be treated through wet, semidry or dry desulfurization processes of either the throwaway type, in which all waste streams are discarded, or the recovery (regenerable) type, in which the  $\mathrm{SO}_{x}$  absorbent is regenerated and reused. To date, wet systems are the most commonly applied. Wet systems generally use alkali slurries as the  $\mathrm{SO}_{x}$  absorbent medium and can be designed to remove well in excess of 90 percent of the incoming  $\mathrm{SO}_{x}$ . Particulate reduction of up to 99 percent is also possible with wet scrubbers, but flyash is often collected by upstream ESPs or baghouses to avoid erosion of the desulfurization equipment and possible interference with the process reactions. Also, the volume of scrubber sludge is reduced with separate flyash removal, and contamination of the reagents and byproducts is prevented. References 7 and 8 give more details on scrubbing and other  $\mathrm{SO}_{x}$  removal techniques.

Nitrogen Oxides  $^{10-11}$  - Nitrogen oxides (NO<sub>X</sub>) emissions from coal combustion are primarily nitrogen oxide (NO). Only a few volume percent are comprised of nitrogen dioxide (NO<sub>2</sub>). NO results from thermal fixation of atmospheric nitrogen in the combustion flame and from oxidation of the nitrogen bound in the coal. Typically, only 20 to 60 percent of the fuel nitrogen is converted to nitrogen oxides. Bituminous and subbituminous coals usually contain from 0.5 to 2 weight percent nitrogen, present mainly in aromatic ring structures. Fuel nitrogen can account for up to 80 percent of total NO<sub>X</sub> from coal combustion.

A number of combustion modifications can be made to reduce  $\mathrm{NO}_{\mathrm{X}}$  emissions from boilers. Low excess air (LEA) firing is the most widespread control modification, because it can be practiced in both old and new units and in all sizes of boilers. LEA firing is easy to implement and has the added advantage of increasing fuel use efficiency. LEA firing is generally only effective above 20 percent excess air for pulverized coal units and above 30 percent excess air for stokers. Below these levels the  $\mathrm{NO}_{\mathrm{X}}$  reduction due to decreased  $\mathrm{O}_2$  availability is offset by increased  $\mathrm{NO}_{\mathrm{X}}$  due to increased flame temperature. Another  $\mathrm{NO}_{\mathrm{X}}$  reduction technique is simply to switch to a coal having a lower nitrogen content, although many boilers may not properly fire coals of different properties.

Off-stoichiometric (staged) combustion is also an effective means of controlling  $NO_X$  from coal fired equipment. This can be achieved by using

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overfire air or low  $\mathrm{NO}_{\mathrm{X}}$  burners designed to stage combustion in the flame zone. Other  $\mathrm{NO}_{\mathrm{X}}$  reduction techniques include flue gas recirculation, load reduction, and steam or water injection. However, these techniques are not very effective for use on coal fired equipment because of the fuel nitrogen effect. Ammonia injection is another technique which can be used, but it is costly. The net reduction of  $\mathrm{NO}_{\mathrm{X}}$  from any of these techniques or combinations thereof varies considerably with boiler type, coal properties and existing operating practices. Typical reductions will range from 10 to 60 percent. References 10 and 60 should be consulted for a detailed discussion of each of these  $\mathrm{NC}_{\mathrm{X}}$  reduction techniques. To date, flue gas treatment is not used to reduce nitrogen oxide emissions due to its higher cost.

Volatile Organic Compounds and Carbon Monoxide - Volatile organic compounds (VOC) and carbon monoxide (CO) are unburnt gaseous combustibles which are generally emitted in quite small amounts. However, during startups, temporary upsets or other conditions preventing complete combustion, unburnt combustible emissions may increase dramatically. VOC and CO emissions per unit of fuel fired are normally lower from pulverized coal or cyclone furnaces than from smaller stokers and handfired units where operating conditions are not as well controlled. Measures used for  $\mathrm{NO}_{\mathrm{X}}$  control can increase CO emissions, so to minimize the risk of explosion, such measures are applied only to the point at which CO in the flue gas reaches a maximum of about 200 parts per million. Control measures, other than maintaining proper combustion conditions, are not applied to control VOC and CO.

Emission Factors and References - Average emission factors for bituminous and subbituminous coal combustion in boilers are presented in Table 1.1-1. The factors for underfeed stokers and handfired units also may be applied to hot air furnaces. In addition to factors for uncontrolled emissions, factors are also presented for emissions after multiple cyclones. Emission factor ratings and references are presented in Table 1.1-2. Further general information on coal, combustion practices, emissions and controls is available in the references cited above.

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#### 1.3 FUEL OIL COMBUSTION

# 1.3.1 General 1,2,22

Fuel oils are broadly classified into two major types, distillate and residual. Distillate oils (fuel oil grade Nos. 1 and 2) are used mainly in domestic and small commercial applications in which easy fuel burning is required. Distillates are more volatile and less viscous than residual oils, having negligible ash and nitrogen contents and usually containing less than 0.3 weight percent sulfur. Residual oils (grade Nos. 4, 5 and 6), on the other hand, are used mainly in utility, industrial and large commercial applications with sophisticated combustion equipment. No. 4 oil is sometimes classified as a distillate, and No. 6 is sometimes referred to as Bunker C. Being more viscous and less volatile than distillate oils, the heavier residual oils (Nos. 5 and 6) must be heated to facilitate handling and proper atomization. Because residual oils are produced from the residue left after lighter fractions (gasoline, kerosene and distillate oils) have been removed from the crude oil, they contain significant quantities of ash, nitrogen and sulfur. Properties of typical fuel oils are given in Appendix A.

#### 1.3.2 Emissions

Emissions from fuel oil combustion are dependent on the grade and composition of the fuel, the type and size of the boiler, the firing and loading practices used, and the level of equipment maintenance. Table 1.3-1 presents emission factors for fuel oil combustion in units without control equipment. The emission factors for industrial and commercial boilers are divided into distillate and residual oil categories because the combustion of each produces significantly different emissions of particulates, SO and NO. The reader is urged to consult the references for a detailed discussion of the parameters that affect emissions from oil combustion.

Particulate Matter 3-7,12-13,24,26-27 - Particulate emissions are most dependent on the grade of fuel fired. The lighter distillate oils result in significantly lower particulate formation than do the heavier residual oils. Among residual oils, Nos. 4 and 5 usually result in less particulate than does the heavier No. 6.

In boilers firing No. 6, particulate emissions can be described, on the average, as a function of the sulfur content of the oil. As shown in Table 1.3-1 (Footnote g), particulate emissions can be reduced considerably when low-sulfur grade 6 oil is fired. This is because low sulfur No. 6, whether refined from naturally occurring low sulfur crude oil or desulfurized by one of several current processes, exhibits substantially lower viscosity and reduced asphaltene, ash and sulfur - all of which results in better atomization and cleaner combustion.

UNCONTROLLED EMISSION FACTORS FOR FUEL OIL COMBUSTION TABLE 1.3-1.

# ¥ EMISSION FACTOR RATING:

| g  | Parti                | Particulate<br>Matter  | Sulfur               | fur Dioxide <sup>c</sup> | Sulfur               | fur<br>Tr1oxide                                       | Ca                   | rbon<br>Monoxide       | Carbon d Nitrogen Oxide Monoxide | Oxide <sup>e</sup>   |                      | Volatile (             | Volatile Organics<br>onmethane | Methane                |
|--|----------------------|--|----------------------|--------------------------|----------------------|---|----------------------|------------------------|----------------------------------|--|----------------------|------------------------|--------------------------------|------------------------|
|  | kg/10 <sup>3</sup> 1 | kg/10 <sup>3</sup> 1 15/10 <sup>3</sup> ga1 kg/10 <sup>3</sup> 1 | kg/10 <sup>3</sup> 1 | 1b/10 <sup>3</sup> ga1   | kg/10 <sup>3</sup> 1 | 1b/10 <sup>3</sup> ga1                                | kg/10 <sup>3</sup> 1 | 1b/10 <sup>3</sup> ga1 | kg/10 <sup>3</sup> 1             | 1 1b/10 <sup>3</sup> gal kg/10 <sup>3</sup> 1 1b/10 <sup>3</sup> gal | kg/10 <sup>3</sup> 1 | 1b/10 <sup>3</sup> ga1 | kg/10 <sup>3</sup> 1           | 1b/10 <sup>3</sup> ga1 |
| Utility Bollers<br>Residual Oil                      | 90                   | <b>50</b>  | 198                  | 1578                     | 0.34Sh               | 0.34S <sup>h</sup> 2.9S <sup>h</sup>                  | 9.0                  | 2                      | 8.0<br>12.6)(5) <sup>1</sup>     | 8.0 67 (12.6)(5) <sup>1</sup> (105)(42) <sup>1</sup>   | 0.09                 | 0.76                   | 0.03                           | 0.28                   |
| Industrial Boilers<br>Residual Oil<br>Distillate Oil | 8<br>0.24            | 20 02  | 19S<br>17S           | 157S<br>142S             | 0.24S<br>0.24S       | 2S<br>2S  | 0.6<br>0.6           | N N                    | 6.6 <sup>1</sup><br>2.4          | 55 <sup>‡</sup><br>20  | 0.034                | 0.28                   | 0.12<br>0.006                  | 1.0                    |
| Commercial Boilers<br>Residual Oil<br>Distillate Oil | g<br>0.24            | 5 08   | 195<br>175           | 157S<br>142S             | 0.24S<br>0.24S       | 2S<br>2S  | 0.6<br>0.6           | N N                    | 6.6                              | 55<br>20   | 0.14                 | 1.13                   | 0.057                          | 0.475                  |
| Residential Furnaces<br>Distillate Oil               | 0.3                  | 2.5  | 178                  | 1428                     | 0.248                | 28  | 9.0                  | 5                      | 2.2                              | 18   | 0.085                | 0.713                  | 0.214                          | 1.78                   |
| Boilers can be approximately classified accor        | oximatel             | y classifie  | d accordi            | ng to their              | r gross ()           | ding to their gross (higher) heat rate as shown below | t rate as            | shown belo             | ow:                              |  |                      |                        |                                |                        |

Villity (power plant) bollers:  $^{\circ}$  >106 x 10<sup>9</sup> J/hr (10 x 10<sup>6</sup> Btu/hr) Industrial bollers:  $^{\circ}$  10.6 x 10<sup>9</sup> J/hr (10 x 10<sup>6</sup> to 100 x 10<sup>6</sup> Btu/hr) Commercial bollers: 0.5 x 10<sup>9</sup> to 10.6 x 10<sup>9</sup> J/hr (0.5 x 10<sup>6</sup> to 10 x 10<sup>6</sup> Btu/hr) Residential furnaces:  $^{\circ}$  <0.5 x 10<sup>9</sup> J/hr (<0.5 x 10<sup>6</sup> Btu/hr)

beferences 3-7 and 24-25. Particulate matter is defined in this section as that material collected by EPA Method 5 (front half catch).

CREferences 1-5. Sindicates that the weight % of sulfur in the oil should be multiplied by the value given.

GREferences 1-5. Sindicates that the weight % of sulfur in the oil should be multiplied by the unit is improperly operated or not well maintained.

Expressed as NO<sub>2</sub>. References 1-5, 8-11, 17 and 26. Test results indicate that at least 95% by weight of NO<sub>x</sub> is NO for all boiler types except residential

furnaces, where about 75% is NO. References 18-21. Volatile organic compound emissions are generally negligible unless boiler is improperly operated or not well maintained, in which case emissions may increase by several orders of magnitude.

\*\*Rearticulate emission factors for residual oil combustion are, on average, a function of fuel oil grade and sulfur content:

Grade 6 oil: 1.25(S) + 0.38 kg/10³ liter [10(S) + 3 1b/10³ gal] where S is the weight % of sulfur in the oil. This relationship is based on 81 individual tests and has a correlation coefficient of 0.65.

Grade 5 oil: 1.25 kg/10³ liter (10 1b/10³ gal)

Grade 4 oil: 0.88 kg/10³ liter (7 1b/10³ gal)

heference 25.

10se 5 kg/10³ liters (42 lb/10³ gal) for tangentially fired boilers, 12.6 kg/10³ liters (105 lb/10³gal) for vertical fired boilers, and 8.0 kg/10³ liters

(67 lb/10³ gal) for all others, at full load and normal (>15%) excess air. Several combustion modifications can be employed for NO<sub>X</sub> reduction: (1)

(1) limited excess air can reduce NO<sub>X</sub> emissions 5-20%, (2) staged combustion 20-40%, (3) using low NO<sub>X</sub> burners 20-50%, and (4) ammonial injection can reduce NO<sub>X</sub> emissions 40-70% but may increase emissions of ammonia. Combinations of these modifications have been employed for further reductions in certain boilers. See Reference 23 for a discussion of these and other NO<sub>x</sub> reducing techniques and their operational and environmental impacts.
Nitrogen oxides emissions from residual oil combustion in industrial and commercial boilers are strongly related to fuel nitrogen content, estimated more

accurately by the empirical relationship:  $kg\ NO_2/10^3$  liters = 2.75 + 50(N)<sup>2</sup> [1b NO<sub>2</sub>/10<sup>3</sup>gal = 22 + 400(N)<sup>2</sup>] where N is the weight % of nitrogen in the oil. For residual oils having high (>0.5 weight %) nitrogen content, use 15 kg NO<sub>2</sub>/10<sup>3</sup> liter (120 lb NO<sub>2</sub>/10<sup>3</sup>gal) as an emission factor.

Boiler load can also affect particulate emissions in units firing No. 6 oil. At low load conditions, particulate emissions may be lowered by 30 to 40 percent from utility boilers and by as much as 60 percent from small industrial and commercial units. No significant particulate reductions have been noted at low loads from boilers firing any of the lighter grades, however. At too low a load condition, proper combustion conditions cannot be maintained, and particulate emissions may increase drastically. It should be noted, in this regard, that any condition that prevents proper boiler operation can result in excessive particulate formation.

Sulfur Oxides  $(\mathrm{SO_X})^{1-5,25,27}$  - Total sulfur oxide emissions are almost entirely dependent on the sulfur content of the fuel and are not affected by boiler size burner design, or grade of fuel being fired. On the average, more than 95 percent of the fuel sulfur is emitted as  $\mathrm{SO_2}$ , about 1 to 5 percent as  $\mathrm{SO_3}$  and about 1 to 3 percent as particulate sulfates. Sulfur trioxide readily reacts with water vapor (both in air and in flue gases) to form a sulfuric acid mist.

Nitrogen Oxides  $(\mathrm{NO_X})^{1-11,14,17,23,27}$  - Two mechanisms form nitrogen oxides, oxidation of fuelbound nitrogen and thermal fixation of the nitrogen in combustion air. Fuel  $\mathrm{NO_X}$  are primarily a function of the nitrogen content of the fuel and the available oxygen (on the average, about 45 percent of the fuel nitrogen is converted to  $\mathrm{NO_X}$ , but this may vary from 20 to 70 percent). Thermal  $\mathrm{NO_X}$ , on the other hand, are largely a function of peak flame temperature and available oxygen - factors which depend on boiler size, firing configuration and operating practices.

Fuel nitrogen conversion is the more important  $\mathrm{NO}_{\mathrm{X}}$  forming mechanism in residual oil boilers. Except in certain large units having unusually high peak flame temperatures, or in units firing a low nitrogen residual oil, fuel  $\mathrm{NO}_{\mathrm{X}}$  will generally account for over 50 percent of the total  $\mathrm{NO}_{\mathrm{X}}$  generated. Thermal fixation, on the other hand, is the dominant  $\mathrm{NO}_{\mathrm{X}}$  forming mechanism in units firing distillate oils, primarily because of the negligible nitrogen content in these lighter oils. Because distillate oil fired boilers usually have low heat release rates, however, the quantity of thermal  $\mathrm{NO}_{\mathrm{X}}$  formed in them is less than that of larger units.

A number of variables influence how much  $\mathrm{NO}_{\mathrm{X}}$  is formed by these two mechanisms. One important variable is firing configuration. Nitrogen oxide emissions from tangentially (corner) fired boilers are, on the average, less than those of horizontally opposed units. Also important are the firing practices employed during boiler operation. Limited excess air firing, flue gas recirculation, staged combustion, or some combination thereof may result in  $\mathrm{NO}_{\mathrm{X}}$  reductions from 5 to 60 percent. See Section 1.4 for a discussion of these techniques. Load reduction can likewise decrease  $\mathrm{NO}_{\mathrm{X}}$  production. Nitrogen oxides emissions may be reduced from 0.5 to 1 percent for each percentage reduction in load from full load operation. It should be noted that most of these variables, with the exception

of excess air, influence the  $\rm NO_X$  emissions only of large oil fired boilers. Limited excess air firing is possible in many small boilers, but the resulting  $\rm NO_X$  reductions are not nearly as significant.

Other Pollutants 18-21 - As a rule, only minor amounts of volatile organic compounds (VOC) and carbon monoxide will be emitted from the combustion of fuel oil. The rate at which VOCs are emitted depends on combustion efficiency. Emissions of trace elements from oil fired boilers are relative to the trace element concentrations of the oil.

Organic compounds present in the flue gas streams of boilers include aliphatic and aromatic hydrocarbons, esters, ethers, alcohols, carbonyls, carboxylic acids and polycylic organic matter. The last includes all organic matter having two or more benzene rings.

Trace elements are also emitted from the combustion of fuel oil. The quantity of trace elements emitted depends on combustion temperature, fuel feed mechanism and the composition of the fuel. The temperature determines the degree of volatilization of specific compounds contained in the fuel. The fuel feed mechanism affects the separation of emissions into bottom ash and fly ash.

If a boiler unit is operated improperly or is poorly maintained, the concentrations of carbon monoxide and VOCs may increase by several orders of magnitude.

#### 1.3.3 Controls

The various control devices and/or techniques employed on oil fired boilers depend on the type of boiler and the pollutant being controlled. All such controls may be classified into three categories, boiler modification, fuel substitution and flue gas cleaning.

Boiler Modification  $^{1-4}$ ,  $^{8-9}$ ,  $^{13-14}$ ,  $^{23}$  - Boiler modification includes any physical change in the boiler apparatus itself or in its operation. Maintenance of the burner system, for example, is important to assure proper atomization and subsequent minimization of any unburned combustibles. Periodic tuning is important in small units for maximum operating efficiency and emission control, particularly of smoke and CO. Combustion modifications, such as limited excess air firing, flue gas recirculation, staged combustion and reduced load operation, result in lowered NO $_{\rm X}$  emissions in large facilities. See Table 1.3-1 for specific reductions possible through these combustion modifications.

Fuel Substitution  $^{3,5,12,28}$  - Fuel substitution, the firing of "cleaner" fuel oils, can substantially reduce emissions of a number of pollutants. Lower sulfur oils, for instance, will reduce  $\mathrm{SO}_{\mathrm{X}}$  emissions in all boilers, regardless of size or type of unit or

grade of oil fired. Particulates generally will be reduced when a lighter grade of oil is fired. Nitrogen oxide emissions will be reduced by switching to either a distillate oil or a residual oil with less nitrogen. The practice of fuel substitution, however, may be limited by the ability of a given operation to fire a better grade of oil and by the cost and availability thereof.

Flue Gas Cleaning 15-16,28 - Flue gas cleaning equipment generally is employed only on large oil fired boilers. Mechanical collectors, a prevalent type of control device, are primarily useful in controlling particulates generated during soot blowing, during upset conditions, or when a very dirty, heavy oil is fired. During these situations, high efficiency cyclonic collectors can effect up to 85 percent control of particulate. Under normal firing conditions or when a clean oil is combusted, cyclonic collectors will not be nearly as effective due to a high percentage of small particles (less than 3 microns diameter) being emitted.

Electrostatic precipitators are commonly used in oil fired power plants. Older precipitators which are also small precipitators generally remove 40 to 60 percent of the particulate matter emissions. Due to the low ash content of the oil, greater collection efficiency may not be required. Today, new or rebuilt electrostatic precipitators have collection efficiencies of up to 90 percent.

Scrubbing systems have been installed on oil-fired boilers, especially of late, to control both sulfur oxides and particulate. These systems can achieve  $\mathrm{SO}_2$  removal efficiencies of up to 90 to 95 percent and provide particulate control efficiencies on the order of 50 to 60 percent.

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#### 1.4 NATURAL GAS COMBUSTION

# 1.4.1 General 1,2

Natural gas is one of the major fuels used throughout the country. It is used mainly for power generation, for industrial process steam and heat production, and for domestic and commercial space heating. The primary component of natural gas is methane, although varying amounts of ethane and smaller amounts of nitrogen, helium and carbon dioxide are also present. Gas processing plants are required for recovery of liquefiable constituents and removal of hydrogen sulfide (H<sub>2</sub>S) before the gas is used (see Natural Gas Processing, Section 9.2). The average gross heating value of natural gas is approximately 9350 kilocalories per standard cubic meter (1050 British thermal units/standard cubic foot), usually varying from 8900 to 9800 kcal/scm (1000 to 1100 Btu/scf).

Because natural gas in its original state is a gaseous, homogenous fluid, its combustion is simple and can be precisely controlled. Common excess air rates range from 10 to 15 percent, but some large units operate at lower excess air rates to increase efficiency and reduce nitrogen oxide (NO $_{\rm X}$ ) emissions.

# 1.4.2 Emissions and Controls $^{3-26}$

Even though natural gas is considered to be a relatively clean fuel, some emissions can occur from the combustion reaction. For example, improper operating conditions, including poor mixing, insufficient air, etc., may cause large amounts of smoke, carbon monoxide and hydrocarbons to be produced. Moreover, because a sulfur containing mercaptan is added to natural gas for detection purposes, small amounts of sulfur oxides will also be produced in the combustion process.

Nitrogen oxides are the major pollutants of concern when burning natural gas. Nitrogen oxide emissions are functions of combustion chamber temperature and combustion product cooling rate. Emission levels vary considerably with the type and size of unit and with operating conditions.

In some large boilers, several operating modifications may be employed for NO control. Staged combustion for example, including off-stoichiometric firing and/or two stage combustion, can reduce NO emissions by 5 to 50 percent. In off-stoichiometric firing, also called "biased firing", some burners are operated fuel rich, some fuel lean, and others may supply air only. In two stage combustion, the burners are operated fuel rich (by introducing only 70 to 90 percent stoichiometric air), with combustion being completed by air injected above the flame zone through second stage "NO-ports". In staged combustion, NO $_{\rm X}$  emissions are reduced because the bulk of combustion occurs under fuel rich conditions.

Other NO<sub>X</sub> reducing modifications include low excess air firing and flue gas recirculation. In low excess air firing, excess air levels are kept as low as possible without producing unacceptable levels of unburned combustibles (carbon monoxide, volatile organic compounds and smoke) and/or other operational problems. technique can reduce  $NO_X$  emissions by 5 to 35 percent, primarily because of lack of oxygen during combustion. Flue gas recirculation into the primary combustion zone, because the flue gas is relatively cool and oxygen deficient, can also lower  $NO_{\rm X}$  emissions by 4 to 85 percent, depending on the amount of gas recirculated. Flue gas recirculation is best suited for new boilers. Retrofit application would require extensive burner modifications. Initial studies indicate that low  $NO_X$  burners (20 to 50 percent reduction) and ammonia injection (40 to 70 percent reduction) also offer NO<sub>x</sub> emission reductions.

Combinations of the above combustion modifications may also be employed to reduce  $\mathrm{NO}_{\mathrm{X}}$  emissions further. In some boilers, for instance,  $\mathrm{NO}_{\mathrm{X}}$  reductions as high as 70 to 90 percent have been produced by employing several of these techniques simultaneously. In general, however, because the net effect of any of these combinations varies greatly, it is difficult to predict what the reductions will be in any given unit.

Emission factors for natural gas combustion are presented in Table 1.4-1, and factor ratings in Table 1.4-2.

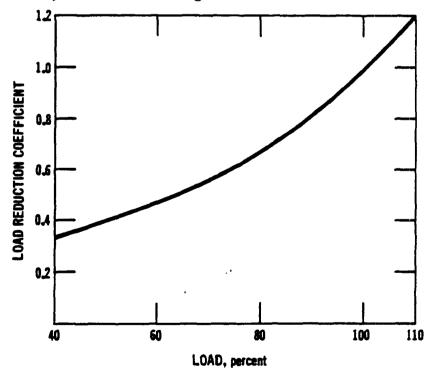


Figure 1.4-1. Load reduction coefficient as function of boiler load. (Used to determine  $NO_X$  reductions at reduced loads in large boilers.)

TABLE 1.4-1. UNCONTROLLED EMISSION FACTORS FOR NATURAL GAS COMBUSTION<sup>a</sup>

| Furnace Size & Type (10 <sup>6</sup> Btu/hr heat input) | Partic<br>kg/10 <sup>6</sup> m <sup>3</sup> | ulates <sup>b</sup><br>1b/10 <sup>6</sup> ft <sup>3</sup> | Particulates Sulfur Nitrogend, Carbonf, 8 Volatile Organics kg/106m3 lb/106ft kg/106m3 lb/106m3 lb/10 | )/10 <sup>6</sup> ft <sup>3</sup> | Nitro<br>Oxite<br>kg/10 <sup>6m3</sup> | gen <sup>d,e</sup><br>de<br>1b/10 <sup>6</sup> ft <sup>3</sup> | Carbon <sup>f,g</sup><br>Monoxide<br>kg/10 <sup>6</sup> m <sup>3</sup> lb/10 <sup>6</sup> f | on <sup>f, 8</sup><br>xide<br>1b/10 <sup>6</sup> ft <sup>3</sup> | Nonmikg/10 <sup>6</sup> m <sup>3</sup> | Volatile<br>ethane<br>1b/10 <sup>6</sup> ft <sup>3</sup> | Organics<br>Meth<br>kg/10 <sup>6</sup> m <sup>3</sup> | ane<br>1b/10 <sup>6</sup> ft <sup>3</sup> |
|---|---|---|---|-----------------------------------|--|--|---|--|--|--|---|---|
| Utility boilers (>100)                                  | 16-80                                       | 1-5   | 9.6   | 9.6                               | 0.6 8800 <sup>h</sup> 550 <sup>h</sup> | 550 <sup>h</sup>   | 049   | 07   | 23                                     | 1.4  | 4.8 0.3   | 0.3                                       |
| Industrial boilers<br>(10 - 100)                        | 16-80                                       | 1-5   | 9.6   | 9.0                               | 2240                                   | 140  | 260   | 35   | 44                                     | 2.8  | 48  | 3   |
| Domestic and commercial boilers (<10)                   | 16-80                                       | 1-5   | 9.6   | 9.0                               | 1600                                   | 100  | 320   | 20   | 84                                     | 5.3  | 43  | 2.7                                       |

References 15-18. CReferences 15-18. CReferences 4-5, 7-8, 11, 11, 18-19, 12. CReferences 4-5, 7-8, 11, 11, 18-19, 12. CReference 4-5, 7-8, 11, 11, 18-19, 12. Can an average sulfur content of natural gas of  $4600 \text{ g/10}^6 \text{ Nm}^3$  (2000  $\text{gr/10}^6 \text{ scf}$ ). Captering the solution of the solution of 4-5, 7-8, 16, 11, 14, 18-19, 12, 12. Captering as 10, 12,

TABLE 1.4-2. FACTOR RATINGS FOR NATURAL GAS COMBUSTION

| Furnace Type        | Particulates | Sulfur | Nitrogen | Carbon    | vo         | C       |
|---------------------|--------------|--------|----------|-----------|------------|---------|
|                     |              | Oxides | Oxides   | Monoxides | Nonmethane | Methane |
| Utility boiler      | В            | A      | A        | A         | С          | С       |
| Industrial boiler   | В            | Α      | A        | A         | C          | С       |
| Commercial boiler   | В            | A      | A        | A         | D          | D       |
| Residential furnace | В            | A      | A        | A         | D          | D       |

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### 1.5 LIQUEFIED PETROLEUM GAS COMBUSTION

### 1.5.1 General 1

Liquefied petroleum gas (LPG) consists of butane, propane, or a mixture of the two, and of trace amounts of propylene and butylene. This gas, obtained from oil or gas wells as a gasoline refining byproduct, is sold as a liquid in metal cylinders under pressure and, therefore, is often called bottled gas. LPG is graded according to maximum vapor pressure, with Grade A being mostly butane, Grade F mostly propane, and Grades B through E being varying mixtures of butane and propane. The heating value of LPG ranges from 6,480 kcal/liter (97,400 Btu/gallon) for Grade A to 6,030 kcal/liter (90,500 Btu/gallon) for Grade F. The largest market for LPG is the domestic/commercial market, followed by the chemical industry and the internal combustion engine.

## 1.5.2 Emissions<sup>1</sup>

LPG is considered a "clean" fuel because it does not produce visible emissions. However, gaseous pollutants such as carbon monoxide, volatile organic compounds (VOC's) and nitrogen oxides do occur. The most significant factors affecting these emissions are burner design, adjustment and venting. Improper design, blocking and clogging of the flue vent, and lack of combustion air result in improper combustion and the emission of aldehydes, carbon monoxide, hydrocarbons and other organics. Nitrogen oxide emissions are a function of a number of variables including temperature, excess air and residence time in the combustion zone. The amount of sulfur dioxide emitted is directly proportional to the amount of sulfur in the fuel. Emission factors for LPG combustion are presented in Table 1.5-1.

TABLE 1.5-1. EMISSION FACTORS FOR LPG COMBUSTION<sup>a</sup> EMISSION FACTOR RATING: C

| Furnace<br>Type and    | Parti        | Particulates                                | Sul                  | Sulfur <sub>b</sub><br>Oxidae               | Nit               | rogen   | Carb                 | 000  | N                 | Volatile Organics   | Organics          | -                  |
|------------------------|--------------|---|----------------------|---|-------------------|---|----------------------|--|-------------------|---|-------------------|--------------------|
| Fuel                   | $kg/10^{9}1$ | kg/10 <sup>3</sup> 1 1h/10 <sup>3</sup> ga1 | kg/10 <sup>3</sup> 1 | kg/10 <sup>3</sup> 1 1b/10 <sup>3</sup> ga1 | $k_{\rm R}/10^31$ | kg/10 <sup>3</sup> 1 1b/10 <sup>3</sup> gal kg/ | kg/10 <sup>3</sup> 1 | kg/10 <sup>3</sup> 1 1b/10 <sup>3</sup> gal kg | $k_{\rm g}/10^31$ | kg/10 <sup>3</sup> 1 1b/10 <sup>3</sup> ga1 kg/10 <sup>3</sup> 1 1b/10 <sup>3</sup> ga1 | $k_{\rm g}/10^31$ | thane<br>1b/10³ga1 |
| industrial             | 0.01-0.06    | 0.10-0.47                                   | 0.015                | 860.0                                       | 85                | 13.9  | 7 0                  | 7  |                   | 76 0  | 60                | 000                |
| Propane                | 0.01-0.05    | 0.09-0.44                                   | 0.018                | 0.098                                       | 1.49              | 12.4  | 0.37                 | 3.1  | 0.03              | 0.25  | 0.03              | 0.27               |
| omestic/<br>commercial |              |   |                      |   |                   |   |                      |  |                   |   |                   |                    |
| Butane                 | 0.01-0.06    |   | 0.018                | 0.098                                       | 1.13              | 9.6   | 0.23                 | 1.9  | 90.0              | 0.5   | 0.03              | 0.25               |
| Propane                | 0.01-0.05    | 0.09-0.44                                   | 0.018                | 0.098                                       | 1.05              | 8.8   | 0.22                 | 1.8  | 90.0              | 0.47  | 0.03              | 0.24               |

Assumes emissions (except sulfur oxides) are the same, on a heat input basis, as for natural gas combustion.

bExpressed as SO<sub>2</sub>. S equals the sulfur content expressed in g/100 m<sup>3</sup> gas vapor. For example, if sulfur content is 0.366 g/100m<sup>3</sup> (0.16 gr/100ft<sup>3</sup>) vapor, the SO<sub>2</sub> emission factor would be 0.01 x 0.366 or 0.0037 kg SO<sub>2</sub>/10<sup>3</sup> liters (0.09 x 0.16 or 0.014 lb of SO<sub>2</sub>/1000 gal) butane burned.

Expressed as NO<sub>2</sub>.

1.5-2 EMISSION FACTORS 8/82

### References for Section 1.5

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#### 1.6 WOOD WASTE COMBUSTION IN BOILERS

## 1.6.1 General 1-3

The burning of wood waste in boilers is mostly confined to those industries where it is available as a byproduct. It is burned both to obtain heat energy and to alleviate possible solid waste disposal problems. Wood waste may include large pieces like slabs, logs and bark strips as well as cuttings, shavings, pellets and sawdust, and heating values for this waste range from about 4,400 to 5,000 kilocalories per kilogram of fuel dry weight (7,940 to 9,131 Btu/1b). However, because of typical moisture contents of 40 to 75 percent, the heating values for many wood waste materials as fired range as low as 2,200 to 3,300 kilocalories per kilogram of fuel. Generally, bark is the major type of waste burned in pulp mills, and a varying mixture of wood and bark waste, or wood waste alone, are most frequently burned in the lumber, furniture and plywood industries.

# 1.6.2 Firing Practices 1-3

A variety of boiler firing configurations is used for burning wood waste. One common type in smaller operations is the dutch oven, or extension type of furnace with a flat grate. This unit is widely used because it can burn fuels with a very high moisture content. Fuel is fed into the oven through apertures at the top of a firebox and is fired in a cone shaped pile on a flat grate. The burning is done in two stages, drying and gasification, and combustion of gaseous products. The first stage takes place in a cell separated from the boiler section by a bridge wall. The combustion stage takes place in the main boiler section. The dutch oven is not responsive to changes in steam load, and it provides poor combustion control.

In a fuel cell oven, the fuel is dropped onto suspended fixed grates and is fired in a pile. Unlike the dutch oven, the fuel cell also uses combustion air preheating and repositioning of the secondary and tertiary air injection ports to improve boiler efficiency.

In many large operations, more conventional boilers have been modified to burn wood waste. These units may include spreader stokers with traveling grates, vibrating grate stokers, etc., as well as tangentially fired or cyclone fired boilers. The most widely used of these configurations is the spreader stoker. Fuel is dropped in front of an air jet which casts the fuel out over a moving grate, spreading it in an even thin blanket. The burning is done in three stages in a single chamber, (1) drying, (2) distillation and burning of volatile matter and (3) burning of carbon. This type of operation has a fast response to load changes, has improved combustion control and can be operated with multiple fuels. Natural gas or oil are often fired in spreader stoker boilers as auxiliary fuel. This is done to maintain constant steam when the wood waste

supply fluctuates and/or to provide more steam than is possible from the waste supply alone.

Sander dust is often burned in various boiler types at plywood, particle board and furniture plants. Sander dust contains fine wood particles with low moisture content (less than 20 weight percent). It is fired in a flaming horizontal torch, usually with natural gas as an ignition aid or supplementary fuel.

# 1.6.3 Emissions and Controls $^{4-28}$

The major pollutant of concern from wood boilers is particulate matter, although other pollutants, particularly carbon monoxide, may be emitted in significant amounts under poor operating conditions. These emissions depend on a number of variables, including (1) the composition of the waste fuel burned, (2) the degree of flyash reinjection employed and (3) furnace design and operating conditions.

The composition of wood waste depends largely on the industry whence it originates. Pulping operations, for example, produce great quantities of bark that may contain more than 70 weight percent moisture and sand and other noncombustibles. Because of this, bark boilers in pulp mills may emit considerable amounts of particulate matter to the atmosphere unless they are well controlled. On the other hand, some operations such as furniture manufacture produce a clean dry (5 to 50 weight percent moisture) wood waste that results in relatively few particulate emissions when properly burned. Still other operations, such as sawmills, burn a variable mixture of bark and wood waste that results in particulate emissions somewhere between these two extremes.

Furnace design and operating conditions are particularly important when firing wood waste. For example, because of the high moisture content that can be present in this waste, a larger than usual area of refractory surface is often necessary to dry the fuel before combustion. In addition, sufficient secondary air must be supplied over the fuel bed to burn the volatiles that account for most of the combustible material in the waste. When proper drying conditions do not exist, or when secondary combustion is incomplete, the combustion temperature is lowered, and increased particulate, carbon monoxide and hydrocarbon emissions may result. Lowering of combustion temperature generally results in decreased nitrogen oxide emissions. Also, emissions can fluctuate in the short term due to significant variations in fuel moisture content over short periods of time.

Flyash reinjection, which is common in many larger boilers to improve fuel efficiency, has a considerable effect on particulate emissions. Because a fraction of the collected flyash is reinjected into the boiler, the dust loading from the furnace, and consequently from the collection device, increases significantly per unit of wood waste burned. It is reported that full reinjection can cause

TABLE 1.6-1. EMISSION FACTORS FOR WOOD AND BARK COMBUSTION IN BOILERS EMISSION FACTOR RATING: B

| Pollutant/Fuel Type                            | kg/Mg                    | lb/ton                   |
|--|--------------------------|--------------------------|
| Particulate <sup>a,b</sup>                     |                          |                          |
| Bark <sup>C</sup>                              |                          |                          |
| Controlled, with flyash reinjection            | 7                        | 14                       |
| Controlled, without flyas                      | h<br>4.5                 | 9                        |
| Uncontrolled                                   | 24                       | 47                       |
| Wood/bark mixture <sup>c</sup>                 |                          |                          |
| Controlled, with flyash reinjection            | 3                        | 6                        |
| Controlled, without flyas reinjection          | h<br>2.7                 | 5.3                      |
| Uncontrolled <sup>f</sup>                      | 3.6                      | 7.2                      |
| Wood <sup>g</sup>                              |                          |                          |
| Uncontrolled                                   | 4.4                      | 8.8                      |
| Gulfur Dioxide <sup>h</sup>                    | 0.074<br>(0.009 — 0.193) | 0.148<br>(0.019 - 0.386) |
| Nitrogen Oxides(as NO <sub>2</sub> )           |                          |                          |
| 50,000-400,000 lb steam/hr <50,000 lb steam/hr | 1.4<br>0.34              | 2.8<br>0.68              |
| Carbon Monoxide <sup>j</sup>                   | 2-24                     | 4-47                     |
| Nonmethane VOC <sup>k</sup>                    | 0.8                      | 1.7                      |

<sup>&</sup>lt;sup>a</sup>References 2,4,9,17-18. For boilers burning gas or oil as an auxiliary fuel, assuming all particulates result from the waste fuel alone.

Reference 30.

fuel alone.

May include condensible hydrocarbons consisting of pitches and tars, mostly from the back half catch of EPA Method 5. Tests reported in Reference 20 indicate that condensible hydrocarbons account for about 4% of total particulate by weight.

Based on moisture content of about 50%.

dAfter the control equipment, assuming an average collection efficiency of 80%. Data from References 4, 7 and 8 indicate that 50% flyash reinjection increases the dust load at the boiler outlet (before control) by 1.2 to 1.5 times, while 100% flyash reinjection increases the load 1.5 to 2 times the load without reinjection.

Based on large dutch ovens and spreader stokers (averaging 23,430 kg

steam/hr) with steam pressures from 10.5 - 42 kg/cm². fBased on small dutch ovens and spreader stokers (usually operating less than 9075 kg/hr of steam), with steam pressures from  $2.8-17.6 \, \text{kg/cm²}$ . Careful air adjustments and improved fuel separation and firing were used on some of these boilers, but the effects cannot be isolated.

References 12-13,19,27. Wood waste includes cuttings, shavings, sawdust and chips, but not bark. Moisture content ranges from 20 to 50% by weight. Based on 28 small boilers (less than 3,300 kg steam/hr) located in the States of New York and North Carolina. Reference 23. Based on tests of fuel sulfur content and sulfur dioxide emissions at four mills burning bark. The lower limit of the range in parentheses should be used for wood, and higher values for bark. A heating value of 4,987 kcal/kg (9,000 Btu/lb) is assumed. The factors are based on the dry weight of fuel. References 7,24-26. It should be noted that several factors can influence emission rates, including combustion zone, temperatures, excess air, boiler operating conditions, fuel moisture and fuel introgen content.

Reference 20. Nonmethane VOC reportedly consists of compounds with a high vapor pressure such as alpha pinene. Emission factors for methane are not available.

a tenfold increase in the dust loadings of some systems, although increases of 1.2 to 2 times are more typical for boilers using 50 to 100 percent reinjection. A major factor affecting this dust loading increase is the extent to which the sand and other noncombustibles can successfully be separated from the flyash before reinjection to the furnace.

Although reinjection increases boiler efficiency from 1 to 4 percent and minimizes the emissions of uncombusted carbon, it also increases boiler maintenance requirements, decreases average flyash particle size and makes collection more difficult. Properly designed reinjection systems should separate sand and char from the exhaust gases, to reinject the larger carbon particles to the furnace and to divert the fine sand particles to the ash disposal system.

Several factors can influence emissions, such as boiler size and type, design features, age, load factors, wood species and operating procedures. In addition, wood is often cofired with other fuels. The effect of these factors on emissions is difficult to quantify. It is best to refer to the references for further information.

The use of multitube cyclone mechanical collectors provides the particulate control for many hogged boilers. Usually, two multicyclones are used in series, allowing the first collector to remove the bulk of the dust and the second collector to remove smaller particles. The collection efficiency for this arrangement is from 65 to 95 percent. Low pressure drop scrubbers and fabric filters have been used extensively for many years. On the West Coast, pulse jets have been used.

Emission factors for wood waste boilers are presented in Table 1.6-1.

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#### 1.7 LIGNITE COMBUSTION

## 1.7.1 General 1-4

Lignite is a relatively young coal with properties intermediate to those of bituminous coal and peat. It has a high moisture content (35 to 40 weight percent) and a low wet basis heating value (1500 to 1900 kilocalories) and generally is burned only close to where it is mined, in some midwestern States and in Texas. Although a small amount is used in industrial and domestic situations, lignite is mainly used for steam/electric production in power plants. In the past, lignite was burned mainly in small stokers, but today the trend is toward use in much larger pulverized coal fired or cyclone fired boilers.

The major advantages of firing lignite are that, in certain geographical areas, it is plentiful, relatively low in cost and low in sulfur content (0.4 to 1 wet basis weight percent). Disadvantages are that more fuel and larger facilities are necessary to generate a unit of power than is the case with bituminous coal. There are several reasons for this. First, the higher moisture content means that more energy is lost in the gaseous products of combustion, which reduces boiler efficiency. Second, more energy is required to grind lignite to the combustion specified size, especially in pulverized coal fired units. Third, greater tube spacing and additional soot blowing are required because of the higher ash fouling tendencies. Fourth, because of its lower heating value, more fuel must be handled to produce a given amount of power, since lignite usually is not cleaned or dried before combustion (except for some drying that may occur in the crusher or pulverizer and during transfer to the burner). Generally, no major problems exist with the handling or combustion of lignite when its unique characteristics are taken into account.

# 1.7.2 Emissions and Controls $^{2-11}$

The major pollutants of concern when firing lignite, as with any coal, are particulates, sulfur oxides, and nitrogen oxides. Volatile organic compound (VOC) and carbon monoxide emissions are quite low under normal operating conditions.

Particulate emission levels appear most dependent on the firing configuration in the boiler. Pulverized coal fired units and spreader stokers, which fire all or much of the lignite in suspension, emit the greatest quantity of flyash per unit of fuel burned. Cyclones, which collect much of the ash as molten slag in the furnace itself, and stokers (other than spreader), which retain a large fraction of the ash in the fuel bed, both emit less particulate matter. In general, the relatively high sodium content of lignite lowers particulate emissions by causing more of the resulting flyash to deposit on the boiler tubes. This is especially so in pulverized coal fired units wherein a high fraction of the ash is

TABLE 1.7-1. EMISSION FACTORS FOR EXTERNAL COMBUSTION OF LIGNITE COAL<sup>a</sup>

| Diring Configuration  | Partic | Particulates | Sul   | Sulfur       | Nitrogen | gen                | Carbon    | VOC<br>Normethene Methene | C         |
|-----------------------|--------|--------------|-------|--------------|----------|--------------------|-----------|---------------------------|-----------|
| Tring com Iguation    | kg/Mg  | kg/Mg 1b/ton | kg/Mg | kg/Mg 1b/ton | kg/Mg    | kg/Mg 1b/ton       |           |                           |           |
| Pulverized Coal Fired |        |              |       |              |          |                    |           |                           |           |
| Dry Bottom            | 3.1A   | 6.3A         | 158   | 30S          | , e , r  | 12 <sup>e, I</sup> | 50        | 60                        | 80        |
| Cyclone Furnace       | 3,3A   | 6.7A         | 158   | 30S          | 8.5      | 17                 | 80        | 60                        | 60        |
| Spreader Stoker       | 3.4A   | 6.8A         | 158   | 308          | 3        | 9                  | <b>60</b> | 80                        | 80        |
| Other Stokers         | 1.5A   | 2.9A         | 158   | 308          | 3        | 9                  | <b>60</b> | 50                        | <b>50</b> |
| q                     |        |              |       |              |          |                    |           |                           |           |

References 5-6,9,12. A is the wet basis percent ash content of the lignite.

(References 2,5-6, 9,12. A is the wet basis percent sulfur content of the lignite by weight. For a high sodium/ash lignite (Na<sub>2</sub>0 8%), use 8.55 kg/Hg (178 lb/ton); for a low sodium/ash lignite (Na<sub>2</sub>0 2%), use 17.55 kg/Hg (358 lb/ton). When the sodium/ash content is unknown, use 155 kg/Hg (308 lb/ton). The conversion of sulfur to sulfur dioxide is shown as Por uncontrolled emissions, and should be applied to lignite consumption as fired.

a function of alkali ash constituents in References 10-11. References 2,5,7-8. Expressed as  $No_2$ .

May be reduced 20 - 40% with low excess air firing and/or staged combustion in front fired and opposed wall fired units and Use 7 kg/Mg (14 lb/ton) for front wall fired and horizontally opposed wall fired units, and 4 kg/Mg (8 lb/ton) for tangentially fired units.

cyclones. <sup>S</sup>Factors reported in Table 1.1-1 may be used, based on the similarity of lignite combustion and bituminous coal combustion.

suspended in the combustion gases and can readily come into contact with the boiler surfaces.

Nitrogen oxide emissions are mainly a function of the boiler firing configuration and excess air. Stokers produce the lowest NO levels, mainly because most existing units are much smaller than the other firing type and have lower peak flame temperatures. In most boilers, regardless of firing configuration, lower excess air during combustion results in lower NO emissions.

Sulfur oxide emissions are a function of the alkali (especially sodium) content of the lignite ash. Unlike most fossil fuel combustion, in which over 90 percent of the fuel sulfur is emitted as  $SO_2$ , a significant fraction of the sulfur in lignite reacts with the ash components during combustion and is retained in the boiler ash deposits and flyash. Tests have shown that less than 50 percent of the available sulfur may be emitted as  $SO_2$  when a high sodium lignite is burned, whereas more than 90 percent may be emitted from low sodium lignite. As a rough average, about 75 percent of the fuel sulfur will be emitted as  $SO_2$ , the remainder being converted to various sulfate salts.

Newer lignite fired utility boilers are equipped with large electrostatic precipitators that may achieve as high as 99.5 percent particulate control. Older and smaller electrostatic precipitators operate at about 95 percent efficiency. Older industrial and commercial units use cyclone collectors that normally achieve 60 to 80 percent collection efficiency on lignite flyash. Flue gas desulfurization systems currently are in operation on several lignite fired utility boilers. These systems are identical to those used on bituminous coal fired boilers (see Section 1.1).

Nitrogen oxide reductions of up to 40 percent can be achieved by changing the burner geometry, controlling excess air and making other changes in operating procedures. The techniques are identical for bituminous and lignite coal.

TABLE 1.7-2. RATINGS OF EMISSION FACTORS FOR LIGNITE COMBUSTION

| Firing Configuration             | Particulates | Sulfur<br>Dioxide | Nitrogen<br>Dioxide |
|----------------------------------|--------------|-------------------|---------------------|
| Pulverized Coal Fired Dry Bottom | A            | A                 | A                   |
| Cyclone Furnace                  | С            | A                 | A                   |
| Spreader Stoker                  | В            | В                 | С                   |
| Other Stokers                    | В            | С                 | D                   |

Emission factors for particulates, sulfur dioxide and nitrogen oxides are presented in Table 1.7-1. Based on the similarity of lignite combustion and bituminous coal combustion, emission factors for carbon monoxide and volatile organic compounds reported in Table 1.1-1 may be used.

### References for Section 1.7

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- 2. G.H. Gronhovd, et al., "Some Studies on Stack Emissions from Lignite Fired Powerplants", Presented at the 1973 Lignite Symposium, Grand Forks, ND, May 1973.
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- 8. "Nitrogen Oxides Emission Measurements for Lignite Fired Power Plants", EPA Project Report No. 75-LSG-3, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1974.
- 9. Coal Fired Power Plant Trace Element Study, A Three Station Comparison, U.S. Environmental Protection Agency, Denver, CO, September 1975.
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  Variables Affecting Uncontrolled Sulfur Emissions from
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  Environmental Protection Agency, Research Triangle Park, NC,
  December 1977.

- 11. C.C. Shih, et al., Emissions Assessment of Conventional
  Stationary Combustion Systems, Volume III: External
  Combustion Sources for Electricity Generation, EPA Contract
  No. 68-02-2197, TRW Inc., Redondo Beach, CA, November 1980.
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#### 3.3.4 STATIONARY LARGE BORE DIESEL AND DUAL FUEL ENGINES

#### 3.3.4.1 General

The primary domestic use of large bore diesel engines, i.e., those greater than 560 cubic inch displacement per cylinder (CID/CYL), is in oil and gas exploration and production. These engines, in groups of three to five, supply mechanical power to operate drilling (rotary table), mud pumping and hoisting equipment, and may also operate pumps or auxiliary power generators. Another frequent application of large bore diesels is electricity generation for both base and standby service. Smaller uses include irrigation, hoisting and nuclear power plant emergency cooling water pump operation.

Dual fuel engines were developed to obtain compression ignition performance and the economy of natural gas, using a minimum of 5 to 6 percent diesel fuel to ignite the natural gas. Dual fuel large bore engines (greater than 560 CID/CYL) have been used almost exclusively for prime electric power generation.

#### 3.3.4.2 Emissions and Controls

The primary pollutant of concern from large bore diesel and dual fuel engines is  $NO_{\rm X}$ , which readily forms in the high temperature, pressure and excess air environment found in these engines. Lesser amounts of carbon monoxide and hydrocarbons are also emitted. Sulfur dioxide emissions will usually be quite low because of the negligible sulfur content of diesel fuels and natural gas.

The major variables affecting  $NO_{\rm X}$  emissions from diesel engines are injection timing, manifold air temperature, engine speed, engine load and ambient humidity. In general,  $NO_{\rm X}$  emissions decrease with increasing humidity.

Because  $\mathrm{NO}_{\mathrm{X}}$  is the primary pollutant from diesel and dual fuel engines, control measures to date have been directed mainly at limiting  $\mathrm{NO}_{\mathrm{X}}$  emissions. The most effective  $\mathrm{NO}_{\mathrm{X}}$  control technique for diesel engines is fuel injection retard, achieving reductions (at eight degrees of retard) of up to 40 percent. Additional  $\mathrm{NO}_{\mathrm{X}}$  reductions are possible with combined retard and air/fuel ratio change. Both retarded fuel injection (8°) and air/fuel ratio change of five percent are also effective in reducing  $\mathrm{NO}_{\mathrm{X}}$  emissions from dual fuel engines, achieving nominal  $\mathrm{NO}_{\mathrm{X}}$  reductions of about 40 percent and maximum  $\mathrm{NO}_{\mathrm{X}}$  reductions of up to 70 percent.

Other  $NO_X$  control techniques exist but are not considered feasible because of excessive fuel penalties, capital cost, or maintenance or operational problems. These techniques include exhaust gas recirculation (EGR), combustion chamber modification, water injection and catalytic reduction.

TABLE 3.3.4-1. EMISSION FACTORS FOR STATIONARY LARGE BORE DIESEL AND DUAL FUEL ENGINES<sup>a</sup>

EMISSION FACTOR RATING: C

| Engine                                  | Nitrogen            | Carbon   | V       | OC         | Sulfur               |
|---|---------------------|----------|---------|------------|----------------------|
| Туре                                    | 0xides <sup>b</sup> | Monoxide | Methane | Nonmethane | Dioxide <sup>d</sup> |
| Diesel                                  |                     |          |         |            |                      |
| 1b/10 <sup>3</sup> hph                  | 24                  | 6.4      | 0.07    | 0.63       | 7                    |
| g/hph                                   | 11                  | 2.9      | 0.03    | 0.29       | 3.2                  |
| g/kWh                                   | 15                  | 3.9      | 0.04    | 0.04       | 4.3                  |
| $1b/10^3$ gal <sup>e</sup>              | 500                 | 130      | 1       | 13         | 150                  |
| 1b/10 <sup>3</sup> gal <sup>e</sup> g/1 | 60                  | 16       | 0.2     | 1.6        | 18                   |
| Dual Fuel                               |                     |          |         |            |                      |
| 1b/10 <sup>3</sup> hph                  | 18                  | 5.9      | 4.7     | 1.5        | 0.70                 |
| g/hph                                   | 8                   | 2.7      | 2.1     | 0.7        | 0.32                 |
| g/kWh                                   | 11                  | 3.6      | 2.9     | 0.9        | 0.43                 |

<sup>&</sup>lt;sup>a</sup>Representative uncontrolled levels for each fuel determined by weighting data from several manufacturers. Weighting based on % of total horsepower sold by each manufacturer during a five year period.

Base on assumed sulfur content of 1% by weight for diesel fuel and 0.46 g/sc (0.20 gr/scf) for pipeline quality natural gas. Dual fuel  $SO_2$  emissions based on 5% oil/85% gas mix. Emissions should be adjusted for other fuel ratios.

efuel ratios.

These factors calculated from the above factors assuming a heating value of 40 MJ/L (145,000 Btu/gal) for oil, 41 MJ/scm (1100 Btu/scf) for natural gas, and an average fuel consumption of 9.9 MJ/kWh (7000 Btu/hph).

#### Reference for Section 3.3.4

1. Standards Support and Environmental Impact Statement Volume I Stationary Internal Combustion Engines, EPA-450/2-78-125a, U. S.
Environmental Protection Agency, Research Triangle Park, NC, July 1979.

Measured as NO<sub>2</sub>. Factors are for engines operated at rated load and speed. Nonmethane VOC accounts for 90% of total VOC from diesel engines but only 25% of total VOC emissions from dual fuel engines. Individual chemical species within the nonmethane fraction are not identified. Molecular dweight of nonmethane gas stream is assumed to be that of methane.

# 4.2.1 NONINDUSTRIAL SURFACE COATING 1,3,5

Nonindustrial surface coating operations are nonmanufacturing applications of surface coating. Two major categories are architectural surface coating and automobile refinishing. Architectural uses are considered to include both industrial and nonindustrial structures. Automobile refinishing pertains to the painting of damaged or worn highway vehicle finishes and not the painting of vehicles during manufacture.

Emissions from a single architectural structure or automobile refinishing are calculated by using total volume and content and weight of volatile constituents for the coating employed in the specific application. Estimating emissions for a large area which includes many major and minor applications of nonindustrial surface coatings requires that area source estimates be developed. Architectural surface coating and auto refinishing emissions data are often difficult to compile for a large geographical area. In cases where a large inventory is being developed and/or resources are unavailable for detailed accounting of actual volume of coatings for these applications, emissions may be assumed proportional to population or number of employees. Table 4.2.1-1 presents factors from national emission data and emissions per population or employee for architectural surface coating and automobile refinishing.

TABLE 4.2.1-1. NATIONAL EMISSIONS AND EMISSION FACTORS
FOR VOC FROM ARCHITECTURAL SURFACE COATING
AND AUTOMOBILE REFINISHING

| EMISSION  | FACTOR | RATING. | C |
|-----------|--------|---------|---|
| TITTOUTON | LUCION | MUTTIO. | ~ |

| Architectural Surface<br>Coating | Automobile<br>Refinishing              |
|----------------------------------|--|
| •                                |  |
| 446,000                          | 181,000                                |
| 491,000                          | 199,000                                |
|                                  |  |
| 21.4 (4.6)                       | 0.84 (1.9)                             |
| 5.8 (0.013) <sup>b</sup>         | 0.84 (1.9)<br>2.7 (0.006) <sup>c</sup> |
|                                  |  |
| _                                | 2.3 (2.6)                              |
| <del>-</del>                     | 2.3 (2.6)<br>7.4 (16.3) <sup>c</sup>   |
|                                  | Coating<br>,<br>446,000                |

References 3 and 5 - 8. All nonmethane organics.
Reference 8. Calculated by dividing kg/yr (1b/yr) by 365 days and converting to appropriate units. Assumes that 75% of annual emissions occurs over a 9 month ozone season. For shorter ozone seasons, adjust accordingly.

Assumes a 6 day operating week (313 days/yr).

The use of waterborne architectural coatings reduces volatile organic compound emissions. Current consumption trends indicate increasing substitution of waterborne architectural coatings for those using solvent. Automobile refinishing often is done in areas only slightly enclosed, which makes control of emissions difficult. Where automobile refinishing takes place in an enclosed area, control of the gaseous emissions can be accomplished by the use of adsorbers (activated carbon) or afterburners. The collection efficiency of activated carbon has been reported at 90 percent or greater. Water curtains or filler pads have little or no effect on escaping solvent vapors, but they are widely used to stop paint particulate emissions.

#### References for Section 4.2.1

- Air Pollution Engineering Manual, Second Edition, AP-40, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1973. Out of Print.
- 2. Control Techniques for Hydrocarbon and Organic Gases from Stationary Sources, AP-68, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1969.
- 3. Control Techniques Guideline for Architectural Surface Coatings
  (Draft), Office of Air Quality Planning and Standards, U.S.
  Environmental Protection Agency, Research Triangle Park, NC,
  February 1979.
- 4. Air Pollutant Emission Factors, HEW Contract No. CPA-22-69-119, Resources Research Inc., Reston, VA, April 1970.
- 5. Procedures for the Preparation of Emission Inventories for Volatile Organic Compounds, Volume I, Second Edition, EPA-450/2-77-028, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1980.
- 6. W.H. Lamason, "Technical Discussion of Per Capita Emission Factors for Several Area Sources of Volatile Organic Compounds", Monitoring and Data Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 15, 1981. Unpublished.
- 7. End Use of Solvents Containing Volatile Organic Compounds, EPA-450/3-79-032, U.S. Environmental Protection Agency, Research Triangle Park, NC, May 1979.
- 8. Written communications between Bill Lamason and Chuck Mann, Monitoring and Data Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, NC, October 1980 and March 1981.

Typical ranges of control efficiencies are given in Table 4.2.2.1-3. Emission controls normally fall under one of three categories - modifications in paint formula, process changes, or addon controls. These are discussed further in the specific subsections which follow.

# 4.2.2.2 Coil and Can Coating 5-8

Process Description - Coil coating is the coating of any flat metal sheet or strip that comes in rolls or coils. Cans are made from two or three flat pieces of metal, so can coating is included within this broad category, as are the coating of screens, fencing, metal doors, aluminum siding and a variety of other products. Figure 4.2.2.2-1 shows a typical coil coating line, and Figure 4.2.2.2-2 depicts a three piece can sheet printing operation.

There are both "toll" and "captive" coil coating operations. The former fill orders to customer specifications, and the latter coat the metal for products fabricated within one facility. Some coil coating operations do both toll and captive work.

NOTE: With Supplement 13, Metal Coil Surface Coating has been updated and expanded into a separate Section.

Please see pages 4.2.2.10-1 through 6.

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Oven temperatures range from 40 to  $380^{\circ}\text{C}$  (100 to  $1000^{\circ}\text{F}$ ), depending on the type and desired thickness of the coating and on the type of metal being coated. A topcoat may be applied and cured in a similar manner.

In can coating, as with coil coating, there are both toll and captive manufacturers. Some plants coat metal sheets, some make three piece cans, some fabricate and coat two piece cans, and some fabricate can ends. Others perform combinations of these processes.

Cans may be made from a rectangular sheet (body blank) and two circular ends ("three piece" cans) or they can be drawn and wall ironed from a shallow cup to which an end is attached after the can is filled ("two piece" cans). There are major differences in coating practices, depending on the type of can and the product packaged in it.

Three piece can manufacturing involves sheet coating and can fabricating. Sheet coating includes base coating and printing or lithographing, followed by curing at temperatures of up to 220°C

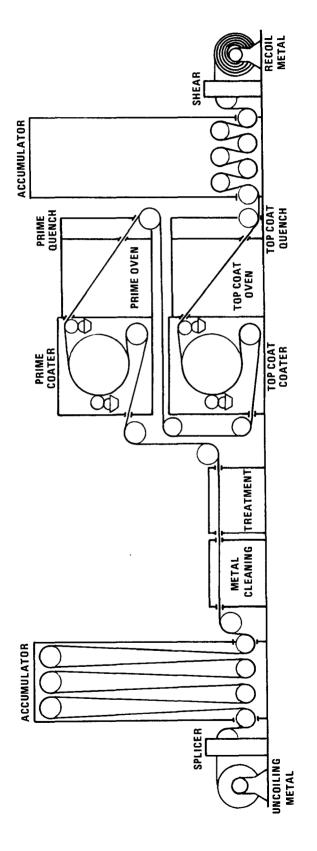


Figure 4.2.2.2 1. Coil coating line emissions. 7

### 4.2.2.8 AUTOMOBILE AND LIGHT DUTY TRUCK SURFACE COATING OPERATIONS

General - Surface coating of an automobile body is a multistep operation carried out on an assembly line conveyor system. Such a line operates at a speed of 3 to 8 meters (9 to 25 feet) per minute and usually produces 30 to 70 units per hour. An assembly plant may operate up to two 8 hour production shifts per day, with a third shift used for cleanup and maintanance. Plants may stop production for a vacation of one and a half weeks at Christmas through New Year's Day and may stop for several weeks in Summer for model changeover.

Although finishing processes vary from plant to plant, they have some common characteristics. Major steps of such processes are:

\*Solvent wipe
Phosphating treatment
Application of prime coat
Curing of prime coat
Application of guide coat

Curing of guide coat Application of topcoat(s) Curing of topcoat(s) Final repair operations

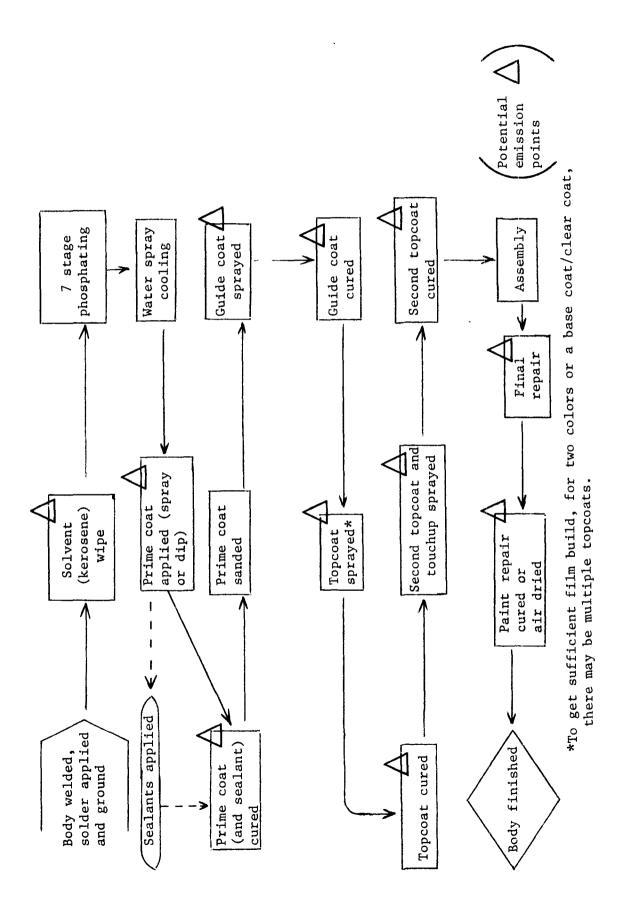
A general diagram of these consecutive steps is presented in Figure 4.2.2.8-1. Application of a coating takes place in a dip tank or spray booth, and curing occurs in the flashoff area and bake oven. The typical structures for application and curing are contiguous, to prevent exposure of the wet body to the ambient environment before the coating is cured.

The automobile body is assembled from a number of welded metal sections. The body and the parts to be coated all pass through the same metal preparation process.

First, surfaces are wiped with solvent to eliminate traces of oil and grease. Second, a phosphating process prepares surfaces for the primer application. Since iron and steel rust readily, phosphate treatment is necessary to retard such. Phosphating also improves the adhesion of the primer and the metal. The phosphating process occurs in a multistage washer, with detergent cleaning, rinsing, and coating of the metal surface with zinc phosphate. The parts and bodies pass through a water spray cooling process. If solventborne primer is to be applied, they are then oven dried.

A primer is applied to protect the metal surface from corrosion and to assure good adhesion of subsequent coatings. Approximately half of all assembly plants use solventborne primers with a combination of manual and automatic spray application. The rest use waterborne primers. As new plants are constructed and exiting plants modernized, the use of waterborne primers is expected to increase.

<sup>\*</sup>The term "solvent" here means organic solvent.



Typical automobile and light duty truck surface coating line. Figure 4.2.2.8-1.

Waterborne primer is most often applied in an electrodeposition (EDP) bath. The composition of the bath is about 5 to 15 volume percent solids, 2 to 10 percent solvent and the rest water. The solvents used are typically organic compounds of higher molecular weight and low volatility, like ethylene glycol monobutyl ether.

When EDP is used, a guide coat (also called a primer surfacer) is applied between the primer and the topcoat to build film thickness, to fill in surface imperfections and to permit sanding between the primer and topcoat. Guide coats are applied by a combination of manual and automatic spraying and can be solventborne or waterborne. Powder guide coat is used at one light duty truck plant.

The topcoat provides the variety of colors and surface appearance to meet customer demand. Topcoats are applied in one to three steps to assure sufficient coating thickness. An oven bake may follow each topcoat application, or the coating may be applied wet on wet. At a minimum, the final topcoat is baked in a high temperature oven.

Topcoats in the automobile industry traditionally have been solventborne lacquers and enamels. Recent trends have been to higher solids content. Powder topcoats have been tested at several plants.

The current trend in the industry is toward base coat/clear coat (BC/CC) topcoating systems, consisting of a relatively thin application of highly pigmented metallic base coat followed by a thicker clear coat. These BC/CC topcoats have more appealing appearance than do single coat metallic topcoats, and competitive pressures are expected to increase their use by U. S. manufacturers.

The VOC content of most BC/CC coatings in use today is higher than that of conventional enamel topcoats. Development and testing of lower VOC content (higher solids) BC/CC coatings are being done, however, by automobile manufacturers and coating suppliers.

Following the application of the topcoat, the body goes to the trim operation area, where vehicle assembly is completed. The final step of the surface coating operation is generally the final repair process, in which damaged coating is repaired in a spray booth and is air dried or baked in a low temperature oven to prevent damage of heat sensitive plastic parts added in the trim operation area.

Emissions and Controls - Volatile organic compounds (VOC) are the major pollutants from surface coating operations. Potential VOC emitting operations are shown in Figure 4.2.2.8-1. The application and curing of the prime coat, guide coat and topcoat account for 50 to 80 percent of the VOC emitted from assembly plants. Final topcoat repair, cleanup, and miscellaneous sources such as the coating of small component parts and application of sealants, account for the remaining 20 percent. Approximately 75 to 90 percent of the VOC emitted during the application and curing process is emitted from the spray booth and flashoff area, and 10 to 25 percent from the bake oven. This emissions split is heavily dependent on the types of

TABLE 4.2.2.8-1. EMISSION FACTORS FOR AUTOMOBILE AND LIGHT DUTY TRUCK SURFACE COATING OPERATIONS

#### EMISSION FACTOR RATING: C

| -                   | Automo     |          |             | uty Truck |
|---------------------|------------|----------|-------------|-----------|
| Coating             | • • •      | of VOC   | kg(1b)      | of VOC    |
|                     | er vehicle | per hour | per vehicle | per hour  |
| Prime Coat          |            |          |             |           |
| Solventborne        |            |          |             |           |
| spray               | 6.61       | 363      | 19.27       | 732       |
|                     | (14.54)    | (799)    | (42.39)     | (1611)    |
| Cathodic            |            |          |             |           |
| electrodeposition   | .21        | 12       | .27         | 10        |
| -                   | (.45)      | (25)     | (.58)       | (22)      |
| Guide Coat          |            |          |             |           |
| Solventborne spray  | 1.89       | 104      | 6.38        | 243       |
|                     | (4.16)     | 229      | (14.04)     | (534)     |
| Waterborne spray    | .68        | 38       | 2.3         | 87        |
| - •                 | (1.50)     | (83)     | (5.06)      | (192)     |
| Topcoat             |            |          |             |           |
| Lacquer             | 21.96      | 1208     |             |           |
| -                   | (48.31)    | (2657)   | NA          | NA        |
| Dispersion lacquer  | 14.50      | 798      |             |           |
| -                   | (31.90)    | (1755)   | NA          | NA        |
| Ename1              | 7.08       | 390      | 17.71       | 673       |
|                     | (15.58)    | (857)    | (38,96)     | (1480)    |
| Basecoat/clear coat | 6.05       | 333      | 18.91       | 719       |
|                     | (13.32)    | (732)    | (41.59)     | (1581)    |
| Waterborne          | 2.25       | 124      | 7.03        | 267       |
|                     | (4.95)     | (273)    | (15.47)     | (588)     |

All nonmethane VOC. Factors are calculated using the following equation and the typical values of parameters presented in Tables 4.2.2.8-2 and 4.2.2.8-3. NA = Not applicable.

$$E_{v} = \frac{A_{v} c_{1} T_{f} V_{c} c_{2}}{S_{c} e_{T}}$$

Where:  $E_v$  = emission factor for VOC, mass per vehicle (lb/vehicle) (exclusive of any addon control devices)

 $A_{y}$  = area coated per vehicle (ft<sup>2</sup>/vehicle)

 $c_1$  = conversion factor: 1 ft/12,000 mil

 $T_f =$ thickness of the dry coating film (mil)

 $V_c = VOC$  (organic solvent) content of coating as applied, less water (1b VOC/gal coating, less water)

 $c_2$  = conversion factor: 7.48 gallons/ft<sup>3</sup>

S<sub>c</sub> = solids in coating as applied, volume fraction (gal solids/gal coating)

 $\mathbf{e}_{\mathrm{T}}^{}$  = transfer efficiency fraction (fraction of total coating solids used which remains on coated parts)

Example: The VOC emissions per automobile from a cathodic electrodeposited prime coat.

$$E_v$$
 mass of VOC = 
$$\frac{(850 \text{ ft}^2)(1/12000)(0.6 \text{ mil})(1.2 \text{ lb/gal-H20})}{(-84 \text{ gal/gal})(1.00)}$$

= .45 1b VOC/vehicle (.21 kg VOC/vehicle)

Base on an average line speed of 55 automobiles/hr.

CBased on an average line speed of 38 light duty trucks/hr.

solvents used and on transfer efficiency. With improved transfer efficiencies and the newer coatings, it is expected that the percent of VOC emitted from the spray booth and the flashoff area will decrease, and the percent of VOC emitted from the bake oven will remain fairly constant. Higher solids coatings, with their slower solvents, will tend to have a greater fraction of emissions from the bake oven.

Several factors affect the mass of VOC emitted per vehicle from surface coating operations in the automotive industry. Among these are:

VOC content of coatings (pounds of coating, less water)
Volume solids content of coating
Area coated per vehicle
Film thickness
Transfer efficiency

The greater the quantity of VOC in the coating composition, the greater will be the emissions. Lacquers having 12 to 18 volume percent solids are higher in VOC than enamels having 24 to 33 volume percent solids. Emissions are also influenced by the area of the parts being coated, the coating thickness, the configuration of the part and the application technique.

The transfer efficiency (fraction of the solids in the total consumed coating which remains on the part) varies with the type of application technique. Transfer efficiency for typical air atomized spraying ranges from 30 to 50 percent. The range for electrostatic spraying, an application method that uses an electrical potential to increase transfer efficiency of the coating solids, is from 60 to 95 percent. Both air atomized and electrostatic spray equipment may be used in the same spray booth.

Several types of control techniques are available to reduce VOC emissions from automobile and light duty truck surface coating operations. These methods can be broadly categorized as either control devices or new coating and application systems. Control devices reduce emissions by either recovering or destroying VOC before it is discharged into the ambient air. Such techniques include thermal and catalytic incinerators on bake ovens, and carbon adsorbers on spray booths. New coatings with relatively low VOC levels can be used in place of high VOC content coatings. Such coating systems include electrodeposition of waterborne prime coatings, and for top coats, air spray of waterborne enamels and air or electrostatic spray of high solids, solventborne enamels and powder coatings. Improvements in the transfer efficiency decrease the amount of coating which must be used to achieve a given film thickness, thereby reducing emissions of VOC to the ambient air.

Calculation of VOC emissions for representative conditions provides the emission factors in Table 4.2.2.8-1. The factors were calculated with the typical value of parameters presented in Tables 4.2.2.8-2 and 4.2.2.8-3. The values for the various parameters for automobiles and light duty trucks represent average conditions existing in the automobile and light duty truck industry in 1980. A more accurate estimate of VOC emissions can be calculated with the equation in Table 4.2.2.8-1 and with site-specific values for the various parameters.

TABLE 4.2.2.8-2. PARAMETERS FOR THE AUTOMOBILE SURFACE COATING INDUSTRY

| Application                   | per vehicle, | riim<br>Thickness,<br>mil | 1b/gal-H <sub>2</sub> 0 | volume fraction solids,<br>gal/gal-H <sub>2</sub> 0 | Iransier<br>Efficiency,<br>% |
|-------------------------------|--------------|---------------------------|-------------------------|---|------------------------------|
| Prime Coat                    |              |                           |                         |   |                              |
| Solventborne spray            | 450          | 0.8                       | 5.7                     | 0.22  | 40                           |
|                               | (220-570)    | (0.3-2.5)                 | (4.2-6.0)               | (,20-,35)   | (32-20)                      |
| Cathodic electrodeposition    | 850          | 9.0                       | 1.2                     | 0.84  | 100                          |
|                               | (660–1060)   | (0.5-0.8)                 | (1.2-1.5)               | (.8487)   | (85-100)                     |
| Guide Coat                    |              |                           |                         |   |                              |
| Solventborne spray            | 200          | 0.8                       | 5.0                     | 0.30  | 40                           |
|                               | (170-280)    | (0.5-1.5)                 | (3.0-5.6)               | (.2555)   | (32-65)                      |
| Waterborne spray              | 200          | 0.8                       | 2.8                     | 0.62  | 30                           |
|                               | (170-280)    | (0.5-2.0)                 | (2.6-3.0)               | (.6065)   | (25–40)                      |
| Topcoat<br>Solventborne sprav |              |                           |                         |   |                              |
| Lacquer                       | 240          | 2.5                       | 6.2                     | 0.12  | 07                           |
| •                             | (170-280)    | (1.0-3.0)                 | (5.8-6.6)               | (.1013)   | (30-65)                      |
| Dispersion lacquer            | 240          | 2.5                       | 5.8                     | 0.17  | 40                           |
|                               | (170-280)    | (1.0-3.0)                 | (4.9~5.8)               | (.1727)   | (30-65)                      |
| Enamel                        | 240          | 2.5                       | 5.0                     | 0.30  | 04                           |
|                               | (170-280)    | (1.0-3.0)                 | (3.0-5.6)               | (.2555)   | (30-65)                      |
| Base $coat/clear$ $coat$      | 240          | 2.5                       | 4.7                     | 0,33  | 40                           |
| Base coat                     | 240          | 1.0                       | 5.6                     | 0,20  | 07                           |
|                               | (170-280)    | (0.8-1.0)                 | (3.4-6.4)               | (.1348)   | (30-20)                      |
| Clear coat                    | 240          | 1.5                       | 4.0                     | 0.42  | 40                           |
|                               | (170-280)    | (1.2-1.5)                 | (3.0-5.1)               | (,30-,54)   | (30-65)                      |
| Waterborne spray              | 240          | 2.2                       | 2.8                     | 0.62  | 30                           |
|                               | (170-280)    | (1.0-2.5)                 | (2.6-3.0)               | (.6065)   | (25-40)                      |

<sup>a</sup>All values for coatings as applied, except for VOC content and volume fraction solids which are for coatings as applied minus water. Ranges in parentheses. Low VOC content (high solids) base coat/clear coats are still undergoing testing and development. Composite of base coat and clear coat.

PARAMETERS FOR THE LIGHT DUTY TRUCK SURFACE COATING INDUSTRY  $^{\mathbf{a}}$ TABLE 4.2.2.8-3.

| Application                | Area Coated<br>per vehicle. | Film<br>Thickness. | VOC Content, | Volume Fraction Solids, | Transfer |
|----------------------------|-----------------------------|--------------------|--------------|-------------------------|----------|
|                            | ft <sup>2</sup>             | m11                | > 7: 8 /     | >7: 1:0 /::0            | %        |
| Prime Coat                 |                             |                    |              |                         |          |
| Solventborne spray         | 875                         | 1.2                | 5.7          | 0.22                    | 40       |
|                            | (300-1000)                  | (0.7-1.7)          | (4.2-6.0)    | (0.2035)                | (32-20)  |
| Cathodic electrodeposition | 1100                        | 9.0                | 1.2          | 0.84                    | 100      |
|                            | (850-1250)                  | (0.5-0.8)          | (1.2-1.5)    | (.8487)                 | (85-100) |
| Guide Coat                 |                             |                    |              |                         |          |
| Solventborne spray         | 675                         | 0.8                | 5.0          | 0.30                    | 07       |
| •                          | (180-740)                   | (0.7-1.7)          | (3.0-5.6)    | (,25-,55)               | (35-65)  |
| Waterborne spray           | 675                         | 0.8                | 2.8          | 0.62                    | 30       |
|                            | (180-740)                   | (0.5-2.0)          | (2.6-3.0)    | (.6065)                 | (25–40)  |
| Topcoat                    |                             |                    |              |                         |          |
| Solventborne spray         |                             |                    |              |                         |          |
| Ename1                     | 750                         | 2.0                | 2.0          | 0.30                    | 40       |
| ,                          | (300000)                    | (1.0-2.5)          | (3.0-5.6)    | (.2555)                 | (30-65)  |
| Base coat/clear coat       | 750                         | 2.5                | 4.7          | 0.33                    | 40       |
| Base coat                  | 750                         | 1.0                | 5.6          | 0.20                    | 04       |
|                            | (300000)                    | (0.8-1.0)          | (3.4-6.4)    | (,13-,48)               | (30-20)  |
| Clear coat                 | 750                         | 1.5                | 4.0          | 0.42                    | 07       |
|                            | (300-900)                   | (1.2-1.5)          | (3.0-5.1)    | (,30-,54)               | (30–65)  |
| Waterborne spray           | 750                         | 2.2                | 2.8          | 0.62                    | 30       |
|                            | (300-900)                   | (1.0-2.5)          | (2.6-3.0)    | (.6065)                 | (25-40)  |

<sup>a</sup>All values are for coatings as applied, except for VOC content and volume fraction solids which are for coatings as applied minus water, banges in parenthesis. Low VOC content (high solids) base coat/clear coats are still undergoing testing and development. Composite of typical base coat and clear coat.

Emission factors are not available for final topcoat repair, cleanup, coating of small parts and application of sealants.

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### 4.2.2.9 PRESSURE SENSITIVE TAPES AND LABELS

General 1-5 - The coating of pressure sensitive tapes and labels (PSTL) is an operation in which some backing material (paper, cloth or film) is coated to create a tape or label product that sticks on contact. The term "pressure sensitive" indicates that the adhesive bond is formed on contact, without wetting, heating or adding a curing agent.

The products manufactured by the PSTL surface coating industry may have several different types of coatings applied to them. The two primary types of coatings are adhesives and releases. Adhesive coating is a necessary step in the manufacture of almost all PSTL products. It is generally the heaviest coating (typically  $0.051 \text{ kg/m}^2$ , or  $0.011 \text{ lb/ft}^2$ ) and therefore has the highest level of solvent emissions (generally 85 to 95 percent of total line emissions).

Release coatings are applied to the backside of tape or to the mounting paper of labels. The function of release coating is to allow smooth and easy unrolling of a tape or removal of a label from mounting paper. Release coatings are applied in a very thin coat (typically 0.00081 kg/m $^2$ , or 0.00017 lb/ft $^2$ ). This thin coating produces less emissions than does a comparable size adhesive coating line.

Five basic coating processes can be used to apply both adhesive and release coatings:

solvent base coating waterborne (emulsion) coating 100 percent solids (hot melt) coating calender coating prepolymer coating

A solvent base coating process is used to produce 80 to 85 percent of all products in the PSTL industry, and essentially all of the solvent emissions from the industry result from solvent base coating. Because of its broad application and significant emissions, solvent base coating of PSTL products is discussed in greater detail.

Process Description  $^{1-2,5}$  - Solvent base surface coating is conceptually a simple process. A continuous roll of backing material (called the web) is unrolled, coated, dried and rolled again. A typical solvent base coating line is shown in Figure 4.2.2.9-1. Large lines in this industry have typical web widths of 152 centimeters (60 in), while small lines are generally 48 centimeters (24 in). Line speeds vary substantially, from three to 305 meters per

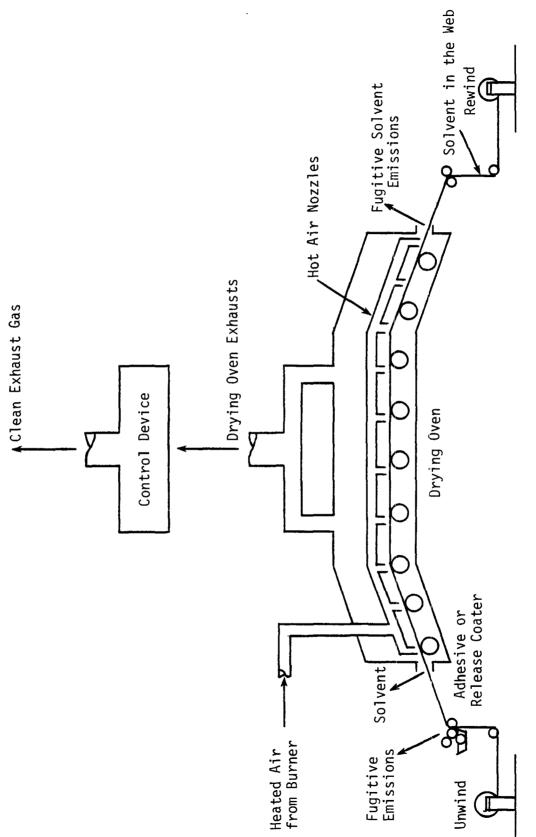


Figure 4.2.2.9-1. Diagram of a Pressure Sensitive Tape and Label Coating Line

minute (10 - 1000 ft/min). To initiate the coating process the continuous web material is unwound from its roll. It travels to a coating head, where the solvent base coating formulation is applied. These formulations have specified levels of solvent and coating solids by weight. Solvent base adhesive formulations contain approximately 67 weight percent solvent and 33 weight percent coating solids. Solvent base releases average about 95 weight percent solvent and 5 weight percent coating solids. Solvents used include toluene, xylene, heptane, hexane and methyl ethyl ketone. The coating solids portion of the formulations consists of elastomers (natural rubber, styrene-butadiene rubber, polyacrylates), tackifying resins (polyterpenes, rosins, petroleum hydrocarbon resins, asphalts), plasticizers (phthalate esters, polybutenes, mineral oil), and fillers (zinc oxide, silica, clay).

The order of application is generally release coat, primer coat (if any) and adhesive coat. A web must always have a release coat before the adhesive can be applied. Primer coats are not required on all products, generally being applied to improve the performance of the adhesive.

Three basic categories of coating heads are used in the PSTL industry. The type of coating head used has a great effect on the quality of the coated product, but only a minor effect on overall emissions. The first type operates by applying coating to the web and scraping excess off to a desired thickness. Examples of this type of coater are the knife coater, blade coater and metering rod coater. The second category of coating head meters on a specific amount of coating. Gravure and reverse roll coaters are the most common examples. The third category of coating head does not actually apply a surface coating, but rather it saturates the web backing. The most common example in this category is the dip and squeeze coater.

After solvent base coatings have been applied, the web moves into the drying oven where the solvents are evaporated from the web. The important characteristics of the drying oven operation are:

source of heat temperature profile residence time allowable hydrocarbon concentration in the dryer oven air circulation

Two basic types of heating are used in conventional drying ovens, direct and indirect. Direct heating routes the hot combustion gases (blended with ambient air to the proper temperature) directly

into the drying zone. With indirect heating, the incoming oven air stream is heated in a heat exchanger with steam or hot combustion gases but does not physically mix with them. Direct fired ovens are more common in the PSTL industry because of their higher thermal efficiency. Indirect heated ovens are less energy efficient in both the production of steam and the heat transfer in the exchanger.

Drying oven temperature control is an important consideration in PSTL production. The oven temperature must be above the boiling point of the applied solvent. However, the temperature profile must be controlled by using multizoned ovens. Coating flaws known as "craters" or "fish eyes" will develop if the initial drying proceeds too quickly. These ovens are physically divided into several sections, each with its own hot air supply and exhaust. By keeping the temperature of the first zone low, and then gradually increasing it in subsequent zones, uniform drying can be accomplished without flaws. After exiting the drying oven, the continuous web is wound on a roll, and the coating process is complete.

Emissions<sup>1,6-10</sup> - The only pollutants emitted in significant quantities from solvent base coating of pressure sensitive tapes and labels are volatile organic compounds (VOC) from solvent evaporation. In an uncontrolled facility, essentially all of the solvent used in the coating formulation is emitted to the atmosphere. Of these uncontrolled emissions, 80 to 95 percent are emitted with the drying oven exhaust. Some solvent (from zero to five percent) can remain in the final coated product, although this solvent will eventually evaporate into the atmosphere. The remainder of applied solvent is lost from a number of small sources as fugitive emissions. The major VOC emission points in a PSTL surface coating operation are indicated in Figure 4.2.2.9-1.

There are also VOC losses from solvent storage and handling, equipment cleaning, miscellaneous spills, and coating formulation mixing tanks. These emissions are not addressed here, as these sources have a comparatively small quantity of emissions.

Fugitive solvent emissions during the coating process come from the evaporative loss of solvent around the coating head and from the exposed wet web prior to its entering the drying oven. The magnitude of these losses is determined by the width of the web, the line speed, the volatility and temperature of the solvent, and the air turbulence in the coating area.

Two factors which directly determine total line emissions are the weight (thickness) of the applied coating on the web and the solvent/solids ratio of the coating formulations. For coating

4.2.2.9-4 EMISSION FACTORS 8/82

formulations with a constant solvent/solids ratio during coating, any increases in coating weight would produce higher levels of VOC emissions. The solvent/solids ratio in coating formulations is not constant industrywide. This ratio varies widely among products. If a coating weight is constant, greater emissions will be produced by increasing the weight percent solvent of a particular formulation.

These two operating parameters, combined with line speed, line width and solvent volatility, produce a number of potentional mass emission situations. Table 4.2.2.9-1 presents emission factors for controlled and uncontrolled PSTL surface coating operations. The potential amount of VOC emissions from the coating process is equal to the total amount of solvent applied at the coating head.

Controls<sup>1,6-18</sup> - The complete air pollution control system for a modern pressure sensitive tape or label surface coating facility consists of two sections, the solvent vapor capture system and the emission control device. The capture system collects VOC vapors from the coating head, the wet web and the drying oven. The captured vapors are directed to a control device to be either recovered (as liquid solvent) or destroyed. As an alternate emission control technique, the PSTL industry is also using low-VOC content coatings to reduce their VOC emissions. Waterborne and hot melt coatings and radiation cured prepolymers are examples of these low-VOC content coatings. Emissions of VOC from such coatings are negligible or zero. Low-VOC content coatings are not universally applicable to the PSTL industry, but about 25 percent of the production in this industry is presently using these innovative coatings.

Capture Systems - In a typical PSTL surface coating facility, 80 to 95 percent of VOC emissions from the coating process is captured in the coating line drying ovens. Fans are used to direct drying oven emissions to a control device. In some facilities a portion of the drying oven exhaust is recirculated into the oven instead of to a control device. Recirculation is used to increase the VOC concentration of the drying oven exhaust gases going to the control device.

Another important aspect of capture in a PSTL facility involves fugitive VOC emissions. Three techniques can be used to collect fugitive VOC emissions from PSTL coating lines. The first involves the use of floor sweeps and/or hooding systems around the coating head and exposed coated web. Fugitive emissions collected in the hoods can be directed into the drying oven and on to a control device, or they can be sent directly to the control device. The second capture technique involves enclosing the entire coating line or the coating application and flashoff areas. By maintaining

TABLE 4.2.2.9-1. EMISSION FACTORS FOR PRESSURE SENSITIVE TAPE AND LABEL SURFACE COATING OPERATIONS

EMISSION FACTOR RATING: C

|                                  | N                | Nonmethane VOC <sup>a</sup> |                  |
|----------------------------------|------------------|-----------------------------|------------------|
|                                  | Uncontrolled     | 85% Control                 | 90% Control      |
| Emission Points                  | kg/kg<br>(1b/1b) | kg/kg<br>(1b/1b)            | kg/kg<br>(1b/1b) |
| Drying Oven Exhaust <sup>b</sup> | 0.80-0.95        | *****                       |                  |
| Fugitives <sup>c</sup>           | 0.01-0.15        | 0.01-0.095                  | 0.0025-0.0425    |
| Product Retention <sup>d</sup>   | 0.01-0.05        | 0.01-0.05                   | 0.01-0.05        |
| Control Device <sup>e</sup>      |                  | 0.045                       | 0.0475           |
| Total Emissions f                | 1.0              | 0.15                        | 0.10             |

<sup>&</sup>lt;sup>a</sup>Expressed as the mass of volatile organic compounds (VOC) emitted per mass of total solvent used. Solvent is assumed to consist entirely of VOC.

References 1, 6-7, 9. Dryer exhaust emissions depend on coating line operating speed, frequency of line downtime, coating composition and oven design.

Determined by difference between total emissions and other point sources. Magnitude is determined by size of the line equipment, line speed, volatility and temperature of the solvents, and air turbulence in the coating area.

dReferences 6-3. Solvent in the product eventually evaporates into the atmosphere.

References 1, 10, 17-18. Emissions are residual content in captured solvent laden air vented after treatment. Controlled coating line emissions are based on an overall reduction efficiency which is equal to capture efficiency times control device efficiency. For 85% control, capture efficiency is 90% with a 95% efficient control device. For 90% control, capture efficiency is 95% with a 95% efficient control device.

Values assume that uncontrolled coating lines eventually emit 100% of all solvents used.

a slight negative pressure within the enclosure, a capture efficiency of 100 percent is theoretically possible. The captured emissions are directed by fans into the oven or to a control device. The third capture technique is an expanded form of total enclosure. The entire building or structure which houses the coating line acts as an enclosure. The entire room air is vented to a control device. The maintenance of a slight negative pressure ensures that very few emissions escape the room.

The efficiency of any vapor capture system is highly dependent on its design and its degree of integration with the coating line equipment configuration. The design of any system must allow safe and adequate access to the coating line equipment for maintenance. The system must also be designed to protect workers from exposure to unhealthy concentrations of the organic solvents used in the surface coating processes. The efficiency of a well designed combined dryer exhaust and fugitive capture system is 95 percent.

Control Devices - The control devices and/or techniques that may be used to control captured VOC emissions can be classified into two categories, solvent recovery and solvent destruction. Fixed bed carbon adsorption is the primary solvent recovery technique used in this industry. In fixed bed adsorption, the solvent vapors are adsorbed onto the surface of activated carbon, and the solvent is regenerated by steam. Solvent recovered in this manner may be reused in the coating process or sold to a reclaimer. The efficiency of carbon adsorption systems can reach 98 percent, but a 95 percent efficiency is more characteristic of continuous long term operation.

The primary solvent destruction technique used in the PSTL industry is thermal incineration, which can be as high as 99 percent efficient. However, operating experience with incineration devices has shown that 95 percent efficiency is more characteristic. Catalytic incineration could be used to control VOC emissions with the same success as thermal incineration, but no catalytic devices have been found in the industry.

The efficiencies of carbon adsorption and thermal incineration control techniques on PSTL coating VOC emissions have been determined to be equal. Control device emission factors presented in Table 4.2.2.9-1 represent the residual VOC content in the exhaust air after treatment.

The overall emission reduction efficiency for VOC emission control systems is equal to the capture efficiency times the control device efficiency. Emission factors for two control levels are presented in Table 4.2.2.9-1. The 85 percent control

level represents 90 percent capture with a 95 percent efficient control device. The 90 percent control level represents 95 percent capture with a 95 percent efficient control device.

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### 4.2.2.10 METAL COIL SURFACE COATING

General 1-2 - Metal coil surface coating (coil coating) is the linear process by which protective or decorative organic coatings are applied to flat metal sheet or strip packaged in rolls or coils. Although the physical configurations of coil coating lines differ from one installation to another, the operations generally follow a set pattern. Metal strip is uncoiled at the entry to a coating line and is passed through a wet section, where the metal is thoroughly cleaned and is given a chemical treatment to inhibit rust and to promote coatings adhesion to the metal surface. In some installations, the wet section contains an electrogalvanizing operation. Then the metal strip is dried and sent through a coating application station, where rollers coat one or both sides of the metal strip. The strip then passes through an oven where the coatings are dried and cured. As the strip exits the oven, it is cooled by a water spray and again dried. If the line is a tandem line, there is first the application of a prime coat, followed by another of top or finish coat. The second coat is also dried and cured in an oven, and the strip is again cooled and dried before being rewound into a coil and packaged for shipment or further processing. Most coil coating lines have accumulators at the entry and exit that permit continuous metal strip movement through the coating process while a new coil is mounted at the entry or a full coil removed at the exit. Figure 4.2.2.10-1 is a flow diagram of a coil coating line.

Coil coating lines process metal in widths ranging from a few centimeters to 183 centimeters (72 inches), and in thicknesses of from 0.018 to 0.229 centimeters (0.007 to 0.090 inches). The speed of the metal strip through the line is as high as 3.6 meters per second (700 feet per minute) on some of the newer lines.

A wide variety of coating formulations is used by the coil coating industry. The more prevalent coating types include polyesters, acrylics, polyfluorocarbons, alkyds, vinyls and plastisols. About 85 percent of the coatings used are organic solvent base and have solvent contents ranging from near 0 to 80 volume percent, with the prevalent range being 40 to 60 volume percent. Most of the remaining 15 percent of coatings are waterborne, but they contain organic solvent in the range of 2 to 15 volume percent. High solids coatings, in the form of plastisols, organosols and powders, are also used to some extent by the industry, but the hardware is different for powder applications.

The solvents most often used in the coil coating industry include xylene, toluene, methyl ethyl ketone, Cellosolve Acetate (TM), butanol, diacetone alcohol, Cellosolve (TM), Butyl Cellosolve (TM), Solvesso 100 and 150 (TM), isophorone, butyl carbinol, mineral spirits, ethanol, nitropropane, tetrahydrofuran, Panasolve (TM), methyl isobutyl ketone, Hisol 100 (TM), Tenneco T-125 (TM), isopropanol, and diisoamyl ketone.

Coil coating operations can be classified in one of two operating categories, toll coaters and captive coaters. The toll coater is a service coater who works for many customers according to the needs and specifications

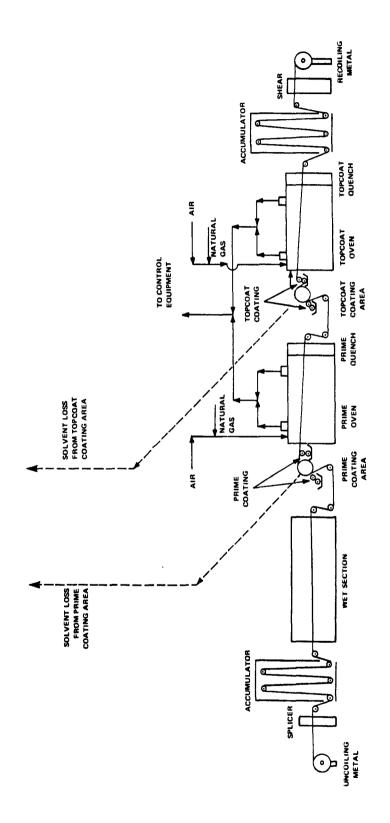


Figure 4.2.2.10-1. Flow Diagram of model coil coating line.

of each. The coated metal is delivered to the customer, who forms the end products. Toll coaters use many different coating formulations and normally use mostly organic solvent base coatings. Major markets for toll coating operations include the transportation industry, the construction industry and appliance, furniture and container manufacturers. The captive coater is normally one operation in a manufacturing process. Many steel and aluminum companies have their own coil coating operations, where the metal they produce is coated and then formed into end products. Captive coaters are much more likely to use water base coatings because the metal coated is often used for only a few end products. Building products such as aluminum siding are one of the more important uses of waterborne metal coatings.

Emission and Controls $^{1-12}$  - Volatile organic compounds (VOC) are the major pollutants emitted from metal coil surface coating operations. Specific operations that emit VOC are the coating application station, the curing oven and the quench area. These are identified in Figure 4.2.2.10-1. VOC emissions result from the evaporation of organic solvents contained in the coating. The percentage of total VOC emissions given off at each emission point varies from one installation to another, but, on the average, about 8 percent is given off at the coating application station, 90 percent the oven and 2 percent the quench area. On most coating lines, the coating application station is enclosed or hooded to capture fugitive emissions and to direct them into the oven. The quench is an enclosed operation located immediately adjacent to the exit end of the oven so that a large fraction of the emissions given off at the quench is captured and directed into the oven by the oven ventilating air. In operations such as these, approximately 95 percent of the total emissions is exhausted by the oven, and the remaining 5 percent escapes as fugitive emissions.

The rate of VOC emissions from individual coil coating lines may vary widely from one installation to another. Factors that affect the emission rate include VOC content of coatings as applied, VOC density, area of metal coated, solids content of coatings as applied, thickness of the applied coating and number of coats applied. Because the coatings are applied by roller coating, transfer efficiency is generally considered to approach 100 percent and therefore does not affect the emission rate.

Two emission control techniques are widespread in the coil coating industry, incineration and use of low VOC content coatings. Incinerators may be either thermal or catalytic, both of which have been demonstrated to achieve consistently a VOC destruction efficiency of 95 percent or greater. When used with coating rooms or hoods to capture fugitive emissions, incineration systems can reduce overall emissions by 90 percent or more.

Waterborne coatings are the only low VOC content coating technology that is used to a significant extent in the coil coating industry. These coatings have substantially lower VOC emissions than most of the organic solventborne coatings. Waterborne coatings are used as an emission control technique most often by installations that coat metal for only a few products, such as building materials. Many such coaters are captive to the firm that produces and sells the products fabricated from the coated coil. Because waterborne

TABLE 4.2.2.10-1. VOC EMISSION FACTORS FOR COIL COATING<sup>a</sup>

### EMISSION FACTOR RATING: C

| Coatings               | kg           | /hr (1b/hr)                 | kg,                | $/m^2$ (1b/ft <sup>2</sup> )         |
|------------------------|--------------|-----------------------------|--------------------|--------------------------------------|
|                        | Average      | Normal range                | Average            | Normal range                         |
| Solventborne           |              |                             |                    |                                      |
| uncontrolled           | 303<br>(669) | 50 - 1,798<br>(110 - 3,964) | 0.060<br>(0.012)   | 0.027 - 0.160<br>(0.006 - 0.033)     |
| $controlled^{\dot{b}}$ | 30<br>( 67)  | 5 - 180<br>(11 - 396)       | 0.0060<br>(0.0012) | 0.0027 - 0.0160<br>(0.0006 - 0.0033) |
| Waterborne             | 50<br>(111)  | 3 - 337<br>(7 - 743)        | 0.0108<br>(0.0021) | 0.0011 - 0.0301<br>(0.0003 - 0.0062) |

<sup>a</sup>All nonmethane VOC. Factors are calculated using the following equations and the operating parameters given in Table 4.2.2.10-2.

(1) 
$$E = \frac{0.623 \text{ ATVD}}{S}$$

where

E = mass of VOC emissions per hour (1b/hr)

A = Area of metal coated per hour (ft<sup>2</sup>)

= Line speed (ft/min) x strip width (ft) x 60 min/hr

V = VOC content of coatings (fraction by volume)

D = VOC Density (assumed to be 7.36 lb/gal)

S = Solids content of coatings (fraction by volume)

T = Total dry film thickness of coatings applied (in).

The constant 0.623 represents conversion factors of 7.48  $\mathrm{gal/ft}^3$  divided by the conversion factor of 12 in/ft.

$$(2) \qquad M = \frac{E}{A}$$

where

M = mass of VOC emissions per unit area coated.

bComputed by assuming a 90 percent overall control efficiency (95 percent capture and 95 percent removal by the control device).

TABLE 4.2.2.10-2. OPERATING PARAMETERS FOR SMALL, MEDIUM AND LARGE COIL COATING LINES<sup>a</sup>

|              |                           |                        | Solventborne  | coatings                                  |  |   |
|--------------|---------------------------|------------------------|---|---|--|---|
| Line<br>size | Line<br>speed<br>(ft/min) | Strip<br>width<br>(ft) | Total<br>dry film<br>thickness <sup>b</sup><br>(in) | VOC<br>content <sup>C</sup><br>(fraction) | Solids<br>content <sup>c</sup><br>(fraction) | VOC<br>density <sup>b</sup><br>(1b/gal) |
| Small        | 200                       | 1.67                   | 0.0018  | 0.40                                      | 0.60   | 7.36                                    |
| Medium       | 300                       | 3                      | 0.0018  | 0.60                                      | 0.40   | 7.36                                    |
| Large        | 500                       | 4                      | 0.0018  | 0.80                                      | 0.20   | 7.36                                    |
|              |                           |                        | Waterborne o  | coatings                                  |  |   |
| Small        | 200                       | 1.67                   | 0.0018  | 0.02                                      | 0.50   | 7.36                                    |
| Medium       | 300                       | 3                      | 0.0018  | 0.10                                      | 0.40   | 7.36                                    |
| Large        | 500                       | 4                      | 0.0018  | 0.15                                      | 0.20   | 7.36                                    |
|              |                           |                        |   |   |  |   |

aObtained from Reference 3.

coatings have not been developed for many coated metal coil uses, most toll coaters use organic solventborne coatings and control their emissions by incineration. Most newer incincerator installations use heat recovery to reduce the operating cost of an incineration system.

Emission factors for coil coating operations and the equations used to compute them are presented in Table 4.2.2.10-1. The values presented therein represent maximum, minimum and average emissions from small, medium and large coil coating lines. An average film thickness and an average solvent content are assumed to compute the average emission factor. Values for the VOC content near the maximum and minimum used by the industry are assumed for the calculations of maximum and minimum emission factors.

The emission factors in Table 4.2.2.10-1 are useful in estimating VOC emissions for a large sample of coil coating sources, but they may not be

bAverage value assumed for emission factor calculations. Actual values should be used to estimate emissions from individual sources.

<sup>&</sup>lt;sup>c</sup>All three values of VOC content and solids content were used in the calculation of emission factors for each plant size to give maximum, minimum and average emission factors.

applicable to individual plants. To estimate the emissions from a specific plant, operating parameters of the coil coating line should be obtained and used in the equation given in the footnote to the Table. If different coatings are used for prime and topcoats, separate calculations must be made for each coat. Operating parameters on which the emission factors are based are presented in Table 4.2.2.10-2.

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### 4.9.2 PUBLICATION GRAVURE PRINTING

Process Description 1-2 - Publication gravure printing is the printing by the rotogravure process of a variety of paper products such as magazines, catalogs, newspaper supplements and preprinted inserts, and advertisements. Publication printing is the largest sector involved in gravure printing, representing over 37 percent of the total gravure product sales value in a 1976 study.

The rotogravure press is designed to operate as a continuous printing facility, and normal operation may be either continuous or nearly so. Normal press operation experiences numerous shutdowns caused by web breaks or mechanical problems. Each rotogravure press generally consists of eight to sixteen individual printing units, with an eight unit press the most common. In publication printing, only four colors of ink are used, yellow, red, blue and black. Each unit prints one ink color on one side of the web, and colors other than these four are produced by printing one color over another to yield the desired product.

In the rotogravure printing process, a web or substrate from a continuous roll is passed over the image surface of a revolving gravure cylinder. For publication printing, only paper webs are used. The printing images are formed by many tiny recesses or cells etched or engraved into the surface of the gravure cylinder. The cylinder is about one fourth submerged in a fountain of low viscosity mixed ink. Raw ink is solvent diluted at the press and is sometimes mixed with related coatings, usually referred to as extenders or varnishes. The ink, as applied, is a mixture of pigments, binders, varnish and solvent. The mixed ink is picked up by the cells on the revolving cylinder surface and is continuously applied to the paper web. After impression is made, the web travels through an enclosed heated air dryer to evaporate the volatile solvent. The web is then guided along a series of rollers to the next printing unit. Figure 4.9.2-1 illustrates this printing process by an end (or side) view of a single printing unit.

At present, only solventborne inks are used on a large scale for publication printing. Waterborne inks are still in research and development stages, but some are now being used in a few limited cases. Pigments, binders and varnishes are the nonvolatile solid components of the mixed ink. For publication printing, only aliphatic and aromatic organic liquids are used as solvents. Presently, two basic types of solvents, toluene and a toluene-xylene-naphtha mixture, are used. The naphtha base solvent is the more common. Benzene is present in both solvent types as an impurity, in concentrations up to about 0.3 volume percent. Raw inks, as purchased, have 40 to 60 volume percent solvent, and the related coatings typically contain about 60 to 80 volume percent solvent. The applied mixed ink consists of 75 to 80 volume percent solvent, required to achieve the proper fluidity for rotogravure printing.

Emissions and Controls 1,3-4 - Volatile organic compound (VOC) vapors are the only significant air pollutant emissions from publication rotogravure printing. Emissions from the printing presses depend on the total amount of solvent used. The sources of these VOC emissions are the solvent components in the raw inks, related coatings used at the printing presses, and solvent added for dilution and press cleaning. These solvent organics are photochemically reactive. VOC emissions from both controlled and uncontrolled publication rotogravure facilities in 1977 were about 57,000 megagrams (63,000 tons), 15 percent of the total from the graphic arts industry. Emissions from ink and solvent storage and transfer facilities are not considered here.

Table 4.9-1 presents emission factors for publication printing on rotogravure presses with and without control equipment. The potential amount of VOC emissions from the press is equal to the total amount of solvent consumed in the printing process (see Footnote f). For uncontrolled presses, emissions occur from the dryer exhaust vents, printing fugitive vapors, and evaporation of solvent retained in the printed product. About 75 to 90 percent of the VOC emissions occur from the dryer exhausts, depending on press operating speed, press shutdown frequency, ink and solvent composition, product printed, and dryer designs and efficiencies. The amount of solvent retained by the various rotogravure printed products is three to four percent of the total solvent in the ink used. The retained solvent eventually evaporates after the printed product leaves the press.

There are numerous points around the printing press from which fugitive emissions occur. Most of the fugitive vapors result from solvent evaporation in the ink fountain, exposed parts of the gravure cylinder, the paper path at the dryer inlet, and from the paper web after exiting the dryers between printing units. The quantity of fugitive vapors depends on the solvent volatility, the temperature of the ink and solvent in the ink fountain, the amount of exposed area around the press, dryer designs and efficiencies, and the frequency of press shutdowns.

The complete air pollution control system for a modern publication rotogravure printing facility consists of two sections, the solvent vapor capture system and the emission control device. The capture system collects VOC vapors emitted from the presses and directs them to a control device where they are either recovered or destroyed. Low-VOC waterborne ink systems to replace a significant amount of solventborne inks have not been developed as an emission reduction alternative.

Capture Systems - Presently, only the concentrated dryer exhausts are captured at most facilities. The dryer exhausts contain the majority of the VOC vapors emitted. The capture efficiency of dryers is limited by their operating temperatures and

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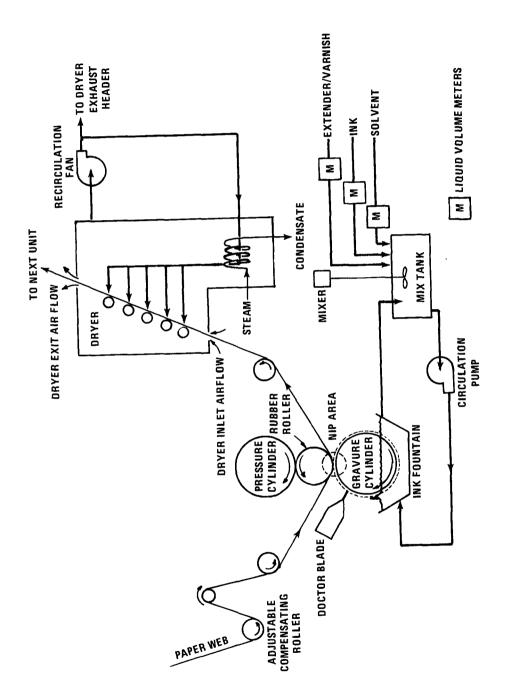


Figure 4.9.2-1. Diagram of a rotogravure printing unit.

EMISSION FACTORS FOR PUBLICATION ROTOGRAVURE PRINTING PRESSES TABLE 4.9.2-1.

# EMISSION FACTOR RATING: C

|                        |                  |              |            |                  | VOC Emi     | VOC Entastons |                  |             |      |
|------------------------|------------------|--------------|------------|------------------|-------------|---------------|------------------|-------------|------|
|                        | Unce             | Uncontrolled |            | 753              | 75% Control |               | 85%              | 85% Control |      |
|                        | Total<br>solvent | Raw          | Raw Ink    | Total<br>solvent | Raw Ink     | l nk          | Fotal<br>solvent | Raw Ink     | - nk |
| Emission<br>Points     | kg/kg<br>(15/16) | kg<br>H ter  | 1 <u>b</u> | kg/kg<br>(1b/1b) | kg          | 1b<br>gal     | kg/kg<br>(1b/1b) | kg<br>Hiter | 1bg  |
| Dryer exhausts         | 0.84             | 1.24         | 10.42      | 1                |             | ı             | ;<br>;<br>;      | 1           | 1    |
| Fugitives <sup>c</sup> | 0.13             | 0.19         | 1.61       | 0.13             | 0.19        | 1.61          | 0.01             | 0.10        | 0.87 |
| d<br>Printed product   | 0.03             | 0.05         | 0.17       | 0.03             | 0.05        | 0.37          | 0.03             | 0.05        | 0.37 |
| Control device         | ı                | ı            | 1          | 0.00             | 0.13        | 1.12          | 0.05             | 0.07        | 0.62 |
| Total emissions        | 1.0              | 1.48         | 12.40      | 0.25             | 0.37        | 3.10          | 0.15             | 0 22        | 1.86 |

consist entirely of VOC. Total solvent used includes all solvent in raw ink and related coatings, all dilution solvent added and all cleaning solvent used. Mass of VOC emitted per volume of raw ink (and coatings) used are general factors, based on typical dilution solvent volume addition. Actual factors based on ink use can vary significantly, as follows: all nonmethane. Mass of VVX emitted per mass of total solvent used are more accurate factors. Solvent assumed to

- Typical total solvent volume/raw luk (and coatings) volume ratio 2.0 liter/liter (gal/gal); range, 1.6 2.4. See References 1, 5-8.
- Solvent density (B) varies with composition and temperature. At  $21^{\circ}$ C ( $10^{\circ}$ F), the density of the most common mixed solvent used is 0.742 kg/liter (6.2 lb/gal); density of toluene solvent used is 0.863 kg/liter (7.2 lb/gal). See Reference 1.
- Mass of VOC emitted/raw ink (and coating) volume ratio determined from the mass emission factor ratio, the solvent/ink volume ratio, and the solvent density,

# 

5 b Reference ) and test data for pressus with dryer exhaust control only (Reference 1). Dryer exhaust emissions depend press operating speed, press shutdown frequency, ink and solvent composition, product printed, and dryer design and efficiencies. Emissions can range from 75-90% of total press emissions.

etype of ink used. Emissions have been reported to range from 1-7% of total press emissions. Based on capture and control device efficiencies (see Note f). Emissions are residual content in captured solvent laden Solvent temporarily retained in product after leaving press depends on dryer efficiency, type of paper and Determined by difference between total emissions and other point emissions. Reference 1.

References 1 and 3. Uncontrolled presses eventually emit 100% of total solvent used. Controlled press emissions are based on overall reduction efficiency equal to capture efficiency x control device efficiency. For 75% control, the capture efficiency is 84% with a 90% efficient control device. For 85% control, the capture efficiency is 90% with a atr vented after treatment. 95% control device. other factors that affect the release of the solvent vapors from the print and web to the dryer air. Excessively high temperatures impair product quality. The capture efficiency of older design dryer exhaust systems is about 84 percent, and modern dryer systems can achieve 85 to 89 percent capture. For a typical press, this type capture system consists of ductwork from each printing unit's dryer exhaust joined in a large header. One or more large fans are employed to pull the solvent laden air from the dryers and to direct it to the control device.

A few facilities have increased capture efficiency by gathering fugitive solvent vapors along with the dryer exhausts. Fugitive vapors can be captured by a hood above the press, by a partial enclosure around the press, by a system of multiple spot pickup vents, by multiple floor sweep vents, by total pressroom ventilation capture, or by various combinations of these. The design of any fugitive vapor capture system needs to be versatile enough to allow safe and adequate access to the press in press shutdowns. The efficiencies of these combined dryer exhaust and fugitive capture systems can be as high as 93 to 97 percent at times, but the demonstrated achievable long term average when printing several types of products is only about 90 percent.

Control Devices - Various control devices and techniques may be employed to control captured VOC vapors from rotogravure presses. All such controls are of two categories, solvent recovery and solvent destruction.

Solvent recovery is the only present technique to control VOC emissions from publication presses. Fixed bed carbon adsorption by multiple vessels operating in parallel configuration, regenerated by steaming, represents the most used control device. A new adsorption technique using a fluidized bed of carbon might be employed in the future. The recovered solvent can be directly recycled to the presses.

There are three types of solvent destruction devices used to control VOC emissions, conventional thermal oxidation, catalytic oxidation and regenerative thermal combustion. These control devices are employed for other rotogravure printing. At present, none are being used on publication rotogravure presses.

The efficiency of both solvent destruction and solvent recovery control devices can be as high as 99 percent. However, the achievable long term average efficiency for publication printing is about 95 percent. Older carbon adsorber systems were designed to perform at about 90 percent efficiency. Control device emission factors presented in Table 4.9-1 represent the residual vapor content of the captured solvent laden air vented after treatment.

Overall Control - The overall emissions reduction efficiency for VOC control systems is equal to the capture efficiency times

the control device efficiency. Emission factors for two control levels are presented in Table 4.9.2-1. The 75 percent control level represents 84 percent capture with a 90 percent efficient control device. (This is the EPA control techniques guideline recommendation for State regulations on old existing presses.) The 85 percent control level represents 90 percent capture with a 95 percent efficient control device. This corresponds to application of best demonstrated control technology for new publication presses.

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### 4.10 COMMERCIAL/CONSUMER SOLVENT USE

# 4.10.1 General 1-2

Commercial and consumer use of various products containing volatile organic compounds (VOC) contributes to formation of tropospheric ozone. The organics in these products may be released through immediate evaporation of an aerosol spray, evaporation after application, and direct release in the gaseous phase. Organics may act either as a carrier for the active product ingredients or as active ingredients themselves. Commercial and consumer products which release volatile organic compounds include aerosols, household products, toiletries, rubbing compounds, windshield washing fluids, polishes and waxes, nonindustrial adhesives, space deodorants, moth control applications, and laundry detergents and treatments.

### 4.10.2 Emissions

Major volatile organic constituents of these products which are released to the atmosphere include special naphthas, alcohols and various chloro- and fluorocarbons. Although methane is not included in these products, 31 percent of the volatile organic compounds released in the use of these products is considered nonreactive under EPA policy.<sup>3,4</sup>

National emissions and per capita emission factors for commercial and consumer solvent use are presented in Table 4.10-1. Per capita emission factors can be applied to area source inventories by multiplying the factors by inventory area population. Note that adjustment to exclude the nonreactive emissions fraction cited above should be applied to total emissions or to the composite factor. Care is advised in making adjustments, in that substitution of compounds within the commercial/consumer products market may alter the nonreactive fraction of compounds.

### References for Section 4.10

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EMISSION FACTOR RATING: C

|                    |                       | Nonmethane VOC <sup>a</sup> | voc <sup>a</sup> |            |                             |                         |
|--------------------|-----------------------|-----------------------------|------------------|------------|-----------------------------|-------------------------|
|                    | National              | National Emissions          |                  | Per Capita | Per Capita Emission Factors | ctors                   |
| Use                | 10 <sup>3</sup> Mg/yr | 10 <sup>3</sup> tons/yr     | kg/yr            | 1b/yr      | g/day <sup>b</sup>          | 10 <sup>-3</sup> 1b/day |
| Aerosol products   | 342                   | 376                         | 1.6              | 3.5        | 4.4                         | 9.6                     |
| Household products | 183                   | 201                         | 0.86             | 1.9        | 2.4                         | 5.2                     |
| Toiletries         | 132                   | 145                         | 0.64             | 1.4        | 1.8                         | 3.8                     |
| Rubbing compounds  | 62                    | 89                          | 0.29             | 0.64       | 08.0                        | 1.8                     |
| Windshield washing | 61                    | 29                          | 0.29             | 0.63       | 0.77                        | 1.7                     |
| Polishes and waxes | 48                    | 53                          | 0.22             | 0.49       | 0.59                        | 1.3                     |
| Nonindustrial      | 29                    | 32                          | 0.13             | 0.29       | 0.36                        | 0.79                    |
| Space deodorant    | 18                    | 20                          | 0.09             | 0.19       | 0.24                        | 0.52                    |
| Moth control       | 16                    | 18                          | 0.07             | 0.15       | 0.19                        | 0.41                    |
| Laundry detergent  | . 4                   | 4                           | 0.02             | 0.04       | 0.05                        | 0.10                    |
| Total <sup>c</sup> | 895                   | 984                         | 4.2              | 9.2        | 11.6                        | 25.2                    |

 $^{\rm a}_{\rm Keferences}$  1 and 2.  $^{\rm b}_{\rm Calculated}$  by 365 and converting to appropriate units.  $^{\rm c}_{\rm C}$  Totals may not be additive because of rounding.

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### 4.11 TEXTILE FABRIC PRINTING

# 4.11.1 Process Description 1-2

Textile fabric printing is part of the textile finishing industry. In fabric printing, a decorative pattern or design is applied to constructed fabric by roller, flat screen or rotary screen methods. Pollutants of interest in fabric printing are volatile organic compounds (VOC) from mineral spirit solvents in print pastes or inks. Tables 4.11-1 and 4.11-2 show typical printing run characteristics and VOC emission sources, respectively, for roller, flat screen and rotary screen printing methods.

In the roller printing process, print paste is applied to an engraved roller, and the fabric is guided between it and a central cylinder. The pressure of the roller and central cylinder forces the print paste into the fabric. Because of the high quality it can achieve, roller printing is the most appealing method for printing designer and fashion apparel fabrics.

In flat screen printing, a screen on which print paste has been applied is lowered onto a section of fabric. A squeegee then moves across the screen, forcing the print paste through the screen and into the fabric. Flat screen machines are used mostly in printing terry towels.

In rotary screen printing, tubular screens rotate at the same velocity as the fabric. Print paste distributed inside the tubular screen is forced into the fabric as it is pressed between the screen and a printing blanket (a continuous rubber belt). Rotary screen printing machines are used mostly but not exclusively for bottom weight apparel fabrics or fabric not for apparel use. Most knit fabric is printed by the rotary screen method, because it does not stress (pull or stretch) the fabric during the process.

Major print paste components include clear and color concentrates, a solvent, and in pigment printing, a low crock or binder resin. Print paste color concentrates contain either pigments or dyes. Pigments are insoluble particles physically bound to fabrics. Dyes are in solutions applied to impart color by becoming chemically or physically incorporated into individual fibers. Organic solvents are used almost exclusively with pigments. Very little organic solvent is used in nonpigment print pastes. Clear concentrates extend color concentrates to create light and dark shades. Clear and color concentrates do contain some VOC but contribute less than I percent of total VOC emissions from textile printing operations. Defoamers and resins are included in print paste to increase color fastness. A small amount of thickening

TYPICAL TEXTILE FABRIC PRINTING RUN CHARACTERISTICS  $^{a}$ TABLE 4.11-1.

| Characteristic  | Roller                                      | !             | Rotary screen                    | en      | Flat screen                                     | ua            |
|---|---|---------------|----------------------------------|---------|---|---------------|
|   | Range                                       | Average       | Range                            | Average | Range   | Average       |
| Wet pickup rate, kg (lb) <sup>b</sup><br>print paste consumed/kg<br>(lb) of fabric <sup>c</sup> | 0.51 - 0.58                                 | 0.56          | 0:10 - 1.89                      | 0.58    | 0.22 - 0.83                                     | 0.35          |
| Fabric weight, $kg/m^2$ (1b/yd <sup>2</sup> ) <sup>d</sup>                                      | 0.116 - 0.116 0.116 (0.213 - 0.213) (0.213) | 0.116         | 0.116 - 0.116 (0.213 - 0.213)    | 0.116   | 0.116 0.314 - 0.314<br>(0.213) (0.579 - 0.579)  | 0.314 (0.579) |
| Mineral spirits added to print paste, weight $%$  | 09 - 0                                      | 26            | 0 - 50                           | e       | 23 - 23   | 23            |
| Print paste used per fabr1c<br>area, kg/m² (1b/yd²)e  | 0.059 - 0.067 0.065 (0.109 - 0.124) (0.119) | 0.065 (0.119) | 0.012 - 0.219<br>(0.021 - 0.403) | 0.067   | 0.067 0.069 - 0.261 (0.124) (0.127 - 0.481)     | 0.110         |
| Mineral spirits used per<br>fabric area, kg/m² (1b/yd²)f  | 0 - 0.040 0.017<br>(0 - 0.074) (0.031)      | 0.017 (0.031) | 0 - 0.109 $(0 - 0.201)$          | 0.0002  | 0.0002 0.016 - 0.060<br>(0.0004)(0.030 - 0.111) | 0.025         |
| Print paste used in run,<br>kg (lb) <sup>8</sup>  | 673 - 764 741<br>(1,490 - 1,695) (1,627)    | 741 (1,627)   | 137 - 2,497 $(287 - 5,509)$      |         | 764 787 – 2,975<br>(1,695) (1,736 – 6,575)      | 1,254 (2,775) |

(13,634 yd<sup>2</sup>); line speed = 40 m/min (44 yd/min); distance, printer to oven = 5 m (5.5 yd). <sup>b</sup>Wet pickup ratio is a method of yield calculation in which mass of print paste consumed is divided by mass of fabric used. <sup>C</sup>Reference 3.

donly average fabric weight is presented. eFabric weight multiplied by wet pickup rate. Fabric weight multiplied by wet pickup multiplied by percent mineral spirits in formulation. Frabric weight multiplied by wet pickup multiplied by percent mineral spirits in formulation. Sprint paste used per fabric area multiplied by area of fabric printed.

SOURCES OF MINERAL SPIRIT EMISSIONS FROM A TYPICAL TEXTILE FABRIC PRINTING RUN TABLE 4.11-2.

|   | Percent of |         | Roller                |         |     | ~         | Rotary screen          |         |     |           | Flat screen |         |     |
|---|------------|---------|-----------------------|---------|-----|-----------|------------------------|---------|-----|-----------|-------------|---------|-----|
| Source  | total      |         | Range                 | Average | age | Range     | ge                     | Average | 1ge |           | Range       | Average | age |
|   | emissions  | kg      | 1b                    | kg      | 116 | kg        | 1b                     | kg      | 1b  | kg<br>kg  | 16          | kg      | 1p  |
| Mineral spirits<br>used in run <sup>b</sup>                     | 100.0      | 0 - 458 | 0 - 458 0 - 1,005 193 | 193     | 425 | 0 - 1,249 | 0 - 1,249 0 - 2,754 23 | 23      | 51  | 181 - 684 | 399 - 1,508 | 288     | 635 |
| Wasted mineral spirits (potential water emissions) <sup>C</sup> | 6.2        | 0 - 28  | 0 - 62                | 12      | 26  | 0 - 77    | 0 - 170                | -       | 2   | 11 - 42   | 24 - 93     | 18      | 40  |
| Overprinted mineral spirit fugitives <sup>d</sup>               | 3,5        | 0 - 16  | 0 - 35                | 7       | 15  | 77 - 0    | 26 - 0                 | 7       | 2   | 6 – 24    | 13 ~ 53     | 10      | 22  |
| Tray and barrel<br>fugitives <sup>e</sup>                       | 0.3        | 0 - 1   | 0 - 2                 | 7       | 2   | 7 - 0     | 6 - 0                  | 0       | 0   | 1 - 2     | 1 - 4       | -       | 2   |
| Flashoff fugitives <sup>e</sup>                                 | 1.5        | 1 - 0   | ÇT - 0                | 6       | 9   | 0 - 19    | 0 - 41                 | 0       | -   | 3 - 10    | 6 - 22      | 4       | 6   |
| Dryer emissions <sup>e</sup>                                    | 88.5       | 0 - 405 | 0 - 889               | 170     | 375 | 0 - 1,105 | 0 - 1,105 0 - 2,436    | 21      | 94  | 160 - 606 | 353 - 1,337 | 255     | 562 |

alength of run = 10,000 m (10,936 yd); fabric width = 1.14 m (1.25 yd); total fabric area = 11,400 m² (13,634 yd²); line speed = 40 m/min (44 yd/min); distance, printer to oven = 5 m (5.5 yd).

\*\*Deprint paste used in run multiplied by mineral spirits added to print paste, weight percent.

\*\*CEstimate provided by industry contacts.

\*\*Deprint deprint paste used in run multiplied by mineral spirits added to print paste, weight percent.

\*\*GESTIMATE OF THE PROVIDED OF THE PRO

agent is also added to each print paste to control print paste viscosity. Print defoamers, resins and thickening agents do not contain VOC.

The majority of emissions from print paste are from the solvent, which may be aqueous, organic (mineral spirits) or both. The organic solvent concentration in print pastes may vary from 0 to 60 weight percent, with no consistent ratio of organic solvent to water. Mineral spirits used in print pastes vary widely in physical and chemical properties. See Table 4.11-3.

TABLE 4.11-3. TYPICAL INSPECTION VALUES FOR MINERAL SPIRITS<sup>a</sup>

| Parameter                       | Range                                     |
|---------------------------------|---|
|                                 |   |
| Specific gravity at 15°C (60°F) | 0.778 - 0.805                             |
| Viscosity at 25°C (77°F)        | 0.83 - 0.95 cP                            |
| Flash point (closed cup)        | 41 - 45° C (105 - 113° F)                 |
| Aniline point                   | $43 - 62^{\circ} C (110 - 144^{\circ} F)$ |
| Kauri-Butanol number            | 32 - 45                                   |
| Distillation range              |   |
| Initial boiling points          | 157 - 166° C (315 - 330° F)               |
| 50 percent value                | 168 - 178° C (334 - 348° F)               |
| Final boiling points            | 199 - 201° C (390 - 394° F)               |
| Composition (%)                 |   |
| Total saturates                 | 81.5 - 92.3                               |
| Total aromatics                 | 7.7 - 18.5                                |
| C <sub>8</sub> and higher       | 7.5 - 18.5                                |

<sup>&</sup>lt;sup>a</sup>References 2,4.

Although some mineral spirits evaporate in the early stages of the printing process, the majority of emissions to the atmosphere is from the printed fabric drying process, which drives off volatile compounds (see Table 4.11-2 for typical VOC emission splits). For some specific print paste/fabric combinations, color fixing occurs in a curing process, which may be entirely separate or merely a separate segment of the drying process.

Two types of dryers are used for printed fabric - steam coil or natural gas fired dryers, through which the fabric is conveyed on belts, racks, etc., and steam cans, with which the fabric makes direct contact. Most screen printed fabrics and practically all printed knit fabrics and terry towels are dried with the first type of dryer, not to stress the fabric. Roller printed fabrics and

apparel fabrics requiring soft handling are dried on steam cans, which have lower installation and operating costs and which dry the fabric more quickly than other dryers.

Figure 4.11-1 is a schematic diagram of the rotary screen printing process, with emission points indicated. The flat screen printing process is virtually identical. The symbols for fugitive VOC emissions to the atmosphere indicate mineral spirits evaporating from print paste during application to fabric before drying. The largest VOC emission source is the drying and curing oven stack, which vents evaporated solvents (mineral spirits and water) to the atmosphere. The symbol for fugitive VOC emissions to the waste water indicates print paste mineral spirits washed with water from the printing blanket (continuous belt) and discharged in waste water.

Figure 4.11-2 is a schematic diagram of a roller printing process in which all emissions are fugitive. Fugitive VOC emissions from the "back grey" (fabric backing material that absorbs excess print paste) in the illustrated process are emissions to the atmosphere because the back grey is dried before being washed. In processes where the back grey is washed before drying, most of the fugitive VOC emissions from the back grey will be discharged into the waste water. In some roller printing processes, steam cans for drying printed fabric are enclosed, and drying process emissions are vented directly to the atmosphere.

## 4.11.2 Emissions and Controls 1,3-12

Presently there is no addon emission control technology for organic solvent used in the textile fabric printing industry. Thermal incineration of oven exhaust has been evaluated in the Draft Background Information document for New Source Performance Standard development, and has been found unaffordable for some fabric printers. The feasibility of using other types of addon emission control equipment has not been fully evaluated. Significant organic solvent emissions reduction has been accomplished by reducing or eliminating the consumption of mineral spirit solvents. The use of aqueous or low organic solvent print pastes has increased during the past decade, because of the high price of organic solvents and higher energy costs associated with the use of higher solvent volumes. The only fabric printing applications presently requiring the use of large quantities of organic solvents are pigment printing of fashion or designer apparel fabric and terry towels.

Table 4.11-4 presents average emission factors and ranges for each type of printing process and an average annual emission factor per print line, based on estimates submitted by individual fabric printers. No emission tests were done. VOC emission rates involve three parameters, organic solvent content of print pastes, consumption of print paste

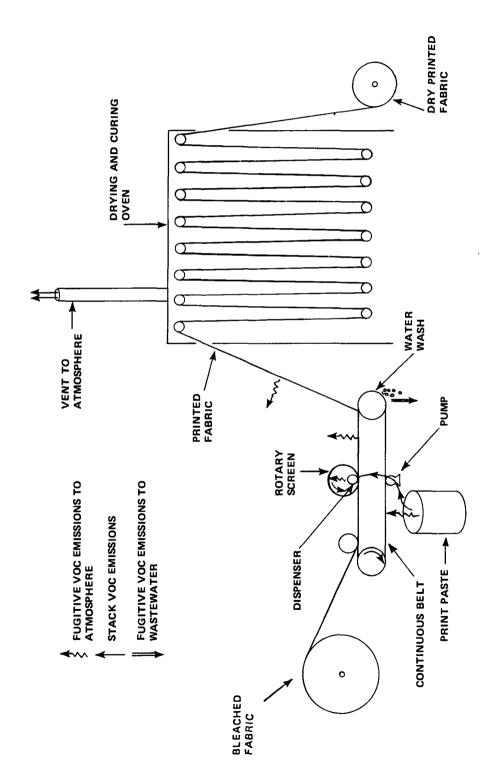


Figure 4.11-1. Schematic diagram of the rotary screen printing process, with fabric drying in a vented oven.

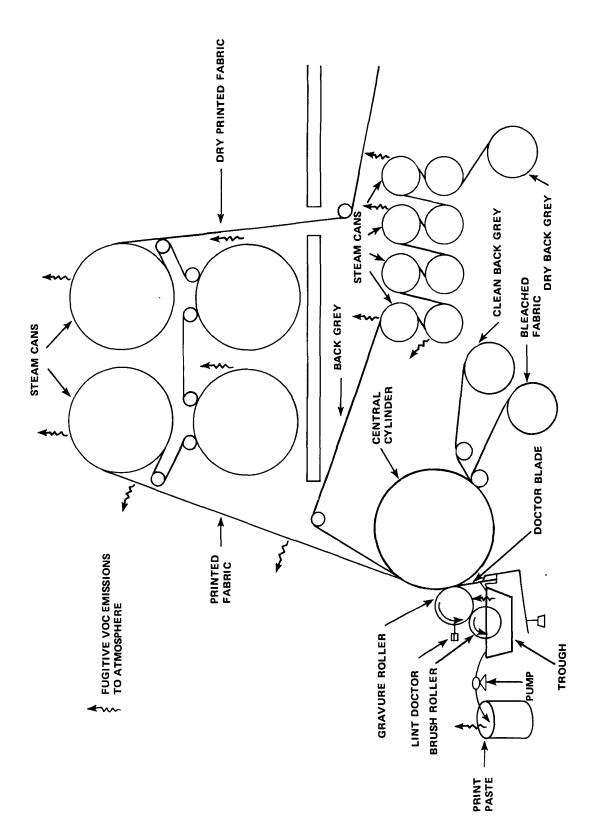


Figure 4.11 $_1$ 2. Schematic diagram of the roller printing process, with fabric drying on steam cans.

(a function of pattern coverage and fabric weight), and rate of fabric processing. With the quantity of fabric printed held constant, the lowest emission rate represents minimum organic solvent content print paste and minimum print paste consumption, and the maximum emission rate represents maximum organic solvent content print paste and maximum print paste consumption. The average emission rates shown for roller and rotary screen printing are based on the results of a VOC usage survey conducted by the American Textile Manufacturers Institute, Inc. (ATMI), in 1979. The average flat screen printing emission factor is based on information from two terry towel printers.

TABLE 4.11-4. TEXTILE FABRIC PRINTING ORGANIC EMISSION FACTORS<sup>a</sup>

EMISSION FACTOR RATING: C

| voc                                   | Roller<br>Range Average   | Rotary screen Range Average          | Flat screenb<br>Range Average         |
|---------------------------------------|---------------------------|--------------------------------------|---------------------------------------|
| kg(1b)/1,000 kg<br>(1b) fabric        | 0 - 348° 142d             | 0 - 945 <sup>c</sup> 23 <sup>d</sup> | 51 - 191 <sup>c</sup> 79 <sup>e</sup> |
| Mg(ton)/yr/print<br>line <sup>C</sup> | 130 <sup>c</sup><br>(139) | 29 <sup>c</sup><br>(31)              | 29 <sup>c</sup><br>(31)               |

<sup>&</sup>lt;sup>a</sup>Transfer printing, carpet printing, and printing of vinyl coated cloth are specifically excluded from this compilation.

Although the average emission factors for roller and rotary screen printing are representative of the use of medium organic solvent content print pastes at average rates of print paste consumption, very little printing is actually done with medium organic solvent content pastes. The distribution of print paste use is bimodal, with the arithmetic average falling between the modes. Most fabric is printed with aqueous or low organic solvent print pastes. However, in applications where the use of organic solvents is beneficial, high organic solvent content print pastes

bFlat screen factors apply to terry towel printing. Rotary screen factors should be applied to flat screen printing of other types of fabric (e.g., sheeting, bottom weight apparel, etc.).

<sup>&</sup>lt;sup>C</sup>Reference 13.

dReference 5.

eReference 6.

are used to derive the full benefit of using organic solvents. The most accurate emissions data can be generated by obtaining organic solvent use data for a particular facility. The emission factors presented here should only be used to estimate actual process emissions.

### References for Section 4.11

- 1. Fabric Printing Industry: Background Information for Proposed Standards (Draft), EPA Contract No. 68-02-3056, Research Triangle Institute, Research Triangle Park, NC, April 21, 1981.
- 2. Exxon Petroleum Solvents, Lubetext DG-1P, Exxon Company, Houston, TX, 1979.
- 3. Memorandum from S. B. York, Research Triangle Institute, to Textile Fabric Printing AP-42 file, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 25, 1981.
- 4. C. Marsden, Solvents Guide, Interscience Publishers, New York, NY, 1963, p. 548.
- 5. Letter from W. H. Steenland, American Textile Manufacturers Institute, Inc., to Dennis Crumpler, U.S. Environmental Protection Agency, Research Triangle Park, NC, April 8, 1980.
- 6. Memorandum from S. B. York, Research Triangle Institute, to textile fabric printing AP-42 file, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 12, 1981.
- 7. Letter from A. C. Lohr, Burlington Industries, to James Berry, U.S. Environmental Protection Agency, Research Triangle Park, NC, April 26, 1979.
- 8. Trip Report/Plant Visit to Fieldcrest Mills, Foremost Screen Print Plant, memorandum from S. B. York, Research Triangle Institute, to G. Gasperecz, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 28, 1980.
- 9. Letter from T. E. Boyce, Fieldcrest Corporation, to S. B. York, Research Triangle Institute, Research Triangle Park, NC, January 23, 1980.
- 10. Telephone conversation, S. B. York, Research Triangle Institute, with Tom Boyce, Foremost Screen Print Plant, Stokesdale, NC, April 24, 1980.

- 11. "Average Weight and Width of Broadwoven Fabrics (Gray)",

  Current Industrial Report, Publication No. MC-22T (Supplement),

  Bureau of the Census, U.S. Department of Commerce, Washington,

  DC, 1977.
- 12. "Sheets, Pillowcases, and Towels", <u>Current Industrial Report</u>, Publication No. MZ-23X, Bureau of the Census, U.S. Department of Commerce, Washington, DC, 1977.
- 13. Memorandum from S. B. York, Research Triangle Institute, to Textile Fabric Printing AP-42 file, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, April 3, 1981.
- "Survey of Plant Capacity, 1977", <u>Current Industrial Report</u>, Publication No. DQ-C1(77)-1, Bureau of the Census, U.S. Department of Commerce, Washington, DC, August 1978.

### 5.16 SODIUM CARBONATE

### 5.16.1 General<sup>1</sup>,<sup>2</sup>

Processes used to produce sodium carbonate ( $Na_2CO_3$ ), or soda ash, are classified as either natural or synthetic. Natural processes recover sodium carbonate from naturally occurring deposits of trona ore (sodium sesquicarbonate) or from brine containing sodium sesquicarbonate and sodium carbonate. The synthetic process (Solvay process) produces sodium carbonate by reacting ammoniated sodium chloride with carbon dioxide. For about a century, almost all sodium carbonate production was by the Solvay process. However, since the mid-1960s, Solvay process production has declined substantially, and natural production has grown by 500 percent. Only one plant in the U.S. now uses the Solvay process. Available data on emissions from the Solvay process are also presented, but because the natural processes are more prevalent in this country, this discussion will focus on emissions from the natural processes.

Three different natural processes are currently in use. These are the monohydrate, sesquicarbonate and direct carbonation processes. The sesquicarbonate process was the first natural process used, but it is used at only one plant and is not expected to be used at future plants. And since data on uncontrolled emissions from this process are not available, emissions from the sesquicarbonate process are not discussed. The monohydrate and direct carbonation processes and emissions are described below, the differences in these two processes being in raw materials processing.

In the monohydrate process, sodium carbonate is produced from trona ore, which consists of 86 to 95 percent sodium sesquicarbonate —  $(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O)$ , 5 to 12 percent gangues (clays and other insoluble impurities) and water. The mined trona ore is crushed and screened and calcined to drive off carbon dioxide and water, forming crude sodium carbonate. Rotary gas fired calciners currently are most commonly used, but the newest plants use coal fired calciners, and future plants are also likely to use coal fired calciners because of the economics and the limited availability of natural gas.

The crude sodium carbonate is dissolved and separated from the insoluble impurities. Sodium carbonate monohydrate ( $Na_2CO_3 \cdot H_2O$ ) is crystallized from the purified liquid by multiple effect evaporators. The sodium carbonate monohydrate is then dried, to remove the free and bound water and to produce the final product. Rotary steam tube, fluid bed steam tube, and rotary gas fired dryers are used, with steam tube dryers more likely in future plants.

In the direct carbonation process, sodium carbonate is produced from brine containing sodium sesquicarbonate, sodium carbonate and other salts. The brine is prepared by pumping liquor into salt deposits, where the salts

are dissolved into a liquor. The recovered brine is carbonated by contact with carbon dioxide to convert all of the sodium carbonate that is present to sodium bicarbonate. The sodium bicarbonate is then recovered from the brine by vacuum crystallizers. The crystal slurry is filtered, and the crystals enter steam heated predryers to evaporate some of the moisture. The partially dried sodium bicarbonate goes to a steam heated calciner where carbon dioxide and the remaining water are driven off, forming impure sodium carbonate. The carbon dioxide evolved is recycled to the brine carbonators. The impure sodium carbonate is bleached with sodium nitrate in a gas fired rotary bleacher to remove discoloring impurities. The bleached sodium carbonate is then dissolved and recrystallized. The resulting crystals of sodium carbonate monohydrate are dried, as in the monohydrate process.

In the Solvay process, ammonia, calcium carbonate (limestone), coal and sodium chloride (brine) are the basic raw materials. The brine is purified in a series of reactors and clarifiers by precipitating the magnesium and calcium ions with soda ash and sodium hydroxide. Sodium bicarbonate is formed by carbonating a solution of ammonia and purified brine which is fed to either steam or gas rotary dryers where it is converted (calcined) to sodium carbonate.

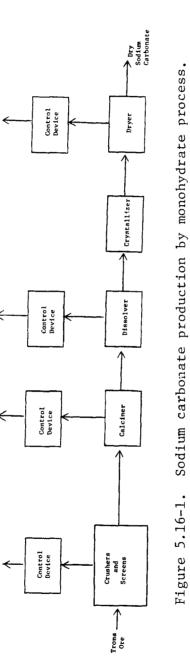
### 5.16.2 Emissions and Controls

The principal emission points in the monohydrate and direct carbonation processes are shown in Figures 5.16-1 and 5.16-2. The major emission sources in the monohydrate process are calciners and dryers, and the major sources in the direct carbonation process are bleachers, dryers and predryers. Emission factors for the emission sources are presented in Table 5.16-1, and emission factors for the Solvay process are presented in Table 5.16-2.

In addition to the major emission points, emissions may also arise from crushing and dissolving operations, elevators, conveyor transfer points, product loading and storage piles. Emissions from these sources have not been quantified.

Particulate matter is the only pollutant of concern from sodium carbonate plants. Emissions of sulfur dioxide ( $SO_2$ ) arise from calciners fired with coal, but reaction of the evolved  $SO_2$  with the sodium carbonate in the calciner keeps  $SO_2$  emissions low. Small amounts of volatile organic compounds (VOC) may also be emitted from calciners, possibly from oil shale associated with the trona ore, but these emissions have not been quantified.

The particulate matter emission rates from calciners, dryers, predryers and bleachers are affected by the gas velocity through the unit and by the particle size distribution of the feed material. The latter affects the emission rate because small particles are more easily entrained in a moving stream of gas than are large particles. Gas velocity through the unit affects the degree of turbulence and agitation. As the gas velocity increases, so does the rate of increase in total particulate matter emissions. Thus, coal fired calciners may have higher particulate emission factors than gas fired calciners because they have higher gas flow rates. The additional particulate emissions contributed by the coal fly ash represent less than one percent of total particulate emissions, and the emission



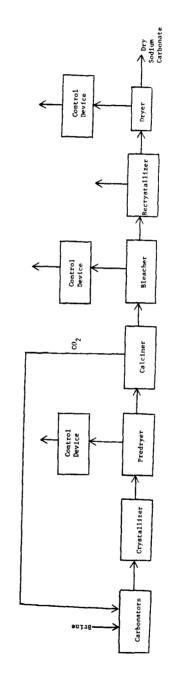


Figure 5.16-2. Sodium carbonate production by direct carbonation process.

TABLE 5.16-1. UNCONTROLLED EMISSION FACTORS FOR NATURAL PROCESS SODIUM CARBONATE PLANTS<sup>a</sup>

EMISSION FACTOR RATING: B

| Source   | Particula | te emissions |
|--|-----------|--------------|
|  | kg/Mg     | lb/ton       |
| Gas fired calciner b                                   | 184.0     | 368.0        |
| Coal fired calciner                                    | 195.0     | 390.0        |
| Rotary steam tube dryer                                | 33.0      | 67.0         |
| Fluid bed steam tube dryer <sup>C</sup>                | 73.0      | 146.0        |
|  | 1.0       | 3.1          |
| Rotary steam heater predryer Rotary gas fired bleacher | 155.0     | 311.0        |

 $<sup>^{\</sup>rm a}_{\rm r}$ References 3-5. Values are averages of 2 - 3 test runs.

TABLE 5.16-2. UNCONTROLLED EMISSION FACTORS FOR A SYNTHETIC SODA ASH (SOLVAY) PLANT<sup>a</sup>

EMISSION FACTOR RATING: D

| Emissions   | kg/Mg   | 1b/ton  |
|---|---------|---------|
| Ammonia losses <sup>b</sup><br>Particulate <sup>c</sup> | 2<br>25 | 4<br>50 |

Reference 6.

b Calculated by subtracting measured ammonia effluent discharges from ammonia

Factor is in kg/Mg (lb/ton) of ore fed to calciner. Includes particulate emissions from coal fly ash. These represent < 1% of the total emissions. Emissions of SO<sub>2</sub> from the coal are roughly 0.0007 kg/Mg (0.014 1b/ton) of ore feed.

Factor is in kg/Mg (lb/ton) of dry product from dryer.
Factor is in kg/Mg (lb/ton) of dry NaHCO3 feed.

eFactor is in kg/Mg (1b/ton) of dry feed to bleacher.

Maximum uncontrolled emissions, from New York State process certificates to operate. Does not include emissions from fugitive or external combustion sources.

factor for coal fired calciners is about 6 percent higher than that for gas fired calciners. Fluid bed steam tube dryers have higher gas flow rates and particulate emission factors than do rotary steam tube dryers. No data on uncontrolled particulate emissions from gas fired dryers are available, but these dryers also have higher gas flow rates than do rotary steam tube dryers and would probably have higher particulate emission factors.

The particulate emission factors presented in Table 5.16-1 represent emissions measured at the inlet to the control devices. However, even in the absence of air pollution regulations requiring emission control, these emissions should be controlled to some degree to prevent excessive loss of product. Because the level of control needed for product recovery is difficult to define, the emission factors do not account for this recovery.

Cyclones in series with electrostatic precipitators (ESP) are most commonly used to control particulate emissions from calciners and bleachers. Venturi scrubbers are also used, but they are not as effective. Cyclone/ESP combinations have achieved removal efficiencies ranging from 99.5 to 99.96 percent for new coal fired calciners, and 99.99 percent for bleachers. Comparable efficiencies should be possible for new gas fired calciners. Venturi scrubbers are most commonly used to control emissions from dryers and predryers, because of the high moisture content of the exit gas. Cyclones are used in series with the scrubbers for predryers and fluid bed steam tube dryers. Removal efficiencies averaging 99.88 percent have been achieved for venturi scrubbers on rotary steam tube dryers at a pressure drop of 6.2 kPa (25 inches water), and acceptable collection efficiences may be achieved with lower pressure drops. Efficiencies of 99.9 percent have been achieved for a cyclone/venturi scrubber on a fluid bed steam tube dryer at a pressure drop of 9.5 kPa (38 inches water). Efficiencies over 98 percent have been achieved for a cyclone/venturi scrubber on a predryer.

Fugitive emissions originating from limestone handling/processing operations, product drying operations and dry solids handling (conveyance and bulk loading) are a significant source of emissions from the manufacture of soda ash by the Solvay process. These fugitive emissions have not been quantified. Ammonia losses also occur because of leaks at pipe fittings, gasket flanges, pump packing glands, discharges of absorber exhaust, and exposed bicarbonate cake on filter wheels and on feed floor prior to calcifying.

### References for Section 5.16

- 1. Sodium Carbonate Industry Background Information for Proposed
  Standards, EPA-450/3-80-029a, U. S. Environmental Protection Agency,
  Research Triangle Park, NC, August 1980.
- 2. Air Pollutant Emission Factors, Final Report, HEW Contract Number CPA-22-69-119, Resources Research, Inc., Reston, VA, April 1970.
- 3. Sodium Carbonate Manufacturing Plant, EPA-79-SOD-1, U. S. Environmental Protection Agency, Research Triangle Park, NC, August 1979.

- 4. Sodium Carbonate Manufacturing Plant, EPA-79-SOD-2, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1980.
- 5. Particulate Emissions from the Kerr-McGee Chemical Corporation Sodium Carbonate Plant, EPA-79-SOD-3, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1980.
- 6. Written communication from W. S. Turetsky, Allied chemical Company, Morristown, NJ, to Frank Noonan, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 17, 1982.

uncontrolled emission factor for SO<sub>2</sub> would be 27.5 kg/Mg (55 pounds per ton) of 100 percent sulfuric acid produced, as shown in Table 5.17-1. For purposes of comparison, note that the Environmental Protection Agency performance standard for new and modified plants is 2 kg/Mg (4 pounds per ton) of 100 percent acid produced, maximum 2 hour average. 3 As Table 5.17-1 and Figure 5.17-3 indicate, achieving this standard requires a conversion efficiency of 99.7 percent in an uncontrolled plant or the equivalent SO2 collection mechanism in a controlled facility. Most single absorption plants have SO<sub>2</sub> conversion efficiencies ranging from 95 - 98 percent.

In addition to exit gases, small quantities of sulfur oxides are emitted from storage tank vents and tank car and tank truck vents during loading operations, from sulfuric acid concentrators, and through leaks in process equipment. Few data are available on the quantity of emissions from these sources.

Of the many chemical and physical means for removing SO2 from gas streams, only the dual absorption and the sodium sulfite/bisulfite scrubbing processes have been found to increase acid production without yielding unwanted byproducts.

TABLE 5.17-1. EMISSION FACTORS FOR SULFURIC ACID PLANTS<sup>a</sup>

| EMISSION FACTOR RATING: | EMISSION | FACTOR | RATING: | Α |
|-------------------------|----------|--------|---------|---|
|-------------------------|----------|--------|---------|---|

|                                    | $\mathfrak{so}_2$ 1                             | Emissions  |
|------------------------------------|---|--|
| Conversion of $SO_2$ to $SO_3$ (%) | kg/Mg of 100%<br>H <sub>2</sub> SO <sub>4</sub> | 1b/ton of 100%<br>H <sub>2</sub> SO <sub>4</sub> |
| 93                                 | 48.0  | 96   |
| 94                                 | 41.0  | 82   |
| 95                                 | 35.0  | 70   |
| 96                                 | 27.5  | 55   |
| 97                                 | 20.0  | 40   |
| 98                                 | 13.0  | 26   |
| 99                                 | 7.0   | 14   |
| 99.5                               | 3.5   | 7  |
| 99.7                               | 2.0   | 4  |
| 100                                | 0.0   | 0  |

a bReference l. This linear interpolation formula can be used for calculating emission factors for conversion efficiencies between 93 and 100%: emission factor =-13.65 (% conversion efficiency) + 1365.

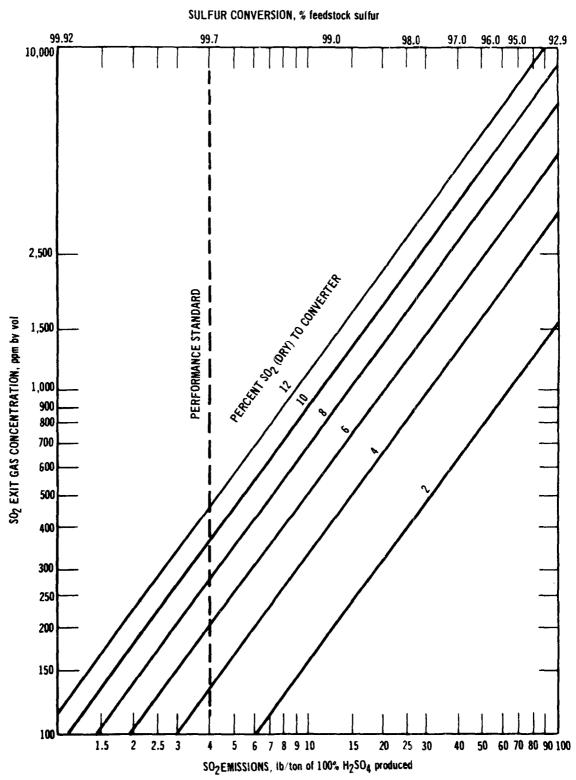


Figure 5.17-3. Sulfuric acid plant feedstock sulfur conversion versus volumetric and mass  $SO_2$  emissions at various inlet  $SO_2$  concentrations by volume.

### 5.20 SYNTHETIC RUBBER

### 5.20.1. Emulsion Styrene-Butadiene Copolymers

General - Two types of polymerization reaction are used to produce styrene-butadiene copolymers, the emulsion type and the solution type. This Section addresses volatile organic compound (VOC) emissions from the manufacture of copolymers of styrene and butadiene made by emulsion polymerization processes. The emulsion products can be sold in either a granular solid form, known as crumb, or in a liquid form, known as latex.

Copolymers of styrene and butadiene can be made with properties ranging from those of a rubbery material to those of a very resilient plastic. Copolymers containing less than 45 weight percent styrene are known as styrene-butadiene rubber (SBR). As the styrene content is increased over 45 weight percent, the product becomes increasingly more plastic.

Emulsion Crumb Process - As shown in Figure 5.20-1, fresh styrene and butadiene are piped separately to the manufacturing plant from the storage area. Polymerization of styrene and butadiene proceeds continuously though a train of reactors, with a residence time in each reactor of approximately 1 hour. The reaction product formed in the emulsion phase of the reaction mixture is a milky white emulsion called latex. The overall polymerization reaction ordinarily is not carried out beyond a 60 percent conversion of monomers to polymer, because the reaction rate falls off considerably beyond this point and product quality begins to deteriorate.

Because recovery of the unreacted monomers and their subsequent purification are essential to economical operation, unreacted butadiene and styrene from the emulsion crumb polymerization process normally are recovered. The latex emulsion is introduced to flash tanks where, using vacuum flashing, the unreacted butadiene is removed. The butadiene is then compressed, condensed and pumped back to the tank farm storage area for subsequent reuse. The condenser tail gases and noncondensibles pass through a butadiene adsorber/desorber unit, where more butadiene is recovered. Some noncondensibles and VOC vapors pass to the atmosphere or, at some plants, to a flare system. The latex stream from the butadiene recovery area is then sent to the styrene recovery process, usually taking place in perforated plate steam stripping columns. From the styrene stripper, the latex is stored in blend tanks.

From this point in the manufacturing process, latex is processed continuously. The latex is pumped from the blend tanks to coagulation vessels, where dilute sulfuric acid ( $\rm H_2SO_4$  of pH 4 to 4.5) and sodium chloride solution are added. The acid and brine mixture causes the emulsion to break, releasing the styrene-butadiene copolymer as crumb product. The coagulation vessels are open to the atmosphere.

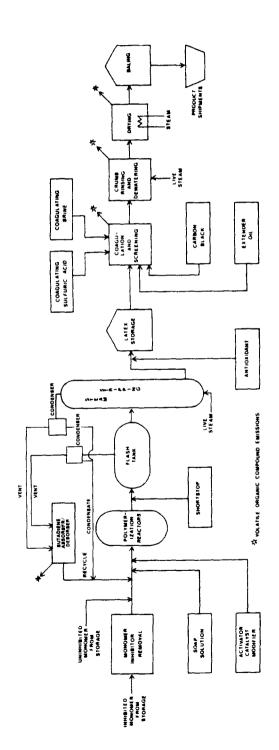


Figure 5.20-1. Typical process for crumb production by emulsion polymerization.

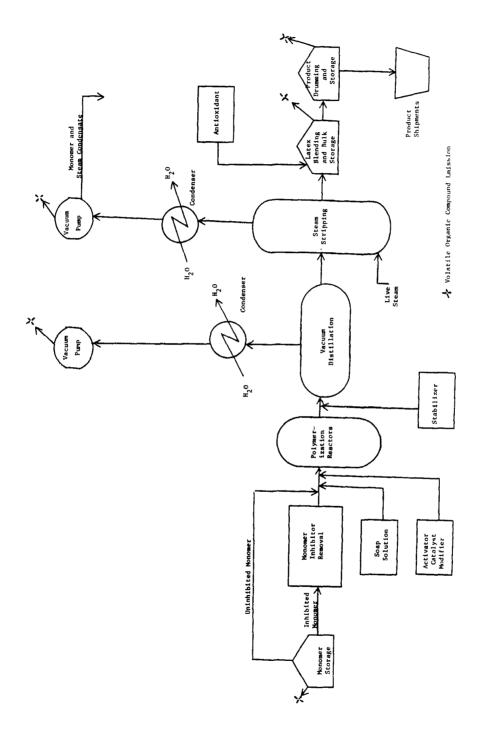


TABLE 5.20-1. EMISSION FACTORS FOR EMULSION STYRENE-BUTADIENE COPOLYMER PRODUCTION<sup>a</sup>

EMISSION FACTOR RATING: B

| Process                                     | Volatile Orga | anic Emissions <sup>b</sup> |
|---|---------------|-----------------------------|
|   | g/kg          | lb/ton                      |
| Emulsion Crumb                              |               |                             |
| Monomer recovery, uncontrolled <sup>c</sup> | 2.6           | 5.2                         |
| Absorber vent                               | 0.26          | 0.52                        |
| Blend/coagulation tank, uncontrolled        | 0.42          | 0.84                        |
| Dryers                                      | 2.51          | 5.02                        |
| Emulsion Latex                              |               |                             |
| Monomer removal f                           |               |                             |
| Condenser vent                              | 8.45          | 16.9                        |
| Blend tanks                                 |               |                             |
| Uncontrolled <sup>†</sup>                   | 0.1           | 0.2                         |

<sup>&</sup>lt;sup>a</sup>Nonmethane VOC, mainly styrene and butadiene. For emulsion crumb and emulsion latex processes only. Factors for related equipment and operations (storage, fugitives, boilers, etc.) are presented in other benefit benefit and operations of AP-42.

Expressed as units per unit of copolymer produced.

Average of 3 industry supplied stack tests.

Average of 1 industry stack test and 2 industry supplied emission estimates.

No controls available. Average of 3 industry supplied stack tests and 1 findustry estimate.

EPA estimates from industry supplied data, confirmed by industry.

Leaving the coagulation process, the crumb and brine acid slurry is separated by screens into solid and liquid. The crumb product is processed in rotary presses that squeeze out most of the entrained water. The liquid (brine/acid) from the screening area and the rotary presses is cycled to the coagulation area for reuse.

The partially dried crumb is then processed in a continuous belt dryer which blows hot air at approximately 93°C (200°F) across the crumb to complete the drying of the product. Some plants have installed single pass dryers, where space permits, but most plants still use the triple pass dryers which were installed as original equipment in the 1940s. The dried product is baled and weighed before shipment.

Emulsion Latex Process - Emulsion polymerization can also be used to produce latex products. These latex products have a wider range of properties and uses than do the crumb products, but the plants are usually much smaller. Latex production, shown in Figure 5.20-2, follows the same basic processing steps as emulsion crumb polymerization, with the exception of final product processing.

As in emulsion crumb polymerization, the monomers are piped to the processing plant from the storage area. The polymerization reaction is taken to near completion (98 to 99 percent conversion), and the recovery of unreacted monomers is therefore uneconomical. Process economy is directed towards maximum conversion of the monomers in one process trip.

Because most emulsion latex polymerization is done in a batch process, the number of reactors used for latex production is usually smaller than for crum production. The latex is sent to a blowdown tank where, under vacuum, any unreacted butadiene and some unreacted styrene are removed from the latex. If the unreacted styrene content of the latex has not been reduced sufficiently to meet product specifications in the blowdown step, the latex is introduced to a series of steam stripping steps to reduce the content further. Any steam and styrene vapor from these stripping steps is taken overhead and is sent to a water cooled condenser. Any uncondensibles leaving the condenser are vented to the atmosphere.

After discharge from the blowdown tank or the styrene stripper, the latex is stored in process tanks. Stripped latex is passed through a series of screen filters to remove unwanted solids and is stored in blending tanks, where antioxidants are added and mixed. Finally, latex is pumped from the blending tanks to be packaged into drums or to be bulk loaded into railcars or tank trucks.

Emissions and Controls - Emission factors for emulsion styrene-butadiene copolymer production processes are presented in Table 5.20-1.

In the emulsion crumb process, uncontrolled noncondensed tail gases (VOC) pass through a butadiene absorber control device, which is 90 percent efficient, to the atmosphere or, in some plants, to a flare stack.

No controls are presently employed for the blend tank and/or coagulation tank areas, on either crumb or latex facilities. Emissions from dryers in the crumb process and the monomer removal part of the latex process do not employ control devices.

Individual plant emissions may vary from the average values listed in Table 5.20-1 with facility age, size and plant modification factors.

References for Section 5.20

- 1. <u>Control Techniques Guideline</u> (Draft), EPA Contract No. 68-02-3168, GCA, Inc., Chapel Hill, NC, April 1981.
- 2. Emulsion Styrene-Butadiene Copolymers: Background Document, EPA Contract No. 68-02-3063, TRW Inc., Research Triangle Park, NC, May 1981.
- 3. Confidential written communication from C. Fabian, U.S. Environmental Protection Agency, Research Triangle Park, NC, to Styrene-Butadiene Rubber File (76/15B), July 16, 1981.

#### 7.15 STORAGE EATTERY PRODUCTION

## 7.15.1 Process Description<sup>1</sup>

Lead acid storage batteries are produced from lead alloy ingots and lead oxide. The lead oxide may be prepared by the battery manufacturer or may be purchased from a supplier. See Section 7.16.

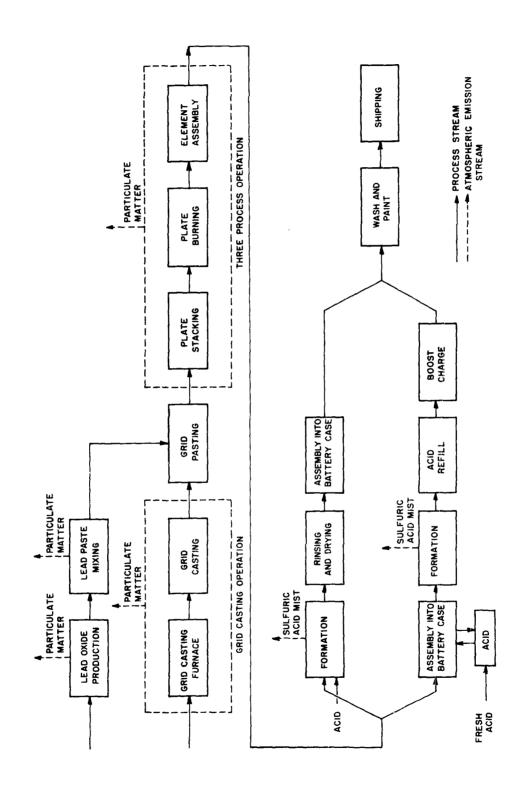
Lead alloy ingots are charged to a melting pot, from which the molten lead flows into molds that form the battery grids. Pasting machines force a paste into the interstices of the grids, after which they are referred to as plates. The grids are often cast in doublets and split apart (slitting) after they have been pasted and cured. The paste is made in a batch type process. Mixing lead oxide powder, water and sulfuric acid produces a positive paste, and the same ingredients in slightly different proportions plus an expander (generally a mixture of barium sulfate, carbon black and organics) make the negative paste.

After the plates are cured, they are sent to the three process operation of plate stacking and burning and element assembly in the battery case. Doublet plates are cut apart and stacked in an alternating positive and negative block formation, with insulators between them. These insulators are of materials such as wood, treated paper, plastic or rubber. Then, in the burning operation, leads are welded to tabs on each positive or negative plate. An alternative to this operation is the cast-on strap process, in which molten lead is poured around the plate tabs to form the connection, and positive and negative terminals are then welded to each such connected element. The completed elements are assembled in battery cases either before (wet batteries) or after (dry batteries) the formation step.

Formation is the immersing of plates in a dilute sulfuric acid solution and the connecting of positive plates to the positive pole of a direct current (dc) source and the negative plates to the negative pole of the dc source. In the wet formation process, this is done in the battery case. After forming, the acid is dumped, fresh acid is added, and a boost charge is applied to complete the battery. In dry formation, the individual plates may be formed in tanks of sulfuric acid before assembly. Also, they may be assembled first and then formed in tanks. The formed elements from either method are then placed in the battery cases, and the batteries are shipped dry. Figure 7.15-1 is a process flow diagram for lead acid battery manufacture.

Defective parts are either reclaimed at the battery plant or are sent to a secondary lead smelter (See Section 7.11). Lead reclamation facilities at battery plants generally are small pot furnaces. Approximately 1 percent of the lead processed at a typical lead acid battery plant is recycled through the reclamation operation.

Lead acid storage battery plants range in production capacity from less than 500 batteries per day to about 10,000 batteries per day. Lead acid storage batteries are produced in many sizes, but the majority is produced for use in automobiles and falls into a standard size range. A standard



Process flow diagram for storage battery production. Figure 7.15-1.

battery contains about 11.8 kilograms (26 lb) of lead, of which about half is present in the lead grids and half in the lead oxide paste.

# 7.15.2 Emissions and Controls $^{1-7}$

Lead oxide emissions result from the discharge of air used in the lead oxide production process. In addition, particulate matter and lead particulate are generated in the grid casting, paste mixing, lead reclamation, three process operations, and other operations such as slitting and small parts casting. These particulates are usually collected by ventilation systems to reduce employee exposure to airborne lead. Sulfuric acid mist emissions are generated during the formation step. Acid mist emissions are significantly higher for dry formation processes than for wet formation processes, because wet formation is conducted in battery cases, while dry formation is conducted in open tanks. Table 7.15-1 presents average uncontrolled emission factors for grid casting, paste mixing, lead reclamation, dry formation, and three process operations, and an average controlled emission factor for lead oxide production. The particulate emission factors presented in the Table include lead and its compounds. The lead emission factors represent emissions of lead in element and compound form, expressed as elemental lead.

A fabric filter is used as part of the process equipment to collect product from the lead oxide facility. Typical air to cloth ratios of fabric filters used for this facility are about 4 to 1. It is estimated that emissions from a facility controlled by a fabric filter with a 3 to 1 air to cloth ratio are about 50 percent less than those from a facility with a typical collection system. <sup>1</sup>

Fabric filters can also be used to control emissions from slitting and three process operations. The paste mixing operation consists of two phases. The first, in which dry ingredients are charged to the mixer, results in major emissions of lead oxide and is usually vented to a baghouse. For the second phase of the cycle, when moisture is present in the exhaust stream, the paste mixer generally is vented to an impingement scrubber. Grid casting machines are sometimes vented to an impingement scrubber. Lead reclamation facilities generally are also vented to impingement scrubbers.

Emission reductions of 99 percent and above can be obtained where fabric filtration is used to control slitting, paste mixing and three process operations. Application of scrubbers to paste mixing, grid casting and lead reclamation facilities can result in emission reductions from 85 percent to over 90 percent.

Wet formation processes usually do not require control. Emissions of sulfuric acid mist from dry formation processes can be reduced by over 95 percent with mist eliminators. Surface foaming agents are also used commonly in dry formation baths to control acid mist emissions.

#### References for Section 7.15

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TABLE 7.15-1. STORAGE BATTERY PRODUCTION EMISSION FACTORS<sup>a</sup>

|                                     | <u>Particulate</u>                  | Lead                                | Emission         |
|-------------------------------------|-------------------------------------|-------------------------------------|------------------|
| Process                             | kg(1b)/10 <sup>3</sup><br>batteries | kg(1b)/10 <sup>3</sup><br>batteries | Factor<br>Rating |
| Grid casting                        | 1.42<br>(3.13)                      | 0.35<br>(0.77)                      | В                |
| Paste mixing                        | 1.96<br>(4.32)                      | 1.13<br>(2.49)                      | В                |
| Lead oxide mill (baghouse outlet) b | 0.05<br>(0.11)                      | 0.05<br>(0.11)                      | С                |
| Three process operation             | 42.0<br>(92.6)                      | 4.79<br>(10.6)                      | В                |
| Lead reclaim furnace <sup>C</sup>   | 3.03<br>(6.68)                      | 0.63<br>(1.38)                      | В                |
| Dry formation <sup>d</sup>          | 14.7<br>(32.4)                      | NA                                  | $B_{\leftarrow}$ |
| Total production                    | 63.2<br>(139)                       | 6.94<br>(15.3)                      |                  |

<sup>&</sup>lt;sup>a</sup>References 1-7. NA = not applicable. Based on standard automotive batteries of about 11.8 kg (26 lb) of lead, of which approximately half is present in the lead grids and half in the lead oxide paste. Particulate emissions include lead and its compounds, as well as other substances. Lead emission factors are expressed as emissions of elemental lead.

bReference 5. Emissions measured for a well controlled facility (fabric filters with an average air:cloth ratio of 3:1) were 0.025 kg (0.055 lb) particulate/1000 batteries and 0.024 kg (0.053 lb) lead/1000 batteries. Factors represent emissions from a facility with typical controls (fabric filtration with an air:cloth ratio of about 4:1). Emissions from a facility with typical controls are estimated to be about twice those from a well controlled facility (Reference 1).

 $<sup>^{\</sup>mathrm{c}}$ Based on the assumption that about 1% of the lead processed at a typical battery plant is processed by the reclaim operation.

d For sulfates in aerosol form, expressed as sulfuric acid, and not accounting for water and other substances which might be present.

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- 5. Source Testing at a Lead Acid Battery Manufacturing Company ESB, Canada, Ltd., Mississauga, Ontario, EPA-76-3, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1976.
- 6. Emissions Study at a Lead Acid Battery Manufacturing Company ESB, Inc., Buffalo, NY, EPA-76-BAT-2, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1976.
- 7. Test Report Sulfuric Acid Emissions from ESB Battery Plant Forming Room,
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  Research Triangle Park, NC, 1977.

#### 8.23 METALLIC MINERALS PROCESSING

### 8.23.1 Process Description 1-6

Metallic mineral processing typically involves the mining of ore, either from open pit or underground mines; the crushing and grinding of ore; the separation of valuable minerals from matrix rock through various concentration steps; and at some operations, the drying, calcining or pelletizing of concentrates to ease further handling and refining. Figure 8.23-1 is a general flow diagram for metallic mineral processing. Very few metallic mineral processing facilities will contain all of the operations depicted in this Figure, but all facilities will use at least some of these operations in the process of separating valued minerals from the matrix rock.

The number of crushing steps necessary to reduce ore to the proper size will vary with the type of ore. Hard ores, including some copper, gold, iron and molybdenum ores, may require as much as a tertiary crushing. Softer ores, such as some uranium, bauxite and titanium/zirconium ores, require little or no crushing. Final comminution of both hard and soft ores is often accomplished by grinding operations using media such as balls or rods of various materials. Grinding is most often performed with an ore/water slurry, which reduces particulate emissions to negligible levels. When dry grinding processes are used, particulate emissions can be considerable.

After final size reduction, the beneficiation of the ore increases the concentration of valuable minerals by separating them from the matrix rock. A variety of physical and chemical processes is used to concentrate the mineral. Most often, physical or chemical separation is performed in an aqueous environment which eliminates particulate emissions, although some ferrous and titaniferous minerals are separated by magnetic or electrostatic methods in a dry environment.

The concentrated mineral products may be dried to remove surface moisture. Drying is most frequently done in natural gas fired rotary dryers. Calcining or pelletizing of some products, such as alumina or iron concentrates, are also performed. Emissions from calcining and pelletizing operations are not covered in this Section.

### 8.23.2 Process Emissions<sup>7-9</sup>

Particulate emissions result from metallic mineral plant operations such as crushing and dry grinding of ore; drying of concentrates; storing and reclaiming of ores and concentrates from storage bins; transfer of materials; and loading of final products for shipment. Particulate emission factors are provided in Table 8.23-1 for various metallic mineral process operations, including primary, secondary and tertiary crushing; dry grinding; drying; and material handling and transfer. Fugitive emissions are also possible from roads and open stockpiles, factors for which are in Section 11.2.

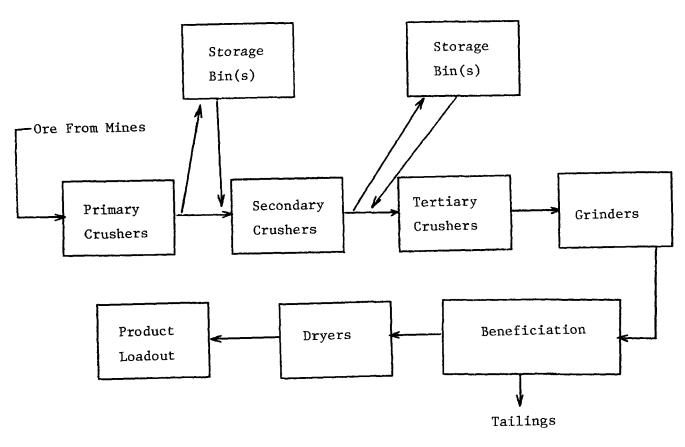


Figure 8.23-1. A metallic mineral processing plant.

The emission factors in Table 8.23-1 are for the process operations as a whole. At most metallic mineral processing plants, each process operation will require several types of equipment. A single crushing operation likely will include a hopper or ore dump, screen(s), crusher, surge bin, apron feeder, and conveyor belt transfer points. Emissions from these various pieces of equipment are often ducted to a single control device. The emission factors provided in Table 8.23-1 for primary, secondary and tertiary crushing operations are for process units that are typical arrangements of the above equipment.

Emission factors are provided in Table 8.23-1 for two types of dry grinding operations, those grinding operations that involve air conveying and/or air classification of material and those that involve screening of material without air conveying. Grinding operations that involve air conveying and air classification usually require dry cyclones for efficient product recovery. The factors in Table 8.23-1 are for emissions after product recovery cyclones. Grinders in closed circuit with screens usually do not require cyclones. Emission factors are not provided for wet grinders, because the high moisture content in these operations can reduce emissions to negligible levels.

8.23-2 EMISSION FACTORS 8/82

The emission factors for dryers in Table 8.23-1 include transfer points integral with the drying operation. A separate emission factor is provided for dryers at titanium/zirconium plants that use dry cyclones for product recovery and for emission control. Titanium/zirconium sand type ores do not require crushing or grinding, and the ore is washed to remove humic and clay material before concentration and drying operations.

At some metallic mineral processing plants, material is stored in enclosed bins between process operations. The emission factors provided in Table 8.23-1 for the handling and transfer of material should be applied to the loading of material into storage bins and the transferring of material from the bin. The emission factor will usually be applied twice to a storage operation, once for the loading operation and once for the reclaiming operation. If material is stored at multiple points in the plant, the emission factor should be applied to each operation and should apply to the material being stored at each bin. The material handling and transfer factors do not apply to small hoppers, surge bins or transfer points that are integral with crushing, drying or grinding operations.

At some large metallic mineral processing plants, extensive material transfer operations, with numerous conveyor belt transfer points, may be required. The emission factors for material handling and transfer should be applied to each transfer point that is not an integral part of another process unit. These emission factors should be applied to each such conveyor transfer point and should be based on the amount of material transferred through that point.

The emission factors for material handling can also be applied to final product loading for shipment. Again, these factors should be applied to each transfer point, ore dump or other point where material is allowed to fall freely.

Test data collected in the mineral processing industries indicate that the moisture content of ore can have a significant effect on emissions from several process operations. High moisture generally reduces the uncontrolled emission rates, and separate emission rates are provided for primary crushers, secondary crushers, tertiary crushers, and material handling and transfer operations that process high moisture ore. Drying and dry grinding operations are assumed to produce or to involve only low moisture material.

For most metallic minerals covered in this Section, high moisture ore is defined as ore whose moisture content, as measured at the primary crusher inlet or at the mine, is 4 weight percent or greater. Ore defined as high moisture at the primary crusher is presumed to be high moisture ore at any subsequent operation for which high moisture factors are provided, unless a drying operation precedes the operation under consideration. Ore is defined as low moisture when a dryer precedes the operation under consideration or when the ore moisture at the mine or primary crusher is less than 4 weight percent.

Separate factors are provided for bauxite handling operations, in that some types of bauxite with a moisture content as high as 15 to 18 weight percent can still produce relatively high emissions during material handling

UNCONTROLLED PARTICULATE EMISSION FACTORS FOR METALLIC MINERAL PROCESSES<sup>a</sup> TABLE 8.23-1.

|   | Low 1                       | Low moisture ore                             | High                        | High moisture ore                            |                              |
|---|-----------------------------|--|-----------------------------|--|------------------------------|
| Process   | Emissions<br>kg/Mg (lb/ton) | Particulate emissions < 10 µm kg/Mg (1b/ton) | Emissions<br>kg/Mg (1b/ton) | Particulate emissions < 10 µm kg/Mg (1b/ton) | Emission<br>Factor<br>Rating |
| Crushing<br>Primary   | 0.2 (0.5)                   | 0.02 (0.05)                                  | 0.01 (0.02)                 | 0.004 (0.009)                                | ပ                            |
| Secondary<br>Tertiary   | 0.6 (1.2)<br>1.4 (2.7)      | NA<br>0.08 (0.16)                            | 0.03 (0.05)                 | 0.012 (0.02)<br>0.001 (0.02)                 | ОВ                           |
| Wet grinding  | Negligible                  | 1  | Negligible                  | ŧ  |                              |
| Dry grinding<br>With air conveying and/or air<br>classification               | 14.4 (28.8)                 | 13.0 (26.0)                                  | ъ                           | ਚ  | U                            |
| Without air conveying or air classification                                   | 1.2 (2.4)                   | 0.16 (0.31)                                  | ď                           | Ū  | Q                            |
| Drying All minerals but titanium/ zirconium sands                             | 9.8 (19.7)                  | 5.9 (12.0)                                   | Q                           | ข  | ပ                            |
| Titanium/zirconium with cyclones  | 0.3 (0.5)                   | NA   | Q                           | æ  | ပ                            |
| Material handling and transfer<br>All minerals but bauxite<br>Bauxite/alumina | 0.06 (0.12)<br>0.6 (1.1)    | 0.03 (0.06)<br>NA                            | 0.005 (0.01)<br>NA          | 0.002 (0.006)<br>NA                          | ပပ                           |

NA = not available, Controlled particulate emission factors are discussed in Section 8.23.3. Defined in Section 8.23.2. References 9-12.

Based on weight of material entering primary crusher.

SO<sub>x</sub> emissions are fuel Based on weight of material entering grinder. Factors are the same for both high moisture and low moisture ores, because material is based on weight of material exiting dryer. Factors are the same for both high moisture and low moisture ores. usually dried before entering grinder.

Based on weight of material transferred. Applies to each loading or unloading operation and to each conveyor belt transfer point.

Bauxite with moisture content as high as 15 - 18% can exhibit the emission characteristics of low moisture ore. Use low moisture factor for bauxite unless material exhibits obvious sticky, nondusting characteristics. dependent (see Chapter 1). NOx emissions depend on burner design, combustion temperature, etc. (see Chapter 1)

procedures. These emissions could be eliminated by adding sufficient moisture to the ore, but bauxite then becomes so sticky that it is difficult to handle. Thus, there is some advantage to keeping bauxite in a relatively dusty state, and the low moisture emission factors given represent conditions fairly typical of the industry.

Particulate matter size distribution data for some process operations have been obtained for control device inlet streams. Since these inlet streams contain particulate matter from several activities, a variability has been anticipated in the calculated size specific emission factors for particulates.

Emission factors for particulate matter equal to or less than  $10\mu m$  aerodynamic diameter, from a limited number of tests performed to characterize the processes, are presented in Table 8.23-1.

In some plants, particulate emissions from multiple pieces of equipment and operations are collected and ducted to a control device. Therefore, examination of reference documents is recommended before application of the factors to specific plants.

Emission factors for particulate matter equal to or less than 10µm from high moisture primary crushing operations and material handling and transfer operations were based on test results usually in the 30 to 40 weight percent range. However, high values were obtained for high moisture ore at both the primary crushing and the material handling and transfer operations, and these were included in the average values in the Table. A similarly wide range occurred in the low moisture drying operation.

Several other factors are generally assumed to affect the level of emissions from a particular process operation. These include ore characteristics such as hardness, crystal and grain structure, and friability. Equipment design characteristics, such as crusher type, could also affect the emissions level. At this time, data are not sufficient to quantify each of these variables.

#### 8.23.3 Controlled Emissions $^{7-9}$

Emissions from metallic mineral processing plants are usually controlled with wet scrubbers or baghouses. For moderate to heavy uncontrolled emission rates from typical dry ore operations, dryers and dry grinders, a wet scrubber with pressure drop of 1.5 to 2.5 kilopascals (6 to 10 inches of water) will reduce emissions by approximately 95 percent. With very low uncontrolled emission rates typical of high moisture conditions, the percentage reduction will be lower (approximately 70 percent).

Over a wide range of inlet mass loadings, a well designed and maintained baghouse will reduce emissions to a relatively constant outlet concentration. Such baghouses tested in the mineral processing industry consistently reduce emissions to less than 0.05 grams per dry standard cubic meter (0.02 grains per dry standard cubic foot), with an average concentration of 0.015 g/dscm (0.006 gr/dscf). Under conditions of moderate to high uncontrolled emission rates of typical dry ore facilities, this level of

controlled emissions represents greater than 99 percent removal of particulate emissions. Because baghouses reduce emissions to a relatively constant outlet concentration, percentage emission reductions would be less for baghouses on facilities with a low level of uncontrolled emissions.

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8.23-6 EMISSION FACTORS 8/82

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