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Sources and Control of Volatile Organic Air Pollutants

Student Manual

APTI Course 482
Third Edition

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Crowder Environmental Associates, Inc.

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1 Introduction

Title 40 of the Code of Federal Regulations, Part 51, Subpart F, Section 51.100, defines a volatile organic compound (VOC) as "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions." Organic compounds that have been shown to have negligible photochemical reactivity and, therefore, and not classed as VOCs include:

- Methane
- Ethane
- Methylene chloride (dichloromethane)
- 1,1,1-trichloroethane (methyl chloroform)
- 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
- Trichlorofluoromethane (CFC-11)
- Dichlorodifluoromethane (CFC-12)
- Chlorodifluoromethane (HCFC-22)
- Trifluoromethane (HFC-23)
- 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114)
- Chloropentafluoroethane (CFC-115)
- 1,1,1-trifluoro-2,2-dichloroethane (HCFC-123)
- 1,1,1,2-tetrafluoroethane (HFC-134a)
- 1,1-dichloro-1-fluoroethane (HCFC-141b)
- 1-chloro-1,1-difluoroethane (HCFC-142b)
- 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124)
- Pentafluoroethane (HFC-125)
- 1,1,2,2-tetrafluoroethane (HFC-134)
- 1,1,1-trifluoroethane (HFC-143a)
- 1,1-difluoroethane (HFC-152a)
- Parachlorobenzotrifluoride (PCBTF)
- Cyclic, branched, or linear, completely methylated siloxanes
- Acetone
- Perchloroethylene (tetrachloroethylene)
- 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca)
- 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb)
- 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee)
- Difluoromethane (HFC-32)

- Ethylfluoride (HFC-161)
- 1,1,1,3,3,3-hexafluoropropane (HFC-236fa)
- 1,1,2,2,3-pentafluoropropane (HFC-245ca)
- 1,1,2,3,3-pentafluoropropane (HFC-245ea)
- 1,1,1,2,3-pentafluoropropane (HFC-245eb)
- 1,1,1,3,3-pentafluoropropane (HFC-245fa)
- 1,1,1,2,3,3-hexafluoropropane (HFC-236ea)
- 1,1,1,3,3-pentafluorobutane (HFC-365mfc)
- Chlorofluoromethane (HCFC-31)
- 1-chloro-1-fluoroethane (HCFC-151a)
- 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a)
- 1,1,1,2,2,3,3,4,4—nonafluoro-4-methoxy-butane ($C_4F_9OCH_3$)
- 2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ($(CF_3)_2CFCF_2OCH_3$)
- 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane ($C_4F_9OC_2H_5$)
- 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ($(CF_3)_2CFCF_2OC_2H_5$)
- Methyl acetate and perfluorocarbon compounds which fall into these classes:

  a. Cyclic, branched, or linear, completely fluorinated alkanes

  b. Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations

  c. Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations

  d. Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine

The purpose of this course is to provide information to regulators and to the regulated community on sources of volatile organic compounds and techniques for controlling their emission to the atmosphere. The focus of the material is on the reduction of VOCs for the purpose of attaining or maintaining the National Ambient Air Quality Standard (NAAQS) for ozone. From 1989 to 1998, peak ambient 1-hour average ozone concentrations in the United States declined by 4 percent, and the average number of days when the daily maximum 1-hour average concentration exceeded the NAAQS decreased by 62 percent. However, in 1999 there were still 32 areas of the country, with a population of approximately 92,505,000 people, that had not yet attained the NAAQS.

In Chapter 2, the reader is provided with information on properties and fundamentals of volatile organic compounds that will aid in understanding the material presented in this course. This chapter is divided into three sections: a brief review of organic chemistry, an overview of the role that VOCs play in the formation of ozone and photochemical smog, and a discussion of important properties of organic vapors.

A source that emits VOCs into the atmosphere must maintain emissions at or below levels that are set forth in the applicable standards. Compliance testing is one method by which these emissions are documented. In Chapter 3, three methods for measuring VOC stack emissions are summarized: Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography; Method 25, Determination of Total Gaseous Non-Methane Organic Emissions as Carbon; and Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer.

In order to gain an understanding of the importance of various VOC source categories, it is useful to explore emissions on a national level. Chapter 4 examines VOC emission trends over about the past one hundred years and the recent emissions in each state. It also looks at a recent national emission inventory for anthropogenic emissions and the total emissions attributed to biogenic sources. Finally, the regulatory approach that is taken at the Federal level to reduce VOC emissions is discussed.

Chapters 5 and 6 and Chapters 8 through 12 discuss VOC source categories that are significant either because of their contribution to national emissions or because they are ubiquitous. Each of these chapters follows the same format. First, the process is described and the nature and sources of emissions from the process are discussed. Next, methods for reducing VOC emissions from the source are presented. Next, applicable RACT recommendations and NSPS and MACT regulatory requirements are discussed. Finally, inspection items that will aid in determining whether the emission reduction techniques are functioning properly are presented. It should be emphasized that the emission regulations that are presented in each chapter are for the purpose of illustrating the types of regulations that are imposed at different levels and are not meant to be comprehensive. The reader is referred to applicable statutes for details of the regulatory requirements and for regulations that may have been promulgated since this text was prepared.

The most significant source of national VOC emissions is surface coating, and this is discussed in Chapter 5. The topics covered include surface preparation, coating types, methods for applying the coatings, and curing methods. Conceptually related to surface coating is the graphic arts industry discussed in Chapter 6. The printing processes covered in this chapter include offset lithography, flexography, rotogravure, and screen printing. Chapter 7 deals with the calculation of the VOC content of coating and inks. Techniques are presented for using the unit balance approach to take information on coating and ink composition and determine the VOC content in the units of typical standards and to determine the VOC reduction achieved by a coating or ink change.

The petroleum industry, including the storage and transport of refined products, is the second most significant source of national VOC emissions.

Petroleum refining is covered in Chapter 8. The complexity of this industry is dealt with by dividing the various refining operations into separation processes, conversion processes, treatment processes and auxiliary processes, and then discussing important processing units within each category. Chapter 9 addresses the storage of volatile organic liquids in fixed roof, internal floating roof and external floating roof tanks, and the distribution of gasoline to bulk terminals, bulk plants, service stations, and to the ultimate user, the automobile.

Chapters 10–12 discuss sources of VOC emissions that are significant primarily because they are ubiquitous. Chapter 10 covers degreasing processes that use cold cleaners, vapor cleaners and in-line cleaners that contain organic solvents. Chapter 11 discusses dry cleaning processes that use chlorinated or petroleum solvents. The use of liquid asphalt to prepare paving materials is addressed in Chapter 12.

Finally, control equipment that can be used to reduce VOC emissions is discussed in Chapter 13. The devices covered are carbon adsorbers, flares, thermal and catalytic oxidizers, condensers, and bioreactors. The operating principles of each device are presented, along with a discussion of parameters that are important to their performance.

References

"National Air Quality and Emissions Trends Report, 1998", EPA 450/R-00-003, March 2000.

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2 Properties and Fundamentals

Organic compounds constitute the largest class of materials described in the field of chemistry. They are composed of carbon and other elements, such as hydrogen, oxygen, nitrogen and chlorine, and they exist as solids, liquids or gases. Some of these compounds are found or produced in nature, but many more have been synthetically developed to serve some need. The environmental effects of these materials are difficult to assess, but two important facts are known:

- Organic compounds volatile enough to be emitted into the atmosphere can contribute to the formation of ozone and photochemical oxidants.
- Organic compounds can have toxic effects on plant and animals.

In order to provide a basis for further study of the industries that produce and emit these materials, this chapter will provide a brief review of organic chemistry, an overview of the role that VOCs play in the formation of ozone and photochemical smog, and a discussion of important properties of organic vapors.

2.1 Review of Organic Chemistry

Organic chemistry is the chemistry of the compounds of carbon. The total number of known organic compounds exceeds 8 million. For comparison, the number of known chemical compounds formed by all other elements except carbon, the inorganic compounds, is approximately 300,000. One reason for the large number of organic compounds is the unique ability of carbon atoms to combine with one another to form carbon-carbon chains that may be straight, branched or cyclic. Another reason is that carbon is capable of combining with many other elements. The carbon atom can combine with the atoms of such widely different elements as oxygen, hydrogen, chlorine, nitrogen, sulfur, and other non-metals, or even with the atoms of metals.

The carbon atom has an atomic number of 6 and an atomic weight of 12. It has 6 electrons, 4 of which are valence electrons that are involved in the formation of bonds. Carbon forms compounds by sharing electrons with other atoms to form covalent bonds. Two carbon atoms, or a carbon atom and an atom of another element, may combine by sharing a pair of electrons, with one electron donated by each of the atoms. This linkage is called a single covalent bond, or simply a single bond. Two carbon atoms, or a carbon atom and an atom of another element, may also combine by sharing two pairs of electrons, with each atom donating two electrons to form two covalent bonds. This type of linkage is called a double covalent bond, or simply a double bond. Another way in which two carbon atoms, or a carbon atom and an atom of another element, may combine is by sharing three pairs of electrons, with each atom donating three electrons to form three covalent bonds. This linkage is called a triple covalent bond, or simply a triple bond. This ability of carbon atoms to combine with one another and with other atoms in various ways accounts, in part, for the great number of organic compounds.

Organic compounds may be represented by molecular formulas, structural formulas or semi-structural formulas. These are illustrated in Figure 2-1. The molecular formula of a compound simply shows the composition of the molecule. However, the structural formula shows how all of the component atoms are bonded together. The semi-structural formula is an abbreviated form of the structural formula.

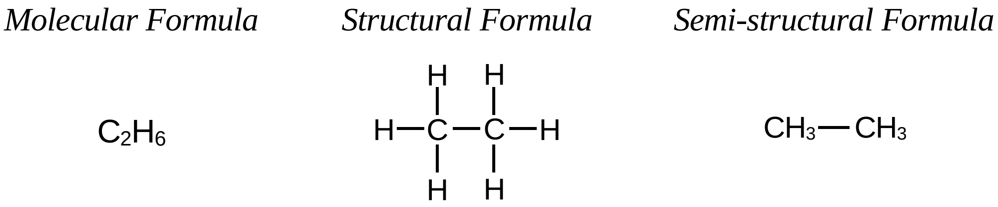


Figure 2-1. Molecular, structural and semi-structural formulas

2.1.1 Hydrocarbons

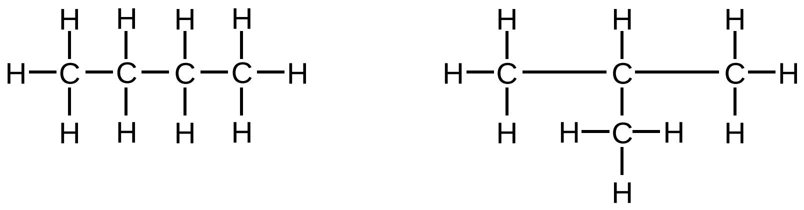
Hydrocarbons are simply compounds that are formed only from carbon and hydrogen. However, because of the different types of bonds that are possible and because of the ability of carbon to form straight, branched or ringed structures, a variety of hydrocarbon compounds are possible.

2.1.1.1 Alkanes

If the carbon atoms are linked together only by single covalent bonds, the compound is referred to as a saturated hydrocarbon, because it contains the maximum proportion of hydrogen. The first five saturated hydrocarbons are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}) and pentane (C_5H_{12}). The formulas for these compounds may be expressed with a simple algebraic formula, C_nH_{2n+2}, where n ranges from 1 to over 1000. Saturated hydrocarbons of the general formula C_nH_{2n+2} are also known as the paraffin hydrocarbons or as the alkanes.

In comparing the molecular formulas of each compound in the alkane series, we find that there is a constant difference of one CH_2 group between each pair. A series of carbon compounds in which each member differs from the preceding member by a CH_2 group is known as an homologous series, and each member of the series is called a homologue. As one would expect, there is a steady gradation of properties from one homologue to the next. For example, boiling point and density increase regularly through a homologous series.

There is only one structural representation for the first three members of the alkane series. However, for the next member of the series, butane, there is the possibility of different structural formulas for the same molecular formula. The molecular formula, C_4H_{10}, only describes a molecule that contains four carbon atoms and ten hydrogen atoms. It does not tell us how these atoms are linked together. By writing down all the ways that four carbon atoms and ten hydrogen atoms could be joined together, we find that there are two, and only two, possible molecules. These are shown in Figure 2-2. Two or more different compounds that are represented by the same molecular formula are called isomers. As the number of atoms in the molecule increases, the number of possible isomers also increases. All saturated hydrocarbons that contain four or more carbon atoms exist as isomers. Saturated hydrocarbons that contain five or more carbon atoms always exist as more than two isomers. Here, compound (a) is called normal butane, or n-butane, and compound (b) is called isobutane, or i-butane. Although they have the same molecular formula, because of their different structures they have different properties. For example, the boiling point of n-butane is 31.1°F, while that of i-butane is 10.9°F.



(a) (b)

Figure 2-2. Isomers of butane

2.1.1.2 Alkenes

Hydrocarbons that contain one double bond, with all the rest of the carbon atoms linked by single bonds, are called olefins. Olefins are important reactants in the generation of ozone and photochemical oxidants, because the double bond provides a reactive site where the molecule can be broken apart or formed into other species. Olefins belong to a class of compounds called unsaturated hydrocarbons. They are called unsaturated because they contain less than the maximum possible proportion of hydrogen. Ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8) and pentylene (C_5H_{10}) are the first four members of the homologous series known as the olefin series or as the alkenes. Again, each member of the series has one more CH_2 group than the preceding member. The general formula for the olefin series is C_nH_{2n}.

Hydrocarbons that contain two double bonds, with all the rest of the carbon atoms linked by single bonds, are called diolefins. The general formula for the diolefin series is C_nH_{2n-2}. Two examples of diolefin compounds are shown in Figure 2-3.

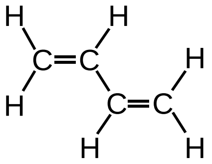
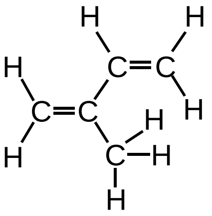
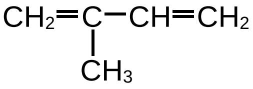
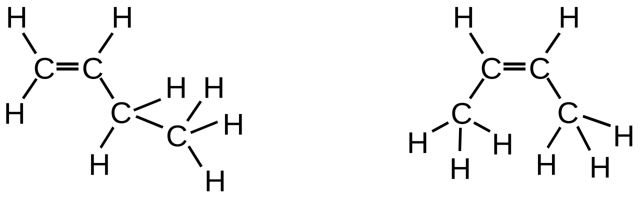
Molecular Formula	***Name***	***Structural Formula***	***Semi-structural Formula***
C_4H_6	butadiene		$CH_2{=}CH{-}CH{=}CH_2$
C_5H_8	2-methyl butadiene		 $CH_2{=}C(CH_3){-}CH{=}CH_2$

Figure 2-3. Examples of diolefin compounds

Olefins also exhibit isomerism. In addition to the structural differences due to branching that is seen in saturated hydrocarbons, olefin series isomerism may occur from different positions of the double bond. An example of this is shown in Figure 2-4 for butylene. One isomer of butylene has the double bond between the first and second carbons, while the second isomer has the double bond between the second and third carbons. These are the only two isomers of butylene.


(a)

(b)

Figure 2-4. Butylene isomers

2.1.1.3 Alkynes

Another homologous series of unsaturated hydrocarbons is the acetylene or alkyne series. All members of this series contain one triple bond, with the rest of the carbon atoms linked by single bonds. Again, each member of the series has one more CH_2 group than the preceding member. The first four members of this series are ethyne or acetylene (C_2H_2), propyne (C_3H_4), butyne (C_4H_6) and pentyne (C_5H_8). The general formula for the alkyne series is C_nH_{2n-2}.

2.1.1.4 Cyclic Compounds

Another special property of carbon is the ability of carbon chains to turn back on themselves to form rings. If the carbon atoms are linked only by single bonds, the resulting ring compounds form a homologous series called the cycloparaffins, where, again, each member has one more CH_2 group that the preceding member. Examples of cycloparaffin compounds are shown in Figure 2-5. Their general formula is C_nH_{2n}.

Cyclopropane

Cyclobutane

Cyclopentane

Cyclohexane

Figure 2-5. Examples of cycloparaffin compounds

Benzene, C_6H_6, shown in Figure 2-6, is a ring compound that is typical of a class of compounds know as aromatic hydrocarbons because many of them have a pronounced odor. Although the bonding is shown in Figure 2-6a as alternating single and double bonds around the ring, the electrons associated with the bonds are actually spread evenly around the ring, as indicated in Figure 2-6b. This delocalization of electrons creates a very stable structure.

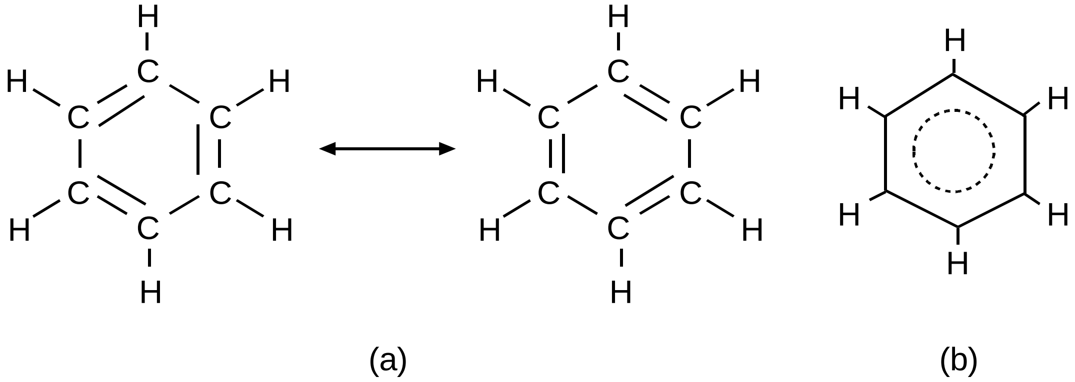


Figure 2-6. Benzene structure

Benzene rings can also be combined to each other. One way of doing this is to join carbon atoms from two benzene or phenyl rings by a single bond to obtain a biphenyl (Figure 2-7). Another way is to produce a network of ring structures such as that show in Figure 2-8. These compounds are called polynuclear aromatics (PNA) or, more recently, polycyclic aromatic hydrocarbons (PAHs). The electrons in these structures are delocalized as they are in benzene.

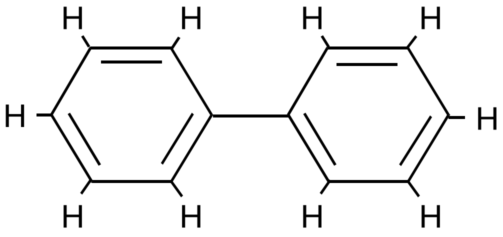


Figure 2-7. Biphenyl

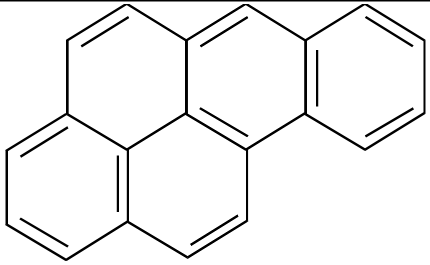


Figure 2-8. Benzo (α) pyrene

2.1.2 Nomenclature

Because of the variety and complexity of organic compounds, nomenclature plays an important role in organic chemistry. So far, we have emphasized the family names of organic compounds. Now we will examine how individual members of a homologous series are named.

The names of many organic compounds are related to the names of the paraffin hydrocarbons. For example, the radical CH_3^-, formed by the loss of one hydrogen atom from methane, is called the methyl radical. Similarly, the ethyl radical, $C_2H_5^-$, is the radical formed by the loss of one hydrogen atom from ethane. Propane may lose a hydrogen atom from either a terminal carbon or from the middle carbon, producing n-propyl or i-propyl radicals, respectively.

Another part of the name of complex organic compounds are the elements or groups of elements that are attached to the hydrocarbon radicals. These are known as functional groups. Some examples of functional groups are the –OH group for alcohols, the $–NH_2$ group for amines, the –SH group for mercaptans, and the –Cl for organic chlorides. The functional group located on a hydrocarbon chain or ring determines the principal chemical properties of the molecule. When a discussion centers around the properties of the functional group and not of the hydrocarbon radical, the radical is often merely represented by the symbol R-. For example, the symbol R-OH or ROH is a general expression for alcohols.

The location of the substitution of a functional group onto a hydrocarbon radical will also affect the properties of the resulting compound. Thus, for many compounds, not only are the number and type of substituted functional groups included in the name, but also the number of the carbon atom or atoms where the substitution is made. For example, 1,1,1-trichloroethane indicates that three chlorine atoms are substituted for the hydrogen atoms on the first carbon of an ethyl radical. Likewise, 2-propylamine indicates that an amine functional group is substituted for one of the hydrogen atoms on the second carbon of a propyl radical. When all of the hydrogen atoms have been substituted by a functional group, the term "per" is used. Thus, 1,1,2,2-tetrachloro-ethylene is also referred to as perchloroethylene.

Finally, it should be recognized that many organic compounds have common names. Ethyne, for example, is also known as acetylene, 1,1,1-trichloroethane is also known as methyl chloroform and chloroethene is also known as vinyl chloride.

2.1.3 Hydrocarbon Derivatives

Despite their diversity, organic compounds that contain only carbon and hydrogen account for less than about 5 percent of all known organic compounds. More than about 95 percent of organic compounds are composed for carbon, hydrogen and some other element or elements. Of primary importance to the environmental scientist are the classes of organic compounds that contain oxygen, halides, nitrogen or sulfur.

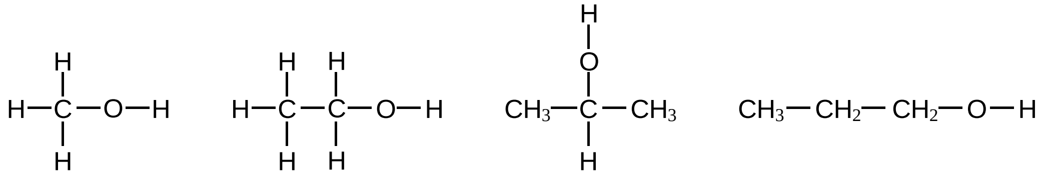
2.1.3.1 Organic Compounds Containing Oxygen

Oxygen has two valence electrons that it can share with other atoms to form covalent bonds. It may share both of those electrons with a single carbon atom to form a double bond, or it may share a single electron with each of two carbon atoms to form two single bonds. It may also share one electron in a single bond with a carbon atom and one electron in a single bond with a hydrogen atom. The result of these bonding options is the formation of six functional groups that characterize the classes of organic compounds that contain oxygen. These functional groups are summarized in Table 2-1.

Table 2-1.
Functional groups containing oxygen

Group	Compound Class	Group	Compound Class
$-O-H$	Alcohols	$-\overset{\overset{O}{\|}}{C}-$	Ketones
$-O-$	Ethers		
$-\overset{\overset{O}{\|}}{C}-H$	Aldehydes	$-\overset{\overset{O}{\|}}{C}-O-H$	Organic Acids
		$-\overset{\overset{O}{\|}}{C}-O-$	Esters

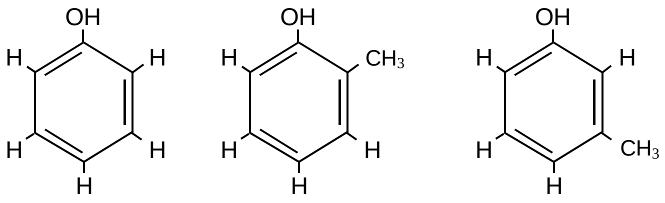
The compounds derived from hydrocarbons by the substitution of an –OH group for a hydrogen atom are called alcohols. In these compounds, the oxygen atom shares one electron with a carbon atom and the other one with a hydrogen atom. Common alcohols are shown in Figure 2-9. Methyl alcohol, or methanol, is sometimes called wood alcohol, because it was once obtained by the destructive distillation of wood.



Methyl alcohol *Ethyl alcohol* *Isopropyl alcohol (Isopropanol)* *n-propyl alcohol*

Figure 2-9. Common alcohols

Ethyl alcohol, or ethanol, is frequently called grain alcohol, because it can be produced by the fermentation of grain. Aromatic alcohols can also be made and are called phenols (Figure 2-10). Phenols tend to behave more like acids than alcohols, because of the properties of the benzene ring. More than one hydrogen atom can be replaced by an –OH group to form compounds called polyhydric alcohols. If these are to be stable organic compounds, the –OH groups must be attached to different carbon atoms. Examples of polyhydric alcohols are shown in Figure 2-11. Ethylene glycol, or simply glycol, is commonly used as an antifreeze; and glycerol, or glycerine, is used in the preparation of cosmetics.



Phenol Ortho-cresol (o-cresol) Meta-cresol (m-cresol)

Figure 2-10. Phenols

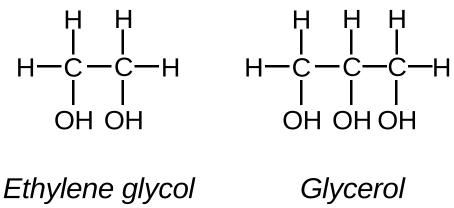


Figure 2-11. Polyhydric alcohols

Ethers form a class of compounds where the oxygen atom shares each of its electrons with a different carbon atom. They have the general form R-O-R, where the hydrocarbon radicals, R, may be the same or they may be different. Diethyl ether, CH_3CH_2-O-CH_2CH_3, is an ether well known as an anesthetic. An example of a mixed ether is methyl ethyl ether, CH_3-O-CH_2CH_3. A special group of ethers, known as cyclic ethers, are important in the plastics industry for making epoxides and other compounds. Two compounds representative of this group are ethylene oxide and propylene oxide (see Figure 2-12).

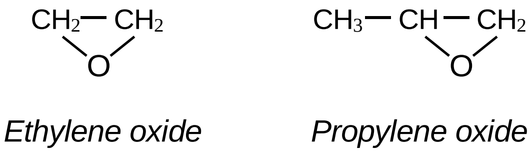
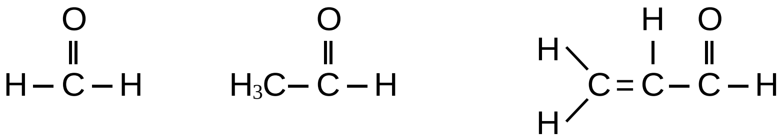


Figure 2-12. Cyclic ethers

Aldehydes are organic compounds whose molecules contain a terminal carbon atom singly bonded to a hydrogen atom and doubly bonded to an oxygen atom. They compose a group of compounds that contribute significantly to the generation of photochemical smog. Whether emitted directly into the atmosphere or produced in atmospheric oxidation reaction sequences, aldehydes provide numerous pathways for the generation of photochemical oxidants. Examples of aldehydes are shown in Figure 2-13. The simplest aldehyde is formaldehyde, which is used extensively as an embalming chemical. Attaching the aldehyde functional group to a methyl radical gives the next simplest aldehyde, acetaldehyde. A more complicated aldehyde, acrolein, is found in photochemical smog and is quite reactive.



$H-\overset{\overset{O}{\|}}{C}-H$ $H_3C-\overset{\overset{O}{\|}}{C}-H$

Formaldehyde *Acetaldehyde* *Acrolein*

Figure 2-13. Aldehydes

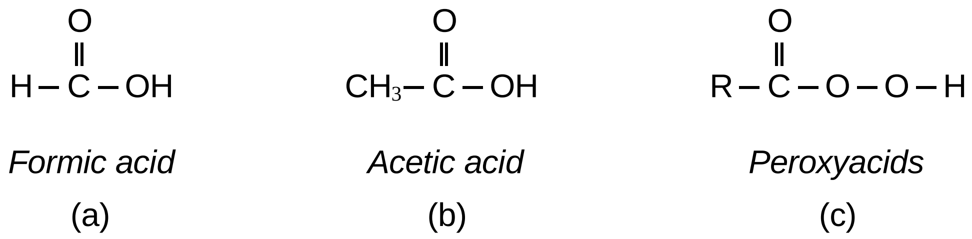
Ketones are widely used as industrial solvents and are closely related to aldehydes, for they both contain the carbonyl group, C=O. Consequently, these two classes of compounds have a great many properties in common. Like aldehydes, ketones are atmospherically reactive and contribute to the formation of photochemical smog. Two common ketones are shown in Figure 2-14.

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

Acetone *Methyl ethyl ketone (MEK)*

Figure 2-14. Ketones

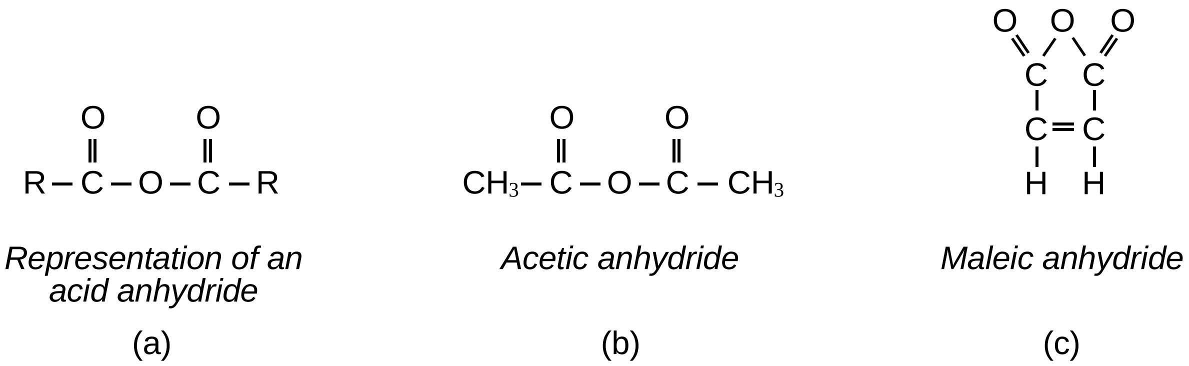
A compound that contains a terminal carbon atom that is doubly bonded to an oxygen atom and singly bonded to an –OH group is called an organic acid. Since this functional group is called the carboxylic acid group, organic acids are also known as carboxylic acids. The simplest organic acid is formic acid (see Figure 2-15a). Acetic acid, found in vinegar, is shown in Figure 2-15b. Another type of acid, the peroxyacid, has an extra oxygen atom to give them the form shown in Figure 2-15c. Peroxyacids are generated in photochemical smog and are extremely reactive, being able to break apart and initiate chain reactions.



Formic acid (a) Acetic acid (b) Peroxyacids (c)

Figure 2-15. Acids

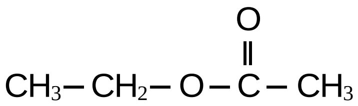
Acid anhydrides are derivatives of organic acids. They are formed from the intermolecular dehydration of two acids, hence the term anhydride. The structure of an acid anhydride is shown in Figure 2-16a. Maleic anhydride (see Figure 2-16c) is an example of a cyclic anhydride and is used in the production of chemicals and plastics.



Representation of an acid anhydride (a) Acetic anhydride (b) Maleic anhydride (c)

Figure 2-16. Acid anhydrides

Esters are compounds that have a non-terminal carbon atom that is singly bonded to one oxygen atom and doubly bonded to another. They are formed by the intermolecular dehydration of an alcohol and an organic acid. For example, ethyl alcohol, CH_3CH_2OH, reacts with acetic acid, CH_3COOH, to give ethyl acetate (see Figure 2-17) and water. The esters are pleasant smelling compounds responsible for the flavor and fragrance of many fruits.



$$CH_3-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Figure 2-17. Ethyl acetate

2.1.3.2 Organic Compounds Containing Halides

Organic compounds containing halides (chlorine, fluorine, bromine and iodine) are widely used as solvents, refrigerants, propellants, anesthetics and as starting compounds for producing other chemicals. Unfortunately, many of them cause serious environmental problems. In addition to contributing to toxicological problems, some compounds in this class have been implicated in the problem of the depletion of the stratospheric ozone layer.

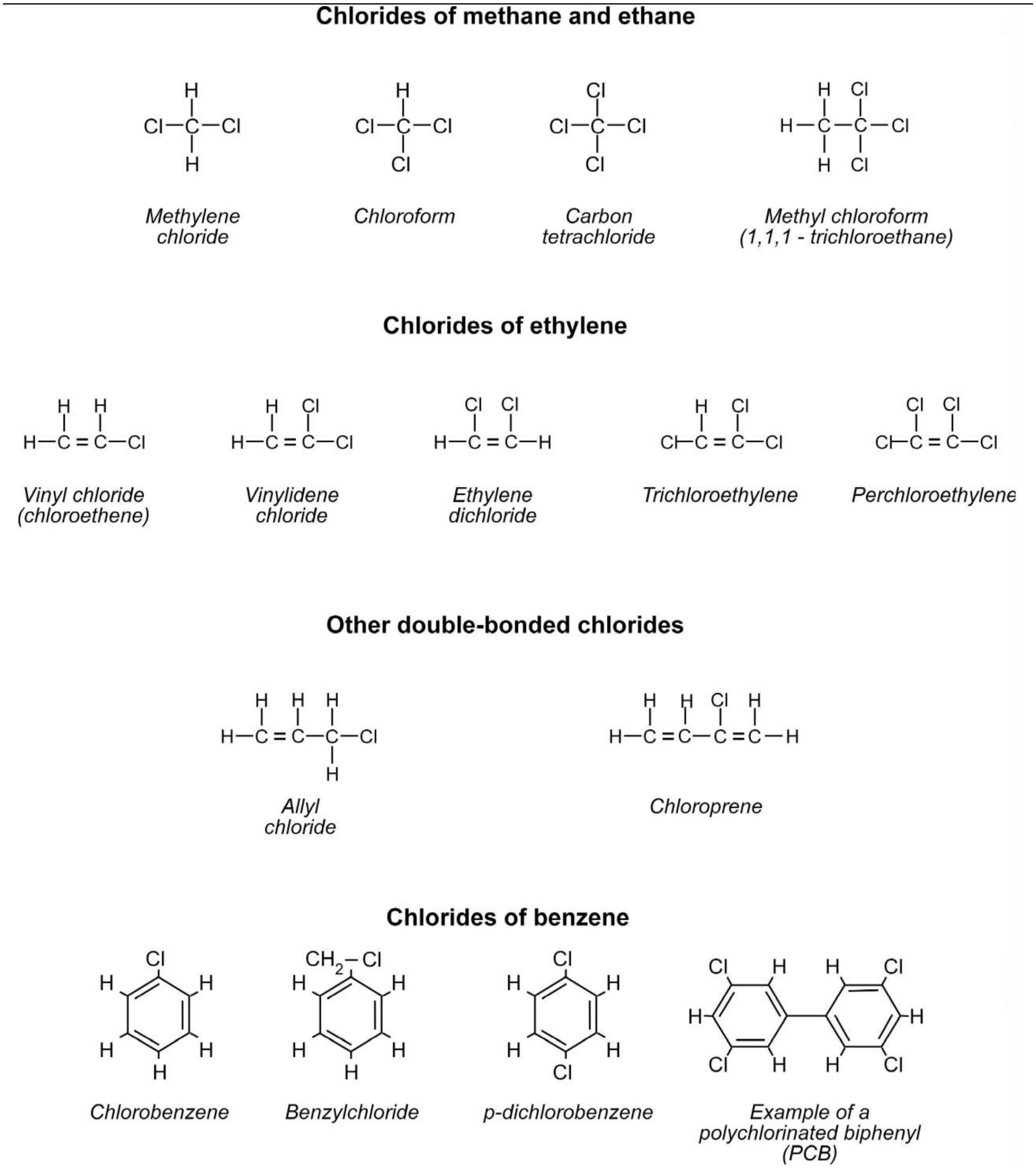
The simplest organic halide is formed when one hydrogen atom from methane, the simplest of the hydrocarbons, is replaced by a halogen atom. When that halogen atom is chlorine, methyl chloride (CH_3Cl) is formed. When the halogen atom is fluorine, bromine or iodine, then methyl fluoride (CH_3F), methyl bromide (CH_3Br) or methyl iodide (CH_3I), respectively, are formed. More complex organic halides can be formed by the substitution of two or more halogen atoms, either the same or different, for the hydrogen atoms of alkanes, alkenes, alkynes and the cyclic compounds. Several examples of organic chlorides are shown in Figure 2-18. Some common chlorofluorocarbons are shown in Figure 2-19. Compounds that contain combinations of carbon, hydrogen, oxygen and halides can also be prepared. Figure 2-20 shows examples of some that are of serious concern.

2.1.3.3 Organic Compounds Containing Nitrogen

Organic compounds that contain nitrogen constitute another important class of substances for the environmental scientist. Amines are odorous materials and have often been the subject of nuisance complaints. The organic nitrates are end products in photochemical oxidation reactions and are responsible for many of the adverse effects of photochemical smog.

Nitrogen has the capability of sharing either three or five electrons with other atoms. The simplest organic nitrogen compounds are the amines, which may be considered as derivatives of ammonia, NH_3. These compounds share three electrons with either carbon or hydrogen. When one hydrogen atom of NH_3 is replaced by a hydrocarbon radical, the resulting compound is called a primary amine and is represented by the general formula RNH_2. Methyl amine (CH_3NH_2) and ethyl amine ($C_2H_5NH_2$) are both examples of primary amines. When two hydrogen atoms are replaced by hydrocarbon radicals, the compound is called a secondary amine and has the general formula R_2NH. Methyl ethyl amine ($(CH_3)(C_2H_5)NH$) and diethyl amine ($(C_2H_5)_2NH$) are examples of secondary amines. The replacement of all three hydrogen atoms with hydrocarbon radicals forms a tertiary amine of the general formula R_3N. Methyl diethyl amine ($(CH_3)(C_2H_5)_2N$) and triethyl amine ($(C_2H_5)_3N$) are examples of tertiary amines.

The more complicated organic nitrogen compounds are those where the nitrogen shares five electrons with other atoms. These include the organic nitro compounds, which have the general formula $R\text{-}NO_2$; and the organic nitrates, which have the general formula $R\text{-}ONO_2$. Nitroethane ($CH_3CH_2\text{-}NO_2$) and ethyl nitrate ($CH_3CH_2\text{-}ONO_2$) are examples of two compounds from this group that are found in photochemical smog. Two important photochemical oxidants from this group are peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN). Both of the compounds, shown in Figure 2-21, are strong eye irritants and cause plant damage.



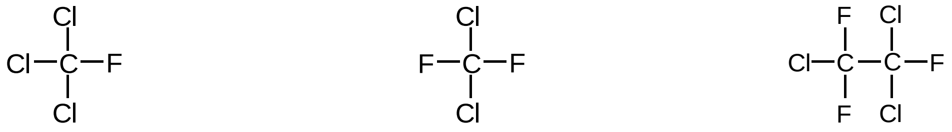
Chlorides of methane and ethane

Chlorides of ethylene

Other double-bonded chlorides

Chlorides of benzene

Figure 2-18. Organic Chlorides



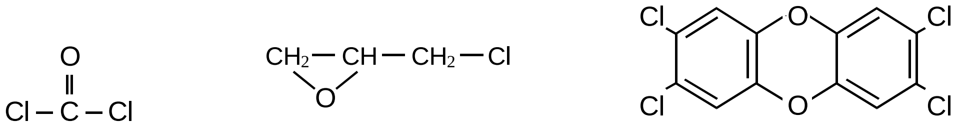
$$\begin{array}{c} Cl \\ | \\ Cl-C-F \\ | \\ Cl \end{array} \qquad \begin{array}{c} Cl \\ | \\ F-C-F \\ | \\ Cl \end{array} \qquad \begin{array}{c} F\ \ \ Cl \\ |\ \ \ \ | \\ Cl-C-C-F \\ |\ \ \ \ | \\ F\ \ \ Cl \end{array}$$

Trichlorofluormethane
(Freon 11)

Dichlorodifluoromethane
(Freon 12)

Trichlorotrifluoroethane
(Freon 13)

Figure 2-19. Chloroflurocarbons



$$Cl-\overset{\overset{O}{\|}}{C}-Cl$$

Phosgene

(a)

Epichlorohydrin

(b)

Dioxin (TCDD)
2,3,7,8, tetrachlorodibenzo-p-dioxin

(c)

Figure 2-20. Compounds containing both oxygen and chlorine

$$CH_3-\overset{\overset{O}{\|}}{C}-O-O-NO_2 \qquad C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-NO_2$$

Peroxyacetyl nitrate

Peroxybenzoyl nitrate

Figure 2-21. PAN and PBN compounds

2.1.3.4 Organic Compounds Containing Sulfur

Kraft pulp mills produce a large number of by-product chemicals in the paper-making process. The sodium sulfide used in these operations reacts with the organic matter in wood chips to produce organic compounds that contain sulfur. One group of these, the mercaptans, has the structure R-SH, which is similar to alcohols. Methyl mecaptan (CH_3SH) has a distinctive, unpleasant odor at very low concentrations. Dimethyl sulfide (CH_3SCH_3) is also a malodorous product of this process. These compounds cause more of a nuisance problem than a problem to public health.

2.2 Formation of Ozone and Photochemical Smog

Photochemical reactions are initiated by the absorption of a photon of energy ($h\nu$) by an atom, molecule, free radical or ion. The first step of a photochemical reaction may be written:

$$A \xrightarrow{h\nu} A^* \qquad (2\text{-}1)$$

Where A* is an excited state of A. The excited molecule may reduce its energy level through dissociation, direct reaction with another molecule, fluorescence, or through collisional deactivation with an energy-absorbing molecule. The mechanism that is most important in atmospheric photochemical reactions is dissociation:

$$A^* \rightarrow B + C + \cdots \qquad (2\text{-}2)$$

The energy for atmospheric photochemical dissociation reactions comes from the sun. In the troposphere, the wavelength range of interest is approximately 280 nm to 730 nm, since stratospheric oxygen and ozone block out most of the ultraviolet radiation below 280 nm and because no photochemical reactions of interest take place at wavelengths above 730 nm.

The major variable that affects these reactions is the change in intensity that occurs with latitude, time of day, time of year, and with the presence of clouds or aerosols. In the U.S., the maximum noontime intensity does not vary significantly with latitude during the summer months. In the 300 nm to 400 nm range, the maximum intensity is about 2×10^{16} photons $cm^{-2}sec^{-1}$ and remains near this value for 4 to 6 hours. In contrast, the winter values vary from 0.7×10^{16} to 1.5×10^{16}, depending on latitude, and the time near this maximum is reduced to 2 to 4 hours.

Nitrogen dioxide (NO_2) is the most important energy absorbing molecule in the atmosphere, absorbing energy over the entire visible and ultraviolet range of the solar spectrum in the lower atmosphere. Between 300 nm and

370 nm, this energy absorption results in over 90 percent of the NO_2 dissociating to NO and O. Other molecules that can undergo photochemical dissociation include O_3, H_2O_2, HNO_2, NO_3, aldehydes and ketones. These photochemical dissociation reactions are important because of the products (mainly free radicals) that result from them. These products then initiate or participate in a large number of other reactions responsible for the conversion of primary air pollutants into ozone and photochemical smog.

2.2.1 Basic Photochemical Cycle

The oxides of nitrogen, NO and NO_2, play an important role in air pollution chemistry. The principle source of these oxides is combustion processes. Approximately 95 percent of the nitrogen oxides emitted from combustion processes are in the form of NO, with the remaining 5 percent emitted as NO_2. However, even small amounts of NO_2 in the atmosphere are sufficient to initiate the complex series of reactions that leads to the formation of ozone and photochemical smog. The process begins with the photolysis of NO_2:

$$NO_2 \xrightarrow{h\nu} NO + O \tag{2-3}$$

The oxygen atom produced by the dissociation reacts rapidly with O_2 to form O_3:

$$O + O_2 \xrightarrow{M} O_3 \tag{2-4}$$

where M represents a third molecule that absorbs the excess vibrational energy and stabilizes the O_3 molecule. There are no significant sources of ozone in the atmosphere other than this reaction. Once formed, O_3 reacts with NO to regenerate NO_2:

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{2-5}$$

The steady-state ozone concentration predicted by Reactions 2-3 through 2-5 can be calculated as a function of initial NO_2 concentration. At a typical maximum urban NO_2 concentration of 0.1 ppm, an ozone concentration of 0.027 ppm is calculated. An ozone concentration of 0.095 ppm is predicted for an initial NO_2 concentration of 1.0 ppm. Since peak 1-hour ozone concentration as high as 0.5 ppm have been measured is some urban areas, it is clear that some other mechanism must be involved. It is equally clear that that mechanism must result in the conversion of NO to NO_2 without consuming O_3. As we will see, that is the role of volatile organic compounds.

2.2.2 Role of Volatile Organic Compounds

To understand the role that volatile organic compounds play in the formation of ozone and photochemical smog, we will use formaldehyde as an initial example. Formaldehyde is directly emitted into the atmosphere by some sources and is also formed by atmospheric oxidation of other organic compounds. Thus, the chemistry of formaldehyde is common to virtually all mechanisms of atmospheric chemistry.

We begin our discussion with the photolysis of O_3. At wavelengths below about
315 nm, ozone dissociates into an excited oxygen atom and an oxygen molecule:

$$O_3 \xrightarrow{h\nu} O^* + O_2 \tag{2-6}$$

Most of the time O* collides with N_2 or O_2, removing the excess energy and quenching the O* to its ground state. Occasionally, however, O* collides with H_2O and produces two hydroxyl radicals:

$$O^* + H_2O \rightarrow 2OH\cdot \tag{2-7}$$

The key to understanding atmospheric chemistry is in understanding the reactions of the hydroxyl radical. This radical, unlike many radicals formed from organic molecules, does not react with oxygen. Instead, it survives to react with most atmospheric compounds, including carbon monoxide, hydrocarbons and aldehydes.

Formaldehyde undergoes two primary reactions in the atmosphere, photolysis (Reaction 2-8) and reaction with OH (Reaction 2-9):

$$HCHO \xrightarrow{h\nu} H\cdot + HCO\cdot \tag{2-8}$$

$$HCHO + OH\cdot \rightarrow HCO\cdot + H_2O \tag{2-9}$$

The hydrogen atom formed in Reaction 2-8 reacts rapidly with O_2 to yield the hydroperoxyl radical, HO_2 (Reaction 2-10). Likewise, the formyl radical, HCO, formed in Reaction 2-9 reacts with O_2 to form another hydroperoxyl radical and carbon monoxide (see Reaction 2-11):

$$H\cdot + O_2 \xrightarrow{M} HO_2\cdot \tag{2-10}$$

$$HCO\cdot + O_2 \rightarrow HO_2\cdot + CO \tag{2-11}$$

The hydroperoxyl radical then reacts with NO to form NO_2 and regenerate the OH radical:

$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot \tag{2-12}$$

Finally, the OH and NO_2 may react to form nitric acid:

$$OH\cdot + NO_2 \rightarrow HNO_3 \tag{2-13}$$

Next, we will consider the reactions of the next aldehyde in the series, acetaldehyde. Like formaldehyde, acetaldehyde reacts by two major pathways, photolysis and reaction with OH:

$$CH_3CHO \xrightarrow{h\nu} CH_3\cdot + HCO\cdot \tag{2-14}$$

$$CH_3CHO + OH\cdot \rightarrow CH_3CO\cdot + H_2O \tag{2-15}$$

The methyl and acetyl radicals produced then react rapidly with O_2:

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot \tag{2-16}$$

$$CH_3CO\cdot + O_2 \rightarrow CH_3COO_2\cdot \tag{2-17}$$

The methylperoxy radical reacts with NO to yield NO_2:

$$CH_3O_2\cdot + NO \rightarrow NO_2 + CH_3O\cdot \tag{2-18}$$

The methoxy radical reacts rapidly with O_2 to produce formaldehyde and HO_2:

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot \tag{2-19}$$

The acetylperoxy radical reacts with both NO and NO_2:

$$CH_3COO_2\cdot + NO \rightarrow NO_2 + CH_3COO\cdot \tag{2-20}$$

$$CH_3COO\cdot + O_2 \rightarrow CH_3O_2\cdot + CO_2 \tag{2-21}$$

$$CH_3COO_2\cdot + NO_2 \rightarrow CH_3COO_2NO_2 \tag{2-22}$$

The product of the last reaction is peroxyacetyl nitrate, commonly referred to as PAN.

Other organic compounds follow similar reaction pathways. With alkanes, since they are not photochemically reactive, hydroxyl radical reaction is the only significant process in the atmosphere. Reaction of an alkane hydrocarbon with OH produces a hydrocarbon radical which reacts rapidly with O_2 to produce a peroxyalkyl radical. The principal fate of the peroxyalkyl radical is reaction with NO to give NO_2 and an alkoxy radical, RO, or to yield an alkyl nitrate, $RONO_2$. Like alkanes, alkenes also undergo hydroxyl radical reaction; however, because of the double-bonded carbon atoms, they will also react with ozone. The initial products of that reaction are aldehydes and peroxyalkyl radicals.

2.2.3 Summary

Photochemical smog is the term used to describe the mixture of reactants and products that result from the interaction of organic compounds with nitrogen oxides. As we have seen, when NO_x is present, ozone formation occurs as a result of the photolysis of NO_2:

$$NO_2 \xrightarrow{h\nu} NO + O \tag{2-23}$$

$$O + O_2 \xrightarrow{M} O_3 \tag{2-24}$$

According to our current understanding of atmospheric chemistry, there are no significant sources of ozone other than this reaction sequence. However, since once O_3 is formed it reacts rapidly with NO to regenerate NO_2, relatively little O_3 is formed by these reactions alone. Organic compounds provide the mechanism for the conversion of NO to NO_2 without consuming O_3.

The key to understanding atmospheric organic chemistry is the OH radical. Its reaction with many hydrocarbons (RH) leads to peroxyalkyl radicals (RO_2):

$$RH + OH\cdot \rightarrow R\cdot + H_2O \tag{2-25}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{2-26}$$

The reaction of OH with aldehydes (RCHO) form acyl (RCO) and acylperoxy ($RCOO_2$) radicals in similar reactions:

$$RCHO + OH\cdot \rightarrow RCO\cdot + H_2O \tag{2-27}$$

$$RCO\cdot + O_2 \rightarrow RCOO_2\cdot \tag{2-28}$$

The peroxy radicals react rapidly with NO to form NO_2 or alkyl nitrates ($RONO_2$):

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot \tag{2-29}$$

$$RO_2\cdot + NO \rightarrow RONO_2 \tag{2-30}$$

$$RCOO_2\cdot + NO \rightarrow NO_2 + RCOO\cdot \tag{2-31}$$

Alkoxy radicals (RO) react with O_2 to produce hydroperoxyl radicals (HO_2) and carbonyl compounds (RCHO):

$$RO\cdot + O_2 \rightarrow HO_2\cdot + RCHO \tag{2-32}$$

Acyloxy radicals (RCOO) decompose to form an alkyl radical (R) and CO_2, with the subsequent generation of another peroxyalkyl radical (RO_2):

$$\mathrm{RCOO}\cdot \rightarrow \mathrm{R}\cdot + \mathrm{CO}_2 \qquad (2\text{-}33)$$

$$\mathrm{R}\cdot + \mathrm{O}_2 \rightarrow \mathrm{RO}_2\cdot \qquad (2\text{-}34)$$

Finally, the hydroperoxyl radicals (HO_2) can react with NO to regenerate OH and complete the cycle:

$$\mathrm{HO}_2\cdot + \mathrm{NO} \rightarrow \mathrm{NO}_2 + \mathrm{OH}\cdot \qquad (2\text{-}35)$$

In summary, the major observed phenomena in a system of nitrogen oxides in an organic-containing atmosphere are conversion of NO to NO_2, formation of a variety of nitrogen-containing species, such as nitric acid and peroxyacyl nitrates, and accumulation of O_3. NO_2 serves both as initiator and terminator of the chain reactions that produce these phenomena.

2.3 Properties of Organic Vapors

In this section, we will present some of the properties of organic vapors. This information will further improve your understanding of the behavior of organic compounds and will provide the tools need to calculate some important parameters.

2.3.1 Gas and Vapor Definitions

The terms gas and vapor are used very loosely. A gaseous material that exists below its critical temperature is called a vapor, because it can be condensed. The critical temperature is the highest temperature at which a pure component liquid and vapor can exist in equilibrium. If you continually compress a vapor at constant temperature, some pressure is eventually reached at which the vapor starts to condense into a liquid. A gaseous material that exists above its critical temperature is called a gas. Compressing a gas at constant temperature will not cause it to condense.

2.3.2 Molecular Weight and the Mole

The molecular weight of a compound is simply the sum of the atomic weights of all the atoms in the molecule. The atomic weight of an atom is based on an arbitrary scale of the relative masses of the elements, usually based on a carbon value of 12. The chemical identity of an atom is determined by the number of protons in its nucleus and is called the atomic number. Values of atomic number and atomic weight can be found in a Periodic Table of Elements.

Mixtures of molecules do not have a true molecular weight; however, they do have an apparent molecular weight that can be calculated from the composition of the mixture:

$$MW_{mixture} = \sum_{i=1}^{n} \chi_i MW_i \tag{2-36}$$

Where χ_i is the mole fraction of component i and MW_i is its molecular weight. Many times properties of a contaminated gas can be approximated by the properties of air, itself a mixture of molecules. The apparent molecular weight of air is 28.95, or approximately 29.

A mole is a mass of material that contains a certain number of molecules. Moles can be expressed in terms of any mass unit; thus, e.g., there are gram-moles, kilogram-moles, ounce-moles, pound-moles and ton-moles. The relationship between the different types of moles is the same as the relationship between the corresponding mass units. Thus, there are 1,000 gram-moles in a kilogram-mole, 453.6 gram-moles in a pound-mole, 16 ounce-moles in a pound-mole and 2,000 pound-moles in a ton-mole.

The gram-mole is the mass of material that contains Avogadro's number of molecules, approximately 6.023×10^{23}. The mass of a mole is numerically equal to the molecular weight. For oxygen, which has a molecular weight of 32, there are 32 grams per gram-mole, 32 kilograms per kilogram-mole, and 32 pounds per-pound mole. However, only the gram-mole contains Avogadro's number of molecules. The kilogram-mole contains 1,000 times Avogadro's number of molecules, and the pound-mole contains 453.6 times.

2.3.3 Equation of State

Equations of state relate the pressure, volume and temperature properties of a pure substance or mixture by semi-theoretical or empirical relationships. Over the range of temperature and pressure usually encountered in air pollution control systems, these values may be related by the ideal or perfect gas law:

$$PV = nRT \tag{2-37}$$

Where: P = absolute pressure
V = gas volume
n = number of moles
R = constant
T = absolute temperature

Here, R is referred to as the universal gas constant, and its value depends on the units of the other terms in the equation. Values of R include:

$$10.73 \text{ psia-ft}^3/\text{lb-mole-°R}$$

0.73 atm-ft^3/lb-mole-°R

82.06 cm^3-atm/g-mole-°K

8.31 x 10^3 kPa-m^3/kg-mole-°K

A useful relationship may be developed from the ideal gas law by noting that PV/T = nR, and that, for a given number of moles of a gas, nR is a constant. Thus, at two different conditions for the same gas, we may write:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{2-38}$$

or

$$V_1 = V_2 \left(\frac{P_2}{P_1} \right) \left(\frac{T_1}{T_2} \right) \tag{2-39}$$

Equation 2-39 allows volumes (or volume rates) to be corrected from one set of temperature and pressure conditions to another.

The ideal gas law may also be rearranged to calculate the volume occupied by a mole of gas, called the molar volume:

$$\frac{V}{n} = \frac{RT}{P} \tag{2-40}$$

For an ideal gas at 68°F and 1 atm, the molar volume is given by:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(0.73 \frac{\text{atm} - \text{ft}^3}{\text{lb} - \text{mole}\ {}^\circ\text{R}} \right)(528\ {}^\circ\text{R})}{(1\,\text{atm})} = 385.4 \frac{\text{ft}^3}{\text{lb} - \text{mole}} \tag{2-41}$$

Finally, we may use the ideal gas law to estimate gas density. Density is the ratio of the mass of a material to the volume that material occupies. For accurate values, gas densities should be determined from reference texts. However, an estimate of the gas density can be determined from the ideal gas law. Recognizing that the number of moles is given by mass (m) divided by molecular weight (MW), the ideal gas law may be written:

$$PV = \left(\frac{m}{MW} \right) RT \tag{2-42}$$

The gas density (ρ) can then be estimated from:

$$\rho = \frac{m}{V} = \frac{P \cdot MW}{RT} \tag{2-43}$$

Density can also be estimated from the molecular weight and molar volume:

$$\rho = \left(\frac{MW}{385.4}\right)\left(\frac{528}{T}\right)\left(\frac{P}{29.92}\right) \tag{2-44}$$

Where: P = absolute pressure (in. Hg)
T = absolute temperature (°R)

2.3.4 Vapor Pressure

At a given temperature, there is only one pressure at which the liquid and vapor phases of a pure substance can exist in equilibrium. That pressure is called the vapor pressure. Empirical correlations of vapor pressure data for various organic compounds are often given in the form of the Antoine equation:

$$\ln(p^*) = A - \frac{B}{T+C} \tag{2-45}$$

Where: p* = vapor pressure
T = temperature
A,B,C = specific constants for each compound

2.3.5 Partial Pressure and Partial Volume

Dalton postulated that the total pressure of a gas mixture is the sum of the individual pressures exerted by each of its components. These individual pressures are called partial pressures. A partial pressure is the pressure that would be obtained if the same mass of individual gas were alone in the same total volume at the same temperature.

From the ideal gas law, it can be seen that, at constant volume and temperature, the partial pressure of a component is a function only of the number of moles of that component that are present in the mixture. Similarly, dividing the ideal gas law for component i by the gas law for the total mixture, at constant volume and temperature, gives:

$$\frac{p_i}{P_T} = \frac{n_i}{n_T} \tag{2-46}$$

Amagat's law of additive volumes is analogous to Dalton's law of additive pressures. Amagat stated that the total volume of a gas mixture is equal to the sum of the volumes of the individual components, if they are measured at the same temperature and total pressure. The individual volumes of each of the components are called partial volumes.

We again see from the ideal gas law that, at constant temperature and total pressure, the partial volume of a component is a function only of the number of moles of that component that are present in the mixture. Again dividing the ideal gas law for component i by the gas law for the total mixture, at constant temperature and total pressure, gives:

$$\frac{\upsilon_i}{V_T} = \frac{n_i}{n_T} \tag{2-47}$$

Combining Equations 2-46 and 2-47 gives:

$$\frac{p_i}{P_T} = \frac{n_i}{n_T} = \frac{\upsilon_i}{V_T} \tag{2-48}$$

In other words, for an ideal gas, pressure fraction equals mole fraction, which equals volume fraction. For a gaseous system, the mole fraction of the ith component is generally written as y_i.

2.3.6 Concentration Expressions

The concentration of an organic vapor is usually expressed as partial pressure, parts per million by volume (ppmv), or mass per unit volume. The use of partial pressure as an expression of concentration is self-explanatory. As noted above, the partial pressure of a vapor is directly proportional to the moles, and hence the mass, of the vapor present in the gas mixture. Conversion from partial pressure to ppmv is straightforward. Dividing the partial pressure by the total pressure gives the pressure fraction. From Equation 2-48, we know that this is numerically equal to the volume fraction. Multiplying the volume fraction by 1 million gives ppmv. The conversion from ppmv to mass per unit volume requires additional calculation:

$$\begin{aligned} 1\text{ ppmv} &= \frac{1\text{ft}^3\text{ VOC}}{10^6\text{ft}^3}\left(\frac{1}{V_{\text{Molar}}}\frac{\text{lb}-\text{mole VOC}}{\text{ft}^3\text{ VOC}}\right)\left(MW_{\text{VOC}}\frac{\text{lb VOC}}{\text{lb}-\text{mole VOC}}\right) \\ &= \frac{MW_{\text{VOC}}}{V_{\text{Molar}}\text{ x}10^6}\frac{\text{lb}}{\text{ft}^3} \end{aligned} \tag{2-49}$$

Where: V_{Molar} = molar volume at system temperature and pressure
MW_{VOC} = VOC molecular weight

2.3.7 Explosive Limits

The explosive limits for a gas mixture are the minimum and maximum concentrations of VOC in air that will support self-sustained combustion. The lower explosive limit (LEL) is defined as the concentration of VOC below which combustion will not be self-sustaining. The upper explosive limit (UEL) is defined as the concentration of VOC which produces a non-burning mixture because of the lack of sufficient oxygen. Table 2-2 lists the explosive limits for some VOCs.

The LEL is the more important of the two terms in describing gas streams with combustible contaminants. Industrial processes which handle combustible vapors are usually required by insurance companies to operate with vapor concentrations in ducts that are less than 25 percent of the LEL, in order to minimize fire and explosion hazards. By using analyzers, alarms and flame arrestors, an insurance company may allow a plant to operate with vapor concentrations as high as 50 percent of the LEL.

Explosive limits are not absolute values, but are affected by temperature, pressure, geometry of the chamber, and the presence of other contaminants. The higher the temperature, the greater the activation energy of combustion and the more likely a flame will propagate. The higher the pressure, the closer the molecules are to one another, decreasing the distance a flame must jump from one combustible point to another. The smaller the diameter of the chamber, the narrower the explosive range becomes. Increased surface-to-volume ratio promotes rapid cooling and flame quenching, limiting flammability. The presence of other compounds can also affect explosive limits, either increasing or decreasing the range, depending on the contaminant.

Table 2-2. Explosive Limits of Selected VOCs

Substance	Explosive Limit (Volume %)	
	Lower	Upper
Methane	5.00	15.00
n-Hexane	1.18	7.40
Ethylene	2.75	28.60
Toluene	1.27	6.75
Xylene	1.00	6.00
Methanol	6.72	36.50
Ethanol	3.28	18.95
Gasoline	1.40	7.60

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Review Questions

1. What is the approximate number of known organic compounds?
    a. 300,000
    b. 1 million
    c. 8 million
    d. 23 million

2. How many valence electrons does carbon have?
    a. 3
    b. 4
    c. 6
    d. 12

3. Which one of the following is not a hydrocarbon?
    a. Aldehydes
    b. Alkynes
    c. Paraffins
    d. Olefins

4. Which classes of organic compounds exhibit isomerism? Select all that apply.
    a. Alkanes
    b. Alkenes
    c. Alkynes
    d. Aromatics

5. Which of the following compounds are identical?
    a. 1,1,1-trichloroethane
    b. 1,1,2,2-tetrachloroethylene
    c. Perchloroethylene
    d. Trichloroethylene

6. Which organic compounds contain the carbonyl group? Select all that apply.
    a. Ethers
    b. Aldehydes
    c. Ketones
    d. Esters

7. Which organic compounds are photochemically reactive? Select all that apply.
    a. Alkanes
    b. Alcohols
    c. Aldehydes
    d. Olefins

8. Which of the following nitrogen-containing compounds are strong eye irritants? Select all that apply
   a. Acrolein
   b. Peroxyacetyl nitrate
   c. Ethyl acetate
   d. Peroxybenzoyl nitrate

9. What is the most important energy-absorbing molecule in the atmosphere?
   a. Nitrogen oxide
   b. Nitrogen dioxide
   c. Ozone
   d. Hydrogen peroxide

10. Understanding the reactions of what radical is key to understanding atmospheric chemistry?
   a. Hydroperoxyl
   b. Peroxyalkyl
   c. Hydroxyl
   d. Acylperoxy

11. What are the primary reactions of aldehydes in the atmosphere? Select all that apply.
   a. Photolysis
   b. Double-bond oxidation
   c. Reaction with OH
   d. Reaction with NO

12. What are the primary reactions of alkanes in the atmosphere? Select all that apply.
   a. Photolysis
   b. Double-bond oxidation
   c. Reaction with OH
   d. Reaction with NO

13. What are the primary reactions of alkenes in the atmosphere? Select all that apply.
   a. Photolysis
   b. Double-bond oxidation
   c. Reaction with OH
   d. Reaction with NO

14. What are the major observed phenomena in a system of nitrogen oxides in an organic-containing atmosphere?
   a. Conversion of NO to NO_2
   b. Formation of a variety of nitrogen-containing species
   c. Accumulation of ozone
   d. All of the above

Review Answers

1. What is the approximate number of known organic compounds?
   c. 8 million

2. How many valence electrons does carbon have?
   b. 4

---

3. Which one of the following is not a hydrocarbon?
   a. Aldehydes

4. Which classes of organic compounds exhibit isomerism? Select all that apply.
   a. Alkanes
   b. Alkenes
   c. Alkynes
   d. Aromatics

5. Which of the following compounds are identical?
   b. 1,1,2,2-tetrachloroethylene
   c. Perchloroethylene

6. Which organic compounds contain the carbonyl group? Select all that apply.
   b. Aldehydes
   c. Ketones

7. Which organic compounds are photochemically reactive? Select all that apply.
   c. Aldehydes

8. Which of the following nitrogen-containing compounds are strong eye irritants? Select all that apply.
   b. Peroxyacetyl nitrate
   d. Peroxybenzoyl nitrate

9. What is the most important energy-absorbing molecule in the atmosphere?
   b. Nitrogen dioxide

10. Understanding the reactions of what radical is key to understanding atmospheric chemistry?
   c. Hydroxyl

11. What are the primary reactions of aldehydes in the atmosphere? Select all that apply.
   a. Photolysis
   c. Reaction with OH

12. What are the primary reactions of alkanes in the atmosphere? Select all that apply.
    - **c.** Reaction with OH

13. What are the primary reactions of alkenes in the atmosphere? Select all that apply.
    - **b.** Double-bond oxidation
    - **c.** Reaction with OH

14. What are the major observed phenomena in a system of nitrogen oxides in an organic-containing atmosphere?
    - **d.** All of the above

Exercise No. 1

Use the Antoine equation to estimate the vapor pressure of acetone at 0°C. For vapor pressure in mm Hg and temperature in K, the Antoine constants are A = 16.65, B = 2,940 and C = -35.93.

Exercise No. 1 Solution

Use the Antoine equation to estimate the vapor pressure of acetone at 0°C. For vapor pressure in mm Hg and temperature in K, the Antoine constants are A = 16.65, B = 2,940 and C = -35.93.

$$\ln(p^*) = A - \frac{B}{T + C} = 16.65 - \frac{2{,}940}{273 - 35.93} = 4.25$$

$$p^* = 70.00 \text{ mm Hg}$$

The experimental value of the vapor pressure is 71.0 mm Hg.

Exercise No. 2

Calculate the mole fraction and gas phase equilibrium concentration in ppmv for acetone in air at 100°F. The total pressure is 1 atm and the vapor pressure of acetone at 100°F is 7.3 psia.

Exercise No. 2 Solution

Calculate the mole fraction and gas phase equilibrium concentration in ppmv for acetone in air at 100°F. The total pressure is 1 atm and the vapor pressure of acetone at 100°F is 7.3 psia.

From Equation 2-48, we know that pressure fraction = mole fraction = volume fraction:

$$y_{\text{acetone}} = \frac{p_{\text{acetone}}}{P_T} = \frac{7.3\,\text{psia}}{14.7\,\text{psia}} = 0.497$$

$$C_{\text{acetone}} = 0.497(10^6) = 496{,}589\,\text{ppmv}$$

Exercise No. 3

A gas stream at 100°F and 1 atm contains 60,000 ppmv of toluene. What temperature must the gas stream be cooled to in order to condense 40% of the toluene vapor? Vapor pressures of toluene in psia are given in the follow table:

40°F	50°F	60°F	70°F	80°F	90°F	100°F
0.2	0.2	0.3	0.4	0.6	0.8	1.0

Exercise No. 3 Solution

A gas stream at 100°F and 1 atm contains 60,000 ppmv of toluene. What temperature must the gas stream be cooled to in order to condense 40% of the toluene vapor? Vapor pressures of toluene in psia are given in the follow table:

40°F	50°F	60°F	70°F	80°F	90°F	100°F
0.2	0.2	0.3	0.4	0.6	0.8	1.0

Determine the toluene concentration after condensation:

$$C_{toluene} = (1-0.4)(60,000) = 36,000 \text{ ppmv}$$

Determine the pressure fraction of the toluene at this concentration:

$$\frac{p_{toluene}}{P_T} = \frac{\upsilon_{toluene}}{V_T} = \frac{36,000}{10^6} = 0.036$$

Calculate the vapor pressure of the toluene:

$$p_{toluene} = 0.036P_T = (0.036)(14.7 \text{ psia}) = 0.529 \text{ psia}$$

Using the table, determine the temperature at this vapor pressure:

$$T = 76.5°F$$

Exercise No. 4

A 70°F gas stream with a flow rate of 1,766 acfm has a heptane concentration of 20,000 ppmv. Determine the mass flow rate of heptane.

Exercise No. 4 Solution

A 70°F gas stream with a flow rate of 1,766 acfm has a heptane concentration of 20,000 ppmv. Determine the mass flow rate of heptane.

Determine the flow rate of pure heptane:

$$Q_{\mathrm{heptane}} = 1{,}766\ \mathrm{acfm}\left(\frac{20{,}000}{10^{6}}\right) = 35.32\ \mathrm{acfm}$$

Calculate the molecular weight of heptane:

$$\text{Heptane} = C_7H_{16}$$

$$MW_{\mathrm{heptane}} = (7)(12) + (16)(1) = 100$$

Use the ideal gas law to determine the mass flow rate of heptane:

$$PV = nRT = \left(\frac{m}{MW}\right)RT$$

$$m = \frac{PV \cdot MW}{RT} = \frac{(1\ \mathrm{atm})\left(35.32\,\frac{\mathrm{ft}^3}{\mathrm{min}}\right)\left(100\,\frac{\mathrm{lb}}{\mathrm{lb-mole}}\right)}{\left(0.73\,\frac{\mathrm{atm}\cdot\mathrm{ft}^3}{\mathrm{lb-mole}\cdot{}^\circ\mathrm{R}}\right)(530\ {}^\circ\mathrm{R})} = 9.13\,\frac{\mathrm{lb}}{\mathrm{min}}$$

Exercise No. 5

Two hundredths of a gallon of liquid propanol is vaporized in a 90,500 ft^3 smog chamber containing air at 60°F and 1 atm. Calculate the concentration of propanol in the chamber in ppmv. Assume the density of the liquid propanol is 7.36 lb/gal.

Exercise No. 5 Solution

Two hundredths of a gallon of liquid propanol is vaporized in a 90,500 ft^3 smog chamber containing air at 60°F and 1 atm. Calculate the concentration of propanol in the chamber in ppmv. Assume the density of the liquid propanol is 7.36 lb/gal.

Determine the mass of the propanol:

$$m_{propanol} = (0.02\ \text{gal})\left(7.36\ \frac{\text{lb}}{\text{gal}}\right) = 0.147\ \text{lb}$$

Calculate the molecular weight of propanol:

$$\text{Propanol} = C_3H_7OH$$

$$MW_{propanol} = (3)(12) + (8)(1) + (1)(16) = 60$$

Use the ideal gas law to determine the volume of propanol:

$$PV = nRT = \left(\frac{m}{MW}\right)RT$$

$$V = \frac{mRT}{P \cdot MW} = \frac{(0.147\ \text{lb})\left(0.73\ \frac{\text{atm}\cdot\text{ft}^3}{\text{lb}-\text{mole}\cdot°\text{R}}\right)(520°\text{R})}{(1\ \text{atm})\left(60\ \frac{\text{lb}}{\text{lb}-\text{mole}}\right)} = 0.930\ \text{ft}^3$$

Calculate the concentration:

$$C_{propanol} = \frac{\upsilon_{propanol}}{V_{chamber}}\text{x}10^6 = \frac{0.93\ \text{ft}^3}{90{,}500\ \text{ft}^3}\text{x}10^6 = 10.276\ \text{ppmv}$$

Exercise No. 6

Determine the minimum volume of air needed to hold 20 lb of evaporated ethanol, if the total pressure is maintained at 740 mm Hg. Assume the evaporation process is isothermal at 70°F. The vapor pressure of ethanol at 70°F is 46.5 mm Hg.

Exercise No. 6 Solution

Determine the minimum volume of air needed to hold 20 lb of evaporated ethanol, if the total pressure is maintained at 740 mm Hg. Assume the evaporation process is isothermal at 70°F. The vapor pressure of ethanol at 70°F is 46.5 mm Hg.

From Dalton, we know that:

$$\frac{n_{air}}{n_{ethanol}} = \frac{p_{air}}{p_{ethanol}}$$

Calculate the molecular weight of ethanol:

$$\text{Ethanol} = C_2H_5OH$$

$$MW_{propanol} = (2)(12) + (6)(1) + (1)(16) = 46$$

Determine the moles of air:

$$n_{air} = n_{ethanol}\left(\frac{p_{air}}{p_{ethanol}}\right) = \left(\frac{20\,\text{lb}}{46\,\frac{\text{lb}}{\text{lb} - \text{mole}}}\right)\left(\frac{740\,\text{mm Hg} - 46.5\,\text{mm Hg}}{46.5\,\text{mm Hg}}\right) = 6.48\,\text{lb} - \text{moles}$$

Calculate the molar volume at 70°F and 740 mm Hg:

$$\frac{V}{n} = \frac{RT}{P} = \frac{\left(0.73\,\frac{\text{atm} - \text{ft}^3}{\text{lb} - \text{mole}\ {}^{o}\text{R}}\right)(530\ {}^{o}\text{R})}{\left(\frac{740}{760}\,\text{atm}\right)} = 397.4\,\frac{\text{ft}^3}{\text{lb} - \text{mole}}$$

Determine the volume of air:

$$V_{air} = (6.48\,\text{lb} - \text{moles})\left(397.4\,\frac{\text{ft}^3}{\text{lb} - \text{mole}}\right) = 2{,}575.2\,\text{ft}^3$$

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Jahnke, J.A., "Measuring the Emission of Organic Compounds to the Atmosphere", EPA 450/2-84-005, September 1984.

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3 Source Measurement Techniques

A source that emits VOCs into the atmosphere must maintain emissions at or below levels that are set forth in the applicable standards. Compliance testing, in which emissions are sampled while the source operates under conditions that are expected to produce maximum emissions, is the means by which these emissions are documented. In this chapter, three methods for measuring VOC stack emissions are summarized: Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography; Method 25, Determination of Total Gaseous Non-Methane Organic Emissions as Carbon; and Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer. The details of these sampling methods are found in 40 CFR 60, Appendix A.

3.1 METHOD 18

In Method 18, a gas sample is extracted from a single point within the stack at a rate proportional to the stack gas velocity. The organic components of the gas sample are then separated by gas chromatography and measured with a suitable detector. This method applies to the measurement of approximately 90 percent of the total gaseous organics emitted from an industrial source in concentrations greater than about 1 ppm. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air or fugitive emission sources. Also, it will not determine compounds that are polymeric, that can polymerize before analysis, or that have very low vapor pressure at stack or instrument conditions.

3.1.1 Sampling

Samples of the stack gas may be collected using one of four techniques:

- Direct interface sampling
- Dilution interface sampling
- Adsorption tube sampling
- Bag sampling

In direct interface sampling, the gas sample is introduced directly into the sample loop of the gas chromatograph (GC). This technique can be used when the moisture content of the sample does not interfere with the analysis procedure and the VOC concentration is low enough that detector saturation is not a problem. If the VOC concentration is high, a dilution interface can be used. The primary advantage of direct or dilution interface sampling is that there is no loss or alteration of the compounds, since a sample collection media (bag or adsorbent) is not used. There are, however, several disadvantages. Since the GC must be located at the site, this method cannot be used if the presence of the hydrogen flame presents a hazard. Also, this method cannot be used on sources with varying flow rate. Since the elution time of the separated VOCs from the GC column is used for compound identification, the sampling system must operate at a constant flow rate. Additionally, a time-integrated sample cannot be obtained. Because of the nature of GC operation, the analysis results represent only grab samples and should not be used on sources with varying concentration. In general, direct or dilution interface sampling is the method of choice for steady state sources where the temperature is below 100°C and the VOC concentrations are suitable for the GC detector.

With adsorption tube sampling, an integrated sample is obtained by collecting the VOCs from the sample gas on adsorbent media contained in primary and backup sampling tubes. The most common adsorbent media is activated charcoal; however, silica gel, Tenax, XAD, or other polymeric adsorbents may be used when appropriate. The collected samples are compact and easily returned to the laboratory for analysis. If necessary, the samples can be stored for up to a week by keeping them at 0°C. However, to be sure that a representative sample is collected, the breakthrough capacity of the adsorbent media for the compounds being collected must be known. Also, the effect of moisture in the stack gas on the adsorbent capacity must be known. Moisture levels above 2 to 3 percent may significantly reduce the capacity of some adsorbents. In addition, to be able to relate the analysis results to the stack concentrations, the quantitative recovery of the compounds from the adsorbent media must be determined. Finally, since the breakthrough capacity is affected by the sampling rate, samples must generally be collected at a constant rate, making this method unsuitable for sources with significantly varying flow rate.

In bag sampling, an integrated sample of the stack gas is collected directly into a Tedlar bag. Usually, the bag is filled by evacuating a rigid air-tight container that holds the bag, as shown in Figure 3-1; however, the bag may also be filled by pumping into it. The sample can be collected with a varying sampling rate, making the technique suitable for sources with varying flow rate. When the sample is placed into the bag, it has the same compounds and concentrations as the stack gas. However, adsorption of the VOC compounds onto the bag surface can reduce their concentration, and reaction of the compounds with the bag material or with each other can change them. To mitigate these potential problems, samples should be analyzed within a few hours of collection, and polar compounds, which have a high affinity for the Tedlar surface, should not be collected with this technique. In general, Tedlar bags are awkward and bulky for shipping to the laboratory and, unless protected, are prone to leaks.

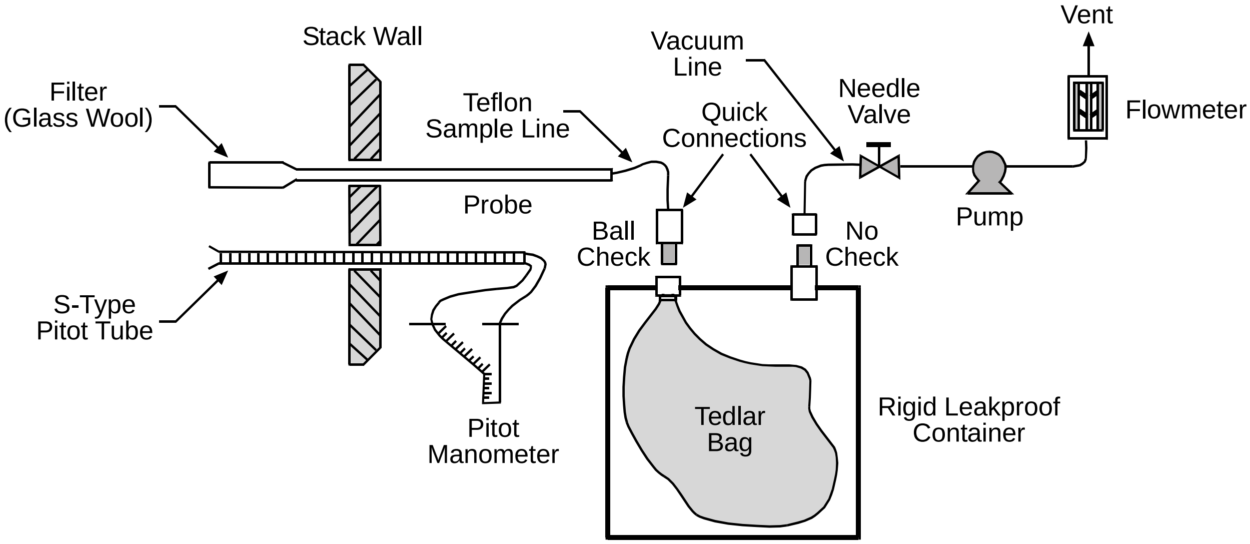

Figure 3-1. Bag sampling system

3.1.2 Analysis

The VOC compounds in samples collected by one of the above techniques are separated by gas chromatography and analyzed with a suitable detector. Chromatographic separations are based on the selective distribution, or partitioning, of compounds between a stationary material and a moving material. In gas chromatography, the moving gas phase passes over a stationary material that is chosen to either absorb or adsorb the organic molecules in the gas. If the stationary material is a liquid, the technique is called gas-liquid chromatography (GLC). If it is a solid, the technique is called gas-solid chromatography (GSC). Because of differences in the sorption rate of the VOC compounds in or on the chosen sorbent, the organic mixture is separated into individual compounds for analysis.

Gas chromatographic instrumentation may be simple or very complex. Basic early systems have developed into today's microprocessor controlled units that provide the analytical chemist with powerful tools for sample separation and identification. However, even the most complex system contains the basic components shown in Figure 3-2.

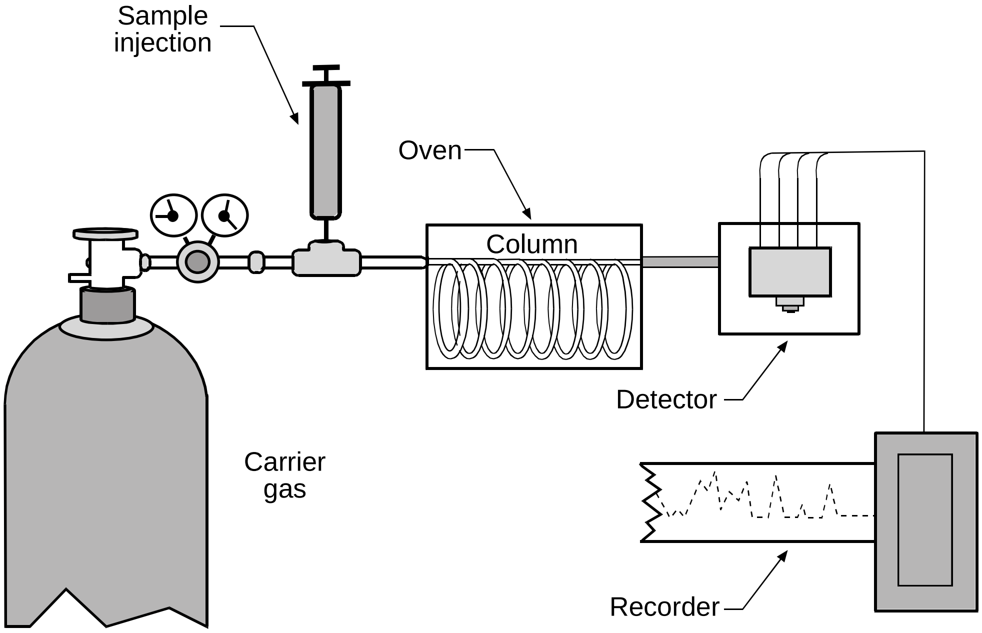

Figure 3-2. Components of a gas chromatograph

The injected sample is moved through the GC system by a carrier gas, such as nitrogen, helium or argon. The method used for injection depends on how the sample was collected. Samples collected in Tedlar bags are referred to as whole air samples. One of the simplest methods of injecting these samples is to use a gas-tight syringe. The sample is withdrawn from the bag and then injected into the GC through a rubber septum. Another method of injecting whole air samples is to use special sampling valves. A pump draws the gas from the bag into a sampling valve that contains a loop of known volume. The loop is closed off from the bag and the carrier gas sweeps the sample into the column.

Samples collected on adsorption tubes must be desorbed before they can be introduced into the GC. A common technique is to heat the tubes and collect the desorbed material in a cryogenic trap. The collected sample is then flash evaporated and injected into the column using an appropriate sampling valve system. With some adsorbents, the sample can be extracted with a liquid solvent. Samples collected on activated carbon, for example, can be extracted with carbon disulfide or methylene chloride. A liquid syringe is then used to inject the extract into a heated injection port that vaporizes the sample before it enters the GC column.

The column is the central component of the GC system. Since the separation of the organic compounds takes place here, the choice of the column type, materials and operating conditions are critical to the analysis. The two types of GC columns are packed and capillary. They can be stainless steel, glass, aluminum or copper and are either U-shaped or wound in coils to fit in the chromatograph oven. Packed column diameters vary from 0.05 to 0.10 inches and they have lengths that range from less than 3 feet to more than 50 feet. They are packed with small diameter solid particles that serve as an adsorbent in GSC or as an inert support for the absorption liquid in GLC. Capillary columns are open tubes with a thin liquid film on the wall or on a solid support coated on the wall. They vary from 0.01 to 0.05 inches in diameter and have lengths that can range beyond 300 feet.

The partitioning capability of the sorbent material in the GC column, whether solid or liquid, must be appropriate for the compounds being separated. Modest sorbent properties for each of the components is usually desired so that the compounds are efficiently separated, but not retained so tightly that analysis times are long. One property that significantly affects the partitioning is the column temperature. GC columns may be operated at a constant temperature or, if the retention times of the compounds differ greatly, the temperature may be programmed for progressive increases. In this manner, compounds of low volatility can be eluted faster, reducing the analysis time.

With proper column design and operating conditions, the components of the sample exit the column in a series of non-overlapping peaks, each corresponding to a normal probability curve. The time each peak eludes is used to identify the compound. Knowing the components in the sample, the analyst runs standards through the column under the same set of experimental conditions. Matching the peaks from the standards with the peaks from the sample is used to identify the specific compounds. The concentration of each compound is determined from the area defined by the elution curve. The area of each peak is divided by the total area of all the peaks to determine the relative proportion of each component in the sample.

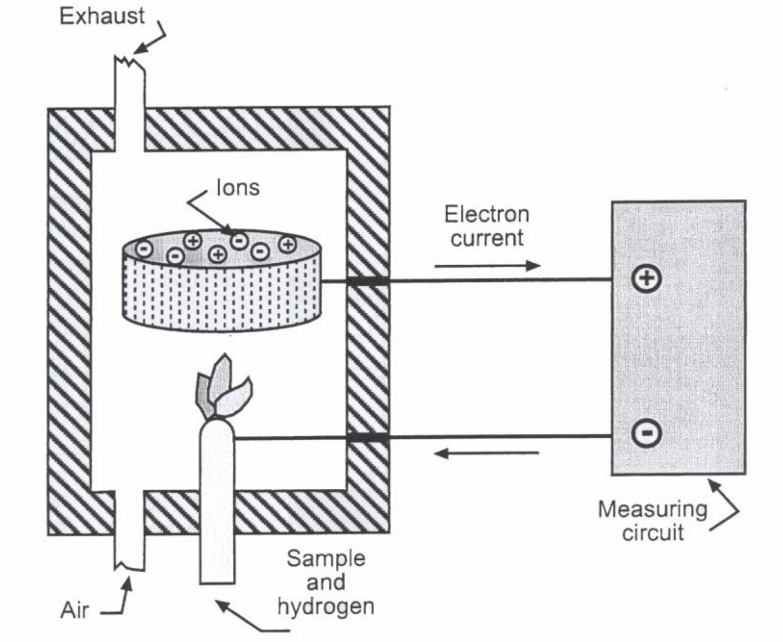

Figure 3-3. Flame ionization detector

The most common detectors used in GC analysis are the flame ionization detector (FID), the photoionization detector (PID) and the electron capture detector (ECD). The most common of these is the flame ionization detector shown in Figure 3-3. The hydrogen flame burns the organic compounds in the gas eluted from the column, forming both positive and negative ions. These ions make the gap between the two electrodes conductive, causing an electric current to flow through the circuit. The current is approximately proportional to the number of carbon atoms entering the flame. However, since the response of the detector varies for different types of organic compounds, it must be calibrated for the specific compounds being studied. The PID is similar to the FID, except that it uses high energy UV radiation to ionize the organic molecules.

The electron capture detector shown in Figure 3-4 is selective for certain groups of organic compounds, such as those containing halogen atoms or nitro groups. In this method, a carrier gas, such as nitrogen, is ionized by a radioactive material, such as Ni^{63} or tritium (H^3), to produce a large number of free electrons. These electrons flow to the positively charged electrode, generating an electric current through the circuit. When the carrier gas contains electron-absorbing molecules, such as halocarbons, the electric current will be reduced. This reduction in current flow can be related to the compound concentration through calibration standards.

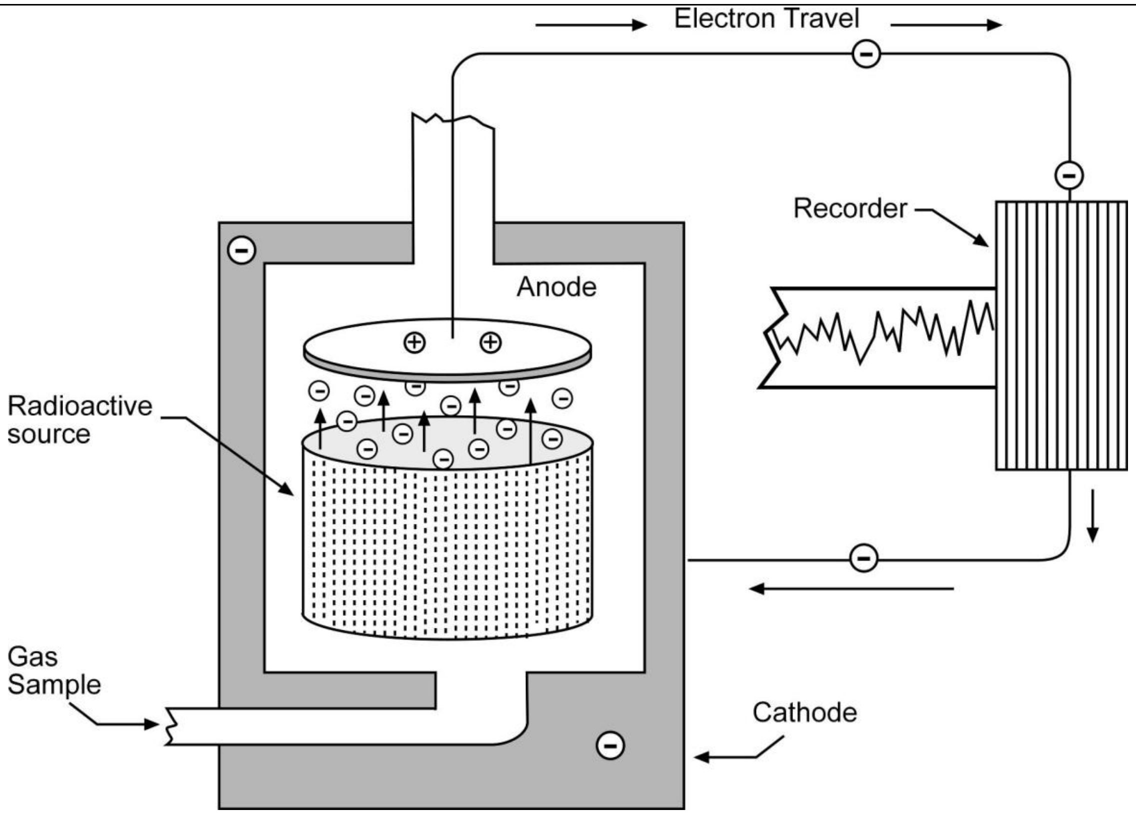

Figure 3-4. Electron capture detector

3.2 METHOD 25

Method 25 applies to the measurement of VOC in source emissions as total gaseous non-methane organics as carbon. Organic compounds that exist as a vapor or that have significant vapor pressure at or below 250°F and are present in concentrations greater than 50 ppm as carbon are subject to measurement by this method. However, a positive bias can result when carbon dioxide (CO_2) and water vapor are present together in the stack. The magnitude of the bias depends on the concentrations. As a guide, if the product of the CO_2 and water vapor concentrations, both expressed as volume percent, is less than 100, the bias can be considered as insignificant.

3.2.1 Sampling

The Method 25 sampling train is shown in Figure 3-5. The sample gas is extracted from the stack through a heated probe, a heated out-of-stack filter, and a dry-ice condensate trap and collected in an evacuated sample tank. The condensate trap consists of 3/8” stainless steel tubing bent into a U shape, packed with coarse quartz wool and submerged in dry ice. The sample tank is either stainless steel or aluminum, with a minimum volume of 4 liters and evacuated to an absolute pressure of 10 mm Hg or less.

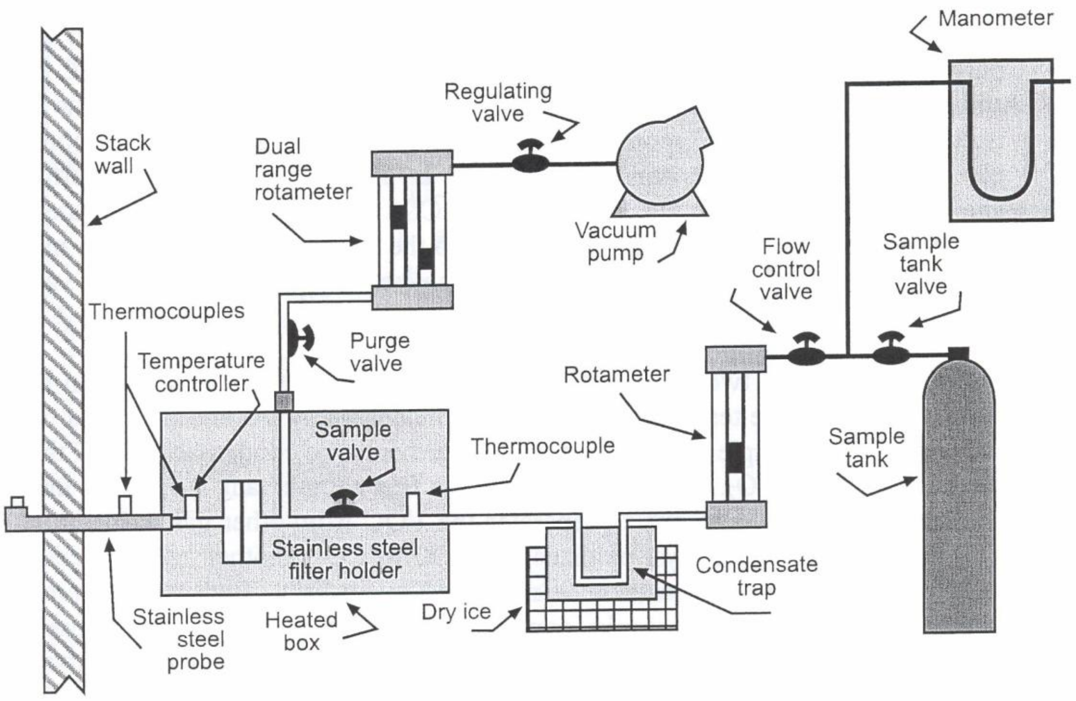

Figure 3-5. Method 25 sampling train

The sampling probe is positioned perpendicular to the stack axis with the 90° nozzle at a point of average velocity and facing away from the direction of gas flow. The probe is heated to 265°F and the filter to 250±5°F. Before sampling, the probe and filter are purged with stack gas for at least 10 minutes using a vacuum pump. When the temperatures at the exit ends of the probe and filter are within their specified values, sampling may begin. The sample is withdrawn from the stack at a constant flow rate (±10 percent) throughout the sampling period. After the sample is collected, the condensate trap and the sample tank are taken to a laboratory for recovery and analysis. The filter catch is discarded.

3.2.2 Analysis

The condensate trap will contain frozen water, condensed organic material and a small volume of sample gas. This gas may contain a significant amount of CO_2. This must be removed from the condensate trap before the sample is recovered, or the CO_2 will be counted as VOC. This is done by purging the condensate trap with zero air and collecting the purged gas in the original sample tank. The zero air purge continues until the CO_2 concentration of the trap effluent is less than 5 ppm. After the purge is completed, the sample tank is pressurized with zero air to approximately 1,060 mm Hg.

A second evacuated tank is used to recover the condensed organic material in the condensate trap. The trap is removed from the dry ice and allowed to warm to ambient temperatures. While the trap is warming, it is purged with zero air. The purged gases are passed through an oxidation catalyst, converting the VOC to CO_2, and are collected in the second tank. The trap is then heated to 200°C, and the purging is continued until the CO_2 concentration in the purged gas is less than 10 ppm. After the purge is completed, this second tank is also pressurized with zero air to approximately 1,060 mm Hg. Note that any CO_2 trapped in the frozen water in the cold trap during sampling and not purged into the first sample tank will be measured as VOC. This is the source of the positive bias when high amounts of water vapor and CO_2 are present in the stack gas.

The tester now has two sample tanks to analyze for VOC. The sample in the first tank, collected at the test site, contains non-condensable VOC and the gases from the CO_2 purge. The sample in the second tank represents the condensable VOC that have been converted to CO_2. A gas sample from the first sample tank is injected into a gas chromatographic column, which separates the VOC from other gases, including CO, CO_2 and methane. A catalyst oxidizes the VOC to CO_2, another catalyst reduces the CO_2 to methane, and the methane is measured by an FID. Because the sample gas contains only a single organic compound, methane, any FID response factor differences have been eliminated. The sample from the second tank is analyzed in a similar manner, with one difference. Since all of the condensable VOCs were oxidized to CO_2 and collected in this tank, the CO_2 peak from this tank is measured and counted as VOC. The total concentration of VOC is the sum of both analyses. The units are ppm as carbon.

Typically, USEPA does not recommend Method 25 for the measurement of mass emissions. Method 25 results will underestimate mass emissions of VOC because molecules containing elements other than carbon, such as chlorine or oxygen, have molecular weights greater than corresponding carbon-hydrogen compounds. However, if the tester knows the composition of the gas, then the final results can be corrected to actual mass emission rates mathematically.

3.3 METHOD 25A

Method 25A is designed to measure total hydrocarbon concentrations in stack gases on a continuous, real-time basis using a flame ionization detector. Alkanes, alkenes and aromatics are the most appropriate compound groups for Method 25A sampling and analysis. Highly substituted or halogenated hydrocarbons, in particular, are not amenable to FID analysis. Method 25A should only be used in situations where an appropriate response factor for the stack gas can be determined and should not be applied to gas streams that cannot be characterized or which have changing composition. The concentrations are measured on a wet basis and are expressed as ppm as propane or other appropriate calibration gas or as ppm as carbon. Adjustments for the percent moisture in the stack gas must be made for the purpose of emission calculations.

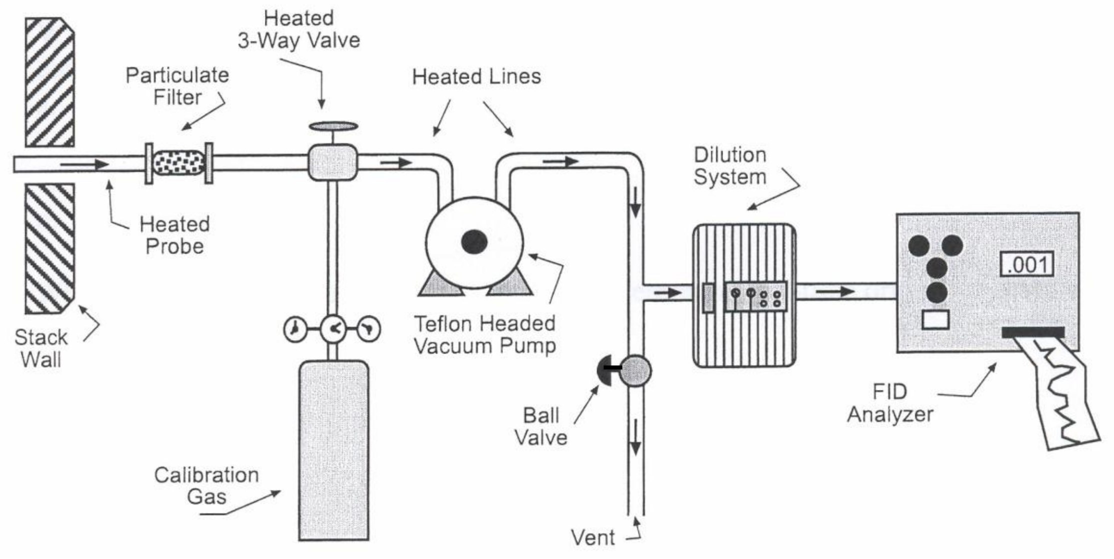

Figure 3-6. Method 25A sampling train

The sampling train for Method 25A is shown in Figure 3-6. The sample gas is extracted from the stack with a stainless steel, or equivalent, 3-hole rake-type probe positioned across the stack centerline or with a single-hole probe located at the center of the stack. The extracted sample is transported to the analyzer through stainless steel or Teflon tubing. If necessary, the sample line should be heated to prevent condensation. An in-stack or out-of-stack glass fiber filter is recommended if the stack gas particulate concentration is significant. If an out-of-stack filter is used, it should be heated to prevent condensation.

Within two hours of the beginning of the test, zero gas and high-level calibration gas should be introduced at the calibration valve assembly and the analyzer output adjusted to appropriate levels. Next, low-level and mid-level calibration gases should be introduced successively and the analyzer output compared to values predicted assuming a linear response between the zero gas and the high-level calibration gas. To be acceptable, the analyzer response must be within ±5 percent of the predicted values. After the test is completed, zero gas and mid-level calibration gas are introduced into the analyzer and the drift from their initial values is determined. To be acceptable, the zero and calibration drift must be within ±3 percent of the span value.

The average organic concentration is determined by the integration of the output recording over the period specified in the applicable regulation.

Review Questions

1. Which of the following is not a method for determining VOC stack emissions?
   a. Method 18
   b. Method 21
   c. Method 25
   d. Method 25A

2. Which test method can be used to determine the concentrations of specific organic compounds in a mixed gas stream?
   a. Method 18
   b. Method 21
   c. Method 25
   d. Method 25A

3. Which test method can be used to directly determine TGNMO in a mixed gas stream?
   a. Method 18
   b. Method 21
   c. Method 25
   d. Method 25A

4. Which test method can be used to directly determine the total gaseous organic concentration in a mixed gas stream?
   a. Method 18
   b. Method 21
   c. Method 25
   d. Method 25A

5. Which test method can be used to continuously determine real-time organic concentration in a mixed gas stream?
   a. Method 18
   b. Method 21
   c. Method 25
   d. Method 25A

6. Which of the following are not appropriate sampling methods for a source with highly varying flow rate? Select all that apply.
   a. Direct interface sampling
   b. Dilution interface sampling
   c. Adsorption tube sampling
   d. Bag sampling

7. Which of the following are not appropriate sampling methods for a source with varying VOC concentration? Select all that apply.
   - a. Direct interface sampling
   - b. Dilution interface sampling
   - c. Adsorption tube sampling
   - d. Bag sampling

8. What is the minimum detectable VOC concentration for Method 18?
   - a. 1 ppm
   - b. 25 ppm
   - c. 50 ppm
   - d. 100 ppm

9. What is the fundamental mechanism of gas-liquid chromatography?
   - a. Sensing of compounds at the end of the column
   - b. Movement of organic molecules in the gas stream
   - c. Dissolving of organic molecules in the liquid phase
   - d. Movement of organic molecules between the gas and liquid phases

10. A sample is injected into a GC column:
   - a. Continuously
   - b. As a plug or pulse
   - c. Until the first peak is eluted
   - d. Until the last peak is eluted

11. What types of detectors are typically used for the analysis of VOC samples?
   - a. TCD and MS
   - b. FPD and HECD
   - c. FID and ECD
   - d. AFD and PID

12. What happens to the ions produced in the flame of a FID?
   - a. They are neutralized by an isotope of hydrogen.
   - b. They are detected by UV absorption methods.
   - c. They produce a current proportional to the number of carbon atoms entering the flame.

13. How do VOC molecules affect the current flow between the electrodes in an ECD?
   - a. Increases
   - b. Decreases
   - c. Has no affect

14. What is the minimum detectable VOC concentration for Method 25?
    a. 1 ppm
    b. 25 ppm
    c. 50 ppm
    d. 100 ppm

15. What type of bias occurs with Method 25 when the stack gas has high concentrations of CO_2 and water vapor?
    a. Positive
    b. Negative
    c. None

16. Which of the following is not part of a Method 25 sampling train?
    a. Evacuated sample tank
    b. Condensate trap
    c. Impingers
    d. Filter

17. What type of detector is used in Method 25 and Method 25A?
    a. FID
    b. ECD
    c. PID
    d. HECD

18. When can Method 25 be used to determine mass emissions of VOC?
    a. Always
    b. Never
    c. When the composition of the gas stream is known

19. Which of the following compounds would not be appropriate for analysis by Method 25A?
    a. Methylene chloride
    b. Benzene
    c. Acetylene
    d. Cyclohexane

20. On what basis does Method 25A determine organic concentration in a mixed gas stream?
    a. Dry
    b. Wet

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Review Answers

1. Which of the following is not a method for determining VOC stack emissions?
   b. Method 21

2. Which test method can be used to determine the concentrations of specific organic compounds in a mixed gas stream?
   a. Method 18

3. Which test method can be used to directly determine TGNMO in a mixed gas stream?
   c. Method 25

4. Which test method can be used to directly determine the total gaseous organic concentration in a mixed gas stream?
   d. Method 25A

5. Which test method can be used to continuously determine real-time organic concentration in a mixed gas stream?
   d. Method 25A

6. Which of the following are not appropriate sampling methods for a source with highly varying flow rate? Select all that apply.
   a. Direct interface sampling
   b. Dilution interface sampling
   c. Adsorption tube sampling

7. Which of the following are not appropriate sampling methods for a source with varying VOC concentration? Select all that apply.
   a. Direct interface sampling
   b. Dilution interface sampling

8. What is the minimum detectable VOC concentration for Method 18?
   a. 1 ppm

9. What is the fundamental mechanism of gas-liquid chromatography?
   d. Movement of organic molecules between the gas and liquid phases

10. A sample is injected into a GC column:
    b. As a plug or pulse

11. What types of detectors are typically used for the analysis of VOC samples?
    c. FID and ECD

12. What happens to the ions produced in the flame of a FID?

c. They produce a current proportional to the number of carbon atoms entering the flame

13. How do VOC molecules affect the current flow between the electrodes in an ECD?
    b. Decreases

14. What is the minimum detectable VOC concentration for Method 25?
    c. 50 ppm

15. What type of bias occurs with Method 25 when the stack gas has high concentrations of CO_2 and water vapor?
    a. Positive

16. Which of the following is not part of a Method 25 sampling train?
    c. Impingers

17. What type of detector is used in Method 25 and Method 25A?
    a. FID

18. When can Method 25 be used to determine mass emissions of VOC?
    c. When the composition of the gas stream is known

19. Which of the following compounds would not be appropriate for analysis by Method 25A?
    a. Methylene chloride

20. On what basis does Method 25A determine organic concentration in a mixed gas stream?
    b. Wet

References

DeWees, B., S. Eckard and C. Davis-Eckard, “Manual for Coordination of VOC Emissions Testing Using EPA Methods 18, 21, 25 and 25A”, EPA 340/1-91-008, September 1991.

Jahnke, J.A., “Measuring the Emission of Organic Compounds to the Atmosphere”, EPA 450/2-84-005, September 1984.

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4 National Sources and the Regulatory Approach

VOC emissions in any particular area will, of course, depend on the types and numbers of emission sources. However, it is useful to explore emissions on a national level to gain an understanding of the importance of various source categories. In this chapter, we will examine VOC emission trends over about the past one hundred years and the recent emissions in each state. We will also look at a recent national emission inventory for anthropogenic emissions and the total emissions attributed to biogenic sources. Finally, we will discuss the regulatory approach that is taken at the Federal level to reduce VOC emissions.

4.1 EMISSION TRENDS

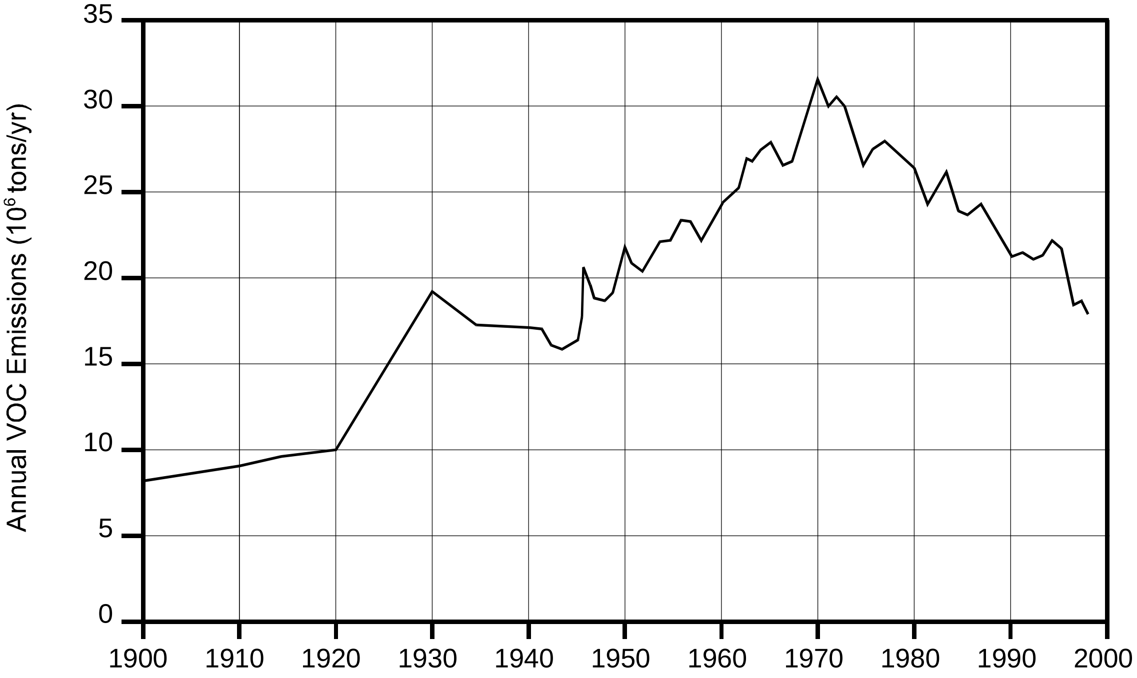

Figure 4-1. Trend in national VOC emissions

The trend in national anthropogenic VOC emissions since 1900 is shown in Figure 4-1. From 1900 to 1970, emissions increased about 264%. However, since 1970, emissions have decreased about 42%, from 30.982 million tons in 1970 to 17.917 million tons in 1998. This represents a significant reduction; however, it is even more significant when one recognizes that population and, accordingly, the number of VOC sources continued to increase over this period. Perhaps a better indication of the effectiveness of our VOC reduction strategies is shown in Figure 4-2, where emissions are expressed in tons per 1,000 people. Here we see that per capita emissions have decreased about 56% since 1970.

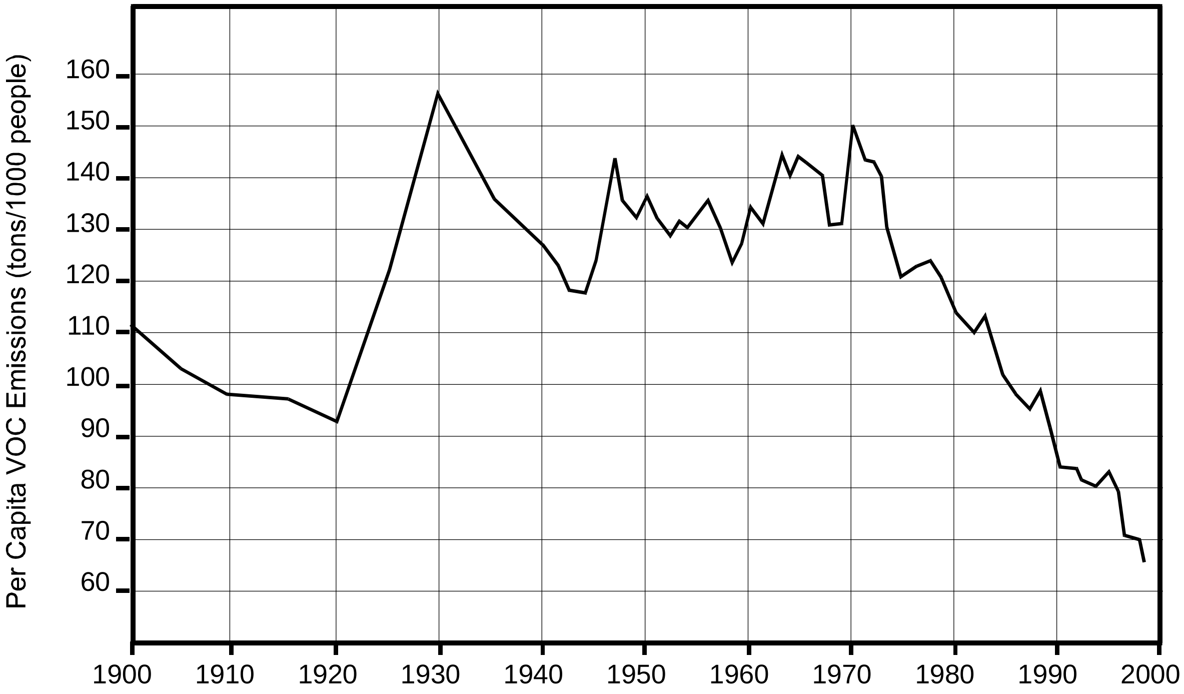

Figure 4-2. Trend in national per capita VOC emissions

Those with the good fortune to live in the Great State of Texas know that it leads the nation in just about everything. Unfortunately, as shown in Table 4-1, this is also true for anthropogenic VOC emissions. In 1998, Texas emitted 1.388 million tons of VOCs, accounting for 7.75% of the national total. Second in emissions was California, with 1.215 million tons or 6.78% of the total. Other significant emitters were Florida, Michigan, New York, Illinois, Ohio, North Carolina, Georgia and Pennsylvania. The state with the lowest VOC emissions was Vermont, with 44 thousand tons or 0.25% of the total. The District of Columbia contributed only 22 thousand tons or 0.12% of the total.

Table 4-1. State Ranking of VOC Emissions for 1998

Rank	State	Emissions (10^3 tons/year)	% of Total
1	Texas	1,388	7.75
2	California	1,215	6.78
3	Florida	891	4.97
4	Michigan	765	4.27
5	New York	753	4.20
6	Illinois	748	4.17
7	Ohio	706	3.94
8	North Carolina	605	3.38
9	Georgia	576	3.21
10	Pennsylvania	575	3.21
11	Tennessee	528	2.95
12	Indiana	518	2.89
13	Virginia	471	2.63
14	Alaska	457	2.55
15	Louisiana	425	2.37
16	Alabama	419	2.34
17	New Jersey	408	2.28
18	Wisconsin	400	2.23
19	Minnesota	381	2.13
20	Missouri	360	2.01
21	Washington	347	1.94
22	South Carolina	334	1.86
23	Kentucky	330	1.84
24	Mississippi	304	1.70
25	Oklahoma	295	1.65
26	Arizona	281	1.57
27	Colorado	274	1.53
28	Oregon	272	1.52
29	Massachusetts	264	1.47
30	Kansas	257	1.43
31	Iowa	239	1.33
32	Arkansas	223	1.24
33	Maryland	183	1.02
34	Utah	161	0.90
35	Connecticut	156	0.87
36	Nebraska	154	0.86
37	West Virginia	141	0.79
38	New Mexico	140	0.78
39	Idaho	115	0.64
40	Maine	109	0.61
41	North Dakota	106	0.59
42	Montana	105	0.59
43	Nevada	98	0.55
44	South Dakota	78	0.44
45	New Hampshire	74	0.41
46	Wyoming	68	0.38
47	Hawaii	54	0.30
48	Delaware	51	0.28
49	Rhode Island	49	0.27
50	Vermont	44	0.25
51	DC	22	0.12
Total		17,917	100.00

4.2 EMISSION INVENTORY

The national inventory of anthropogenic VOC emissions is shown in Table 4-2 for 1970, 1980, 1990 and 1998. The percentage contribution for each source category in 1998 is also shown. The category that was the greatest contributor to national VOC emissions in 1998 was industrial processes, with emissions of 6.006 million tons or 33.5% of the total. This represented a reduction of about 44% since 1970, when it was the second greatest contributor. The inventory for industrial processes will be discussed further below.

Table 4-2. National Anthropogenic VOC Emissions

Source Category	Emissions (10^3 tons/year)				%
	1970	1980	1990	1998	1998
On-road vehicles	12,972	8,979	6,313	5,326	29.7
Light-duty gas vehicles & motorcycles	9,193	5,907	3,947	2,832	15.8
Light-duty gas trucks	2,770	2,059	1,622	2,015	11.2
Heavy-duty gas vehicles	743	611	432	257	1.4
Diesel vehicles	266	402	312	222	1.2
Non-road vehicles and engines	1,878	2,312	2,545	2,461	13.7
Aircraft	97	146	180	177	1.0
Railroads	22	33	52	50	0.3
Marine vessels	7	19	32	35	0.2
Recreational marine vessels	736	830	787	783	4.4
Recreational equipment	138	152	129	136	0.8
Lawn and garden equipment	514	587	710	655	3.7
Farm equipment	49	155	146	132	0.7
Commercial equipment	122	135	184	172	1.0
Construction equipment	121	174	225	229	1.3
Industrial equipment	63	61	73	64	0.4
Other non-road equipment	9	20	27	28	0.2
Stationary fuel combustion	721	1,050	1,005	893	5.0
Electric utility	30	45	47	54	0.3
Industrial	150	157	182	161	0.9
Commercial	11	11	12	16	0.1
Residential	530	837	756	654	3.7
Other			8	8	0.0
Industrial processes	10,653	11,101	7,114	6,006	33.5
Non-industrial solvent use	1,674	1,002	1,900	2,012	11.2
Cutback asphalt	1,045	323	199	144	0.8
Pesticide application	241	241	258	405	2.3
Adhesives			361	313	1.7
Consumer solvents			1,082	1,099	6.1
Other	388	438		51	0.3

Waste disposal and recycling	1,984	758	986	433	2.4
Natural sources			14	14	0.1
Miscellaneous	1,100	1,134	1,059	772	4.3
Total	30,982	26,336	20,936	17,917	100.0

The source category making the second greatest contribution to VOC emissions in 1998 was on-road vehicles, with emissions of 5.326 million tons or 29.7% of the total. This represented a reduction of about 59% since 1970, when it was the greatest contributor. This category was dominated by light-duty gas vehicles and motorcycles, whose emissions had decreased about 69% since 1970, and by light-duty gas trucks, whose emissions had decreased about 27%.

The next most significant source category in 1998 was non-road vehicles and engines. These sources contributed 2.461 million tons of VOC emissions or 13.7% of the total. This category was dominated by recreational marine vessels and lawn and garden equipment, which accounted for over half of the emissions.

Non-industrial solvent use was the next most important category in 1998, with emissions of 2.012 million tons or 11.2% of the total. This represented an increase of about 20% since 1970. The most significant sources in this category were consumer solvents, which accounted for over half of the emissions, and pesticide application. A relatively minor contributor was the use of cutback asphalt, which had decreased about 86% since 1970.

Stationary fuel combustion contributed only 5% of the VOC emissions in 1998, with most of that coming from residential wood combustion. Other small contributors were waste disposal and recycling at 2.4%, natural anthropogenic sources at 0.1%, and miscellaneous sources at 4.3%.

The emission inventory for industrial processes is shown in Table 4-3 for 1970, 1980, 1990 and 1998. The percentage contribution for each industrial source category in 1998 is also shown. As might be expected, the category that was the greatest contributor to national industrial VOC emissions in 1998 was solvent utilization, with emissions of 3.265 million tons or 54.4% of the total for industrial processes. This represented a reduction of about 41% since 1970. The most significant source in this category was surface coating, with 37.0% of the total for industrial processes.

The source category making the second greatest contribution to industrial VOC emissions in 1998 was storage and transport of organic materials. These sources contributed 1.323 million tons of VOC emissions or 22.0% of the total for industrial processes. This represented a reduction of about 32% since 1970. The most significant sources in this category were service stations and petroleum product storage.

The next most significant industrial source category in 1998 was petroleum industries, with VOC emissions of 497 thousand tons or 8.3% of the total for industrial processes. This represented a reduction of about 58% since 1970. The most important contributors in this category were oil and gas production and petroleum refining.

Table 4-3. National Industrial VOC Emissions

Source Category	Emissions (10^3 tons/year)				%
	1970	1980	1990	1998	1998
Chemical manufacturing	1,341	1,595	634	396	6.6
Organic chemicals	629	884	192	137	2.3
Inorganic chemicals	65	93	2	3	0.0
Polymers and resins	271	384	242	125	2.1
Pharmaceuticals	40	77	20	8	0.1
Other	336	157	178	123	2.0
Metals processing	394	273	122	75	1.2
Petroleum industries	1,195	1,440	612	497	8.3
Oil and gas production	411	379	301	268	4.5
Petroleum refining	773	1,045	308	224	3.7
Asphalt manufacturing	11	16	3	5	0.1
Solvent utilization	5,499	5,581	3,850	3,265	54.4
Degreasing	707	513	744	457	7.6
Graphic arts	319	373	274	311	5.2
Dry cleaning	263	320	215	169	2.8
Surface coating	3,570	3,685	2,523	2,224	37.0
Other	640	690	94	104	1.7
Storage and transport	1,954	1,975	1,495	1,323	22.0
Petroleum product storage	899	823	516	395	6.6
Petroleum product transport	92	61	151	122	2.0
Service stations	937	1,045	786	773	12.9
Organic chemical storage/transport	26	46	40	31	0.5
Other			2	2	0.0
Other industrial processes	270	237	401	450	7.5
Agricultural and food products	208	191	138	125	2.1
Rubber and plastic products	60	44	58	52	0.9
Wood, pulp and paper products			96	148	2.5
Textile, leather & apparel products			20	15	0.2
Mineral products	2	2	18	31	0.5
Miscellaneous			71	79	1.3
Total	10,653	11,101	7,114	6,006	100.0

Chemical manufacturing contributed 396 thousand tons of VOC emissions in 1998 or 6.6% of the total for industrial processes. This represented a reduction of about 70% since 1970. Other industrial process contributed the remaining 450 thousand tons.

Biogenic VOC emission estimates for 1998 were not available at the time of writing. However, in 1997, total biogenic emissions were estimated to be 28.194 million tons. Once again, the leading contributor was the State of Texas with 2.431 million tons. Other significant contributors were California (1.623 million tons), Alabama (1.579 million tons), Arkansas (1.517 million tons), Mississippi (1.419 million tons), Georgia (1.405 million tons), Florida (1.307 million tons), Louisiana (1.187 million tons), Oregon (1.075 million tons) and Missouri (1.045 million tons). Anthropogenic VOC emissions for 1997 were estimated to be 18.876 million tons. This gives a total national VOC emission for 1997 of 47.070 million tons, about 40% anthropogenic and about 60% biogenic.

4.3 REGULATORY APPROACH

On December 2, 1970, Congress created the U.S. Environmental Protection Agency (USEPA) and charged it with the responsibility of setting National Ambient Air Quality Standards (NAAQS). In response to this mandate, the USEPA promulgated NAAQS on April 30, 1971, for photochemical oxidants, nitrogen oxides, sulfur dioxide, total suspended particulate matter, carbon monoxide and hydrocarbons. Of these, only the hydrocarbon standard was not set because of health considerations, but rather as an aid to attaining the photochemical oxidants standard. That standard was later removed as the ozone (photochemical oxidants) attainment strategy changed.

The photochemical oxidants standard formulated by USEPA set an hourly average level of 0.08 ppm that was not to be exceeded more than once per year. In 1979, USEPA changed the designation of the NAAQS from photochemical oxidants to ozone and revised the 1-hour standard to 0.12 ppm. Compliance with this standard is attained when the expected exceedance, as determined by Appendix H of 40CFR50, is equal to or less than 1.

On July 18, 1997, USEPA once again revised the ozone standard, returning it to 0.08 ppm, but with an averaging time of 8 hours. Compliance with this standard is based on the 3-year average of the fourth highest daily maximum 8-hour ozone concentration. In May of 1999, the U.S. Court of Appeals for the D.C. District ruled that Congress had delegated too much power to USEPA when revising NAAQS and that there was no determinate criteria provided to guide them, thus placing the status of the new standard in question. However, on February 27, 2001, the U.S. Supreme Court ruled that the Clean Air Act does not delegate legislative power to USEPA in violation of the U.S. Constitution, opening the way for implementation of the new standard.

Although the Supreme Court opened the way for implementation of the new standard, it further ruled that the plan proposed by USEPA was illegal. While this issue has not been resolved at the time of writing, it is likely that areas will be required to achieve the 1-hour standard before their status with regard to the 8-hour standard is determined. Areas that attain the 1-hour standard but not the 8-hour standard will likely be classed as transitional and additional requirements for these areas developed by USEPA.

4.3.1 Nonattainment Area Classifications and Requirements

Areas that fail to meet the 1-hour ozone NAAQS or that contribute to the failure of nearby areas are designated as nonattainment. In addressing ozone nonattainment, Congress adopted a graduated program in which areas with more significant ozone problems are allowed more time for compliance but are required to implement more stringent controls. These area classifications, along with their respective attainment dates, are shown in Table 4-4. USEPA may authorize two 1-year extensions beyond the specified deadline if the state containing the area has complied with all State Implementation Plan (SIP) requirements and the area has had no more than one exceedance of the NAAQS in the preceding year. The SIP requirements for each of these areas are summarized in the following paragraphs.

Table 4-4. Ozone Nonattainment Classifications

Classification	Concentration (ppm)	Attainment Date
Marginal	0.121-0.138	November 15, 1993
Moderate	0.138-0.160	November 15, 1996
Serious	0.160-0.180	November 15, 1999
Severe	0.180-0.190 0.190-0.280	November 15, 2005 November 15, 2007
Extreme	0.280 and above	November 15, 2010

4.3.1.1 Marginal Areas

Forty-three areas were originally designated as marginal in 1991. By August 2, 2001, that number had decreased to 21. The following summarizes the SIP requirements for these areas:

- Existing motor vehicle inspection and maintenance programs must comply with USEPA guidelines.
- Reasonable available control technology (RACT) in accordance with USEPA guidelines must be required for existing sources of VOCs.
- New or modified major sources (those that emit or have the potential to emit at least 100 tons of VOCs per year) must obtain permits and undergo review.
- The VOC emission offset ratio for new or modified major sources must be at least 1.1 to 1.
- VOC emissions must be inventoried every three years.

- Stationary sources of VOCs or NO_x must submit annual emission statements. This requirement may be waived for sources emitting less than 25 tons/year, if the state included the emissions in its 3-year inventory.

4.3.1.2 Moderate Areas

Thirty-one areas were originally designated as moderate in 1991. By August 2, 2001, that number had decreased to 10. In addition to the provisions for marginal areas, the following summarizes the SIP requirements that must be met in these areas:

- A basic motor vehicle inspection and maintenance program must be implemented.
- RACT must be required for all existing sources of VOC for which a Control Technique Guideline (CTG) has been issued by USEPA. It must also be required for all existing major sources of VOC for which a CTG has not been issued.
- The VOC offset ratio for new or modified major sources must be at least 1.15 to 1.
- In order to show reasonable further progress, VOCs must be reduced at least 15% each year over the 6-year period allowed to reach attainment.
- Contingency measures that will be automatically undertaken if an area fails to make reasonable further progress or to achieve attainment by the deadline must be developed.

4.3.1.3 Serious Areas

Fourteen areas were originally designated as serious in 1991. By August 2, 2001, that number had not changed. In addition to the provisions for moderate areas, the following summarizes the SIP requirements that must be met in these areas:

- Programs for improved monitoring of ambient ozone and ozone precursors and for improved monitoring of VOC and NO_x emissions must be implemented.
- A major source must be defined as any stationary source that emits or has the potential to emit at least 50 tons of VOCs per year.
- The VOC offset ratio for new or modified major sources must be at least 1.2 to 1.
- If a major source undertaking modification offsets any increase in emissions by a ratio of at least 1.3 to 1, only best available control technology (BACT), rather than lowest achievable emission rate (LAER), will be required.
- In general, any change that results in an increase in VOC emissions from a major source is considered a modification triggering the permit requirements.

- Any gasoline dispensing facility that sells more than 10,000 gallons per month and independent small business marketers that sell more than 50,000 gallons per month must install and operate a Stage II emission control system. An exemption may be granted if USEPA determines that the use of on-board vapor recovery systems is widespread.
- An enhanced program to reduce VOC and NO_x emissions from in-use vehicles must be implemented in urban areas with a 1980 population of 200,000 or more.
- In order to show reasonable further progress, VOCs must be reduced at least 3% each year averaged over each consecutive 3-year period until the attainment deadline.
- Transportation control measures consistent with USEPA guidelines and capable of bringing emissions within projected levels must be implemented.

4.3.1.4 Severe Areas

Four areas with a compliance deadline in 2005 and 5 areas with a compliance deadline in 2007 were originally designated as severe in 1991. By August 2, 2001, those numbers had not changed. In addition to the provisions for serious areas, the following summarizes the SIP requirements that must be met in these areas:

- A major source must be defined as any stationary source that emits or has the potential to emit at least 25 tons of VOCs per year.
- The VOC offset ratio for new or modified major sources must be at least 1.3 to 1. If all existing major sources are required to use BACT, the required offset ratio is 1.2 to 1.
- Transportation control measures must be implemented to offset growth in emissions from an increase in vehicle miles traveled.
- Any company employing 100 or more persons must reduce employee work-related vehicle trips and increase average vehicle ridership, unless an alternative plan for reducing emissions is approved.

4.3.1.5 Extreme Areas

Only 1 area was originally designated as extreme in 1991, the Los Angeles South Coast Air Basin. That had not changed by August 2, 2001. In addition to the provisions for severe areas, the following summarizes the SIP requirements that must be met in this area:

- A major source must be defined as any stationary source that emits or has the potential to emit at least 10 tons of VOCs per year.

- The VOC offset ratio for new or modified major sources must be at least 1.5 to 1. If all existing major sources are required to use BACT, the required offset ratio is 1.2 to 1.
- Any VOC increase from a major source will trigger new source review.
- Electric utilities and industrial and commercial boilers that have actual emissions of more than 25 tons/year must burn clean fuel 90% of the time or use advanced control technology for the control of NO_x emissions.
- Traffic control measures must be established during heavy traffic hours to reduce the use of high-polluting vehicles.
- The hoped-for development of new control technologies or improved existing technologies may be used for reductions, provided it is not needed in the first 10 years.

4.3.1.6 Ozone Transport Regions

Under Title I of the Clean Air Act, all SIPs must prohibit emissions that interfere with the Clean Air Act requirements of other states. To ensure that this is met, the 1990 Amendments established a new provision to address the interstate transport of air pollutants. When it is determined that the interstate transport of pollutants from one or more states is significantly contributing to a violation of a NAAQS in another state or states, USEPA may establish a transport region that includes those states. After designating a transport region, USEPA must establish a transport commission made up of representatives of the states. The following summarizes the SIP requirements that must be met in an ozone transport region:

- An enhanced inspection and maintenance program for motor vehicles in all metropolitan statistical areas with a population of 100,000 or more must be implemented.
- RACT must be required for all existing sources of VOC for which a Control Technique Guideline (CTG) has been issued by USEPA. It must also be required for all existing major sources of VOC for which a CTG has not been issued.
- Major stationary sources of VOCs must undergo new source review. A major source must be defined as any stationary source that emits or has the potential to emit at least 50 tons of VOCs per year.
- Major stationary sources of NO_x may be required to comply with RACT and new source review.
- A Stage II gasoline vapor recovery program or other measures identified by USEPA as capable of achieving comparable reductions must be implemented.

The only ozone transport region created to date is the Northeast Ozone Transport Region. It consists of the states of Connecticut, Delaware, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, Vermont and the CMSA that includes the District of Columbia (which includes part of northern Virginia).

The provisions for the regulation of stationary sources and for the demonstration of reasonable further progress that are outlined in the paragraphs above focus on the reduction of VOC emissions. Where NO_x reductions are mentioned, they are generally optional and can be used if it is determined that they would contribute to attainment. The reason for this flexibility is the complex nature of the relationship between NO_x and ozone. Although NO_x emissions play an important role in ozone formation, the scavenging ability of NO_x under some conditions can cause increased ozone levels when NO_x emissions are decreased. In general, the requirements for major stationary sources of VOCs also apply to major stationary sources of NO_x, unless USEPA determines that NO_x reductions would not be beneficial.

4.3.2 Regulation of Existing Sources

The Federal policies for existing sources are shown in Figure 4-3. The large circle represents nonattainment areas and the space outside of it represents attainment areas. The smaller circles show how the different control policies apply and overlap between the areas. No Federal policies are indicated for attainment areas. This is because, with the exception of Title III provisions, regulation of existing sources in an attainment area is the primary responsibility of the states. However, whether the source is located in an attainment or nonattainment area, it must comply with permitting provisions and may bank emission reductions for future expansion.

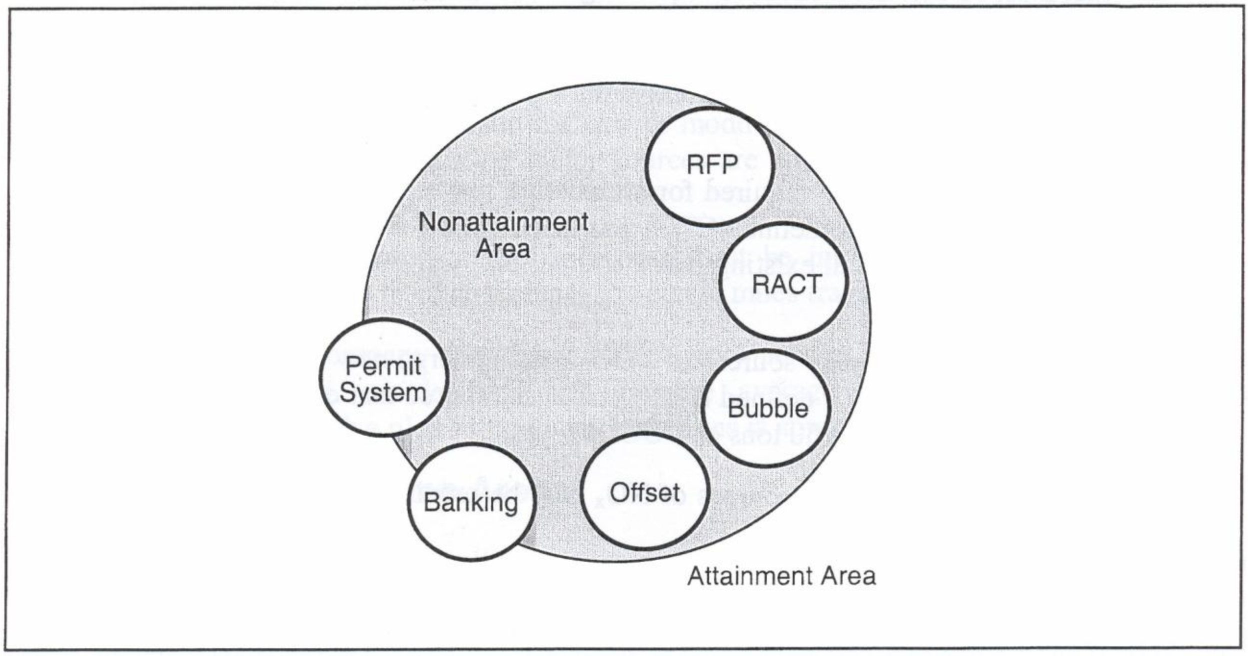

Figure 4-3. Existing source policies

Existing sources located in a nonattainment area must apply RACT so that the area can reach attainment status according to the reasonable further progress (RFP) schedule developed in the SIP. By reducing emissions more than required, an existing source may provide an offset for a new source or it may bank them for future expansion. Existing sources may also elect to bubble emissions. This policy treats a plant as if an imaginary bubble were placed over it. Changes can be made in different plant operations so long as the overall VOC emissions from the bubble are reduced.

In order to provide the states guidance in setting RACT emission limits, USEPA has published a series of documents referred to as Control Technique Guidelines (CTGs). These documents are not regulations, but serve only as an information base from which state and local agencies can develop their own regulations. Tables 4-5 through 4-8 list the stationary source categories for which a CTG has been developed. There is no significance to the Group I, Group II, Group III and Post-1990 designations, other than the date the CTG was promulgated. However, it should be noted that the more significant sources of surface coating, graphic arts and petroleum product refining, storage and distribution were addressed in the earlier groups.

Table 4-5. Group I Control Technique Guideline Documents

Source Category	Reference No.
Surface coating operations	EPA 450/2-76-028
Surface coating of cans, coils, paper, fabrics, automobiles, and light-duty trucks	EPA 450/2-77-008
Surface coating of metal furniture	EPA 450/2-77-032
Surface coating of insulation of magnet wire	EPA 450/2-77-033
Surface coating of large appliances	EPA 450/2-77-034
Storage of petroleum liquids in fixed roof tanks	EPA 450/2-77-036
Bulk gasoline tanks	EPA 450/2-77-035
Solvent metal cleaning	EPA 450/2-77-022
Use of cutback asphalt	EPA 450/2-77-037
Refinery vacuum producing systems, wastewater separation, and process unit turnarounds	EPA 450/2-77-025
Hydrocarbons from tank truck gasoline loading terminals	EPA 450/2-77-026
Design criteria for Stage I vapor control systems--gasoline service stations	USEPA, OAQPS, November 1975

Table 4-6. Group II Control Technique Guideline Documents

Source Category	Reference No.
Control techniques for volatile organic emissions from stationary sources	EPA 450/2-78-022
Leaks from petroleum refinery equipment	EPA 450/2-78-036
Surface coating of miscellaneous metal parts and products	EPA 450/2-78-015
Manufacture of vegetable oils	EPA 450/2-78-035
Surface coating of flat wood paneling	EPA 450/2-78-032
Manufacture of synthesized pharmaceutical products	EPA 450/2-78-029
Manufacture of pneumatic rubber tires	EPA 450/2-78-030
Graphic arts--rotogravure and flexography	EPA 450/2-78-033
Petroleum liquid storage in external floating roof tanks	EPA 450/2-78-047
Perchloroethylene dry cleaning systems	EPA 450/2-78-050
Leaks from gasoline tank trucks and vapor collection systems	EPA 450/2-78-051

Table 4-7. Group III Control Technique Guideline Documents

Source Category	Reference No.
Manufacture of high-density polyethylene, polypropylene, and polystyrene resins	EPA 450/3-83-008
Synthetic organic chemical, polymer, and resin manufacturing equipment	EPA 450/3-83-006
Large petroleum dry cleaners	EPA 450/3-82-009
Air oxidation processes in synthetic organic chemical manufacturing industry	EPA 450/3-84-015
Leaks from natural gas/gasoline processing plants	EPA 450/3-83-007

Table 4-8. Post-1990 Control Technique Guideline Documents

Source Category	Reference No.
Control techniques for VOC emissions from stationary sources	EPA 453/R-92-018
Reactor processes and distillation operations in SOCMI	EPA 450/4-91-031
Offset lithographic printing	EPA 453/D-95-001
Wood furniture manufacturing operations	EPA 453/R-96-007
Shipbuilding and ship repair operations (surface coating)	61FR44050 August 27, 1996
Coating operations at aerospace manufacturing and rework operations	EPA 453/R-97-004
Beyond VOC RACT CTG requirements	EPA 453/R-95-010
Batch processes	EPA 453/R-93-017
Industrial wastewater	EPA 450/D-93-056
Volatile organic liquid storage tanks	EPA 453/D-93-057

The following information is contained in a CTG document:

- Definition of the affected facilities
- Number of affected facilities in the country
- National VOC emissions from the facilities
- VOC emission range per facility
- Source size emitting at least 100 tons/year
- Recommended RACT emission limit
- VOC reduction per facility after RACT is applied
- Capital and annual costs of control and the cost per ton of VOC removed

Promulgation of a CTG is a time intensive process. A draft document is prepared and published for review. Relevant comments on the draft are addressed and the final document promulgated. Although the CTG process is still alive, it has not been very active since the mid-1990s. With the 1990 Amendments, there was a need to get timely guidance to the states. To accomplish this, Alternative Control Technology (ACT) documents were developed. These documents are issued without review; however, they contain only descriptions of alternative controls, with no recommended

RACT emission limit. Table 4-9 lists the ACTs that have been published to date for VOC sources.

Another source for RACT guidance is the RACT/BACT/LAER Clearinghouse or RBLC. The RBLC provides data on prevention and control technology determinations made by state and local agencies. It is designed to help permit applicants and reviewers make pollution prevention and control technology decisions for stationary sources and includes data submitted by states and territories on over 200 different air pollutants and 1,000 industrial processes. The Clearinghouse also has a regulation database that summarizes all emission standards and CTGs issued by USEPA. The database is organized so that a rule is associated with the type of facility that is governed by the regulation. Facility-level information includes rule status, statutory basis for emission limits, proposed and effective dates, references to supporting technical documentation, and explanatory notes. Pollutant-level information includes details about add-on equipment and/or pollution prevention methods that can satisfy the rule, estimated capital costs, annualized costs, and cost effectiveness in dollars per ton. The RBLC can be accessed on-line at http://cfpub1.epa.gov/rblc/htm/bl02.cfm.

Table 4-9. Alternative Control Technology Documents

Source Category	Reference No.
Halogenated solvent cleaners	EPA 450/3-89-030
Application of traffic markings	EPA 450/3-88-007
Ethylene oxide sterilization/fumigation operations	EPA 450/3-89-007
Automobile refinishing	EPA 453/R-94-031
Organic waste process vents	EPA 450/3-91-007
Polystyrene foam manufacturing	EPA 450/3-90-020
Bakery oven emissions	EPA 453/R-92-017
Carbon reactivation processes	EPA 453/R-92-019
Surface coating operations at shipbuilding and ship repair facilities	EPA 453/R-94-032
Batch processes	EPA 453/R-94-020
Industrial cleaning solvents	EPA 453/R-94-015
Air emissions from industrial wastewater	CTG with revised option tables: 4/94
Offset lithographic printing	EPA 453/R-94-054
Application of agricultural pesticides	EPA 453/R-92-011
Surface coating of automotive/transportation and business machine plastic parts	EPA 453/R-94-017
Volatile organic liquids storage in floating and fixed roof tanks	EPA 453/R-94-001

4.3.3 Regulation of New and Modified Sources

The Federal policies for new and modified sources are shown in Figure 4-4. New or modified sources located in attainment areas must comply with any applicable New Source Performance Standard (NSPS) or, in general, apply Best Available Control

Technology (BACT). They must also comply with Prevention of Significant Deterioration (PSD) provisions. Whether the source is located in an attainment or nonattainment area, it must comply with permitting provisions and may bank emission reductions for future expansion. New or modified sources located in a nonattainment area must meet a Lowest Achievable Emission Rate (LAER) level of control, comply with the RFP provisions of the SIP and obtain offsets. All of this is overseen by USEPA's New Source Review (NSR) program.

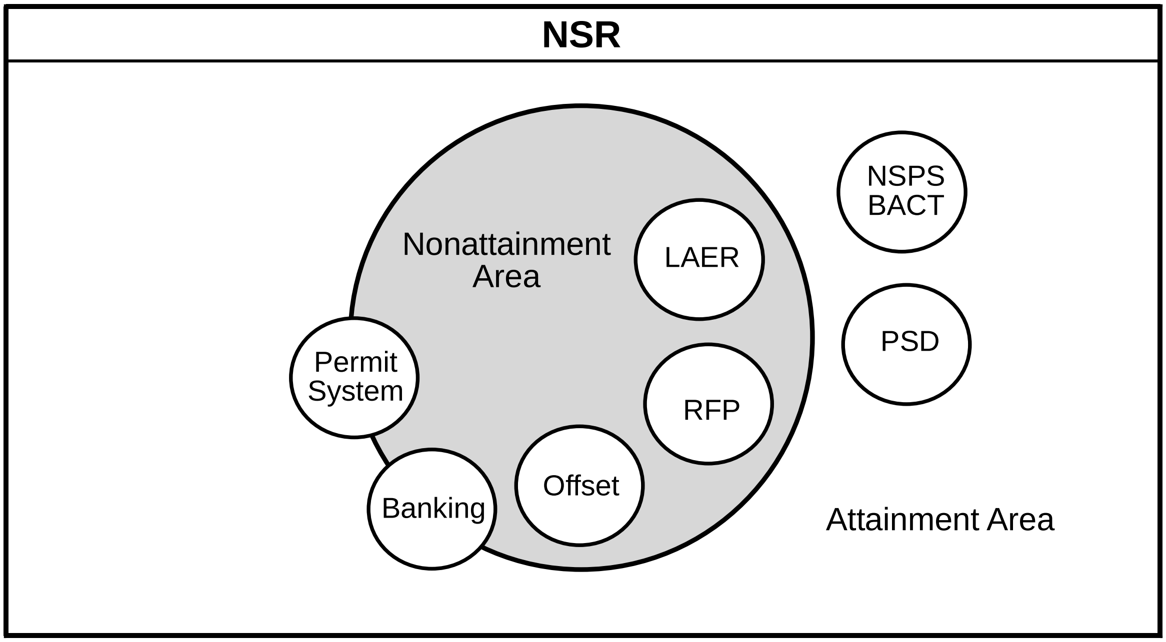

Figure 4-4. New and modified source policies

NSPS standards that apply to VOC sources are listed in Table 4-10. Guidance in determining BACT and LAER levels of control is available in the RBLC.

Table 4-10. New Source Performance Standards for VOC Sources (40CFR60)

Subpart	Source Category
K	Storage vessels for petroleum liquids (constructed after June 11, 1973)
Ka	Storage vessels for petroleum liquids (constructed after May 18, 1978)
Kb	Volatile organic liquid storage vessels (constructed after July 23, 1984)
EE	Surface coating of metal furniture
MM	Automobile and light-duty truck surface coating operations
QQ	Graphic arts industry: Publication rotogravure printing
RR	Pressure sensitive tape and label surface coating operations
SS	Industrial surface coating: Large appliances
TT	Metal coil surface coating
VV	Equipment leaks of VOC in the SOCMI
WW	Beverage can surface coating industry
XX	Bulk gasoline terminals
BBB	Rubber tire manufacturing industry
DDD	VOC emissions from the polymer manufacturing industry
FFF	Flexible vinyl and urethane coating and printing
GGG	Equipment leaks of VOC in petroleum refineries
HHH	Synthetic fiber production facilities
III	VOC emissions from the SOCMI air oxidation unit processes
JJJ	Petroleum dry cleaners
KKK	Equipment leaks of VOC from onshore natural gas processing plants

Table 4-10. New Source Performance Standards for VOC Sources (40CFR60) (cont.)

Subpart	Source Category
NNN	VOC emissions from SOCMI distillation operations
QQQ	VOC emissions from petroleum refinery wastewater systems
RRR	VOC emissions from SOCMI reactor processes
SSS	Magnetic tape coating facilities
TTT	Industrial surface coating: Plastic parts for business machines
VVV	Polymeric coating of supporting substrates facilities
WWW	Municipal Solid Waste Landfills

4.3.4 Regulation of Hazardous Air Pollutants

Although toxic air pollutants are not specifically addressed in this course, many VOCs are also classified as volatile hazardous air pollutants (VHAP). New or existing sources that emit more than 10 tons/year of a single VHAP or more than 25 tons/year of a combination of VHAPs must apply Maximum Achievable Control Technology (MACT). The MACT standards for VHAPs at the time of writing are listed in Table 4-11. Students with specific interests in hazardous air pollutants are referred to APTI Course 400.

Table 4-11. MACT Standards for VHAP Sources (40CFR63)

Subpart	Source Category
F	Organic hazardous air pollutants from the SOCMI
G	Organic hazardous air pollutants from the SOCMI for process vents, storage vessels, transfer operations and wastewater
H	Organic hazardous air pollutants for equipment leaks
I	Organic hazardous air pollutants for certain processes subject to the negotiated regulation for equipment leaks
M	Perchloroethylene dry cleaning facilities
O	Ethylene oxide emissions from sterilization facilities
R	Gasoline distribution facilities
T	Halogenated solvent cleaning
U	Group I polymers and resins
W	Epoxy resins production and non-nylon polyamides production
Y	Marine tank vessel loading operations
CC	Petroleum refineries
DD	Off-site waste and recovery operations
EE	Magnetic tape manufacturing operations
GG	Aerospace manufacturing and re-work facilities
HH	Oil and natural gas production
II	Shipbuilding and ship repair (surface coating)
JJ	Wood furniture manufacturing operations
KK	Printing and publishing industry
GGG	Pharmaceuticals production
HHH	Natural gas transmission and storage

Table 4-11. MACT Standards for VHAP Sources (cont.)

Subpart	Source Category
III	Flexible polyurethane foam production
JJJ	Group IV polymers and resins
MMM	Pesticide active ingredient production
OOO	Group III polymers and resins
PPP	Polyether polyols production
CCCC	Manufacturing nutritional yeast
GGGG	Solvent extraction for vegetable oil production
VVVV	Boat manufacturing

Review Questions

1. What is the current national emission rate of anthropogenic VOC emissions?
   a. Less than 18 million tons/year
   b. 20 million tons/year
   c. 25 million tons/year
   d. More than 30 million tons/year

2. How do biogenic emissions of VOCs compare to anthropogenic emissions?
   a. Less than
   b. Greater than
   c. About the same

3. What source category is responsible for the greatest amount of VOC emissions?
   a. Stationary combustion
   b. On-road vehicles
   c. Off-road vehicles
   d. Industrial processes

4. What source category is responsible for the second greatest amount of VOC emissions?
   a. Stationary combustion
   b. On-road vehicles
   c. Off-road vehicles
   d. Industrial processes

5. What industrial source category is responsible for the greatest amount of VOC emissions?
   a. Chemical manufacturing
   b. Petroleum industries
   c. Solvent utilization
   d. Storage and transport of organic materials

6. What industrial source category is responsible for the second greatest amount of VOC emissions?

a. Chemical manufacturing
b. Petroleum industries
c. Solvent utilization
d. Storage and transport of organic materials

7. What is the current NAAQS for ozone? Select all that apply.

a. 0.08 ppm, 1-hour average

b. 0.08 ppm, 8-hour average

c. 0.12 ppm, 1-hour average

d. 0.12 ppm, 8-hour average

8. What level of control must be applied to existing sources in a nonattainment area?

- **a. RACT**
- **b. BACT**
- **c. LAER**

9. What level of control must be applied to new sources in a nonattainment area?

a. RACT

b. BACT

c. LAER

10. What level of control must be applied to new sources in an attainment area?

- **a. RACT**

- **b. BACT**

- **c. LAER**

Review Answers

1. What is the current national emission rate of anthropogenic VOC emissions?
   a. Less than 18 million tons/year

2. How do biogenic emissions of VOCs compare to anthropogenic emissions?
   b. Greater than

3. What source category is responsible for the greatest amount of VOC emissions?
   d. Industrial processes

4. What source category is responsible for the second greatest amount of VOC emissions?
   b. On-road vehicles

5. What industrial source category is responsible for the greatest amount of VOC emissions?
   c. Solvent utilization

6. **What industrial source category is responsible for the second greatest amount of VOC emissions?**
   d. Storage and transport of organic materials

7. What is the current NAAQS for ozone? Select all that apply.

b. **0.08 ppm, 8-hour average**

c. **0.12 ppm, 1-hour average**

8. What level of control must be applied to existing sources in a nonattainment area?

a. **RACT**

9. What level of control must be applied to new sources in a nonattainment area?

c. **LAER**

10. What level of control must be applied to new sources in an attainment area?

b. **BACT**

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5 Surface Coating

Surface coating involves the application of a wet or dry coating material to the surface of another material, either for decoration or for protection against damage or corrosion. Coatings are applied to a wide variety of materials or substrates, including metal, wood, paper, plastic and fabric. The shapes made from these materials range from flat panels and sheets to automotive bodies. The composition of the coating used depends on the substrate to which it will be applied, the shape of the object to be coated and the desired characteristics of the final surface. The method used to apply and cure the coating depends on the characteristics of the coating and the shape of the object being coated.

5.1 PROCESS DESCRIPTION

Although there is considerable diversity among surface coating operations, the basic steps involved in the process are similar. First, the material to be coated is prepared by having its surface cleaned and treated. This preparation may involve simply the removal of dust or may include degreasing, corrosion treatment or surface etching. Next, the coating is applied to the prepared surface. Application methods include spraying, dipping, flow coating, roller coating, and electrostatic deposition. Finally, the deposited coating is dried or cured to form the final surface. Drying or curing may be done at ambient temperature, in elevated temperature ovens or by exposure to radiation.

5.1.1 Surface Preparation

Preparation of the surface to be coated is necessary to insure proper bonding between the coating and the surface. Typically, the surface is cleaned with a detergent or aqueous alkaline solution in order to remove dirt, oil, grease and other contaminants. In some cases, organic degreasers may be used to remove heavy machine grease and milling agents. In automotive manufacturing and refinishing, a solvent wipe is often used after the initial cleaning step to remove any traces of oil and grease that might remain. Many surface preparation operations include acid etching to increase the surface area or a phosphate treatment or chromate conversion coating to promote good coating adhesion and provide for corrosion resistance. After the surface preparation is completed, the parts are dried prior to the application of the coating.

5.1.2 Types of Coatings

The types of coatings used in the surface coating industries are conventional solvent-borne coatings, high-solids coatings, waterborne coatings, powder coatings and radiation-cured coatings. With the exception of powder and radiation-cured coatings, they are all composed of solid resins, pigments and additives that are dispersed in a volatile carrier.

5.1.2.1 Conventional Coatings

For many years, coatings have been used that employ only organic solvents as the volatile carrier. Once the coating is applied, the organic solvent evaporates and the coating hardens. These coatings have been traditionally used because the solvent evaporates rapidly, allowing the coating to dry quickly, and they produce a durable, high quality surface. However, because of limitations in solubility, viscosity and related factors, only a limited number of monomers and pre-polymers can be used in the formulations. Solvent contents of conventional coatings used in the coil coating industry are shown in Table 5-1 and for other industries in Table 5-2.

Table 5-1

Conventional Coatings Used in Coil Coating

Coating	Volatile Content wt %
Acrylics	40% to 45%
Adhesives	70% to 80%
Alkyds	50% to 70%
Epoxies	45% to 70%
Fluorocarbons	55% to 60%
Phenolics	50% to 75%
Polyesters	45% to 50%
Silicones	35% to 50%
Vinyls	60% to 75%
Zincromet®	35% to 40%

5.1.2.2 High-Solids Coatings

High-solids coatings have higher solids content and, therefore, lower solvent content than conventional coatings. Because of the increased solids, a given quantity of the coating will cover more surface than a conventional coating and have less VOC emissions. There will also be less drum handling, reduced freight costs and reduced solvent removal energy. However, the viscosity of high-solids coatings is greater than for conventional coatings, which may require heating of the coating or modification of the application equipment or rate. Table 5-3 shows the emissions reductions achieved when various high-solids coatings are substituted for a conventional coating containing 65% solvent.

Table 5-2

Typical Solvent Content of Conventional Coatings Used in Various Industries

Industry	Coating	Volatile Content vol %
Metal furniture	Not specified	65%
Automobile and light-duty truck	Enamel	67% to 76%
Automobile and light-duty truck	Lacquer	82% to 88%
Automobile refinishing	Enamel	72% to 76%
Automobile refinishing	Lacquer	87% to 91%
Large appliance	Not specified	70%
Traffic marking	Alkyd	50%

Table 5-3

Emission Reductions for High-Solids Coatings

Coating	Emission Reduction, %
60% solids by volume	61% to 62%
65% solids by volume	69%
70% solids by volume	75%
80% solids by volume	85%

5.1.2.3 Waterborne Coatings

Waterborne solvents use water as the primary volatile carrier. They also contain 2% to 15% by volume of organic solvent to aid in wetting the pigments, to enhance solubility, and to promote good flow and viscosity characteristics. There are three forms of waterborne coatings: water-soluble dispersions, water-soluble polymers and emulsions. The water-soluble dispersions are usually transparent, water-soluble polymers are translucent and emulsions are opaque. Because of the lower organic solvent content of waterborne coatings, significant emission reductions can be realized. Table 5-4 shows the emission reductions achieved when different water-to-solvent ratio coatings are substituted for a conventional coating containing 65% solvent.

Table 5-4

Emission Reductions for Waterborne Coatings

Coating	Application Method	Emission Reduction, %
82/18 waterborne	Electrostatic spraying	80% to 82%
82/18 waterborne	Dip and flow coating	82%
82/18 waterborne	Electrodeposition	95%
67/33 waterborne	Electrostatic spraying	67%
67/33 waterborne	Dip and flow coating	67%

Waterborne coatings can use a larger number of different monomers and pre-polymers than conventional coatings, providing for a wide range of formulations. Waterborne coatings have reduced flammability and reduced toxicity. They are easier to clean up and the cleaning operations have lower VOC losses. They can also be used with higher solids concentrations without the significant increase in viscosity that occurs with solvent-borne coatings. However, water has a much higher heat of vaporization than organic solvents, but the coatings require less air flow in the oven to maintain appropriate humidity levels and avoid potentially explosive VOC concentrations. As a result of the combination of these two factors, energy input is approximately 20% to 25% higher than for conventional coatings. Also, temperature and humidity must be better controlled during curing in order to maintain surface quality and line speed. Special care must be taken when using electrostatic application, and both application and curing equipment are subject to corrosion. Metal parts require better surface preparation to remove traces of oil or grease that could inhibit adhesion. Some waterborne coatings exhibit poor surface quality, high rub-off and reduced weathering properties. However, more recent formulations have a higher gloss and improved weathering properties, and chalking and fade resistance are better than for conventional coatings.

5.1.2.4 Powder Coatings

Powder coatings are composed of fine, dry particles of paint solids and contain no solvent carrier. These coatings are either thermoplastic or thermosetting. Thermoplastic coatings melt when heat is applied, but continue to have the same chemical composition after cooling and hardening. Thermosetting coatings also melt when exposed to heat but then polymerize with themselves or with other reactive components to form a surface that is chemically different from the applied solids. Small quantities of VOC, usually less than 4%, may be emitted as by-products of the polymerization process. Because there is no solvent carrier and polymerization by-products of thermosetting powder coatings are low, large emission reductions can be realized. Table 5-5 shows the emission reductions achieved when different powder coatings are substituted for a conventional coating containing 65% solvent.

Table 5-5
Emission Reductions for Powder Coatings

Coating	Type	Emission Reduction, %
Epoxy	Thermosetting	97% to 99%
Acrylics	Thermosetting	99%
Urethane polyester	Thermosetting	96% to 98%
Polyester	Thermoplastic	99%
Acrylics	Thermoplastic	99%

Powder coatings have better chemical and abrasion resistance properties than conventional coatings. Because of the low VOC emissions, lower air flow rates can be used in the curing ovens, reducing energy requirements. Any excess powder from the application process can be easily recovered and either recycled or discarded, and touchup of parts prior to curing is easily accomplished. However, the cost of powder coatings is higher and there are a limited number of formulations. The capital costs of powder coating equipment are somewhat higher than for conventional coating, and higher temperatures are required for curing. Because of the difficulty in removing the powder from application equipment, mixing of colors may occur during color changes.

5.1.2.5 Radiation-Cured Coatings

Radiation-cured coatings are composed of low molecular weight polymers or oligomers dissolved in acrylic monomers. These formulations contain no solvent carriers and are cured by polymerizing them with either ultraviolet or electron-beam radiation. Like powder coatings, small quantities of VOC may be emitted as by-products of the polymerization process. Curing times are very fast—a few seconds for ultraviolet radiation and a second or less for electron-beam radiation—allowing for high line speeds. The operating costs of a radiation-cure system are considerably less than a conventional system, and the floor space requirement is greatly reduced. However, like powder coatings, the cost of the coatings is higher and there are a limited number of formulations. The capital costs of the coating equipment are also higher than for conventional systems, and ultraviolet and electron-beam energy systems can cause injuries to workers if they are not carefully shielded and operated.

5.1.3 Coating Application

After preparation of the surface, one or more coatings are applied. Typically, the first coating applied is a primer. This coating provides corrosion resistance, fills in imperfections on the surface and provides a bonding surface for the top coat. The top coat, or series of coats, is applied over the cured primer coat and determines the final quality and color of the surface. Techniques for applying coatings included spray coating (air, airless and electrostatic), dip coating, flow coating, roller coating and electrodeposition. Table 5-6 shows the types of industries that typically use each application method.

One parameter that affects VOC emissions from coating application is the transfer efficiency of the application method. Transfer efficiency is the percent ratio of the amount of coating solids applied to the surface to the total amount of solids used. Application methods with low transfer efficiencies will use more coating to achieve a level of applied solids and will have higher VOC emissions. Transfer efficiencies for each of the application methods will be indicated in the following discussions.

Table 5-6
Coating Application Methods for Various Industries

Application Method	Coil Coating	Metal Furniture	Auto & Light Truck	Large Appliances	Can	Auto Refinish	Traffic Marking	Wood Building Products	Fabric
Air-atomized spray			X	X	X	X	X	X	X
Airless spray				X		X		X	X
Electrostatic spray		X	X	X		X		X	X
HVLP			X			X		X	X
Electrostatic bell & disk				X				X	X
Dip		X		X				X	X
Flow		X		X				X	
Roller	X				X			X	X
Electrodeposition	X		X	X					

5.1.3.1 Spray Coating

The basic types of spray application methods are air-atomized spray, airless spray, electrostatic spray and high-volume, low-pressure spray. Typically, coatings are applied in a spray booth to protect the coated surface from dust and to provide a ventilated area that protects workers from solvent vapors. The transfer efficiency for spray application depends on the air velocity, temperature and humidity, the properties of the coating, the time between mixing and applying the coating, the surface configuration, the skill of the operator, and on the type of spray system that is used. Table 5-7 shows typical transfer efficiencies for different spraying methods and surface types.

Table 5-7
Transfer Efficiencies For Different Spraying Methods and Surface Types

Spraying Method	Flat Surface	Table-Leg Surface	Bird-Cage Surface
Air-atomized	50	15	10
Airless	75-80	10	10
Electrostatic air-atomized	75	65	65
Electrostatic airless	80	70	70
Electrostatic disk	95	90-95	90-95

In air-atomized spray, the coating is atomized and propelled by forced air. The spray gun, sometimes referred to as a two-fluid gun, is supplied with compressed air at pressures up to 60 psi and with coating at pressures of 10 to 30 psi. As the high-pressure air mixes with the coating, it atomizes it into small droplets and propels it in a turbulent mist toward the part to be coated.

Airless spray uses a single-fluid gun and hydraulic atomization. The coating is supplied to the gun at pressures of 1,000 to 3,000 psi and then forced through a specially designed nozzle. A diagram of an airless spray gun is shown in Figure 5-1. As the coating exits the gun, the sudden decrease to atmospheric pressure atomizes the coating and the force of ejection propels it toward the part.

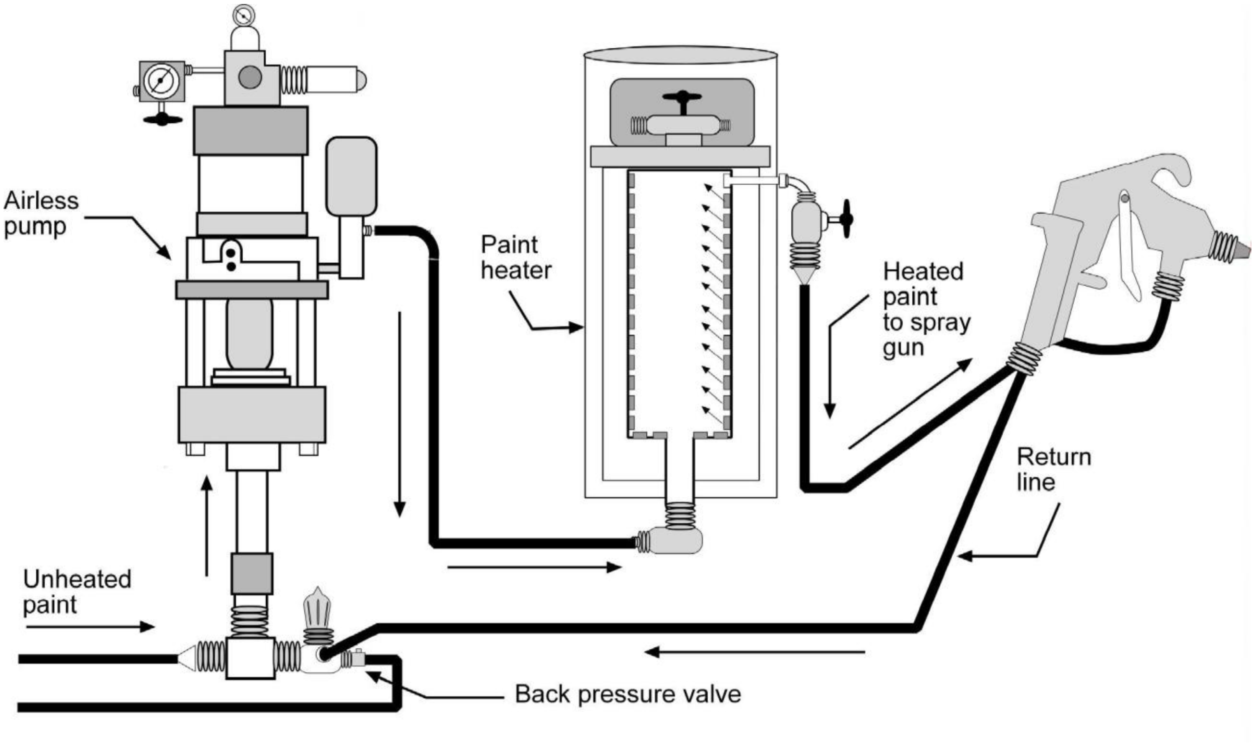

Figure 5-1. Diagram of airless spray gun with an attached paint heater

There are electrostatically enhanced versions of both air-atomized and airless spray guns. Electrostatic spraying uses a transformer to create an electrical potential of up to 60 kilovolts DC between the coating particles and the part to be coated. The part is positively grounded and the coating is given a negative charge at the spray applicator. The charged coating particles are electrostatically attracted to the part to be coated, increasing the transfer efficiency over that of conventional air-atomized and airless spray guns.

Other electrostatic application methods use spinning bells or disks (see Figures 5-2 and 5-3). The surface of the bell or disk is negatively charged, giving a negative charge to the coating particles passing across it. Atomization occurs primarily because of the repelling forces between the individual particles and between the particles and the applicator surface. Some atomization occurs because of the centrifugal forces imparted by the rapidly spinning bell or disk. The atomized coating particles are attracted to the positively grounded parts. The bell or disk may reciprocate up and down or back and forth to allow complete coating of the part.

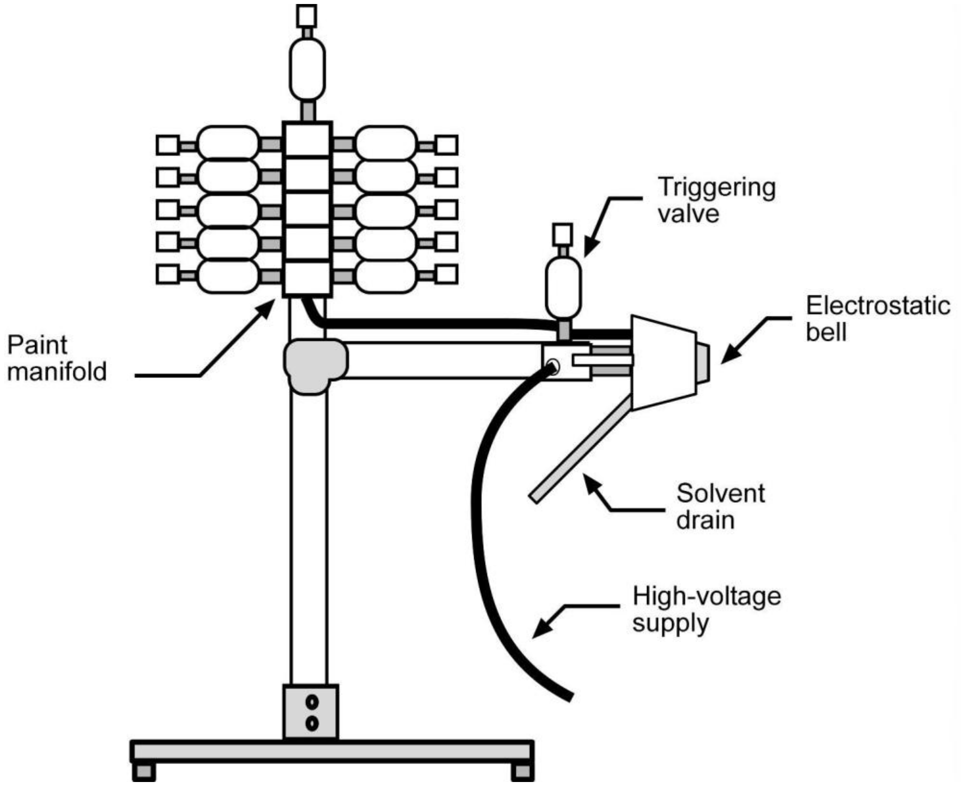

Figure 5-2. Diagram of stationary electrostatic bell

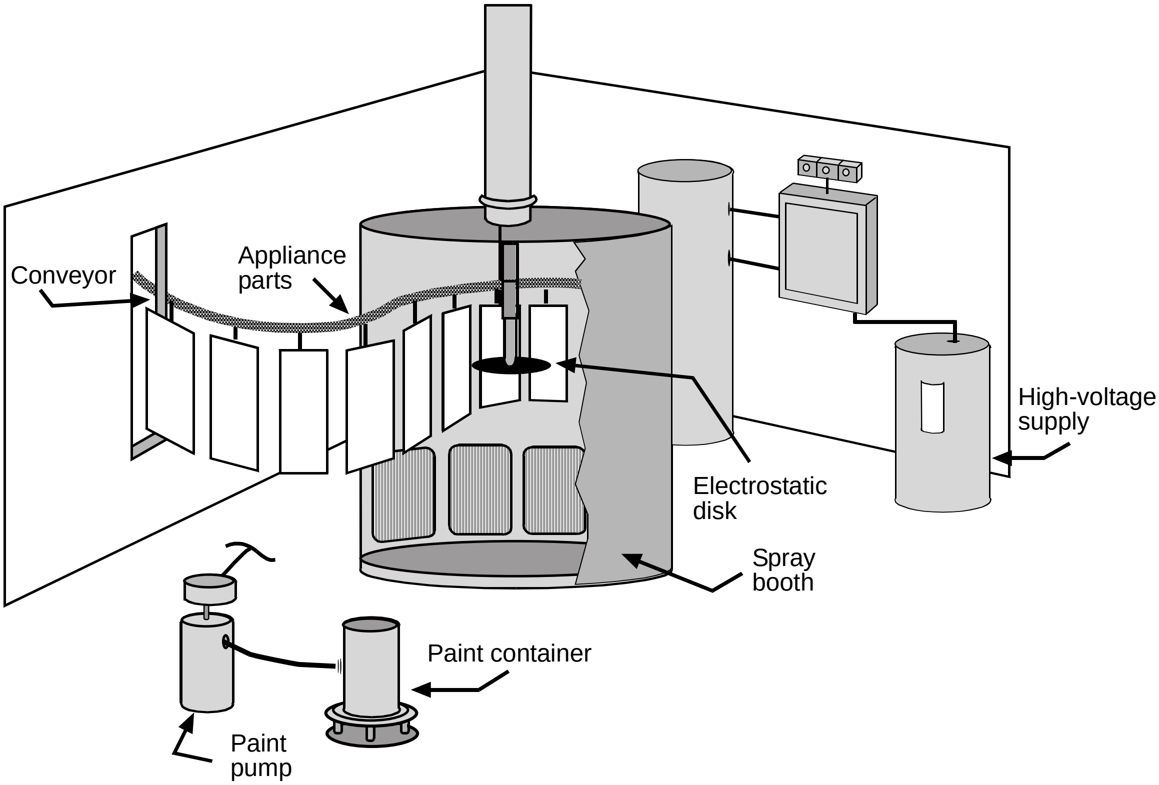

Figure 5-3. Diagram of a reciprocating disk and spray booth

A relatively new development in spray application equipment is the high-volume, low-pressure (HVLP) or turbine spray gun. With this system, a turbine is used to generate and deliver the atomizing air. The turbine draws in filtered air and drives it through several stages that rotate at up to 10,000 rpm. This results in a high volume of warm, dry atomizing air that is delivered to the spray gun at pressures of 4 to 6 psi. This low-pressure air gives greater control over the spray, with less of the overspray and fogging that accompanies the blasting effect common with conventional high-pressure systems. Transfer efficiencies of 60% to 70% have been reported for this application method.

5.1.3.2 Dip Coating

Dip coating involves the immersion of individual parts into a tank containing the coating. The parts, usually on hangers or trays, may be dipped individually, in batches or by a continuous conveyor line. After the coated parts emerge, they may be held over the tank to allow the excess coating to drip back into the tank or they may move to an area where the excess coating is collected and returned to the tank. The coating in the tank is kept at a constant solids concentration by the addition of fresh coating and solvent to make up for usage and evaporation. Transfer efficiency for this application method is approximately 85%.

5.1.3.3 Flow Coating

In flow coating, the coating is pumped through overhead nozzles and allowed to flow over the parts to be coated. In some cases, warm air jets may be directed toward the parts to improve coating uniformity. The excess coating drips off the parts and is collected and returned to the main tank for reuse. Fresh coating and solvent are added to make up for usage and evaporation. Transfer efficiency for this application method is also approximately 85%.

5.1.3.4 Roller Coating

Roller coating involves the transfer of a coating from a trough or vat to a flat surface by a series of rollers. Roller coating machines typically have three power-driven rollers. One roller runs partially immersed in the coating vat and transfers the coating to the second roller. The strip or sheet to be coated is run between the second and third rollers and is coated by transfer of the coating from the second roller. The distance between the rollers determines the amount of coating that is transferred. If the second roller turns in the same direction as the surface to be coated, the system is referred to as a direct roll coater. If they turn in opposite directions, the system is a reverse roll coater. Transfer efficiency for this application method is typically greater than 95%.

5.1.3.5 Electrodeposition Coating

In the electrodeposition process (EDP), a DC voltage is applied between the coating bath, or carbon or stainless-steel electrodes in the bath, and the part to be coated. The coatings used in EDP tanks are waterborne solutions. The part, which can act as the cathode or anode, is dipped into the bath. Coating particles are attracted from the bath to the part because they are oppositely charged, producing an extremely even coating. Transfer efficiency for this application method is also typically greater than 95%.

5.1.4 Curing

After the coating has been applied, it must be dried or cured to form the final hardened surface. For coatings that contain a volatile carrier, this process typically begins with pre-drying. This is usually done in an open area as the parts move from the application area to the finishing or curing oven. The purpose of pre-drying is to evaporate enough of the volatile carrier before the part reaches the oven so that bubbling or blistering of the surface does not occur. Pre-drying also allows time for the coating to level itself, if it has been applied unevenly.

With the exception of radiation-cured coatings, final curing of the coating is done in an elevated temperature oven. To further mitigate against bubbling or blistering of the surface, ovens typically have multiple zones that operate at successively higher temperatures. Oven temperatures can range from 150°F to 650°F, depending on the substrate, the type of coating and the oven zone. As the coated materials pass through the oven, the remaining volatile carrier is evaporated, and the substrate is heated to the temperature necessary to achieve proper curing of the coating.

Ovens must have sufficient air flow to prevent evolved solvents from interfering with the drying and curing process. With solvent-borne coatings, there must also be sufficient air flow to prevent explosive concentrations from being reached. Typically, ovens are operated with VOC concentrations less than 25% of the lower explosive limit (LEL).

After the coated materials exit the oven, they must be cooled. Conveyorized systems usually accomplish this by simply moving the parts through an open area, letting them cool by natural or forced convection. Paper, fabrics and plastic films are typically passed over chilled rollers, while metal strips are cooled with water sprays.

5.2 EMISSION CONTROL TECHNIQUES

The amount of VOC emissions that result from a surface coating process are determined by the composition of the applied coating and the total quantity of coating used. The quantity of coating used is determined by the area of the surface to be coated, the thickness of the coating and the efficiency of the application method. Accordingly, control measures that can be applied to these processes can be categorized into three areas: reduced-VOC coating, higher transfer efficiency application, and add-on control devices.

5.2.1 Reduced-VOC Coating

A relatively inexpensive way to reduce VOC emissions is to reduce the VOC content of the coating. Changing from a conventional solvent-borne coating to a high-solids or waterborne coating can usually be done with little or no change in the coating process and can produce significant VOC reductions. Changing to a powder or radiation-cured coating can produce dramatic VOC reductions, but at the expense of new processing equipment.

5.2.2 Higher Transfer Efficiency Application

Using a higher transfer efficiency application method will reduce the amount of coating that is used to deposit a given level of solids on the surface, thereby reducing VOC emissions. The application method that offers the greatest opportunity for doing this is spraying. For a modest cost, an air-atomization system could be replaced with an airless system and a modest reduction in VOC emissions could be achieved. With a greater capital investment, conventional spraying equipment could be replaced with electrostatic equipment, yielding an even greater reduction in VOC emissions.

Potentially, some coating processes could replace conventional spraying with the higher transfer efficiency dip or flow coating methods.

5.2.3 Add-On Control Equipment

When it is not possible to change from conventional coatings or when coating changes alone do not achieve the required VOC reduction, add-on control equipment can be employed. It is generally assumed that all of the organic solvent in the coating will be emitted during the coating process. However, where in the coating process those solvents are evolved will depend on the application method, and that will determine which areas should be controlled to achieve the greatest level of reduction. Table 5-8 shows the typical percentage of total VOC emissions that are expected from each coating step for different coating methods. Based on these values, it is likely that a RACT level of control could be achieved for dip or roller coating by only controlling the oven. However, for spray and flow coating, control of both the application area and the oven would likely be required. Greater levels of control for all application methods would likely require control of the pre-dry area.

Table 5-8

Percent of Total Emissions by Coating Step for Different Coating Methods

Coating Method	Application	Pre-Dry	Oven
Spray coating	30-50	10-30	20-40
Dip coating	5-10	10-30	50-70
Flow coating	30-50	20-40	10-30
Roller coating	0-5	10-20	60-80

The type of add-on control equipment that is used will depend on the characteristics of the gas stream and will be strongly influenced by the temperature. Gas streams collected from application and pre-dry areas could be controlled by either adsorption or catalytic or thermal incineration. Because of the elevated temperatures, gas streams collected from ovens can only practically be controlled by incineration. Some care must be exercised in applying catalytic incinerators to surface coating processes, since many of the pigments used in coatings contain metals that may poison the catalyst.

5.3 EMISSION REGULATION

At the time of writing, USEPA had issued RACT recommendations for the surface coating of cans, coils, paper, fabric, automobiles, light-duty trucks, metal furniture, magnetic wire, large appliances, miscellaneous metal parts, flat wood paneling, and wood furniture. NSPS requirements had been promulgated for the surface coating of metal furniture, automobiles, light-duty trucks, pressure sensitive tape, labels, large appliances, metal coils, beverage cans, flexible vinyl and urethane, magnetic tape, plastic parts and for the polymeric coating of supporting substrates. MACT standards had been issued for magnetic tape manufacturing, aerospace manufacturing and re-work, shipbuilding and ship repair, and wood furniture manufacturing. As an example, the recommended and required standards for large appliances and metal coil coating are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and record keeping requirements.

Surface Coating of Large Appliances, Control Technique Guideline Document, EPA-450/2-77-034

Recommended standard:

An emission limit of 2.8 lbs of VOC per gallon of coating less water.

Standards of Performance for Industrial Surface Coating: Large Appliances, 40CFR60, Subpart SS

Applicability Date: December 24, 1980

Applicability Size: All

Standard:
An emission limit of 7.51 lbs of VOC per gallon of solids applied.

Surface Coating of Metal Coils, Control Technique Guideline Document, EPA-450/2-77-008

Recommended standard:
An emission limit of 2.6 lbs of VOC per gallon of coating less water.

Standards of Performance for Metal Coil Surface Coating, 40CFR60, Subpart TT

Applicability Date: January 5, 1981

Applicability Size: All

Standard:

- An emission limit of 2.34 lbs of VOC per gallon of solids applied for each calendar month for each facility that does not use an emission control device; or
- An emission limit of 1.17 lbs of VOC per gallon of solids applied for each calendar month for each facility that continuously uses an emission control device operated at the most recently demonstrated overall efficiency; or
- An emission limit of 10% of the VOCs applied for each calendar month (90% emission reduction) for each facility that continuously uses an emission control device operated at the most recently demonstrated overall efficiency; or

- An emission limit between 1.17 lbs of VOC per gallon of solids applied (or a 90% emission reduction) and 2.34 lbs of VOC per gallon of solids applied for each calendar month for each facility that intermittently uses an emission control device operated at the most recently demonstrated overall efficiency.

5.4 PROCESS INSPECTION

There should be two goals in any field inspection. First is to evaluate the source's compliance with any rule-specific monitoring and record keeping requirements and with the provisions of the Title V permit. In addition, changes in operating conditions or parameters that could result in increased emissions should be evaluated. In surface coating processes, increased emissions usually result from changes in coating composition, changes in the method and rate of application, and from reduced performance of the air pollution control device. Recommended general inspection items include the following:

- ***Review coating composition and consumption records.*** Coating composition data should be evaluated to determine compliance with the operating permit and with applicable regulations. These data typically include the solvent, solids and water content of the coating, the coating density and the solvent density. Techniques for calculating the VOC content of the coating in the units of the applicable standard will be presented in Chapter 7. Coating and solvent consumption records should be reviewed and compared to the operating permit limitations.

- ***Observe coating preparation*.** Determine if the coating preparation area is ventilated and what type of control device is used. Note if the coating and solvent drums are kept closed when not being used. Observe how spills are cleaned up. Question plant personnel regarding the types of solvents in the coatings and those used as diluents and if they have been changed. If carbon adsorbers are used for control of any portion of the surface coating process, they may not function as designed if the solvents have been changed. If more volatile solvents are being used, VOC losses from the application and pre-drying areas will likely be greater. If carbon adsorbers are used to control these areas, they may not have sufficient capacity to handle the increased emissions. If a separate catalytic incinerator is used for these areas, the increased VOC concentration may cause high temperature problems in the catalyst bed. If it is necessary to confirm the coating composition, samples of the "as applied" coating should be taken for Method 24 analysis.

- ***Observe coating application*.** Determine if the coating application area is ventilated and what type of control device is used. Note if they have made changes in the application method. Question plant personnel regarding any changes in the application rate. Determine if any changes are made in the control system parameters to accommodate any changes in solvents or application rates. Observe how spills are cleaned up.

- ***Observe pre-drying area.*** Determine if the pre-drying area is ventilated and what type of control device is used. Determine if any changes are made in the control system parameters to accommodate any changes in solvents or application rates.
- ***Observe curing area.*** Check physical integrity of the oven and oven temperatures. Determine what type of control device is used. Question plant personnel regarding any changes in line speed. Determine if any changes are made in the control system parameters to accommodate any changes in solvents, application rates or line speed.

The inspection of carbon adsorbers and catalytic and thermal incinerators is covered in APTI Course 455, Inspection of Gas Control Devices and Selected Industries. The reader is referred to this course for guidance.

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Review Questions

1. Which of the following is not a step in a surface coating process? Select all that apply.
   a. Surface preparation
   b. Coating application
   c. Curing
   d. Final assembly

2. What is the purpose of surface preparation? Select all that apply.
   a. To insure proper bonding of the coating
   b. To provide corrosion resistance
   c. To select parts capable of being coated
   d. To decide how the part will be coated

3. Which type of coating typically has the highest VOC content?
   a. Conventional coating
   b. High-solids coating
   c. Waterborne coating
   d. Powder coating

4. Which type of coating typically has the lowest VOC content?
   a. Conventional coating
   b. High-solids coating
   c. Waterborne coating
   d. Powder coating

5. What are disadvantages of high-solids coatings? Select all that apply.
   a. Higher freight costs
   b. Higher viscosity
   c. Higher solvent removal energy
   d. Poor adhesion

6. What are advantages of waterborne coatings? Select all that apply.
   a. No organic solvent content
   b. Wide range of formulations
   c. Reduced oven energy
   d. Easier clean up

7. What are the two types of powder coatings?
   a. Thermoresistant
   b. Thermoplastic
   c. Thermoelastic
   d. Thermosetting

8. Which type of powder coating produces a surface that is chemically different from the applied solids?
   a. Thermoresistant
   b. Thermoplastic
   c. Thermoelastic
   d. Thermosetting

9. What type of energy is used to polymerize radiation-cured coatings? Select all that apply.
   a. Ultraviolet
   b. Infrared
   c. Electron beam
   d. Solar

10. What is the purpose of primer coating? Select all that apply.
    a. Corrosion resistance
    b. Color enhancement
    c. Fill in surface imperfections
    d. Improve final coat bonding

11. Which coating method has the lowest transfer efficiency?
    a. Dip coating
    b. Flow coating
    c. Air-atomized spray coating
    d. Electrostatic spray coating

12. Which coating method has the highest transfer efficiency?
    a. Dip coating
    b. Flow coating
    c. Air-atomized spray coating
    d. Electrostatic spray coating

13. What is the purpose of pre-drying? Select all that apply.
    a. Increases line speed
    b. Prevents blistering of the surface
    c. Provides time for leveling of the coating
    d. Reduces oven energy

14. What techniques are used to reduce VOC emissions from surface coating processes?
    a. Reduced-VOC coating
    b. Higher transfer efficiency application
    c. Add-on control equipment
    d. All of the above

15. Which of the following should be included in a general inspection of a surface coating facility?
    a. Review coating composition and consumption records
    b. Observe coating preparation
    c. Observe coating process
    d. All of the above

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Review Answers

1. Which of the following is not a step in a surface coating process? Select all that apply.
   d. Final assembly

2. What is the purpose of surface preparation? Select all that apply.
   a. To insure proper bonding of the coating
   b. To provide corrosion resistance

3. Which type of coating typically has the highest VOC content?
   a. Conventional coating

4. Which type of coating typically has the lowest VOC content?
   d. Powder coating

5. What are disadvantages of high-solids coatings? Select all that apply.
   b. Higher viscosity

6. What are advantages of waterborne coatings? Select all that apply.
   b. Wide range of formulations
   d. Easier clean up

7. What are the two types of powder coatings?
   b. Thermoplastic
   d. Thermosetting

8. Which type of powder coating produces a surface that is chemically different from the applied solids?
   d. Thermosetting

9. What type of energy is used to polymerize radiation-cured coatings? Select all that apply.
   a. Ultraviolet
   c. Electron beam

10. What is the purpose of primer coating? Select all that apply.
    a. Corrosion resistance
    c. Fill in surface imperfections
    d. Improve final coat bonding

11. Which coating method has the lowest transfer efficiency?
    c. Air-atomized spray coating

12. Which coating method has the highest transfer efficiency?
    d. Electrostatic spray coating

13. What is the purpose of pre-drying? Select all that apply.

b. Prevents blistering of the surface
c. Provides time for leveling of the coating

14. What techniques are used to reduce VOC emissions from surface coating processes?
d. All of the above

15. Which of the following should be included in a general inspection of a surface coating facility?
d. All of the above

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Kumar, A., and T. Shenoy, "Evaporative Emissions and Surface Coating: Surface Coatings", *Air Pollution Engineering Manual*, Second Edition, Chapter 10, W.T. Davis, ed., John Wiley & Sons, New York, 2000.

Turner, M.B., "Surface Coating", *Air Pollution Engineering Manual*, Chapter 10, A.J. Buonicore and W.T. Davis, eds., Van Nostrand Reinhold, New York, 1992.

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6 Graphic Arts

The graphic arts industry is often referred to as the printing, publishing and packaging industry. In this chapter, we will focus on the printing operations currently used in the graphic arts industry: offset lithography, flexography, rotogravure and screen printing. Each type of printing operation employs distinctive processes and materials and has its own unique air emission characteristics and control measures.

6.1 OFFSET LITHOGRAPHY

6.1.1 Process Description

Offset lithography uses a planographic printing surface that has been chemically treated to form a hydrophobic (oleophilic) ink-receptive image area and an oleophobic (hydrophilic) water-loving non-image area. To keep the hydrophobic ink film from migrating into the non-image area of the plate, a second fluid, a dampening fluid, is applied to the plate along with the ink. A typical printing unit, shown in Figure 6-1, consists of the following:

- An inking system composed of multiple metal and polymeric rollers that produce and deliver a thin, uniform ink film to the printing plate.
- A dampening system that delivers fountain solution to the printing plate, preferentially wetting the nonprinting areas.
- A plate cylinder on which the printing plate with its images is mounted. Only the inked images are transferred from the printing plate to the blanket cylinder.
- A blanket cylinder on which a rubber-covered lithographic blanket is mounted. The blanket receives the images from the printing plate and transfers them to the substrate or web.
- An impression cylinder that controls the force imposed on the substrate, so that the images are transferred properly.

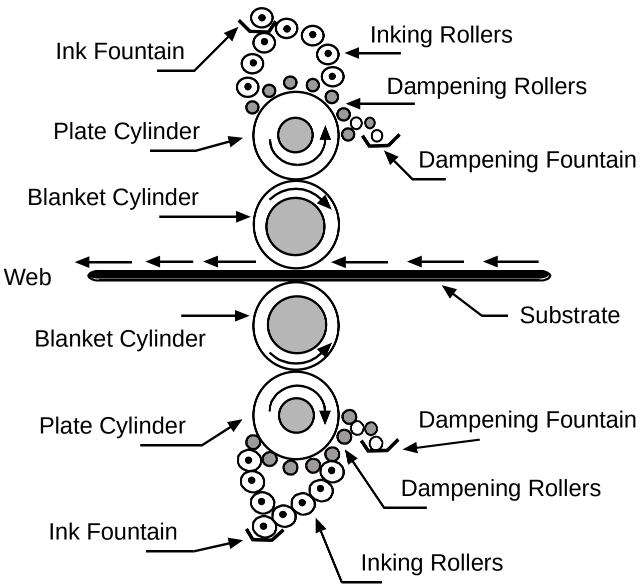

Figure 6-1. Diagram of an offset lithography printing unit

There are three common offset lithography processes: nonheatset web printing, heatset web printing and sheetfed printing.

6.1.1.1 Nonheatset Web Printing

In web printing, a rotary press is used to print an image on a continuous web of paper at speeds between 600 and 2100 feet per minute. After printing, the web is mechanically cut and manipulated into its final form.

Nonheatset web printing represents about 35% of lithographic processes, with newspaper printing being the most common application. A typical unit is shown in Figure 6-2. This printing process can be distinguished from other web printing processes by its unique ink and paper requirements. Nonheatset inks are semifluid materials that depend on the rapid absorption of the liquid component of the ink by the surface of the paper. The capillary action of the paper draws the liquid into the surface and sets the ink. This precludes the use of coated papers and permits only a minimum of filler materials or machine finishing. This process does not require the application of heat to evaporate the liquid component or cure the resin.

Fountain solutions used in the dampening system of nonheatset web printers are usually greater than 99.5% water. The remaining components are typically high-boiling-point glycols and glycol ethers. The contact dampening system applies a film of the fountain solution directly to the printing plate, using either rollers or misting sprays. The ink-train dampening system applies the fountain solution to the ink roller train, forming an emulsion. The ink-water emulsion is then transferred to the printing plate, where the shear of the printing nip causes the emulsion to break into its hydrophobic ink component and hydrophilic water component. Both types of dampening systems are open to the atmosphere.

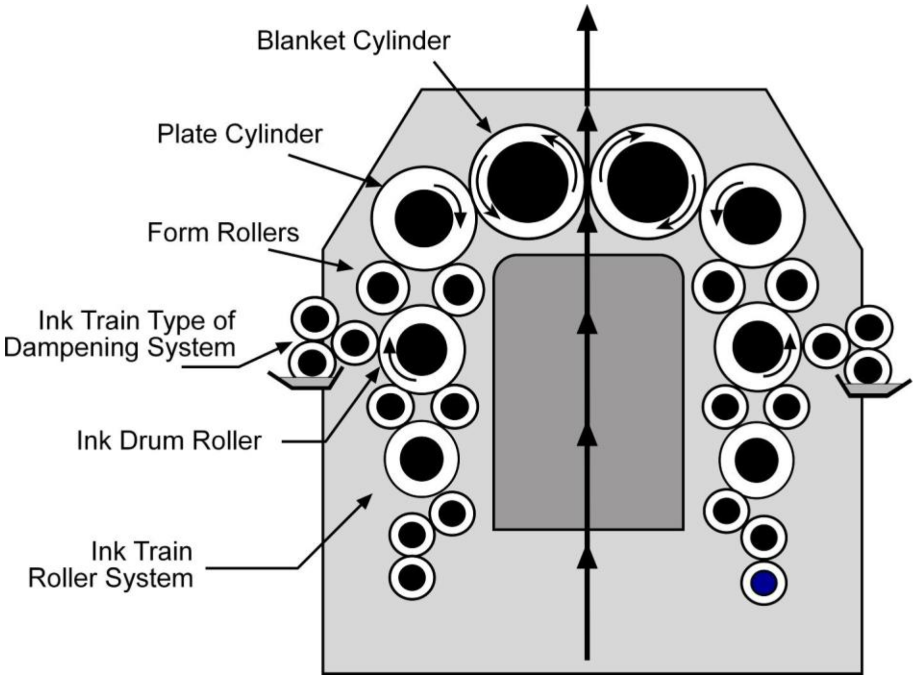

Figure 6-2. Typical components of offset nonheatset web printing units

6.1.1.2 Heatset Web Printing

Heatset web printing is used to produce over 75% of magazines, books, catalogs and tabloids. The process varies in complexity from simple, one-color printing stations to complex multicolor presses that utilize eight or more printing units. It is similar to other offset lithography processes in the type of plates used and in the requirement for a fountain solution to maintain the printing image. Differences include the web speed, inks that require energy to dry, energy application devices to dry the ink and web cooling devices. A typical unit is shown in Figure 6-3.

Printing is typically applied to both sides of the web. Depending on the number of colors to be used, the web will pass through one or more printing stations before entering the dryer. Dryers for heatset web printers are typically recirculating hot air systems; however, some direct flame impingement and infrared dryers are still in use. Typically, energy is applied to both sides of the web to raise the web temperature to about 225°F to 325°F. Depending on the ink application rate and the type of paper being printed, approximately 40% to 90% of the solvent in the ink is evaporated in the dryer. The remaining solvent is retained in the paper web. Fountain solution transferred to the web will also be evaporated in the dryer, and presses with automatic blanket washers will evaporate cleaning solvent in the dryer during the wash cycle. The web exiting the dryer is passed over chilled rollers to cool it to about 20°F above ambient temperature before folding and cutting.

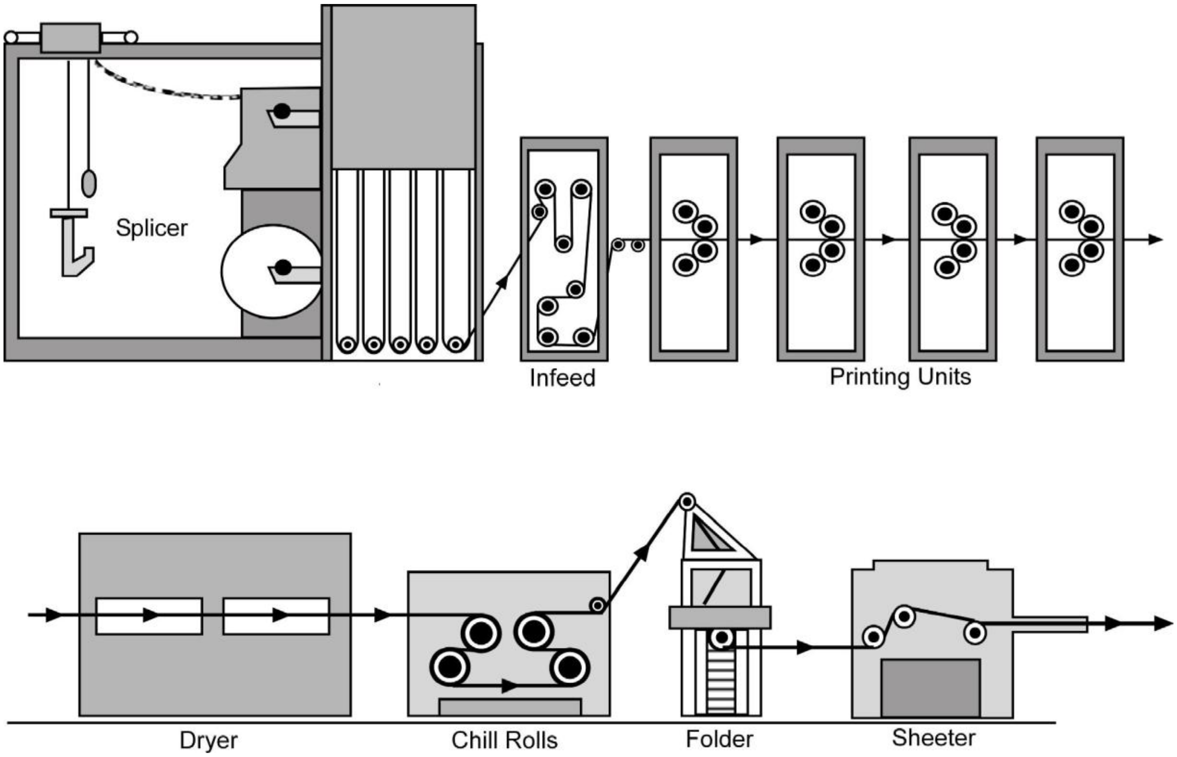

Figure 6-3. Web offset press with optional delivery to a folder or sheeter

In addition to inks that dry by evaporation, others cure by chemical reaction. Reactive-cure inks contain only pigments and a nonvolatile reactive binder. The energy needed to cure these inks is usually supplied by high-energy UV lamps, electron beam generators or thermal ovens. The absorption of energy by the ink causes the binder to cure and harden. Few, if any, VOCs are emitted.

The fountain solutions used in heatset web printing are aqueous solutions containing 5% to 20% isopropyl alcohol or 2% to 5% alcohol substitutes, such as 2-butoxyethanol or ethylene glycol. As much as 75% of the isopropyl alcohol will evaporate into the room, while up to 25% of 2-butoxyethanol will evaporate. Ethylene glycol is even less volatile. The amount of solvent remaining in the dried web is also variable, ranging from essentially zero to as much as 5%.

6.1.1.3 Sheetfed Printing

As the name implies, sheetfed printing applies images to individual sheets, rather than to a continuous web. While paper is the dominant substrate, significant volumes of paperboard, tinplate and plastic are printed with the process. The products printed range in size from individual envelopes, newsletters, advertising brochures, books, magazines and folding cartons to billboards. It is again similar to other offset lithography processes in the type of plates used and in the requirement for a fountain solution to maintain the printing image. The primary differences are in the form of the substrate being printed and in the use of inks that cure at ambient conditions through oxidation and polymerization.

The sheetfed lithographic printing press consists of a feeder, a printing unit and a delivery unit. The feeder supplies sheeted substrates to the printing unit. Any number of printing units can be installed sequentially, with a six-unit press being the most common. Printing is done on one side of the substrate at a time using inks that are formulated to set quickly at ambient temperatures, usually within minutes. In some units, UV, electron beam or infrared radiation may be used for ink drying and curing. The primary solvents in sheetfed inks are petroleum distillates. The ink-setting mechanism involves the penetration of the solvent phase into the substrate and deposition of the solids phase onto the substrate surface for subsequent oxidation and polymerization. The delivery unit stacks the printed sheets. Atomizers are typically used to deposit chemically modified cornstarch onto the surface of the sheets to prevent contact in the pile.

The fountain solutions used in sheetfed printing are similar to those used in heatset web printing. They are either applied directly to the printing plate or to the surface of the ink rollers. Some presses use dampening systems that function with fountain solutions that do not require the use of isopropyl alcohol or alcohol substitutes.

Printers frequently use in-line coating finishes following printing, either as the last unit of the printing press or as auxiliary equipment. This coating provides a glossy or dull finish for protection of the surface. The three main types of coating compositions are varnish, aqueous coating and UV-cured coating. Press varnish is essentially a sheetfed ink without pigments.

6.1.2 Emission Control Techniques

The three potential sources of VOC emissions from offset lithography are the ink, the fountain solution, and press-cleaning operations. Because of differences in ink and fountain solution compositions used in the different lithographic processes, control techniques vary.

6.1.2.1 Inks

Nonheatset web inks are formulated with low volatility petroleum solvents and are applied at temperatures that are relatively low in comparison to the solvent’s boiling point. It is generally assumed that all materials transferred to the paper penetrate the surface and are retained within the product. Method 24 tests have indicated VOC contents in the inks of 2% to 20%. However, there is some question as to whether it is appropriate to apply this test method to non-evaporative systems. Also, the method does not take into consideration the pacification of the solvent component within the set resin and pigments complex or the absorption of the material within the cellulose fiber. USEPA guidelines contained in the CTG and ACT documents for lithographic printing suggest that 5% of the solvent is emitted as fugitive emissions and that 95% is retained in the paper. If nonheatset web inks were considered a significant source of VOC, the best control technique would be in ink reformulation.

Emissions from heatset web inks that cure by evaporation in a dryer are controlled with add-on control equipment. The primary methods are incineration and condenser-droplet-removal systems. Condenser-droplet-removal systems consist of air-to-air heat exchangers followed by fiberglass filters or electrostatic precipitators to remove the condensed droplets. USEPA guidelines suggest that 80% of the solvent is emitted in the dryer and that 20% in retained in the paper.

Like nonheatset web inks, sheetfed inks are formulated with low volatility petroleum solvents and are applied at temperatures that are relatively low in comparison to the solvent’s boiling point. Because of this, the emissions are very low. USEPA guidelines suggest that 5% of the solvent is emitted as fugitive emissions and that 95% is retained in the paper. If sheetfed inks were considered a significant source of VOC, the best control technique would be in ink reformulation.

6.1.2.2 Fountain Solution

Although fountain solutions are mostly water, they do contain organic additives that evaporate during printing and drying operations. The most volatile of these is isopropyl alcohol. One technique for reducing emissions is to use other dampening agents, such as 2-butoxyethanol, ethylene glycol or glycol ethers. These substitutes are considerable less volatile than isopropyl alcohol and can be used in much lower concentration. When alcohol must be used, refrigeration of the fountain solution to 55°F to 60°F can significantly reduce the evaporation rate. USEPA guidelines suggest that 100% of the fountain solution additives in nonheatset web and sheetfed printing are emitted as fugitive emissions. For heatset web printing, the guidelines suggest that 70% of the additives are emitted in the dryer and that 30% are emitted as fugitive emissions.

6.1.2.3 Press Cleaning

Press cleaning to remove built-up layers of ink and paper dust is a necessary maintenance operation in offset lithography processes and can be a significant source of VOC emissions. Press cleaning is estimated to be the source of 90% to 95% of all emissions from nonheatset web printing and second to isopropyl alcohol dampening solutions in sheetfed printing. Cleaning operations are usually performed manually using rags or paper wipes soaked with solvent; however, some heatset web and sheetfed presses are equipped with automatic blanket washing systems.

Emissions from press-cleaning operations can be reduced by decreasing the VOC content of the cleaning solution or by using less volatile solvents. Emissions can also be limited by placing the cleaning rags and wipes in sealed containers as they are used. One method of reducing VOC content is to add water and detergent to form the cleaning solution. In some cases, it may be possible to use an aqueous cleaner. USEPA guidelines suggest that 40% of the solvent used in automatic blanket washers on heatset web presses is emitted through the dryer and that 60% is emitted as fugitive emissions.

6.1.3 Emission Regulation

At the time of writing, USEPA had issued draft RACT recommendations for offset lithographic printing. These recommended standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Control of Volatile Organic Compound Emissions from Offset Lithographic Printing, Control Technique Guideline Document, EPA-453/D-95-001

Recommended standard:

- Reduce VOC emissions from the dryer of a heatset web press by 90%.
- Use fountain solutions in a nonheatset web press that contain less than 3% by volume of non-alcohol additives or alcohol substitutes.
- Use fountain solutions in a heatset web press that have VOC contents equivalent to less than 1.6% alcohol by volume.
- Use fountain solutions in a sheetfed press that have VOC contents equivalent to less than 5% alcohol by volume.
- Use cleaning solutions that have less than 30% by weight VOC.

Offset Lithographic Printing,
Alternative Control Techniques Document, EPA-453/D-94-054

Additional Recommendations:

- An applicability cutoff of 15 pounds per day of actual VOC emissions without control devices for all printing activities (inks, coating, fountain solution and press cleaning).
- Use fountain solutions in all types of lithographic presses that contain less than 5% by volume of alcohol substitutes.
- Use blanket and ink roller cleaning solutions with a VOC composite partial vapor pressure less than 10 mm Hg at 20°C.
- Keep cleaning materials and used towels in closed containers.

6.2 FLEXOGRAPHY

6.2.1 Process Description

Flexography is a method of direct rotary printing that uses raised-image rubber printing plates and fluid inks and that can run at speeds of more than 2,200 feet per minute. The inks, which contain up to about 75% solvent by weight, are applied to the plate with a metering system called an anilox roll and then transferred directly to the web from the plate. Prior to 1980, flexography was used almost exclusively for packaging and specialty printing, an application that still represents a significant majority of all flexography processes. Products include labels, wrapping paper, bread bags, cartons, multi-walled bags, and paper towels. Development of publication flexography began in the late 1970s and grew rapidly. Today, flexography has become a viable process for printing newspapers, newspaper inserts, flyers, direct mailers, phone directories and catalogs, with a print quality rivaling offset lithography and rotogravure.

6.2.1.1 Press Designs

Flexographic press designs fall into one of five categories, depending on the printing application:

- Central impression
- In-line
- Stacked
- Newspaper unit
- Publication unit

The central impression design uses one common impression cylinder, with two to eight printing stations distributed around it. A six-color central impression press is shown in Figure 6-4. This design has the advantages of compactness, excellent registration of multi-color images and excellent control of the web. In between each printing station, a between color dryer uses forced air to partially dry the ink before the next color application. This limited drying capacity is one of the disadvantages of this design. The web enters the main dryer after the last color station for final drying of all the colors. The main dryer is typically a recirculating air system that operates at 150°F to 250°F, depending on the web material.

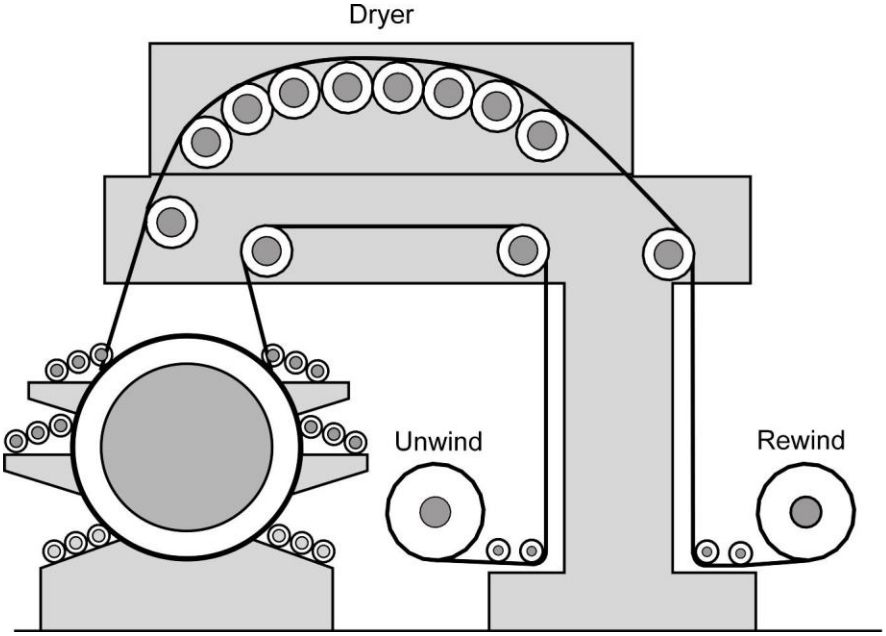

Figure 6-4. Flexographic central impression press

In the in-line design, the printing stations are separate, discrete units mounted in line with one another (see Figure 6-5). Any number of stations can be used, and the distance between color units provides for longing drying times and better drying capacity. However, color registration on thin flexible materials can be difficult to control.

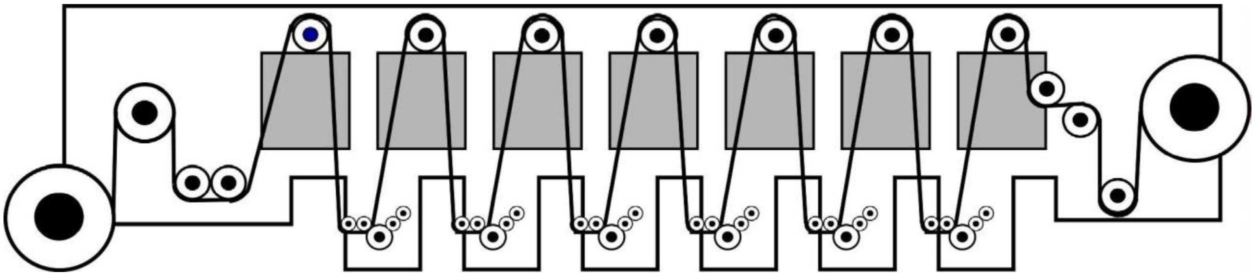

Figure 6-5. Flexographic in-line press

In the stack design shown in Figure 6-6, individual printing stations are stacked one over another, usually on one or both sides of a main press frame. One advantage of this design is that it is usually possible to reverse the web so that both sides can be printed with one pass through the press. Also, the printing stations are very accessible, making changeovers and clean-ups between jobs easier.

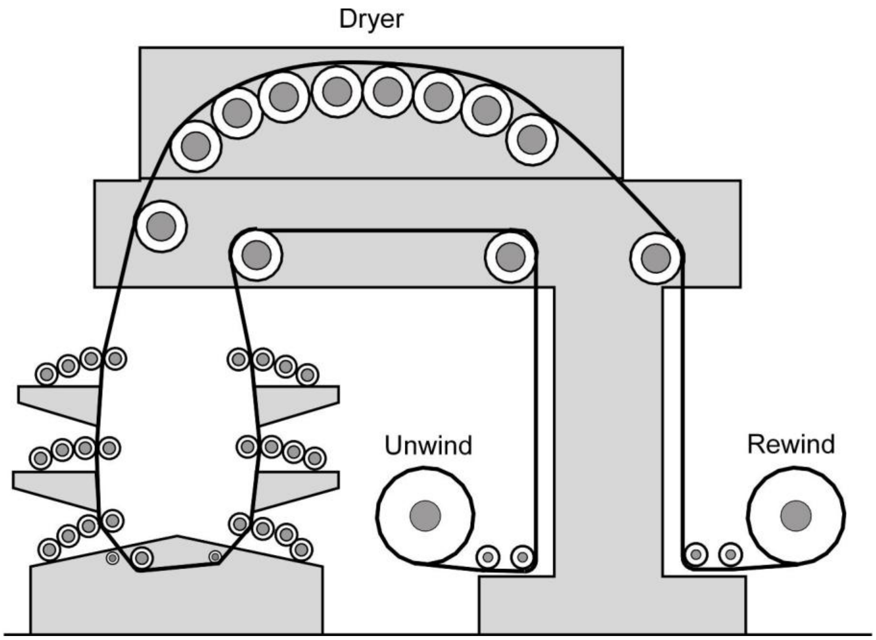

Figure 6-6. Flexographic stack press

A newspaper printing unit, shown in Figure 6-7, consists of two printing stations located back-to-back in a common pair of frames. This arrangement permits the printing of black images on both sides of the web. Multiple units are arranged in a pressline to print the many pages required of a large newspaper. Color decks, each consisting of one printing station, are placed above those positions where the publisher wants to add a single color. Occasionally, double decks, stacked units or multiple color units are added where single colors are wanted on both sides of the web or for multiple color printing on section fronts or center spreads.

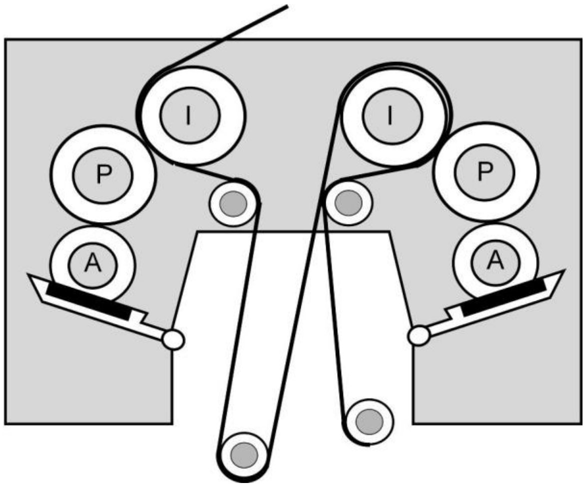

Figure 6-7. Flexographic newspaper printing unit

Publication flexographic presses use dedicated four-color units (see Figure 6-8). Two units are typically combined into one press for printing four colors on both sides of the web. The advantages of this design include wide web capability, high operating speed and compact design. Dryers, usually infrared, are used to insure adequate drying of the ink after each side of the web is printed.

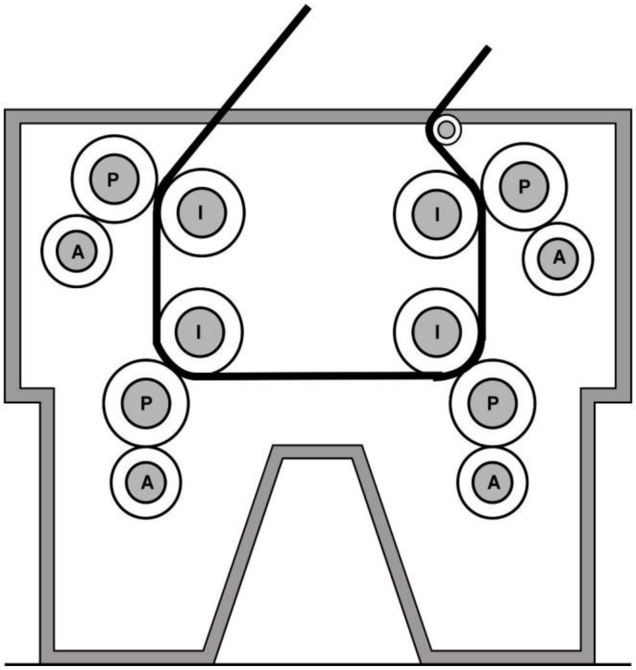

Figure 6-8. Publication flexographic printing unit

6.2.1.2 Inking Systems

The anilox roll is the primary ink control device in a flexographic inking system. Engraved cells in the chrome or ceramic roll surface hold the ink for transfer to the printing plate. The applied ink volume and the ink film thickness are controlled by the anilox roll.

There are several systems used to meter the ink from the anilox roll. In the two-roll system shown in Figure 6-9, a fountain roller rotating in an ink bath transfers the ink to the anilox roll, which, in turn, transfers it to the printing plate and the web. This type of metering system deposits the heaviest volume of ink.

In a second system, the anilox roll rotates in an open ink fountain, directly in contact with the ink (see Figure 6-10). A single reverse-angle doctor blade is used to scrape or doctor the excess ink off of the anilox surface before it is transferred to the printing plate. This system generally has superior ink thickness control and is used where print quality is more critical.

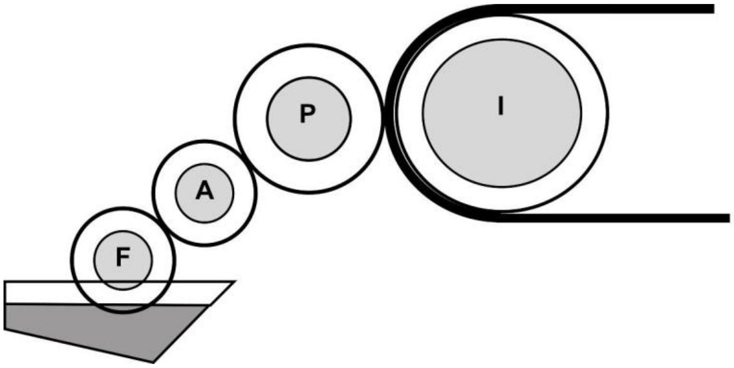

Figure 6-9. Fountain roller style of printing station

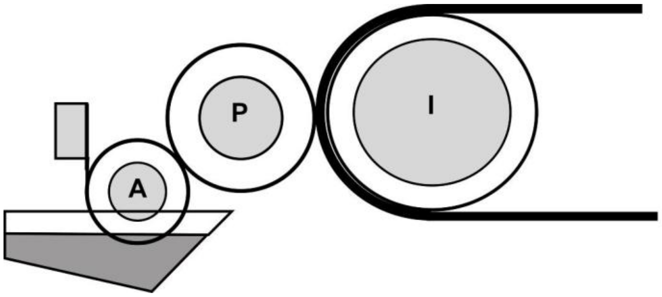

Figure 6-10. Single-doctor-bladed style of printing station

The most common inking system design, shown in Figure 6-11, uses an enclosed ink chamber and two doctor blades. Ink containment and reversibility of the printing station are two of this system's advantages. Ink is pumped into the chamber and doctored from the anilox roll by one of the blades before it is transferred to the printing plate. The double-doctor-bladed ink chamber is often used when both high-speed and high-quality printing are required.

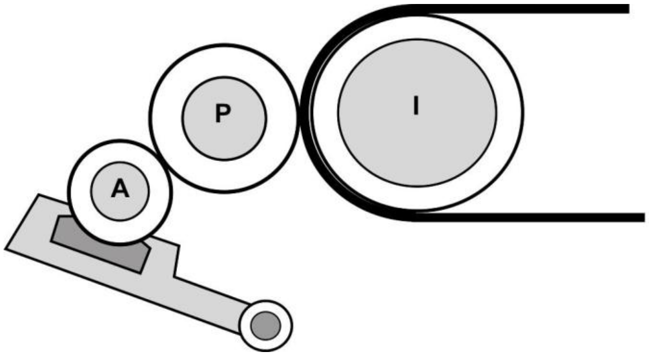

Figure 6-11. Double-doctor-bladed style of printing station

6.2.1.3 Types of Inks

There are three ink types common to flexography: organic solvent-based, water-based and radiation curable. Organic solvent-based inks represent a little more than half of all flexographic inks used today. Higher production speeds are generally possible with these inks because of the low solvent boiling point and quick solvent release from the ink film layer. They also require lower airflow rates for drying, typically 3,000 cfm to 7,000 cfm. Common solvents include ethanol, isopropanol, n-propanol, toluene, hexane, isopropyl acetate, n-propyl acetate, glycols and glycol ethers. These solvents are often blended in various percentages to control drying rates and end use properties.

Water-based inks represent nearly half of all inks used. They work best when the web is hydrophilic and porous. The more hydrophobic the web and the higher the press speed, the less suitable water-based inks become. They also require higher airflow rates for drying, typically 6,000 cfm to 12,000 cfm. Plastic film and foil are two examples of web materials that are not very compatible with water-based inks. Newsprint, however, is an excellent web material. The inks used for newspaper printing have low viscosity and absorb quickly into the newsprint, minimizing the need for high-volume air dryers.

Water-based inks may contain organic solvents, although in much smaller amounts than in solvent-based inks. These are required to optimize the solubility of the resins in the water and to improve the flow of the ink film onto the web. The solvents used in water-based inks include alcohols, amines, glycols and glycol ethers. In publication flexography, amines and glycols are used in quantities less than 5% of the ink formulation, prior to dilution with water. Alcohols are not used. The solvent content may be higher than 5% in packaging flexography, particularly if alcohols are used as co-solvents.

Radiation-cured inks are set by exposure to ultraviolet or electron beam radiation. They are very fast drying and have high quality image formation. However, they are currently limited to narrow web printing, such as labels, and a few wide web specialty products.

6.2.2 Emission Control Techniques

VOC emissions from flexographic printing come from organic solvents in the ink and from solvents used for press cleaning. Accordingly, control measures that can be applied to this process can be categorized into three areas: reduced-VOC ink, reduced-VOC cleaning, and add-on control devices.

6.2.2.1 Reduced-VOC Ink

A relatively inexpensive way to reduce VOC emissions is to reduce the VOC content of the ink. Changing from an organic solvent-based ink to a high-solids or water-based ink can usually be done with little change in the printing process and can produce significant VOC reductions. However, there have been some difficulties in applying high-solids technology to solvent-based inks. Changing to a radiation-cured ink can produce dramatic VOC reductions, but at the expense of new processing equipment.

6.2.2.2 Reduced-VOC Cleaning

Organic solvents are generally used to clean presses that use solvent-based inks. However, it may be possible to reduce the VOC content by adding water and detergent to form the cleaning solution. Lower volatility solvents may also be used. In some cases, mechanical cleaning with baking soda or dry ice blasting may be possible. Where water-based inks are used, non-organic cleaning techniques using highly alkaline solutions are applicable.

6.2.2.3 Add-On Control Equipment

When it is not possible to change from solvent-based inks or when ink changes alone do not achieve the required VOC reduction, add-on control equipment can be employed. The type of add-on control equipment that is used will depend on the characteristics of the gas stream and the cost effectiveness of the strategy. While some solvent recovery techniques such as adsorption and condensation have been employed at a few flexographic facilities, gas streams collected from dryers are most frequently controlled by incineration. Some care must be exercised in applying catalytic incinerators to flexographic printing, since some of the pigments used in the inks contain metals that may poison the catalyst.

6.2.3 Emission Regulation

At the time of writing, USEPA had issued RACT recommendations and MACT requirements for flexographic printing. These recommended and required standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Control of Volatile Organic Emissions from Existing Stationary Sources--Volume VIII: Graphic Arts--Rotogravure and Flexography, Control Technique Guideline Document, EPA-450/2-78-033

Recommended standard:

- Achieve an overall VOC reduction efficiency of 60%.

National Emission Standards for the Printing and Publishing Industry, 40CFR63, Subpart KK

Applicability: Each new and existing facility that is a major source of hazardous air pollutants (HAP) at which wide-web (>18 inches) flexographic printing presses are operated.

Standard:

- Limit emissions to no more than 5% of the organic HAP applied for the month; or
- Limit emissions to no more than 4% of the total mass or inks, coatings, varnishes, adhesives, primers, solvents, reducers, thinners, and other materials applied for the month; or
- Limit emissions to no more than 20% of the mass of solids applied for the month; or
- Limits emissions to a calculated equivalent allowable mass based on the organic HAP and solids contents of the inks, coatings, varnishes, adhesives, primers, solvents, reducers, thinners, and other materials applied for the month.

6.3 ROTOGRAVURE

6.3.1 Process Description

The rotogravure printing industry consists of three branches: publication rotogravure, packaging rotogravure and product rotogravure. Publication rotogravure plants print magazines, catalogs and advertising materials. Presses can accommodate webs up to 139 inches wide and run at speeds up to 3,000 feet per minute. Packaging rotogravure is used to print cartons, paper wraps, labels, plastic film and aluminum foil. Press widths range from 12 to 64 inches and they run at speeds from 300 to over 1,000 feet per minute. Product rotogravure is used to print wrapping paper, wall coverings, wood grains for laminates, some postage stamps and other specialty products. Press widths and speeds vary considerably.

In rotogravure printing, the image areas from which inks or coatings are transferred consist of small, recessed cells engraved into the surface of a gravure cylinder. The material that is engraved is typically an electroplated layer of copper. After engraving, the cylinder is protected from wear by a very thin electroplated layer of chromium.

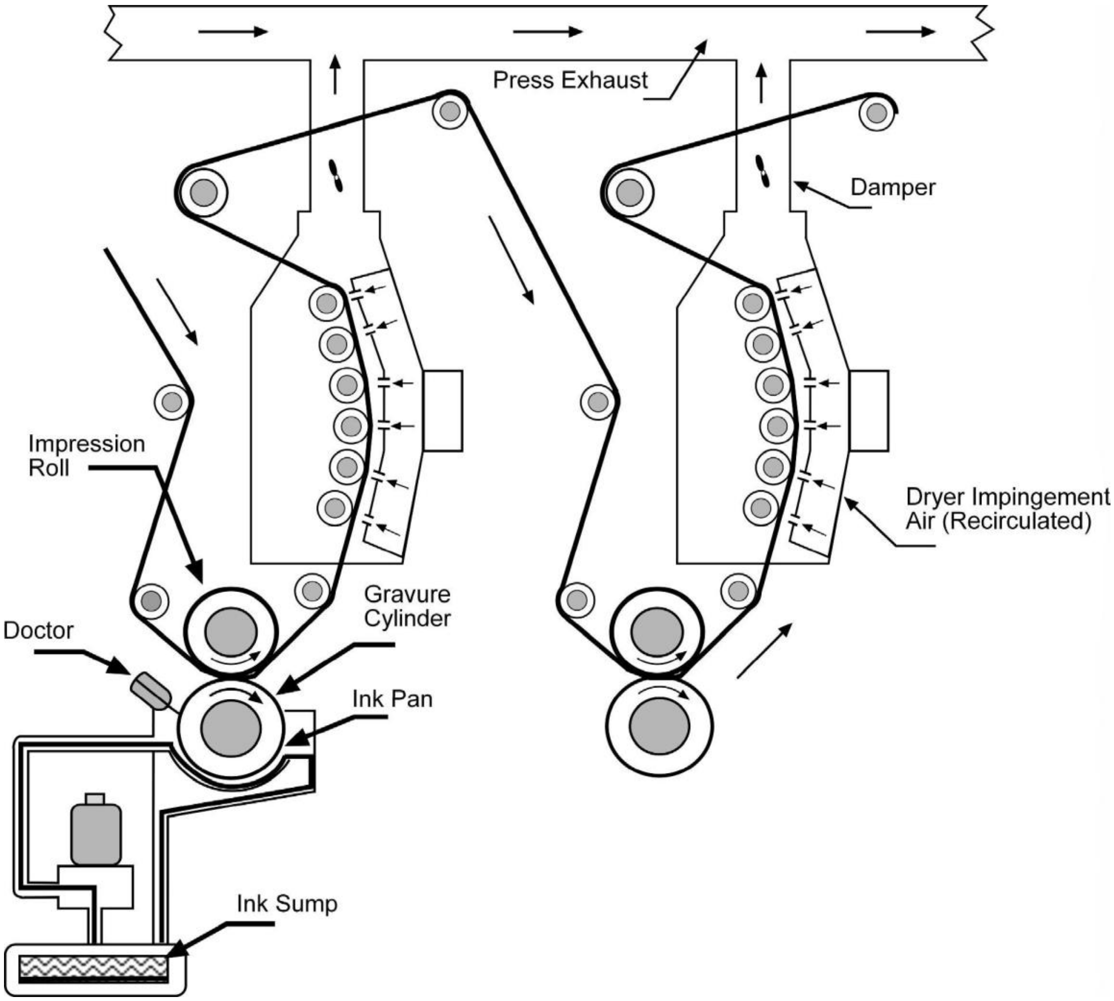

Figure 6-12. Section of rotogravure press

A section of a rotogravure press is shown in Figure 6-12. As the gravure cylinder rotates, its lower portion is flooded with liquid ink. A doctor blade removes the ink from the non-printing surface of the cylinder, leaving ink only in the recessed cells. The ink is then transferred to the web by pressing the web against the gravure cylinder with a rubber-covered impression roll. Each printing station is followed by a high-volume air dryer to dry the ink before the next color or coating is applied. The ink dries by evaporation at temperatures that typically range from 80°F to 150°F for publication rotogravure and up to 280°F for packaging rotogravure.

Rotogravure inks can contain as much as 75% solvent by weight. They have to be highly fluid to provide for proper flooding of the cylinder, for doctoring and for transfer of the ink from the cells to the web. Traditionally, low ink viscosity and fast drying have been achieved by the use of low-boiling-point organic solvents, and this is still essentially the case for publication rotogravure. However, certain packaging and product rotogravure plants are routinely using water-based inks.

6.3.2 Emission Control Techniques

VOC emissions from rotogravure printing come from organic solvents in the ink and from solvents used for press cleaning. Accordingly, control measures that can be applied to this process can be categorized into three areas: reduced-VOC ink, reduced-VOC cleaning, and add-on control devices.

6.3.2.1 Reduced-VOC Ink

A relatively inexpensive way to reduce VOC emissions is to reduce the VOC content of the ink. Changing from an organic solvent-based ink to a water-based ink can produce significant VOC reductions. The use of high-solids technology reduce VOC emissions has not been successful in rotogravure printing.

6.3.2.2 Reduced-VOC Cleaning

Organic solvents are generally used to clean presses that use solvent-based inks. However, it may be possible to reduce the VOC content by adding water and detergent to form the cleaning solution. Lower volatility solvents may also be used. In some cases, mechanical cleaning with baking soda or dry ice blasting may be possible. Where water-based inks are used, non-organic cleaning techniques using highly alkaline solutions are applicable.

6.3.2.3 Add-On Control Equipment

When it is not possible to change from solvent-based inks or when ink changes alone do not achieve the required VOC reduction, add-on control equipment can be employed. The type of add-on control equipment that is used will depend on the characteristics of the gas stream and the cost effectiveness of the strategy. Solvent recovery with activated carbon adsorbers is used in all publication rotogravure plants and in some packaging plants, when the solvent can be reused without too much further processing. When a variety of solvents or water-soluble solvents are used, VOC emissions are generally controlled by incineration. Some care must be exercised in applying catalytic incinerators to rotogravure printing, since some of the pigments used in the inks contain metals that may poison the catalyst.

6.3.3 Emission Regulation

At the time of writing, USEPA had issued RACT recommendations for publication and packaging rotogravure, NSPS requirements for publication rotogravure and MACT requirements for publication, packaging and product rotogravure. These recommended and required standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Control of Volatile Organic Emissions from Existing Stationary Sources--Volume VIII: Graphic Arts--Rotogravure and Flexography, Control Technique Guideline Document, EPA-450/2-78-033

Recommended standard:

- Achieve an overall VOC reduction efficiency of 75% for publication rotogravure.
- Achieve an overall VOC reduction efficiency of 65% for packaging rotogravure.

Standards of Performance for the Graphic Arts Industry: Publication Rotogravure Printing, 40CFR60, Subpart QQ

Applicability Date: October 28, 1980

Standard:

- VOC emitted must be less than or equal to 16% of the total mass of VOC solvent and water used during any consecutive 30 day averaging period.

National Emission Standards for the Printing and Publishing Industry, 40CFR63, Subpart KK

Applicability: Each new and existing facility that is a major source of hazardous air pollutants (HAP) at which publication rotogravure or product and packaging rotogravure printing presses are operated.

Standard:

For publication rotogravure printing:

- Limit emissions to no more than 8% of the total volatile matter used each month.

For product and packaging rotogravure printing:

- Limit emissions to no more than 5% of the organic HAP applied for the month; or
- Limit emissions to no more than 4% of the total mass or inks, coatings, varnishes, adhesives, primers, solvents, reducers, thinners, and other materials applied for the month; or
- Limit emissions to no more than 20% of the mass of solids applied for the month; or
- Limits emissions to a calculated equivalent allowable mass based on the organic HAP and solids contents of the inks, coatings, varnishes, adhesives, primers, solvents, reducers, thinners, and other materials applied for the month.

6.4 SCREEN PRINTING

6.4.1 Process Description

The screen printing process involves the flow of ink through a porous screen mesh that has a stencil bonded to it to define the image. The ink flows through the imaged screen by hydraulic pressure that is provided by a flexible rubber or synthetic blade known as a squeegee. The squeegee blade moves across the surface of the imaged screen, pressing the ink through those areas of the screen not blocked by the stencil and onto the substrate. The substrate is then either placed into drying racks or onto a conveyor for transport into a drying unit.

Unlike other printing processes, screen printing is able to use a wide variety of substrates. These include plastic, fabric, metal, paper, leather, masonite, wood and electronic circuit boards. Products include imprinted textile garments, banners, billboards, posters, containers, labels, decals, emblems, flags, pennants, nameplates, wallpaper and product-identification markings. Substrates may be printed individually or as a continuous web.

Four types of inks are used in screen printing: solvent-based, water-based, UV-curable and plastisols. Conventional solvent-based inks are widely used in the industry. They contain up to 60% organic solvent and cure by evaporation. Water-based inks use water as all or part of their solvent component and typically contain 65% to 70% solids. They also cure by solvent evaporation. UV-curable inks contain monomers and oligomers that polymerize when exposed to ultraviolet radiation. Plastisols contain PVC resins and plasticizers and are essentially 100% solids. They form their final surface by fusing at about 320°F.

Drying units utilize hot air, infrared radiation and UV radiation to dry or cure the wet ink and have exhaust systems to remove the resulting emissions from the workplace. The most common system is the hot-air convection oven. Typically, 80% of the air is recirculated and 20% is exhausted. Infrared systems use inductive energy to create heat within the material to dry it. Air is circulated within the heating system; however, very little is exhausted to the outside. UV curing units use ultraviolet radiation to polymerize the ink into a solid film. This process takes place in a fraction of a second and is about 10 times more energy efficient than traditional hot-air units.

The screens used in the printing process are reclaimed for reuse. First, ink residue is removed from the screen using water-soluble ink degraders or appropriate solvents. The screen must then be degreased, since any remaining chemical or solvent residue will impede the effectiveness of the stencil remover. After the stencil remover is applied, the emulsion begins to dissolve and is completely removed with a high-pressure washer. After repeated uses, ghost images of previous stencil applications will remain. Ghost or haze removers are used to remove this condition. After using the haze removers, the screen material must again be degreased before it can be reused.

6.4.2 Emission Control Techniques

VOC emissions from screen printing come from organic solvents in the ink and from solvents used for press cleaning and screen reclamation. Accordingly, control measures that can be applied to this process can be categorized into three areas: reduced-VOC ink, reduced-VOC cleaning, and add-on control devices.

6.4.2.1 Reduced-VOC Ink

A relatively inexpensive way to reduce VOC emissions is to reduce the VOC content of the ink. For some substrates, changing from an organic solvent-based ink to a high-solids or water-based ink can usually be done with little change in the printing process and can produce significant VOC reductions. Changing to a radiation-cured ink can produce dramatic VOC reductions, but at the expense of new processing equipment.

6.4.2.2 Reduced-VOC Cleaning

Organic solvents are generally used to clean presses and reclaim screens that use solvent-based inks. However, it may be possible to reduce the VOC content by adding water and detergent to form the cleaning solution. Lower volatility solvents may also be used. In some cases, mechanical press cleaning with baking soda or dry ice blasting may be possible. Where water-based inks are used, non-organic cleaning and reclamation techniques using highly alkaline solutions may be applicable.

6.4.2.3 Add-On Control Equipment

When it is not possible to change from solvent-based inks or when ink changes alone do not achieve the required VOC reduction, add-on control equipment can be employed. The most common control devices used in screen printing are thermal and catalytic incinerators. Some care must be exercised in applying catalytic incinerators to screen printing, since some of the pigments used in the inks contain metals that may poison the catalyst.

6.4.3 Emission Regulation

At the time of writing, USEPA had not issued any emission control recommendations or standards for screen printing.

6.5 PROCESS INSPECTION

There should be two goals in any field inspection. First is to evaluate the source's compliance with any rule-specific monitoring and recordkeeping requirements and with the provisions of the Title V permit. In addition, changes in operating conditions or parameters that could result in increased emissions should be evaluated. In graphic arts processes, increased emissions usually result from changes in ink composition and in the method and rate of application and from reduced performance of the air pollution control device. Recommended general inspection items include the following:

- ***Review ink composition and consumption records.*** Ink composition data should be evaluated to determine compliance with the operating permit and with applicable regulations. These data typically include the solvent, solids and water content of the ink, the ink density and the solvent density. Techniques for calculating the VOC content of the ink in the units of the applicable standard will be presented in Chapter 7. Ink and solvent consumption records should be reviewed and compared to the operating permit limitations.
- ***Observe ink preparation.*** Determine if the ink preparation area is ventilated and what type of control device is used. Note if the ink and solvent drums are kept closed when not being used. Observe how spills are cleaned up. Question plant personnel regarding the types of solvents in the inks and those used as diluents and if they have been changed. If carbon adsorbers are used for control of any portion of the process, they may not function as designed if the solvents have been changed. If more volatile solvents are being used, VOC losses from the printing area will likely be greater. If it is necessary to confirm the ink composition, samples of the "as applied" ink should be taken for Method 24, Method 24a or other appropriate analysis.
- ***Observe printing area.*** Determine if the printing area is ventilated and what type of control device is used. Note if they have made changes in the printing method. Question plant personnel regarding any changes in the application rate. Determine if any changes are made in the control system parameters to accommodate any changes in solvents or application rates. Observe how spills are cleaned up.
- ***Observe curing area.*** Check physical integrity of the oven and oven temperatures. Determine what type of control device is used. Question plant personnel regarding any changes in line speed. Determine if any changes are made in the control system parameters to accommodate any changes in solvents, application rates or line speed.

The inspection of carbon adsorbers and catalytic and thermal incinerators is covered in APTI Course 455, Inspection of Gas Control Devices and Selected Industries. The reader is referred to this course for guidance.

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Review Questions

1. Which of the following is not a graphic arts process?
   a. Metallography
   b. Flexography
   c. Lithography
   d. Rotogravure

2. Which graphics arts process uses a planographic printing plate?
   a. Screen printing
   b. Flexography
   c. Lithography
   d. Rotogravure

3. Which lithographic printing processes retain most of the ink solvent in the substrate? Select all that apply.
   a. Nonheatset web
   b. Heatset web
   c. Sheetfed

4. What is the major component of fountain solutions used in lithographic printing?
   a. Isopropyl alcohol
   b. Water
   c. Ethylene glycol
   d. Glycol ethers

5. What type of energy is used to polymerize radiation-curable inks? Select all that apply.
   a. Ultraviolet
   b. Electron beam
   c. Infrared
   d. Solar

6. What are potential sources of VOC emissions from lithographic printing processes? Select all that apply.
   a. Inks
   b. Suppressants
   c. Fountain solutions
   d. Cleaning solutions

7. Which graphics arts process uses a raised-image rubber printing plate?
   a. Screen printing
   b. Flexography
   c. Lithography
   d. Rotogravure

8. Which of the following is not a type of flexographic printing press?
   a. Stacked
   b. Offset
   c. In-line
   d. Central impression

9. What type of roll is used to transfer ink to the printing plate in a flexography press?
   a. Rubber
   b. Planar
   c. Anilox
   d. Trifid

10. What is the most common control device used on flexographic press dryers?
    a. Incinerators
    b. Adsorbers
    c. Absorbers
    d. Condensers

11. Which graphics arts process uses an engraved printing plate?
    a. Screen printing
    b. Flexography
    c. Lithography
    d. Rotogravure

12. Which of the following are divisions of the rotogravure printing industry? Select all that apply.
    a. Product
    b. Commercial
    c. Packaging
    d. Publishing

13. Which graphics arts process uses the greatest variety of substrates?
    a. Screen printing
    b. Flexography
    c. Lithography
    d. Rotogravure

14. What techniques are used to reduce VOC emissions from graphic arts processes?
    a. Reduced-VOC ink
    b. Reduced-VOC cleaning
    c. Add-on control equipment
    d. All of the above
15. Which of the following should be included in a general inspection of a graphic arts facility?
    a. Review ink composition and consumption records
    b. Observe ink preparation
    c. Observe printing and curing process
    d. All of the above

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Review Answers

1. Which of the following is not a graphic arts process?
   a. Metallography

2. Which graphics arts process uses a planographic printing plate?
   c. Lithography

3. Which lithographic printing processes retain most of the ink solvent in the substrate? Select all that apply.
   a. Nonheatset web
   c. Sheetfed

4. What is the major component of fountain solutions used in lithographic printing?
   b. Water

5. What type of energy is used to polymerize radiation-curable inks? Select all that apply.
   a. Ultraviolet
   b. Electron beam

6. What are potential sources of VOC emissions from lithographic printing processes? Select all that apply.
   a. Inks
   c. Fountain solutions
   d. Cleaning solutions

7. Which graphics arts process uses a raised-image rubber printing plate?
   b. Flexography

8. Which of the following is not a type of flexographic printing press?
   b. Offset

9. What type of roll is used to transfer ink to the printing plate in a flexography press?
   c. Anilox

10. What is the most common control device used on flexographic press dryers?
    a. Incinerators

11. Which graphics arts process uses an engraved printing plate?
    d. Rotogravure

12. Which of the following are divisions of the rotogravure printing industry? Select all that apply.
    a. Product
    c. Packaging
    d. Publishing

13. Which graphics arts process uses the greatest variety of substrates?
    a. Screen printing

14. What techniques are used to reduce VOC emissions from graphic arts processes?
    d. All of the above

15. Which of the following should be included in a general inspection of a graphic arts facility?
    d. All of the above

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7 Calculating the VOC Content of Coatings and Inks

In order to comply with regulations for surface coating and graphic arts processes, the source may elect to change to low VOC content coatings or inks, to improve the application transfer efficiency or to use add-on controls, such as incineration or carbon adsorption. When compliance is achieved by a change in the coating or ink composition alone, emissions can be calculated from the VOC content of the applied coating or ink. When add-on controls or transfer efficiency improvements are used, more complex calculations can be made to determine the effectiveness of the control strategy. It is more convenient, and often more reliable, to establish compliance status through these calculations than it is to measure the VOC emission directly.

7.1 INFORMATION NEEDS

Calculations for determining compliance with surface coating and graphic arts regulations require four types of information. First, the form of the emission limitation must be known. Second, data on the properties and compositions of the coatings or inks must be available. Third, the transfer efficiency of the application method and the performance specifications for any add-on control devices must be known. And, finally, production rates and coating or ink usage rates must be known. In this section, the regulatory basis for emission limitations will be presented, along with a description of the sources of data necessary for compliance determinations.

7.1.1 Emission Limitations

The first type of information that is needed to determine the compliance status of a source is the emission limitation the source is required to meet. The form in which that emission limit is expressed depends, in part, on the establishing regulatory program. A number of Federal programs, such as reasonably available control technology (RACT), new source performance standards (NSPS) and maximum achievable control technology (MACT), apply to surface coating and graphic arts industries. In addition, states may have their own individual control programs designed to reduce VOC emissions. Common forms of emission limitations for the surface coating industry are:

- Weight of VOC per volume of coating less water and exempt solvents
- Weight of VOC per area of surface covered
- Weight of VOC per volume of solids
- Weight of VOC per volume of applied solids

Emission limitations for the graphic arts industry are typically on a different basis. Common forms are:

- Volume percent VOC in the volatile fraction
- Volume percent water in the volatile fraction
- Volume percent solids in the ink less water

Compliance determination calculations are typically done in the units of the emission limitation. In some cases, that emission limitation may be specified for the "as applied" coating, i.e., for the composition that is actually used in the process. The composition of the "as applied" coating is determined from the composition of the coating "as supplied" by the manufacturer and the quantity and composition of diluent or cut solvents that are added. Regulations generally require continuous compliance over some time period, typically an hour or a day.

Calculations for sources which comply by reformulating the coating are typically done on the basis of the weight of VOC per gallon of coating. However, it is sometimes necessary to compare compliant coatings with other forms of emission limitation. These types of calculations are called *equivalency calculations* and are done on the basis of solids content. The reason for this is that the amount of solids it takes to coat a surface to a particular thickness is the same regardless of the coating formulation or application method. Calculations are also done on the basis of solids content when compliance is achieved by the use of add-on controls or improved transfer efficiencies.

7.1.2 Coating and Ink Data

The second type of information that is needed to make a compliance determination calculation is the properties and composition of the coating or ink. These data include coating and VOC densities and VOC, solids and water contents. Common methods and sources for obtaining the necessary data are summarized below.

7.1.2.1 Standard Methods

The USEPA has promulgated Reference Methods 24 and 24A (40CFR60, Appendix A) for determining the properties and composition of coatings and inks. Both methods rely on American Society of Testing Materials (ASTM) procedures. Method 24 is used to determine the following information for paint, varnish, lacquer and related surface coatings:

- Weight fraction of volatile matter
- Weight fraction of water

- Volume fraction of solids
- Coating density

Although Method 24 is suitable for most coatings, Method 24A is more appropriate for inks which contain a high volatile fraction. Method 24A is used to determine:

- Weight fraction of VOC
- Ink density
- Solvent density

7.1.2.2 Data Sheets

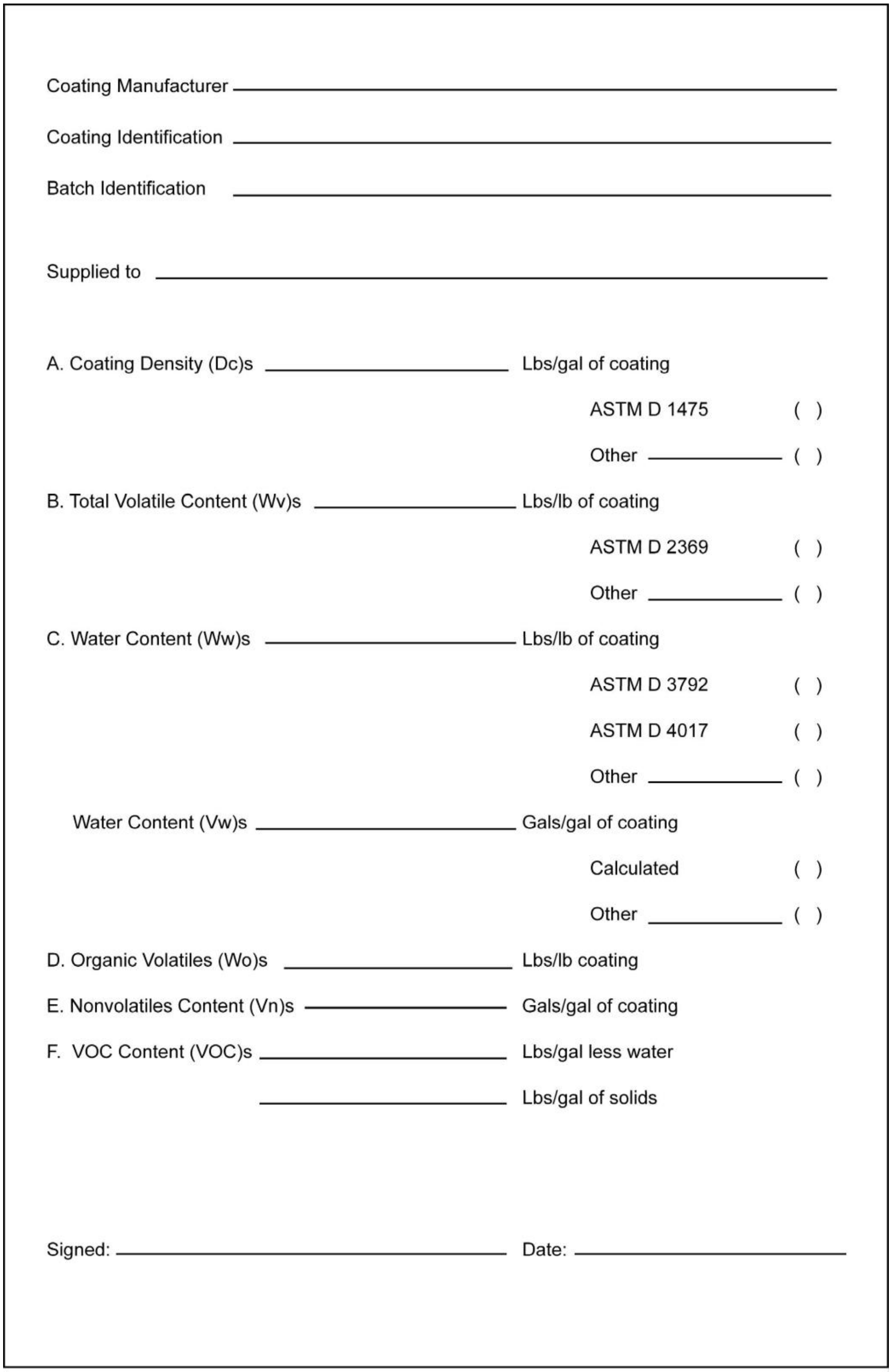
The USEPA, in conjunction with the National Painting and Coatings Association, has developed two data sheets to facilitate evaluation of the VOC content of a coating. Simplified versions of these forms are shown in Figures 7-1 and 7-2. Figure 7-1 is for the "as supplied" data obtained from the coating manufacturer, while Figure 7-2 is for the "as applied" data, after the user has added diluent solvents to obtain the desired coating properties.

7.1.2.3 Material Safety Data Sheets

Material Safety Data Sheets (MSDS) are supplied by the manufacturer and contain information on the properties and composition of the "as supplied" coating. MSDS may also be used as a source of information on diluent solvents.

7.1.3 Transfer Efficiency

The third type of information that is necessary to determine the compliance status of a source is the transfer efficiency of the application method and the degree of emission reduction that can be expected from add-on control devices. Minimum or baseline transfer efficiencies that can be used in compliance calculations are specified in some Control Technique Guideline (CTG) documents and NSPS. Many sources, however, take advantage of improved or enhanced transfer efficiencies. The enhanced transfer efficiency is determined under actual operating conditions. When enhanced transfer efficiency is used, compliance is determined by comparing the VOC emission from the baseline case to the enhanced case.



Coating Manufacturer ____________________

Coating Identification ____________________

Batch Identification ____________________

Supplied to ____________________

A. Coating Density (Dc)s ____________ Lbs/gal of coating

ASTM D 1475 ( )

Other ________ ( )

B. Total Volatile Content (Wv)s ____________ Lbs/lb of coating

ASTM D 2369 ( )

Other ________ ( )

C. Water Content (Ww)s ____________ Lbs/lb of coating

ASTM D 3792 ( )

ASTM D 4017 ( )

Other ________ ( )

Water Content (Vw)s ____________ Gals/gal of coating

Calculated ( )

Other ________ ( )

D. Organic Volatiles (Wo)s ____________ Lbs/lb coating

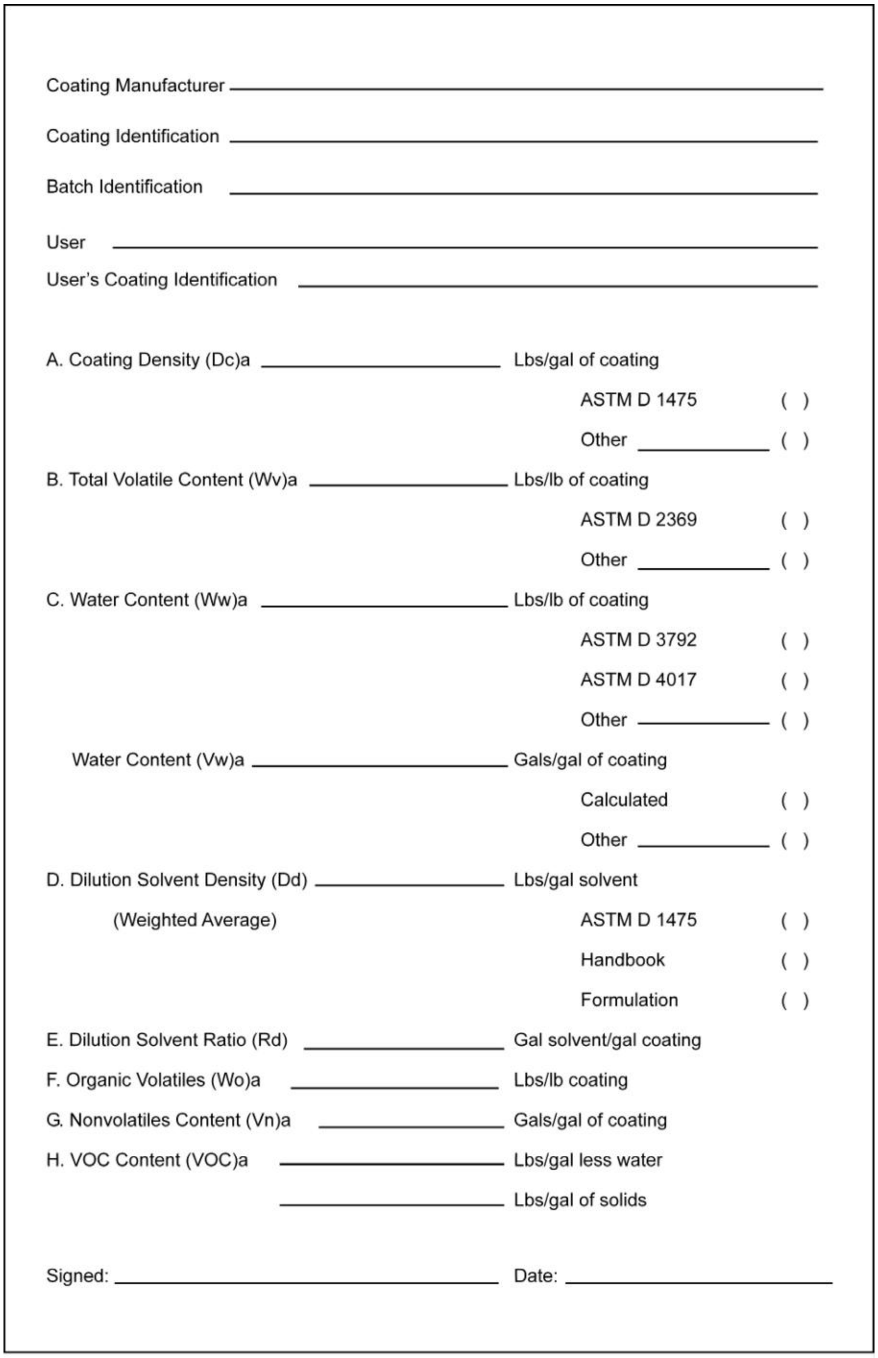
E. Nonvolatiles Content (Vn)s ____________ Gals/gal of coating

F. VOC Content (VOC)s ____________ Lbs/gal less water

____________ Lbs/gal of solids

Signed: ____________________ Date: ____________________

Figure 7-1. Properties of the coating “as supplied” by the coating manufacturer



Coating Manufacturer ____________________

Coating Identification ____________________

Batch Identification ____________________

User ____________________

User's Coating Identification ____________________

A. Coating Density (Dc)a ____________ Lbs/gal of coating

ASTM D 1475 ( )

Other ________ ( )

B. Total Volatile Content (Wv)a ____________ Lbs/lb of coating

ASTM D 2369 ( )

Other ________ ( )

C. Water Content (Ww)a ____________ Lbs/lb of coating

ASTM D 3792 ( )

ASTM D 4017 ( )

Other ________ ( )

Water Content (Vw)a ____________ Gals/gal of coating

Calculated ( )

Other ________ ( )

D. Dilution Solvent Density (Dd) ____________ Lbs/gal solvent

(Weighted Average)

ASTM D 1475 ( )

Handbook ( )

Formulation ( )

E. Dilution Solvent Ratio (Rd) ____________ Gal solvent/gal coating

F. Organic Volatiles (Wo)a ____________ Lbs/lb coating

G. Nonvolatiles Content (Vn)a ____________ Gals/gal of coating

H. VOC Content (VOC)a ____________ Lbs/gal less water

____________ Lbs/gal of solids

Signed: ____________________ Date: ____________

Figure 7-2. Properties of the coating “as applied” by the coating user

The claimed efficiency of capture and control equipment can be determined from manufacturer's information. The actual efficiency is determined by performance testing on the specific source.

7.1.4 Process Records

The fourth type of information that is necessary for compliance determinations is coating or ink usage rates and production rates. Most regulations require sources to maintain a record of coating usage and other process data. Although recordkeeping requirements vary, generally the minimum information that must be maintained includes:

- Coating formulation and analytical data
- Coating consumption data
- Capture and control equipment performance data
- Transfer efficiency data
- Process information

Sources are only required to submit data that is applicable to their operation. For example, if a source uses only compliant coatings to meet emission limitations, it does not need to maintain records on transfer efficiencies or control equipment performance. Sources subject to NSPS or construction or operating permits may have other recordkeeping requirements specific to those programs.

7.2 EMISSION CALCULATIONS

7.2.1 VOC Emissions on the Basis of Coating Volume

To illustrate the calculation of VOC emissions on the basis of coating volume, consider a coating that is 35 weight percent solids and 10 weight percent water. The solids density is 29.7 lbs/gal, and the density of water is 8.34 lbs/gal. The composition of the organic solvent is 83.3 volume percent xylene and 16.7 volume percent MEK.

The first step in the calculation process is to determine the density of the mixed organic solvent. From reference texts, it is determined that the density of xylene is 7.5 lbs/gal and the density of MEK is 6.7 lbs/gal. To determine the mixed solvent density, we find the proportional contribution of each solvent to a gallon of the mixture and then add them together.

$$\left(7.5\,\frac{\text{lbs xylene}}{\text{gal xylene}}\right)\left(0.833\,\frac{\text{gal xylene}}{\text{gal solvent}}\right)=6.25\,\frac{\text{lbs xylene}}{\text{gal solvent}}$$

$$\left(6.7\,\frac{\text{lbs MEK}}{\text{gal MEK}}\right)\left(0.167\,\frac{\text{gal MEK}}{\text{gal solvent}}\right)=1.11\,\frac{\text{lbs MEK}}{\text{gal solvent}}$$

$$\text{Solvent density} = 6.25\,\frac{\text{lbs xylene}}{\text{gal solvent}} + 1.11\,\frac{\text{lbs MEK}}{\text{gal solvent}} = 7.36\,\frac{\text{lbs solvent}}{\text{gal solvent}}$$

The next step is to determine the coating density. To determine this, we use each component density to determine the volume occupied by the weight of that component. We add these volumes together to determine the total volume and then divide that into the total weight to get the coating density. However, we must first determine the weight of solvent in the coating. Assume that we have 100 lbs of coating. From the given composition information, we know that we have 35 lbs of solids and 10 lbs of water in that 100 lbs of coating. Therefore:

Solvent content = 100 lbs coating – 35 lbs solids – 10 lbs water = 55 lbs solvent

$$\frac{35\,\text{lbs solids}}{29.7\,\dfrac{\text{lbs solids}}{\text{gal solids}}} = 1.18\,\text{gal solids}$$

$$\frac{10\,\text{lbs water}}{8.34\,\dfrac{\text{lbs water}}{\text{gal water}}} = 1.20\,\text{gal water}$$

$$\frac{55\,\text{lbs solvent}}{7.36\,\dfrac{\text{lbs solvent}}{\text{gal solvent}}} = 7.47\,\text{gal solvent}$$

1.18 gal solids + 1.20 gal water + 7.47 gal solvent = 9.85 gal coating

$$\text{Coating density} = \frac{100\,\text{lbs coating}}{9.85\,\text{gal coating}} = 10.15\,\frac{\text{lbs coating}}{\text{gal coating}}$$

From the information above, we can easily determine the composition of the coating on a volume basis. Dividing the volume of each component by the total volume and then multiplying by 100 gives the volume percentage of that component in the coating: 12.0 volume percent solids, 12.2 volume percent water and 75.8 volume percent solvent.

Now we are ready to calculate the VOC emissions on the basis of coating volume. We know we want to end up with an answer that has pounds of solvent in the numerator and gallons of coating in the denominator, so we choose as our beginning point the solvent density. But solvent density has gallons of solvent in its denominator, and we want gallons of coating — so, we multiply the solvent density by the volume fraction of solvent in the coating:

$$\text{Emissions} = \left(7.36\,\frac{\text{lbs solvent}}{\text{gal solvent}}\right)\left(0.758\,\frac{\text{gal solvent}}{\text{gal coating}}\right) = 5.58\,\frac{\text{lbs solvent}}{\text{gal coating}}$$

This calculation uses coating composition information that is on a volume basis. We could get the same result using the weight-based information. Again, we know we want to end up with an answer that has pounds of solvent in the numerator and gallons of coating in the denominator, so this time we choose the weight fraction of solvent in the coating as our starting point. But this parameter has pounds of coating in the denominator, and we want gallons of coating — so, we multiply the weight fraction of solvent in the coating by the coating density:

$$\text{Emissions} = \left(0.55\,\frac{\text{lbs solvent}}{\text{lb coating}}\right)\left(10.15\,\frac{\text{lbs coating}}{\text{gal coating}}\right) = 5.58\,\frac{\text{lbs solvent}}{\text{gal coating}}$$

Some regulations express the VOC emission limit on the basis of the coating volume less water and exempt solvents. To convert our answer to that basis, we must divide it by the gallons of coating less water and exempt solvents per gallon of coating. To determine that factor, we first write that there is one gallon of coating in a gallon of coating and then subtract the volume fractions of water and exempt solvents from it. Since there are no exempt solvents in our coating, that relationship becomes:

$$1\,\frac{\text{gal coating}}{\text{gal coating}} - 0.122\,\frac{\text{gal water}}{\text{gal coating}}$$

Since both of these terms have the same denominator, we can combine them to get:

$$\frac{1\,\text{gal coating} - 0.122\,\text{gal water}}{\text{gal coating}}$$

or

$$\frac{(1-0.122)\,\text{gal coating less water}}{\text{gal coating}}$$

We can now divide this into our previous answer to get the VOC emissions on the basis of coating volume less water. The complete calculation looks like this:

$$\text{Emissions} = \frac{\left(7.36\,\frac{\text{lbs solvent}}{\text{gal solvent}}\right)\left(0.758\,\frac{\text{gal solvent}}{\text{gal coating}}\right)}{\frac{(1-0.122)\,\text{gal coating less water}}{\text{gal coating}}} = 6.35\,\frac{\text{lbs solvent}}{\text{gal coating less water}}$$

If we had had exempt solvents in our coating, we would have simply subtracted their volume fraction from the 1 in the denominator, just as we did for the water.

7.2.2 VOC Emissions on the Basis of Solids Volume

Some regulations express the emission limit on the basis of solids volume. Since we already know how to get the emissions on the basis of coating volume, all we need to do to change gallons of coating in the denominator to gallons of solids is divide by the volume fraction of solids in the coating. The complete calculation looks like this:

$$\text{Emissions} = \frac{\left(7.36\,\frac{\text{lbs solvent}}{\text{gal solvent}}\right)\left(0.758\,\frac{\text{gal solvent}}{\text{gal coating}}\right)}{0.12\,\frac{\text{gal solids}}{\text{gal coating}}} = 46.49\,\frac{\text{lbs solvent}}{\text{gal solids}}$$

or

$$\text{Emissions} = \frac{\left(0.55\,\frac{\text{lbs solvent}}{\text{lb coating}}\right)\left(10.15\,\frac{\text{lbs coating}}{\text{gal coating}}\right)}{0.12\,\frac{\text{gal solids}}{\text{gal coating}}} = 46.52\,\frac{\text{lbs solvent}}{\text{gal solids}}$$

To express our result in terms of the gallons of solids applied, all we need to do is divide by the transfer efficiency of the application method. Assume that our coating is being applied by electrostatic spraying with a transfer efficiency of 75%. The emission rate then becomes:

$$\text{Emissions} = \frac{46.49\,\frac{\text{lbs solvent}}{\text{gal solids}}}{0.75\,\frac{\text{gal solids applied}}{\text{gal solids}}} = 61.99\,\frac{\text{lbs solvent}}{\text{gal solids applied}}$$

7.2.3 Graphic Arts Compliance Calculations

Graphic arts emission limitations are typically expressed in terms of the volume percent VOC in the volatile fraction, the volume percent water in the volatile fraction, or the volume percent solids in the ink less water. To illustrate these calculations, consider an ink that is 10 volume percent solids, 20 volume percent solvent and 70 volume percent water.

7.2.3.1 Volume Percent VOC in the Volatile Fraction

To determine the VOC content on this basis, we want to end up with an answer that has gallons of solvent in the numerator and gallons of volatiles in the denominator, so we choose as our beginning point the volume fraction of solvent in the ink. But this parameter has gallons of ink in the denominator, and we want gallons of volatiles. The volatile components in the ink are the solvent and the water, and the fraction of volatiles is one minus the fraction of solids. So, to change our denominator from gallons of ink to gallons of volatiles, we divide the volume fraction of solvent in the ink by one minus the volume fraction of solids:

$$\text{VOC content} = \frac{0.20\,\dfrac{\text{gal solvent}}{\text{gal ink}}}{(1-0.10)\,\dfrac{\text{gal volatiles}}{\text{gal ink}}} = 0.222\,\frac{\text{gal solvent}}{\text{gal volatiles}} \text{ or } 22.2\% \text{ of the volatiles}$$

7.2.3.2 Volume Percent Water in the Volatile Fraction

Expressing the water content on this basis is done exactly like the previous example for VOC content, except we start with the volume fraction of water in the ink:

$$\text{Water content} = \frac{0.70\,\dfrac{\text{gal water}}{\text{gal ink}}}{(1-0.10)\,\dfrac{\text{gal volatiles}}{\text{gal ink}}} = 0.778\,\frac{\text{gal water}}{\text{gal volatiles}} \text{ or } 77.8\% \text{ of the volatiles}$$

7.2.3.3 Volume Percent Solids in the Ink Less Water

Determining the VOC content on this basis requires that we end up with an answer that has gallons of solids in the numerator and gallons of ink less water in the denominator, so we choose as our beginning point the volume fraction of solids in the ink. But this parameter has gallons of ink in the denominator, and we want gallons of ink less water. So, to change our denominator from gallons of ink to gallons of ink less water, we divide the volume fraction of solids in the ink by one minus the volume fraction of water:

$$\text{VOC content} = \frac{0.10\,\dfrac{\text{gal solids}}{\text{gal ink}}}{(1-0.70)\,\dfrac{\text{gal ink less water}}{\text{gal ink}}} = 0.333\,\frac{\text{gal solids}}{\text{gal ink less water}} \text{ or } 33.3\%$$

Exercise No. 1

A coater is required to meet an emission limit of 3.5 pounds of VOC per gallon of coating less water. Does a coating with the following specifications comply?

Coating density: 9.0 lbs/gal
Total volatiles: 70 weight percent
Water content: 30 weight percent

Exercise No. 1 Solution

A coater is required to meet an emission limit of 3.5 pounds of VOC per gallon of coating less water. Does a coating with the following specifications comply?

Coating density:	9.0 lb/gal
Total volatiles:	70 weight percent
Water content:	30 weight percent

The volume fraction of water in the coating is:

$$\frac{\left(9.0\,\frac{\text{lbs coating}}{\text{gal coating}}\right)\left(0.30\,\frac{\text{lbs water}}{\text{lb coating}}\right)}{8.34\,\frac{\text{lbs water}}{\text{gal water}}} = 0.32\,\frac{\text{gal water}}{\text{gal coating}}$$

The solvent content of the coating is:

$$0.70\,\frac{\text{lbs volatiles}}{\text{lb coating}} - 0.30\,\frac{\text{lbs water}}{\text{lb coating}} = 0.40\,\frac{\text{lbs solvent}}{\text{lb coating}}$$

The VOC emitted per volume of coating less water is:

$$\frac{\left(9.0\,\frac{\text{lbs coating}}{\text{gal coating}}\right)\left(0.40\,\frac{\text{lbs solvent}}{\text{lb coating}}\right)}{\frac{(1-0.32)\,\text{gal coating less water}}{\text{gal coating}}} = 5.3\,\frac{\text{lbs solvent}}{\text{gal coating less water}}$$

This coating does not comply.

Exercise No. 2

a. A coater is required to meet an emission limit of 4.0 pounds of VOC per gallon of solids. Does a coating with the following specifications comply?

Coating density: 10.0 lbs/gal
Total volatiles: 60 weight percent
Water content: 45 weight percent
Solids content: 30 volume percent

b. Could the above coating meet an emission limit of 6.5 pounds of VOC per gallon of solids applied, if it is applied with a transfer efficiency of 80%?

Exercise No. 2 Solution

a. A coater is required to meet an emission limit of 4.0 pounds of VOC per gallon of solids. Does a coating with the following specifications comply?

Coating density:	10.0 lbs/gal
Total volatiles:	60 weight percent
Water content:	45 weight percent
Solids content:	30 volume percent

b. Could the above coating meet an emission limit of 6.5 pounds of VOC per gallon of solids applied, if it is applied with a transfer efficiency of 80%?

The solvent content of the coating is:

$$0.60\,\frac{\text{lbs volatiles}}{\text{lb coating}} - 0.45\,\frac{\text{lbs water}}{\text{lb coating}} = 0.15\,\frac{\text{lbs solvent}}{\text{lb coating}}$$

a. The VOC content of the coating is:

$$\frac{\left(10.0\,\dfrac{\text{lbs coating}}{\text{gal coating}}\right)\left(0.15\,\dfrac{\text{lbs solvent}}{\text{lb coating}}\right)}{0.30\,\dfrac{\text{gal solids}}{\text{gal coating}}} = 5.0\,\frac{\text{lbs solvent}}{\text{gal solids}}$$

This coating does not comply.

b. The VOC content of the coating is:

$$\frac{5.0\,\dfrac{\text{lbs solvent}}{\text{gal solids}}}{0.80\,\dfrac{\text{gal solids applied}}{\text{gal solids}}} = 6.3\,\frac{\text{lbs solvent}}{\text{gal solids applied}}$$

This coating complies.

Exercise No. 3

A coater is required to meet an emission limit of 3.7 pounds of VOC per gallon of coating less water. What percent emission reduction is needed if the coater uses a conventional solvent-borne coating with a solvent content of 5.0 pounds of VOC per gallon and solids content of 25 volume percent? Assume a solvent density of 7.36 lbs/gal.

Exercise No. 3 Solution

A coater is required to meet an emission limit of 3.7 pounds of VOC per gallon of coating less water. What percent emission reduction is needed if the coater uses a conventional solvent-borne coating with a solvent content of 5.0 pounds of VOC per gallon and solids content of 25 volume percent? Assume a solvent density of 7.36 lbs/gal.

Convert the emission limit to a solids basis:

$$\left(3.7\,\frac{\text{lbs solvent}}{\text{gal coating less water}}\right)\left(\frac{(1-0.0)\,\text{gal coating less water}}{\text{gal coating}}\right)=3.7\,\frac{\text{lbs solvent}}{\text{gal coating}}$$

$$\frac{3.7\,\dfrac{\text{lbs solvent}}{\text{gal coating}}}{7.36\,\dfrac{\text{lbs solvent}}{\text{gal solvent}}}=0.50\,\frac{\text{gal solvent}}{\text{gal coating}}$$

$$1.00\,\frac{\text{gal coating}}{\text{gal coating}}-0.50\,\frac{\text{gal solvent}}{\text{gal coating}}=0.50\,\frac{\text{gal solids}}{\text{gal coating}}$$

$$\frac{3.7\,\dfrac{\text{lbs solvent}}{\text{gal coating}}}{0.50\,\dfrac{\text{gal solids}}{\text{gal coating}}}=7.4\,\frac{\text{lbs solvent}}{\text{gal solids}}$$

Determine the VOC content of the actual coating:

$$\frac{5.0\,\dfrac{\text{lbs solvent}}{\text{gal coating}}}{0.25\,\dfrac{\text{gal solids}}{\text{gal coating}}}=20.0\,\frac{\text{lbs solvent}}{\text{gal solids}}$$

Calculate the percent reduction:

$$\frac{20.0-7.4}{20.0}\,\text{x}\,100=63.0\%$$

Exercise No. 4

A coater uses 10 gallons per hour of a solvent-borne coating that has a solvent content of 5.0 pounds of VOC per gallon and a solids content of 25 volume percent. Regulations require that the coating formulation meet an emission limit of 3.0 pounds of VOC per gallon of coating or the coater must control the emissions to an equivalent level. Assuming that the production rate, film thickness and transfer efficiency remain constant, what are the allowable hourly VOC emissions? Assume a solvent density of 7.36 lbs/gal.

Exercise No. 4 Solution

A coater uses 10 gallons per hour of a solvent-borne coating that has a solvent content of 5.0 pounds of VOC per gallon and a solids content of 25 volume percent. Regulations require that the coating formulation meet an emission limit of 3.0 pounds of VOC per gallon of coating or the coater must control the emissions to an equivalent level. Assuming that the production rate, film thickness and transfer efficiency remain constant, what are the allowable hourly VOC emissions? Assume a solvent density of 7.36 lbs/gal.

The solids usage rate is:

$$\left(10.0\,\frac{\text{gal coating}}{\text{hr}}\right)\left(0.25\,\frac{\text{gal solids}}{\text{gal coating}}\right)=2.5\,\frac{\text{gal solids}}{\text{hr}}$$

The VOC volume fraction for the complying coating is:

$$\frac{3.0\,\dfrac{\text{lbs solvent}}{\text{gal coating}}}{7.36\,\dfrac{\text{lbs solvent}}{\text{gal solvent}}}=0.41\,\frac{\text{gal solvent}}{\text{gal coating}}$$

The solids volume fraction for the complying coating is:

$$1.0\,\frac{\text{gal coating}}{\text{gal coating}}-0.41\,\frac{\text{gal solvent}}{\text{gal coating}}=0.59\,\frac{\text{gal solids}}{\text{gal coating}}$$

The volume of complying coating required is:

$$\frac{2.5\,\dfrac{\text{gal solids}}{\text{hr}}}{0.59\,\dfrac{\text{gal solids}}{\text{gal coating}}}=4.24\,\frac{\text{gal coating}}{\text{hr}}$$

The emission rate is:

$$\left(3.0\,\frac{\text{lbs solvent}}{\text{gal coating}}\right)\left(4.24\,\frac{\text{gal coating}}{\text{hr}}\right)=12.72\,\frac{\text{lbs solvent}}{\text{hr}}$$

NOTE: This example presents a method for determining hourly VOC emissions for offset calculations. Regulatory limitations would normally be based on either applicable coating formulations or control efficiency requirements. An hourly cap would only normally be used in addition to these regulatory requirements.

Exercise No. 5

A printer uses a solvent-borne ink that is 80 weight percent solvent and has a density of 7.44 pounds per gallon. The plant uses 10,000 55-gallon drums of ink each year. Tests show a 75%

efficiency for the capture system and a 90 percent efficiency for the control device. What are the plant's potential VOC emissions? If the regulatory requirement is to control 60% of the VOC emissions, is the plant in compliance? What would the VOC emissions be if the plant just met the regulatory requirement? What are the actual VOC emissions?

Exercise No. 5 Solution

A printer uses a solvent-borne ink that is 80 weight percent solvent and has a density of 7.44 pounds per gallon. The plant uses 10,000 55-gallon drums of ink each year. Tests show a 75% efficiency for the capture system and a 90% efficiency for the control device. What are the plant's potential VOC emissions? If the regulatory requirement is to control 60% of the VOC emissions, is the plant in compliance? What would the VOC emissions be if the plant just met the regulatory requirement? What are the actual VOC emissions?

The potential (uncontrolled) emissions are:

$$\left(55\,\frac{\text{gal ink}}{\text{drum}}\right)\left(7.44\,\frac{\text{lbs ink}}{\text{gal ink}}\right)\left(0.8\,\frac{\text{lbs solvent}}{\text{lb ink}}\right)\left(10{,}000\,\frac{\text{drums}}{\text{yr}}\right)=3{,}273{,}600\ \text{lbs solvent}$$

The control efficiency is:

$$(0.75 \text{ x } 0.90) \text{ x } 100 = 67.5 \text{ percent}$$

The plant is in compliance.

The VOC emissions at the regulatory limit are:

$$3{,}273{,}600 \text{ x } (1 - 0.60) = 1{,}309{,}440 \text{ lbs solvent}$$

The actual VOC emissions are:

$$3{,}273{,}600 \text{ x } [1-(0.75 \text{ x } 0.90)] = 1{,}063{,}920 \text{ lbs solvent}$$

Exercise No. 6

A printer uses an ink concentrate that has 30.55 weight percent solvent and a density of 10.8 lbs/gal. This concentrate is diluted with 1.5 gallons of water to each gallon of ink. What is the VOC content of the volatile portion? Assume a solvent density of 6.6 lbs/gal.

Exercise No. 6 Solution

A printer uses an ink concentrate that has 30.55 weight percent solvent and a density of 10.8 lbs/gal. This concentrate is diluted 1.5:1 with water. What is the VOC content of the volatile portion? Assume a solvent density of 6.6 lbs/gal.

The VOC content of the concentrate is:

$$\frac{\left(10.8\,\frac{\text{lbs ink}}{\text{gal ink}}\right)\left(.3055\,\frac{\text{lbs solvent}}{\text{lb ink}}\right)}{6.6\,\frac{\text{lbs solvent}}{\text{gal solvent}}} = 0.50\,\frac{\text{gal solvent}}{\text{gal ink}}$$

The volatile content of the "as applied" ink is:

$$0.50\,\frac{\text{gal solvent}}{\text{gal ink}} + 1.50\,\frac{\text{gal water}}{\text{gal ink}} = 2.00\,\frac{\text{gal volatiles}}{\text{gal ink}}$$

The VOC content of the volatile portion is:

$$\frac{0.50\,\frac{\text{gal solvent}}{\text{gal ink}}}{2.00\,\frac{\text{gal volatiles}}{\text{gal ink}}} = 0.25\,\frac{\text{gal solvent}}{\text{gal volatiles}} \text{ or } 25\% \text{ of volatiles}$$

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"A Guideline for Graphic Arts Calculations", EPA-340/1-88-004, June 1988.

“A Guideline for Surface Coating Calculations", EPA-340/1-86-016, July 1986.

"Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings", EPA-450/3-84-019, December 1984.

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8 Petroleum Refining

Crude oils are a mixture of paraffinic, naphthenic, and aromatic hydrocarbon compounds that contain small amounts of water, sand, sulfur, oxygen, nitrogen and metals as typical impurities. The refining industry uses various physical, thermal, catalytic and chemical processes to convert these oils into a wide range of products, including liquefied petroleum gas, gasoline, jet fuel, diesel fuel, lubricating oils and feedstocks for the petrochemical industry.

Petroleum refining involves a collection of complex processes that can be intimidating to agency personnel. Contributing to this is that there are probably no two refineries in the world that are exactly alike. The main reason for this is that refineries are designed to refine certain types of crude oil. The quality of crude oil ranges from the heavily contaminated black oil from Saudi Arabia and the U.S. Gulf Coast to the clear, honey-colored oils from Nigeria and Indonesia. Also, each refinery is designed to produce a certain range of products and that product mix usually changes with the seasons.

The purpose of this chapter is to give the reader a basic understanding of refining processes and their control and the regulations that apply to them. Inspection of refinery processes will not be discussed. To help with some of the complexity, we will divide refining operations into four categories:

- Separation processes
- Conversion processes
- Treatment processes
- Auxiliary processes

8.1 PROCESS DESCRIPTION

In general, crude oil is separated by distillation into fractions designated as (1) light ends; (2) straight-run gasolines; (3) middle distillates, from which kerosene, heating oils, and fuels for diesel, jet, rocket and gas turbine engines are made; (4) wide-cut gas oil, from which waxes, lubricating oil and feedstocks for producing gasoline are produced; and (5) residual oil, from which asphalt, coke and tar are made. The typical processing steps are shown in Figure 8-1.

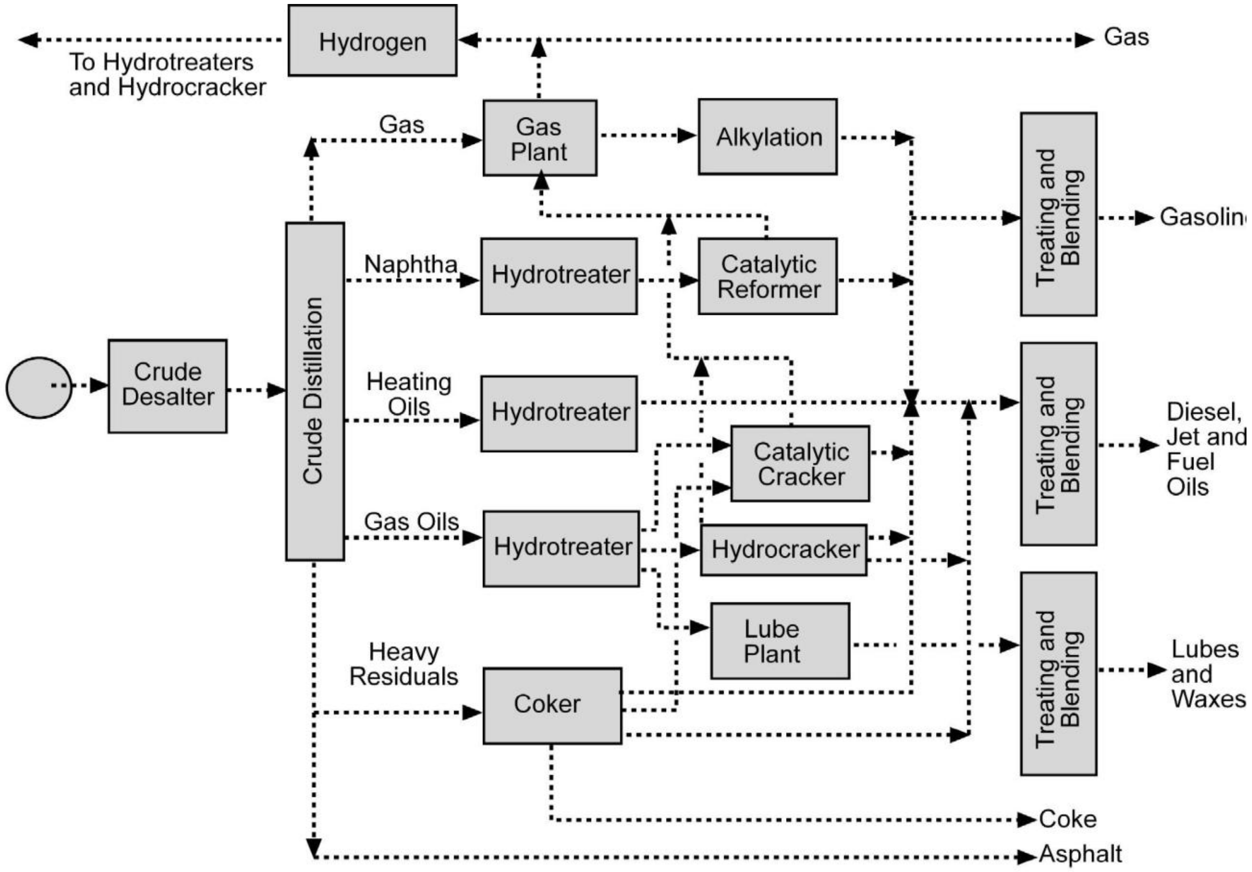

Figure 8-1. Typical processing steps in a petroleum refinery

8.1.1 Separation Processes

8.1.1.1 Desalting

Most refineries include some form of crude desalting as the first step. Although most of the free water and sand settle out and separate during storage, dissolved salts or suspended salt crystals are present in water that is emulsified with the crude oil. These salts can cause corrosion and plugging of processing equipment if they are not removed. Crude oil desalting is a separation and reaction process in which an imposed electrical field and/or chemical additives are used to coalesce the salt particles, which are then washed away with water. The process also removes arsenic and other trace metals that can poison catalysts in later processes.

In electrical desalting, the most common technique, water and demulsifier chemicals are added to the crude oil to dissolve the impurities. The crude, water and chemical mixture is heated under pressure to 160°F to 300°F and then subjected to a high-potential electrostatic field that causes the water droplets to agglomerate and settle to the lower portion of the vessel. The salt-containing water is removed from the vessel and sent to the wastewater treatment facility and the desalted crude flows to the distillation units.

In chemical desalting, the salts are separated from the crude oil by water washing in the presence of chemicals. The crude, chemicals and wash water are heated under pressure to 150°F to 350°F and sent to a settler with a residence time of 20 to 60 minutes. The heating lowers the surface tension and viscosity of the oil, allowing the water droplets to coagulate and settle. The salt-containing water is removed from the settler and sent to the wastewater treatment facility and the desalted crude flows to the distillation units.

8.1.1.2 Distillation

The first major separation step in refining is crude oil distillation. Here, the desalted crude is separated into various constant-boiling-range fractions using distillation columns or towers. The lowest boiling fraction is withdrawn at the top of the column and the highest boiling fraction is removed from the bottom. Products of intermediate boiling ranges may be withdrawn as sidestreams from various points along the column. These sidestreams are further processed in small columns called strippers, where steam is used to free the sidestream cut from its more volatile components so that the boiling point of the product can be adjusted to a specified value.

The first distillation column, shown in Figure 8-2, operates at essentially atmospheric pressure. Before entering the column, the desalted crude oil flows through a process heater where its temperature is raised to about 750°F. The column normally consists of 30 to 50 fractionation trays and three or more sidestream draws. Here, the crude is typically separated into light gases, light naphtha with a boiling range of 100°F to 250°F, heavy naphtha with a boiling range of 200°F to 350°F, light gas oil with a boiling range of 325°F to 500°F, heavy gas oils with a boiling range of 450°F to 650°F, and residuum.

The gases drawn from the top of the tower are condensed and sent to an accumulator for separation. The gas phase contains light hydrocarbons (propane and butane) and is usually compressed and sent to the refinery fuel gas system. The liquid phase contains water, pentane and lighter crude fractions. Some of the pentane and lighter crude fractions are returned to the top of the tower and the rest is sent to a fractionator where the propane and butane are removed. The water is sent to the wastewater treatment system.

The atmospheric distillation column usually has three or more sidestream draws that contain low-boiling components. These light ends are stripped from each sidestream in a separate column containing 4 to 10 trays. Steam is introduced under the bottom tray and the steam and stripped light ends are returned to the main column above the corresponding side draw tray. The hot residuum is steam stripped in the base of the main column and typically flows to a vacuum distillation column for additional separation.

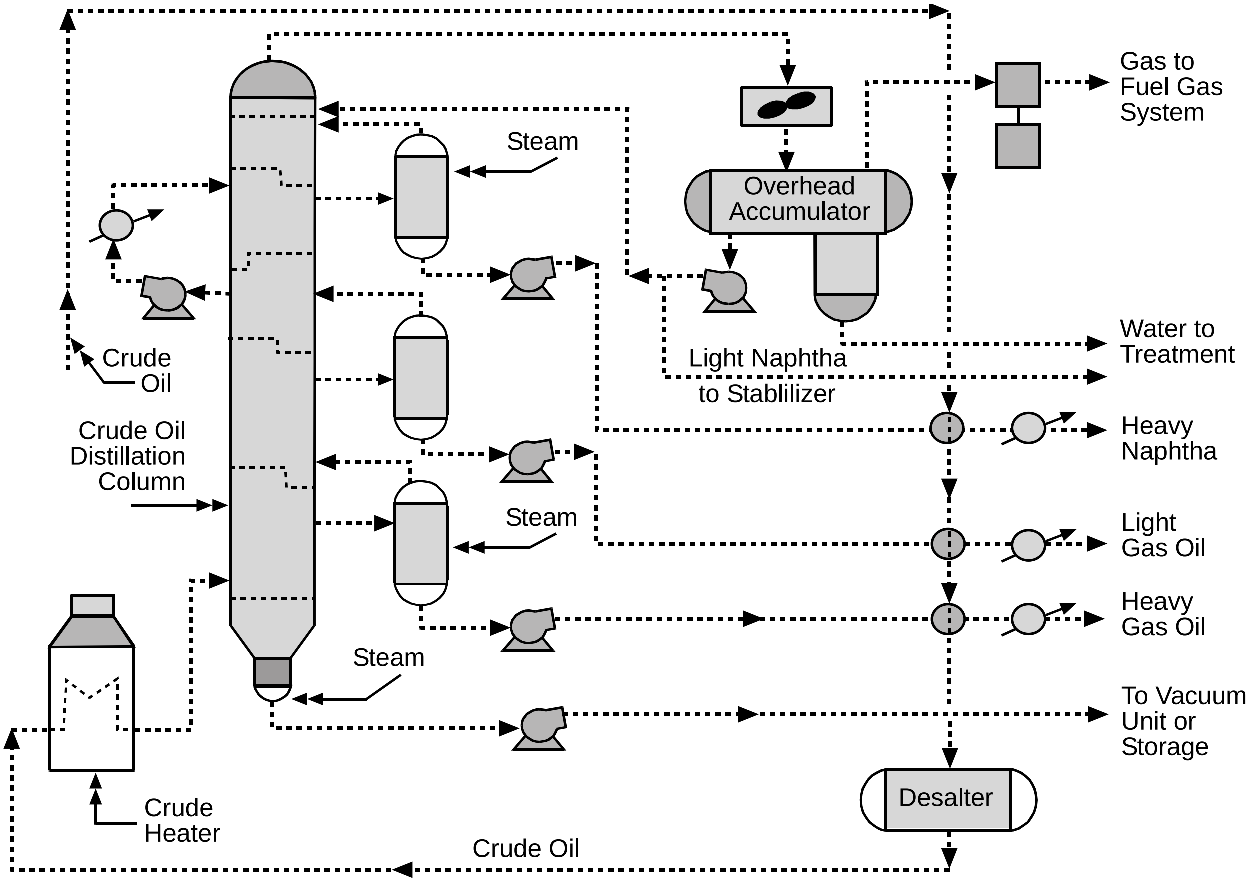

Figure 8-2. Typical atmospheric distillation unit

The temperatures required for atmospheric distillation of the heavier fractions of crude oil are so high that thermal cracking would occur, resulting in lost product and equipment fouling. Therefore, these materials are further distilled under vacuum, since the boiling temperature decreases with decreasing pressure. A typical vacuum distillation column is shown in Figure 8-3. The residual bottoms from the atmospheric distillation column, referred to as topped crude, flows to a process heater and then to the vacuum column where fractionation takes place at temperatures of 730°F to 850°F and a pressure of 0.5 to 1.0 psia. Fractionation is further improved when the effective pressure is lowered to about 0.2 psia by the addition of steam at the bottom of the tower. The residuum from the bottom of the vacuum tower is usually sent to the coking unit for further processing.

The pressure in the vacuum distillation column is generated by the use of steam ejectors with contact condensers or vacuum pumps with surface condensers. With the steam ejector, a steam nozzle discharges a jet of high-velocity steam across a suction chamber that is connected to the column. The gases drawn out of the column by the suction, together with the steam, are condensed by direct contact with water. The mixed stream of condensed steam, condensed organic vapors and cooling water flow to what is referred to as the hot well for separation. The recovered organic is sent to a waste oil tank and the water is sent to the wastewater treatment facility. Although more costly than contact condensers, the recent trend is to use vacuum pumps with surface condensers to reduce the contamination of water with condensed organic. The noncondensed vapor from either system is sent directly to a process heater or to the refinery fuel gas system.

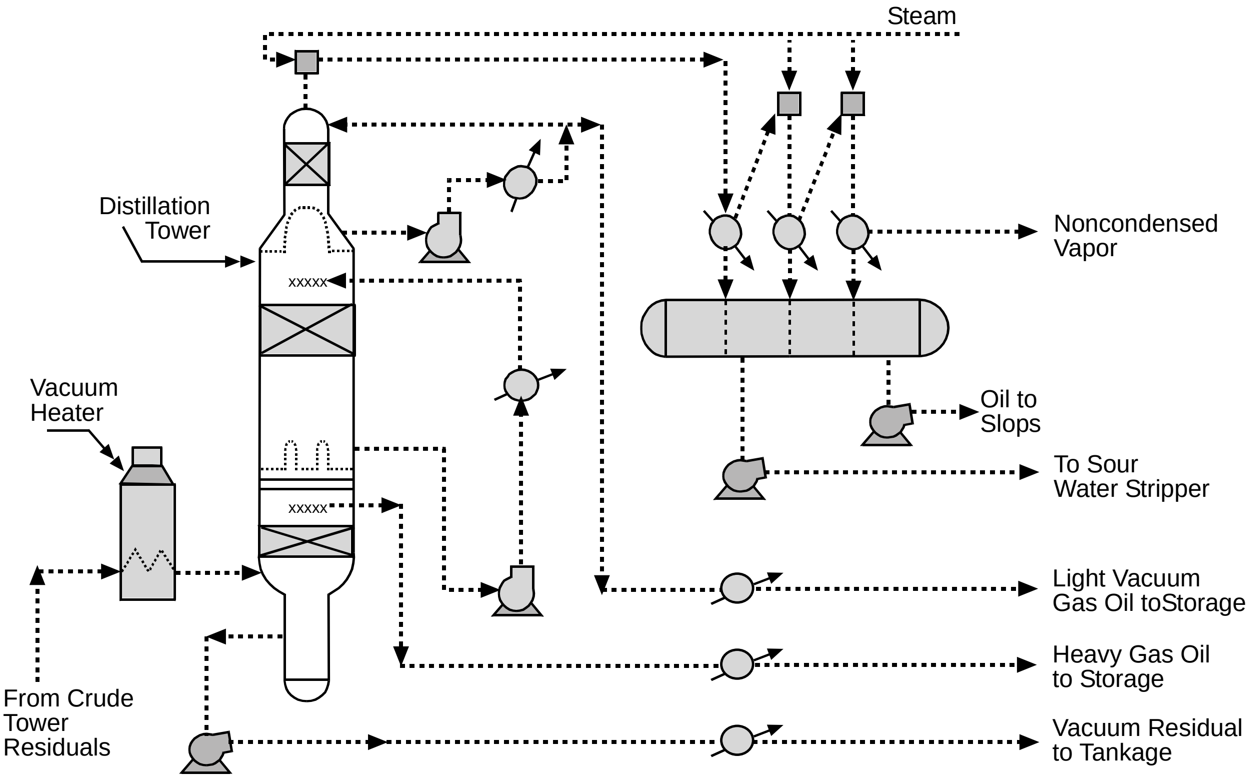

Figure 8-3. Typical vacuum distillation unit

8.1.1.3 Deasphalting

Deasphalting separates asphalts or resins from more viscous fractions using liquid-liquid extraction. Residuum from the vacuum tower is mixed with liquid propane, heated and fed to the deasphalting tower. The tower separates the material into two phases. The asphalt phase is heated and steam stripped for removal of residual propane and sent to the asphalt blowing tower for further processing. Propane is removed from the deasphalted oil phase by a two-stage evaporation process and steam stripping. The propane recovered from both phases is recycled.

8.1.2 Conversion Processes

After the crude oil is separated into various fractions, a series of conversion processes are used to meet the specifications for high-octane gasoline, jet fuel, and diesel fuel, and to upgrade components such as residual oils and light ends to gasoline. Coking, visbreaking and cracking processes are used to break large molecules into smaller molecules. Polymerization and alkylation processes are used to combine small molecules into larger ones. Isomerization and reforming processes rearrange the structure of molecules to produce higher-value products of a similar molecular size.

8.1.2.1 Coking

Coking is a thermal cracking process that converts low-value residual materials to higher value gas oil and petroleum coke. Typical feeds include crude oil residue, decanted oils and tar pitch. In addition to the coke, products include gas, naphtha, gasoline, and heavy and light gas oil. There are three types of coking processes: delayed coking, flexicoking and fluid coking. Delayed coking, the most common process, will be discussed here.

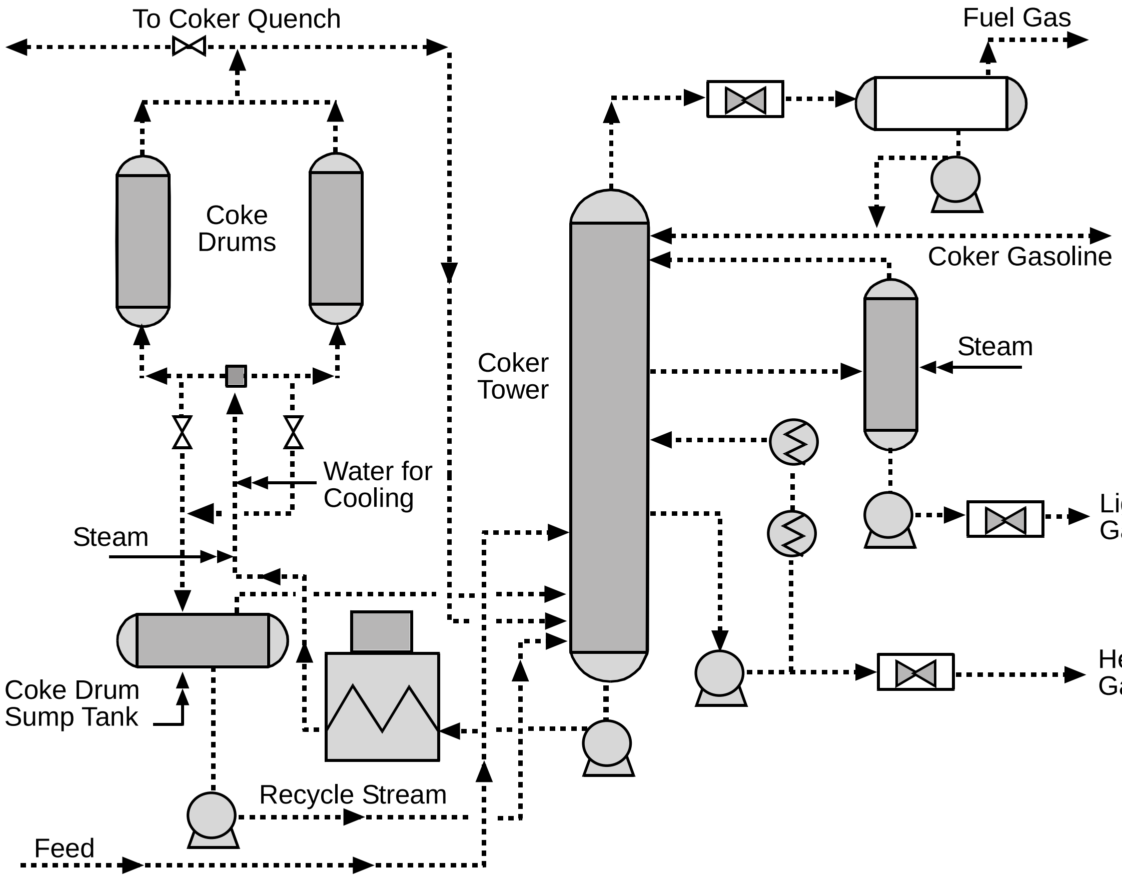

Figure 8-4. Flow diagram of delayed coking unit

In the delayed coking process, shown in Figure 8-4, the feed first enters the coker tower where gas oil, gasoline, and lighter fractions are flashed off and recovered. The tower bottoms are combined with a recycle stream and heated to 900°F to 1,100°F in a process heater, where some cracking and vaporization begins. The heated vapor-liquid stream then enters the coke drum, where the primary coking reaction takes place at a typical pressure of 25 to 30 psig, but may be as high as 100 psig. The vapor portion of the feed undergoes further cracking as it passes through the drum, and the liquid portion undergoes successive cracking and polymerization until it is converted to vapor and coke. The vapors from the coke drum are recycled to the coker tower for separation and recovery.

A coking unit has at least two drums and may have as many as four. Once the drum in service is filled with coke, the material flow is switched to an empty drum and the removal process is initiated. First, steam is injected into the drum to remove hydrocarbon vapors. The resulting gas stream is collected, condensed and separated. The condensed water will contain coke particles and is added to the coke removal stream. The recovered organic liquid is sent to the waste oil system, and the noncondensable vapors are sent to a flare or a process heater. After purging, the drum is filled with water, opened and drained. The coke is then cut out with a high-pressure water jet or a mechanical drill. The coke particles are separated from the water using screens. Fine particles remaining in the water are removed in a thickener, and the water is recycled to the coke cutting process.

8.1.2.2 Visbreaking

Viscosity breaking, or visbreaking, is a milder form of thermal cracking than coking. It is used to reduce the viscosity of residual fractions so that they may be blended into fuel oils. It is typically applied when the demand for middle distillates exceeds that for gasoline.

Residues from atmospheric and vacuum distillation are fed to a process heater where mild cracking produces a mixture of residual oil, naphtha and gas. This process takes place at temperatures of 800°F to 950°F and at pressures of 100 to 300 psig to as high as 750 psig. Some coke may also be formed and deposited on the heater tube surfaces, requiring them to be cleaned regularly to maintain efficient heat transfer. The reaction products are quenched with a recycle stream of gas oil and sent to a fractionator. The visbroken tars accumulate in the bottom of the tower and the flashed vapors are fractionated into light ends, gasoline, and light and heavy gas oils in the upper section of the tower. The heavy gas oil is stripped of light ends and may be blended with the visbreaker bottoms or used as feed for the catalytic cracker. The light ends are sent either to a gas recovery plant or to the refinery fuel gas system. Visbreaker bottoms that are not blended with oil may be used a feed for the coking unit.

8.1.2.3 Catalytic Cracking

Catalytic cracking is used to convert a gas oil feed stream into fuel gas, liquified petroleum gas, high-octane gasoline, and distillate fuel. The fluid catalytic cracking process shown in Figure 8-5 is the most common. Fresh feed is heated in a process heater and introduced into the bottom of a vertical transfer line or riser, along with a catalyst in the form of very fine particles. The catalyst vaporizes the feed, bringing both to the desired reaction temperature of 880°F to 980°F. The high activity of modern catalysts causes most of the cracking reactions to take place in the riser as the catalyst and vapor mixture flows upward into the reactor. The hydrocarbon vapors are separated from the catalyst particles by cyclones in the reactor.

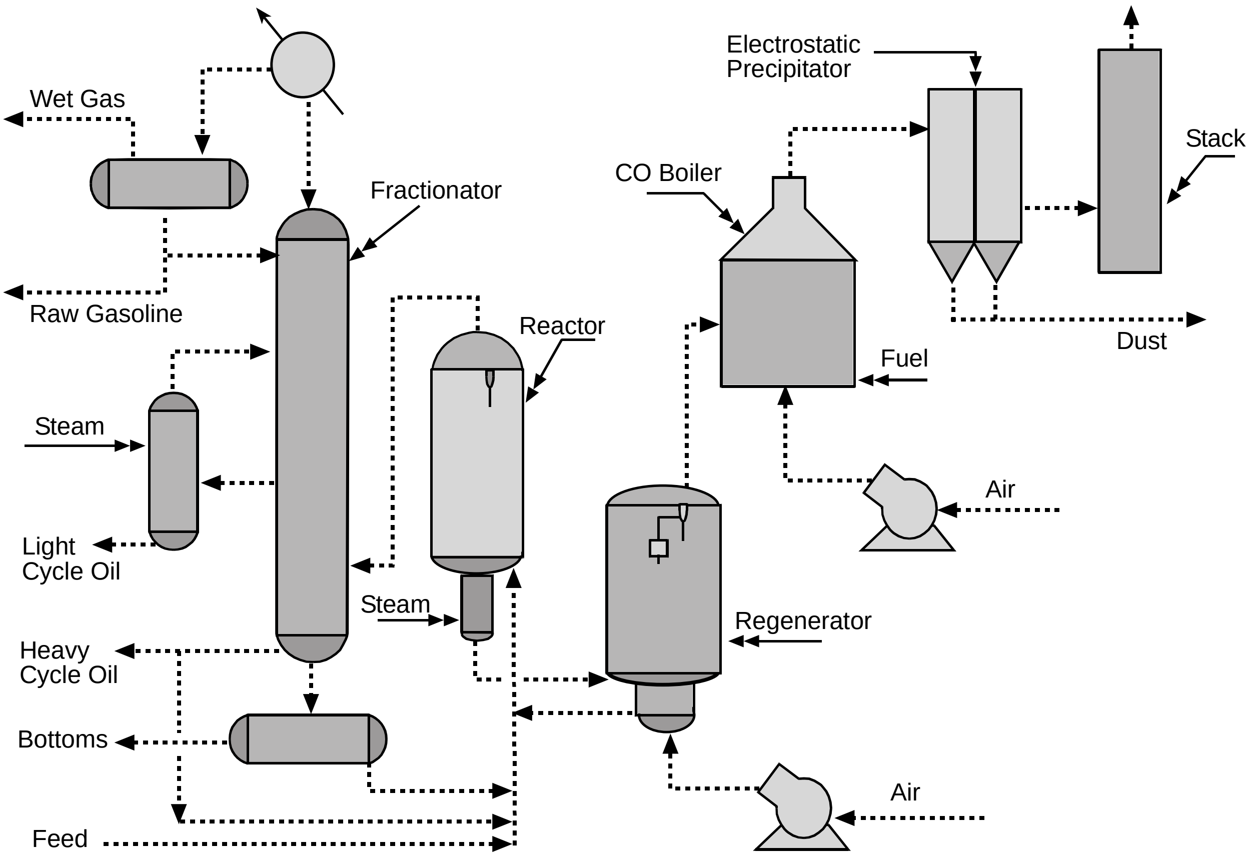

Figure 8-5. Diagram of a fluid catalytic cracking unit

The vapors exiting the reactor are condensed and sent to a fractionator for separation and recovery. The vapors from the top of the fractionator are condensed to recover gasoline, and the noncondensables are sent to the gas recovery system. Other cuts from the fractionator may include alkylation unit feed and light and heavy oils. The bottoms from the fractionator may be recycled to the reactor or sent to the coking unit.

The spent catalyst falls to the bottom of the reactor and is steam stripped to remove adsorbed hydrocarbons as it exits the reactor bottom. The spent catalyst is then conveyed to a regenerator, where coke deposited on the catalyst surface during cracking reactions is burned off at 1,100°F to 1,250°F using controlled combustion air that fluidizes the catalyst. The resulting combustion gases, usually rich in carbon monoxide (CO), flow through cyclones to remove the entrained catalyst and are then burned in a CO boiler to generate steam. The particulate emissions from the CO boiler are usually controlled by an electrostatic precipitator. The regenerated catalyst is recycled.

8.1.2.4 Polymerization

Polymerization is the continuous, catalytic conversion of olefin gases to liquid condensation products. It was first introduced to provide a gasoline blending stock when octane levels were very low. It is rarely used in refineries today. The octane gain from blending of polymer gasoline was soon replaced by blending of alkylate from alkylation units. Polymers are valuable in some applications, however, such as additives for motor oil.

In the liquid catalyst polymerization process, the olefin feed is polymerized with a liquid phosphoric acid catalyst in a reactor that operates at a temperature of 300°F to 400°F and a pressure of 150 to 400 psig. The hydrocarbon polymer from the reactor is separated from the acid in a settler and sent to a fractionator. Liquid petroleum gas is recovered from the top of the fractionator, and the product, polymer gasoline, is recovered as bottoms.

In the solid catalyst polymerization process, the olefin feed is mixed with recycled propane and water and introduced into a multiple-fixed-bed reactor that contains pellets impregnated with the phosphoric acid catalyst. Depending on the feedstock, this reactor operates at a temperature between 350°F and 425°F and a pressure between 400 and 1,200 psig. The effluent from the reactor flows to a depropanizer, where propane and lighter gases are removed from the top. The depropanizer bottoms flow to a debutanizer, where butane is removed from the top, and the product, polymer gasoline, is removed from the bottom.

8.1.2.5 Alkylation

In alkylation, branched hydrocarbons are synthesized by the addition of a paraffinic or aromatic hydrocarbon to an olefin in the presence of a sulfuric or hydrofluoric acid catalyst. The product, alkylate, is used as an antiknock additive in motor and aviation fuels.

Sulfuric acid alkylation is an exothermic process. In the effluent refrigeration system, olefin and isobutane streams are mixed before entering a horizontal reactor. In the reactor, the hydrocarbon mixture is contacted with concentrated sulfuric acid, resulting in an exothermic reaction that forms an emulsion that is 35% to 50% hydrocarbons and 50% to 65% sulfuric acid. This emulsion is sent to a settler for separation. The acid phase is treated and recycled to the process. The separated hydrocarbons undergo pressure reduction, which causes vaporization and cooling. The cooled hydrocarbons flow through the reactor cooling elements, acting as a refrigerant, and to a vapor-liquid separator. The recovered hydrocarbon liquid is treated with caustic and water washes and sent to a deisobutanizer. The alkylate product is in the deisobutanizer bottoms. Typically, these bottoms are sent to a debutanizer to produce the final alkylate that is used in aviation and motor fuels.

Sulfuric acid alkylation with cascade autorefrigeration is similar to effluent refrigeration except that a multicompartment reactor-settler vessel is used instead of a single compartment reactor and a separate settling vessel. The olefin enters each compartment of the reactor simultaneously in a parallel flow. The isobutane and sulfuric acid are mixed before entering the reactor and flow from compartment to compartment in a series or cascade flow. The mixing of the components in each compartment results in the exothermic reaction; however, the light hydrocarbons evaporate directly from the reaction mixture, cooling the process. The liquids from the last reactor compartment flow into the settler section of the vessel, where the acid is separated from the hydrocarbon. The acid phase is treated and recycled to the process. The recovered hydrocarbon liquid undergoes treatment, deisobutanizing, and debutanizing to produce the final alkylate product.

In hydrofluoric acid alkylation, olefins, isobutane and hydrofluoric acid are introduced into a single vessel that serves as the reactor and settler. The separated acid phase is treated and recycled to the process. The recovered hydrocarbon liquid undergoes treatment, deisobutanizing, and debutanizing to produce the final alkylate product.

8.1.2.6 Isomerization

The isomerization processes rearrange the molecular structure of the feedstock in order to produce branched-chain compounds from straight-chain compounds. The process is usually applied to butane or to mixtures of pentane and hexane. When butane is the feedstock, the isobutane product is normally used as feed to an alkylation unit. Pentane-hexane feeds are processed to improve their octane rating.

In butane isomerization, a mixed butane feedstock enters a deisobutanizer tower, where the isobutane is recovered from the top. The normal butane from the deisobutanizer is mixed with hydrogen, raised to 300°F to 400°F and passed over a fixed-bed noble metal catalyst at a pressure of 200 to 400 psig. The reactor effluent is cooled and sent to a separator for recovery of the hydrogen, which is recycled. The liquid from the separator is sent to a fractionator for removal of the light gases. This gas is sent to the refinery fuel gas system. The bottoms from the fractionator are returned to the deisobutanizer, where isobutane from the fresh feed and that produced in the reactor are recovered from the top. The normal butane is recycled until it is converted to isobutane.

Similarly, pentane, hexane or a mixture of the two is mixed with hydrogen, raised to 300°F to 500°F and passed over a fixed-bed noble metal catalyst at about 300 psig. If hexane or a mixture or pentane and hexane is the feedstock, the effluent from the first reactor is cooled to 250°F to 400°F and sent to a second reactor operated at about the same pressure. The final reactor effluent is cooled and sent to a separator for recovery of the hydrogen, which is recycled. The liquid from the separator is sent to a fractionator for removal of the light gases. This gas is sent to the refinery fuel gas system. The fractionator bottoms are the final product.

8.1.2.7 Reforming

Catalytic reforming is used to convert straight-chain naphtha compounds to ring or branched structures. The predominated reaction is the dehydrogenation of naphthenes to form aromatics. Some of these aromatics are isolated to become petrochemical feedstocks, but most become motor fuel blending stocks of high antiknock quality. The types of catalytic reforming systems in use include Platforming, Ultraforming, Powerforming, Magna-forming and Houdriforming. Platforming, the most widely used, will be discussed here.

In Platforming, the naphtha feed is mixed with hydrogen, heated to 800°F to 900°F and fed to a series of reactors containing a fixed-bed noble metal catalyst and operating at pressures of 300 to 500 psig. Because the reaction in highly endothermic, it is necessary to reheat the feed before it enters each reactor. The effluent from the last reactor is cooled and sent to a receiver, where it is separated into gas and liquid phases. Hydrogen is recovered from the gas phase and recycled to the reactors. The liquid from the separator is sent to a fractionator for removal of the light gases. This gas is sent to the refinery fuel gas system. The fractionator bottoms are the final reformate product.

Most of the variation in the design of Platforming units is in the catalyst regeneration cycle. In systems that operate at higher pressures and with high hydrogen-to-naphtha ratios, the catalyst degenerates slowly, allowing for uninterrupted process runs that range from a few months to over a year. These catalysts may be regenerated in place or replaced with new catalyst. In systems that operate at lower pressures and with low hydrogen-to-naphtha ratios, the catalyst degenerates rapidly and is regenerated in place about once a day. To avoid process shut downs, these systems are usually equipped with a spare reactor. In-place regeneration burns the carbon deposits from the catalyst by circulating air and combustion products through the reactor at 900°F to 1,050°F. The regeneration gases are usually incinerated in a process heater.

8.1.3 Treatment Processes

Treatment processes are used to improve the quality of intermediate fractions and final products, usually by removing undesirable impurities. The most common processes are hydrotreating, amine treating, chemical sweetening and asphalt blowing. These will be discussed briefly in the following sections.

8.1.3.1 Hydrotreating

Hydrotreating is used to remove sulfur, nitrogen and metal compounds from intermediate petroleum fractions in order to prevent downstream corrosion and catalyst poisoning. It is the most common process for treating catalytic reformer and catalytic cracker feedstocks. Hydrotreating is also used to sweeten and improve the color and stability of kerosene, jet fuels and lubricating oils.

There are several hydrotreating processes. In hydrodesulfurization, the stream to be treated is mixed with hydrogen, heated to 550°F to 800°F and sent to a fixed-bed catalytic reactor operating at 200 to 1,500 psig. The higher temperatures and pressures are used when treating high-boiling or highly contaminated feedstocks. In the reactor, the sulfur and nitrogen in the feed are converted to hydrogen sulfide and ammonia. The reaction product is cooled and sent to a high-pressure separator, where the hydrogen is recovered and recycled. The oil from the bottom of the separator is fed to a low-pressure separator, where the hydrogen sulfide and ammonia are recovered and sent to the amine-treating unit.

8.1.3.2 Amine Treating

The amine treater removes acidic impurities, mainly hydrogen sulfide and carbon dioxide, from refinery gas streams. In some refineries it is part of the sulfur recovery plant, rather than a separate unit. The amine treater is also known as a gas sweetening unit, an acid gas treating unit or an amine scrubber.

The process is a single absorption-regeneration cycle circulating an aqueous amine solution. The feed gas stream containing the impurities is contacted with the amine solution in a tray tower or countercurrent packed tower. The amine solution recovered from the bottom of the tower is heated and steam stripped, reversing the absorption reaction, regenerating the amine solution and producing a concentrated acid gas stream. The regenerated amine solution is recycled to the absorber. The acid gas stream is sent to the sulfur recovery plant.

8.1.3.3 Chemical Sweetening

Sweetening of distillates is accomplished by the extraction of mercaptans or by their conversion to disulfides, which remain in the product. The conversion process uses a reactor that contains a fixed-bed catalyst that is wetted by caustic solution. Air is injected into the sour feed, which causes the mercaptans to oxidize to disulfides as the feed stream passes through the catalyst bed. The effluent from the reactor is sent to a separator, where the caustic solution is recovered and recycled. The sweetened product is sent to storage or to further processing.

In the extraction process, the sour distillate is contacted with a caustic solution in a countercurrent packed tower. The mercaptans are soluble in the caustic solution and are extracted from the distillate. The sweetened product is sent to storage or to further processing. The mercaptan-rich caustic stream is mixed with powdered catalyst and sent to an oxidizer. Air is injected into the mixture, causing the mercaptans to oxidize to disulfides. The oxidizer effluent is sent to a separator, where the caustic solution is recovered and recycled to the extractor tower. The disulfides are sent to a hydrotreating unit or sold as a specialty product. The air from both the conversion and the extraction process is usually sent to a process heater.

8.1.3.4 Asphalt Blowing

The asphalt used in making paving materials is usually the bottoms from vacuum or atmospheric distillation and requires no further processing. However, the asphalt used in shingles and composition roofing must be harder. This is accomplished by blowing air through the distillation residuals to polymerize the asphalt by oxidation. When a very high melting point product with extreme hardness is desired, a catalyst such as ferric chloride or phosphorous pentoxide is added to the asphalt before it is blown.

Before entering the asphalt-blowing reactor, the feed is typically heated to 400°F to 600°F. In the batch process, heated compressed air is injected into the asphalt through a sparger at the bottom of the reactor. In the continuous process, heated air is passed countercurrent to the feed flow. The oxygen in the air reacts with the asphalt, resulting in oxidation, polymerization and increased cross-linkage of the asphalt molecules. The reaction is exothermic and quench steam is sometimes used for temperature control. The emissions from the reactor include acetaldehyde, benzene, formaldehyde, metals, PAH, toluene and sulfur compounds. They are usually controlled by incineration.

8.1.4 Auxiliary Processes

There are a number of processes that are vital to the operation of a refinery, even though they are not directly involved in the refining of crude oil. These include sulfur recovery, wastewater treatment, fuel gas recovery and blowdown systems.

8.1.4.1 Sulfur Recovery

Sulfur compounds in various petroleum fractions are converted into H_2S by treating processes. This H_2S is collected and sent to the sulfur recovery plant where it is converted to elemental sulfur. The most widely used method of recovering sulfur from acid gases is the Claus process. In the Claus process, a portion of the H_2S is oxidized with air to form SO_2:

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$$

This SO_2 is combined with the remaining H_2S over a fixed-bed catalyst to produce sulfur:

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

The tail gases exiting the last reactor are sent to a desulfurization system where most of the remaining sulfur compounds are removed before the gas stream is discharged to the atmosphere.

8.1.4.2 Wastewater Treatment

All refineries employ some form of wastewater treatment prior to discharge to the environment or reuse in the refinery. The specific design of wastewater treatment systems is dictated by the types of refinery pollutants that must be removed; however, drain systems, oil-water separators and air flotation systems are generally included and are the source of most of the VOC emissions from wastewater treatment.

Drain systems consist of individual process drains, where oily water from various sources is collected, and junction boxes, which receive the oily water from several drains. Oil-water separators are usually the first step in the treatment of refinery wastewater. The separation and removal of oil from the water are accomplished through density differences that cause the oil to rise to the top, allowing it to be skimmed off. Air flotation usually follows the oil-water separator and is used to remove remaining oil and solids by introducing air bubbles into the wastewater by mechanical means.

Additional wastewater treatment may involve secondary processes that utilize biological oxidation to degrade soluble organic contaminants. These processes include oxidation ponds, aerated lagoons, activated sludge and trickling filters. Tertiary treatment processes such as chlorination, ion exchange, membrane separation, activated carbon adsorption, and filtration may be used to further reduce wastewater contamination.

8.1.4.3 Fuel Gas Recovery

The fuel gas plant or light-ends unit incorporates a system of operations for recovering useful hydrocarbon vapor mixtures from crude oil distillation, catalytic cracking, reforming and other refinery processes. The collected gases are compressed, condensed and separated into mixtures having constant vapor pressure. These mixtures may be used as refinery fuel, sold as liquefied petroleum gases, used as feedstock for hydrogen production, used as alkylation feedstock, or sold as petrochemical feedstock.

8.1.4.4 Blowdown Systems

Blowdown systems allow for the safe disposal of liquid and gaseous hydrocarbons discharged from pressure-relief devices. Refinery equipment subject to planned and unplanned discharges is manifolded into a collection unit. The blowdown is separated into liquid and vapor, with the liquid being recycled into the refinery and the vapor either recycled or flared.

8.2 EMISSION CONTROL TECHNIQUES

Direct discharges of VOC emissions from refinery processes are generally controlled by some type of vapor recovery or destruction system. The emission stream may be recycled to fuel gas production or the heating value of the stream may be recovered by combustion in a flare, incinerator or process heater. Fugitive emissions are reduced by the use of covers and by inspection and maintenance of components with a potential to leak.

8.2.1 Flares

Flaring is generally considered a control option when the heating value of the emission stream cannot be recovered because of uncertain or intermittent flow, as in process upsets or emergencies. There are several different types of flares, but the most common is the elevated steam-assisted flare. They are designed and operated to handle large fluctuations in flow rate and VOC content. If the waste gas does not have sufficient heating value to sustain combustion, auxiliary fuel is added. Destruction efficiencies of 98% can be achieved by steam-assisted flares when controlling emission streams with heat contents greater than 300 Btu/scf.

8.2.2 Incinerators

Thermal and catalytic incinerators are typically applied to continuous emission streams that contain dilute concentrations of VOCs; however, catalytic incinerators are not as widely applied as thermal incinerators, because of catalyst sensitivities to pollutants and process conditions. Destruction efficiencies up to 95% to 99+% are achievable. Although they can accommodate minor fluctuations in flow, incinerators are not well suited to streams with highly variable flow, because of reduced residence time and poor mixing during increased flow conditions. Also, because concentrations are dilute, supplementary fuel may be required to maintain desired combustion temperature. Fuel requirements may be reduced by recovering the energy contained in the hot flue gases from the incinerator.

8.2.3 Process Heaters

Process heaters and boilers can be used to control emission streams by recovering their heating value and destroying the VOCs at efficiencies greater than 98%. Typically, emission streams are controlled in process heaters or boilers only if they have a heating value greater than 150 Btu/scf. In some cases, emission streams with high heat content may be the main fuel. Emission streams with low heat content can also be burned in boilers or process heaters when the flow rate is small compared with that of the fuel-air mixture. Because these combustion devices are essential to the operation of the refinery, only those emission streams that will not reduce their performance or reliability can be controlled. Streams not suitable for control include those with varying flow rate and/or heating value, high-volume/low-heating-value streams, and streams with corrosive compounds.

8.2.4 Covers

Covering a liquid surface or the vapor space above a liquid surface suppresses VOC emissions to the atmosphere. Emissions from wastewater drains can be reduced 40% to 50% by either a physical cover at ground level or a U-tube water seal in the drain pipe. Junction boxes can also be controlled with covers; however, to prevent siphoning and vapor locks, they must be equipped with a vent pipe. To minimize emissions, this vent pipe must also have a water seal. Emissions from oil-water separators can be controlled at efficiencies ranging from 85% to 98% by installing a fixed or floating roof. In addition to covering components in the wastewater system, the system can be completely enclosed and vented to a control device. The emission reduction in this case would depend on the efficiency of the control device.

8.2.5 Fugitive Emission Control

Fugitive emissions in the form of liquid or vapor losses often result from poor maintenance or housekeeping. The most efficient way to reduce these emissions is an effective program of inspection, maintenance and training. Equipment operators and maintenance personnel should be taught to inspect and identify liquid and vapor leaks and to repair these leaks immediately. Leak detection and repair programs are covered in APTI Course 380, Inspection Techniques for Fugitive VOC Emission Sources, and the reader is referred to this course for guidance.

8.3 EMISSION REGULATION

At the time of writing, USEPA had issued RACT recommendations for refinery vacuum producing systems, wastewater separators and process unit turnarounds, NSPS requirements for petroleum refinery wastewater systems and MACT requirements for petroleum refineries. These recommended and required standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Control of Refinery Vacuum Producing Systems, Wastewater Separators and Process Unit Turnarounds, Control Technique Guideline Document, EPA-450/2-77-025

Recommended standard:

- Incinerate, or compress and add to the refinery fuel gas system, non-condensable vapors from the vacuum producing system.

- Cover the forebay and separator sections of wastewater separators.
- Vent all vapors to a flare or vapor recovery system when a process unit is shut down for a turnaround.

Standards of Performance for VOC Emissions from Petroleum Refinery Wastewater Systems, 40CFR60, Subpart QQQ

Applicability Date: May 4, 1987

Standard: Individual Drain Systems

- Each drain shall be equipped with water seal controls.
- Junction boxes shall be equipped with a tightly sealed cover and may have an open vent pipe.
- Sewer lines shall be covered or enclosed.
- Wastewater routed through new process drains and a new first common downstream junction box shall not be routed through a downstream catch basin.
- Modified or reconstructed drain systems that had a catch basin in the existing configuration prior to May 4, 1987, are exempt from the provisions of this section.
- An alternative standard allows for a completely closed drain system.

Standard: Oil-Water Separators

- Each separator shall be equipped with a fixed roof that completely covers the separator with no separation between the roof and wall. An alternative standard allows for the use of a floating roof.
- Separators designed to treat greater than 250 gallons per minute shall be equipped with a closed vent system and control device with at least 95 percent efficiency. Modified or reconstructed separators handling less than 600 gallons per minute that were equipped with a fixed roof prior to May 4, 1987, are exempt from this requirement.
- Slop oil and oily wastewater shall be collected, stored, transported, recycled, reused or disposed of in an enclosed system.
- Separator tanks, slop oil tanks, storage vessels and other required auxiliary equipment may be equipped with a pressure control valve set at the maximum pressure for proper system operation, but may not vent continuously.
- Storage vessels subject to 40CFR60, subparts K, Ka or Kb are not subject to this section.

Standard: Closed Vent Systems and Control Devices

- Combustion devices shall be at least 95 percent efficient or have a minimum residence time of 0.75 seconds at 1,500°F.
- Vapor recovery system shall be at least 95 percent efficient.
- Closed vent systems shall operate with no detectable emissions, be equipped with a flow indicator, and direct the vapors to a control device.

National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries, 40CFR63, Subpart CC

Applicability: All process vents, storage vessels, wastewater streams and treatment operations, equipment leaks, gasoline loading racks and marine vessel loading racks that are located at major sources and that handle one or more HAPs listed in the subpart.

Standard: Process Vents (Group 1)

- Reduce emissions using a flare that operates with no visible emissions and meets 40CFR63.11(b); or
- Reduce emissions using a control device by 98 percent by weight or to an outlet concentration of 20 ppmv, whichever is less stringent.

Standard: Storage Vessels (Group 1)

The provisions for Group 1 storage vessels are essentially the same as 40CFR60, Subpart Kb, and are summarized in Chapter 9.

Standard: Wastewater (Group 1)

Comply with the provisions of 40CFR61, Subpart FF, for tanks, surface impoundments, containers, individual drain systems, oil-water separators, treatment processes, and closed vent systems and control devices. The basic requirements of these provisions are as follows:

Tanks

Install, operate and maintain a fixed-roof and closed-vent system that routes all organic vapors vented from the tank to a control device.

Surface Impoundments

Install, operate and maintain on each surface impoundment a cover and closed-vent system that routes all organic vapors vented from the impoundment to a control device.

Containers

Install, operate and maintain a cover on each container used to handle, transfer or store waste; transfer waste into the container using a submerged fill pipe; use a closed-vent system and route vapors to a control device if waste treatment is performed in the container.

Individual Drain Systems

Install, operate and maintain on each drain system opening a cover and closed-vent system that routes all organic vapors vented from the drain system to a control device; or

Equip each drain with water seal controls or a tightly sealed cap or plug; equip each junction box with a cover and use water seal controls or a closed-vent system on any vent pipe; and cover or enclose each sewer line.

Oil-Water Separators

Install, operate and maintain a fixed-roof and closed-vent system that routes all organic vapors vented from the oil-water separator to a control device.

Treatment Processes

Install, operate and maintain a treatment process that either reduces benzene in the waste stream to less than 10 ppmw, or removes 99% or more of the benzene on a mass basis, or destroys the benzene by incineration in a combustion unit that achieves a destruction efficiency of 99% or greater; seal all openings in the treatment system and keep them closed at all times waste is being treated.

Closed-Vent Systems and Control Devices

The closed-vent system must operate with no detectable emissions. If the control device is a combustion unit, it must provide a minimum residence time of 0.5 seconds at a minimum temperature of 1,400°F, or reduce organic emissions by 95 weight percent or greater, or achieve an outlet concentration of 20 ppmv. If the control device is a vapor recovery system, it must control organic compounds with an efficiency of 95 weight percent or greater and benzene emissions with an efficiency of 98 weight percent or greater.

Standard: Equipment Leaks

- Existing sources shall comply with 40 CFR 60, Subpart VV.
- New sources shall comply with 40 CFR 63, Subpart H.

Standard: Gasoline Loading Racks

Comply with 40 CFR 63, Subpart R. The provisions of this standard are summarized in Chapter 9.

Standard: Marine Tank Vessel Loading

Comply with 40CFR63, Subpart Y. In general, this subpart requires that each terminal be equipped with a system that collects vapors displaced during the loading of a marine tank vessel and that prevents vapors collected at one loading berth from being discharged to the atmosphere through another loading berth. The collected vapors must then be reduced by 95% to 98%, depending on the applicable section, before being emitted to the atmosphere.

8.4 PROCESS INSPECTION

Inspection of petroleum refineries for fugitive leaks is covered in APTI Course 380, Inspection Techniques for Fugitive VOC Emission Sources, and the reader is referred to this course for guidance.

Review Questions

1. What are the basic categories of refining operations? Select all that apply.
   a. Separation processes
   b. Conversion processes
   c. Treatment processes
   d. Auxiliary processes

2. What of the following is the principal separation process?
   a. Desalting
   b. Distillation
   c. Deasphalting

3. Which separation process is used on topped crude?
   a. Desalting
   b. Atmospheric distillation
   c. Vacuum distillation
   d. Deasphalting

4. Which of the following is not a conversion process?
   a. Delayed coking
   b. Alkylation
   c. Reforming
   d. Hydrogenation

5. What is the primary source of emissions from catalytic cracking?
   a. Equipment leaks
   b. Catalyst regeneration
   c. Air sparging
   d. Reactor cyclones

6. Which conversion processes are used to increase the molecular weight of crude oil fractions? Select all that apply.
   a. Isomerization
   b. Alkylation
   c. Polymerization
   d. Reforming

7. Which conversion processes are used to rearrange the structure of molecules? Select all that apply.
   a. Isomerization
   b. Alkylation
   c. Polymerization
   d. Reforming

8. What contaminants are removed by hydrotreating? Select all that apply.
   a. Hydrogen
   b. Sulfur
   c. Sodium
   d. Nitrogen

9. What is the primary source of emissions from chemical sweetening?
   a. Equipment leaks
   b. Catalyst regeneration
   c. Air sparging
   d. Extraction

10. Which treatment process has the greatest potential to emit PAHs?
    a. Hydrotreating
    b. Amine treating
    c. Asphalt blowing
    d. Chemical sweetening

11. What type of process is typically used for sulfur recovery?
    a. Claus process
    b. Clausius process
    c. Clapeyron process
    d. Clausius-Clapeyron process

12. Which of the following are the most significant sources of VOC emissions from wastewater treatment? Select all that apply.
    a. Trickling filters
    b. Drain systems
    c. Membrane separators
    d. Oil-water separators

13. What types of emission control techniques are used in refinery processes? Select all that apply.
    a. Fabric filters
    b. Incinerators
    c. Covers
    d. Leak detection and repair programs

14. For which refinery operation has USEPA issued RACT recommendations and both NSPS and MACT requirements?
    a. Vacuum producing systems
    b. Oil-water separators
    c. Drain systems
    d. Process turnarounds

Review Answers

1. What are the basic categories of refining operations? Select all that apply.
   a. Separation processes
   b. Conversion processes
   c. Treatment processes
   d. Auxiliary processes

2. What of the following is the principal separation process?
   b. Distillation

3. Which separation process is used on topped crude?
   c. Vacuum distillation

4. Which of the following is not a conversion process?
   d. Hydrogenation

5. What is the primary source of emissions from catalytic cracking?
   b. Catalyst regeneration

6. Which conversion processes are used to increase the molecular weight of crude oil fractions? Select all that apply.
   b. Alkylation
   c. Polymerization

7. Which conversion processes are used to rearrange the structure of molecules? Select all that apply.
   a. Isomerization
   d. Reforming

8. What contaminants are removed by hydrotreating? Select all that apply.
   b. Sulfur
   d. Nitrogen

9. What is the primary source of emissions from chemical sweetening?
   c. Air sparging

10. Which treatment process has the greatest potential to emit PAHs?
    c. Asphalt blowing

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    a. Claus process

12. Which of the following are the most significant sources of VOC emissions from wastewater treatment? Select all that apply.
    b. Drain systems
    d. Oil-water separators

13. What types of emission control techniques are used in refinery processes? Select all that apply.
    b. Incinerators
    c. Covers
    d. Leak detection and repair programs

14. For which refinery operation has USEPA issued RACT recommendations and both NSPS and MACT requirements?
    b. Oil-water separators

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9 Petroleum Product Storage and Distribution

The marketing of petroleum products at the wholesale and retail level requires an extensive distribution network. Many products, such as lubricating oils and solvents, may be put in drums and shipped by truck to warehouses, dealers or customers. Specialty products, such

as solvents, thinners, lubricating oils and some fuels, may be transported from the refinery directly to the customer by railroad cars. However, gasoline, diesel fuel, jet fuel and heating oil are generally distributed to the customer through a series of intermediate storage and transfer facilities. The VOC sources, control, regulation and inspection of these storage and transfer operations are the subject of this chapter.

9.1 PETROLEUM PRODUCT STORAGE

9.1.1 Process Description

Three types of vessels are commonly used to store volatile organic liquids:

- Fixed roof tanks
- Internal floating roof tanks
- External floating roof tanks

These tanks are cylindrical in shape with the axis oriented perpendicular to the foundation. The tanks are almost exclusively above ground, although below ground vessels and horizontal vessels may also be used in volatile organic liquid service.

9.1.1.1 Fixed Roof Tanks

The fixed-roof tank is the least expensive to construct and is generally considered the minimum acceptable equipment for storing volatile organic liquids. A typical fixed roof tank, shown in Figure 9-1, consists of a cylindrical shell with a cone-shaped, dome-shaped or flat roof that is permanently affixed to the tank shell. Most recently built tanks are of all-welded construction and are designed to be both liquid and vapor tight. However, many older tanks may be of riveted or bolted construction and may not be vapor tight. A pressure-vacuum valve is commonly installed on the tank to allow operation at a slight internal pressure or vacuum, typically about 0.75 in. H_2O. Because this valve prevents the release of vapor only during very small changes in temperature, barometric pressure or liquid level, VOC emissions from a fixed roof tank can be significant. In addition, gauge hatches, sample wells, float gauges and access hatches also serve as potential sources of VOC emissions.

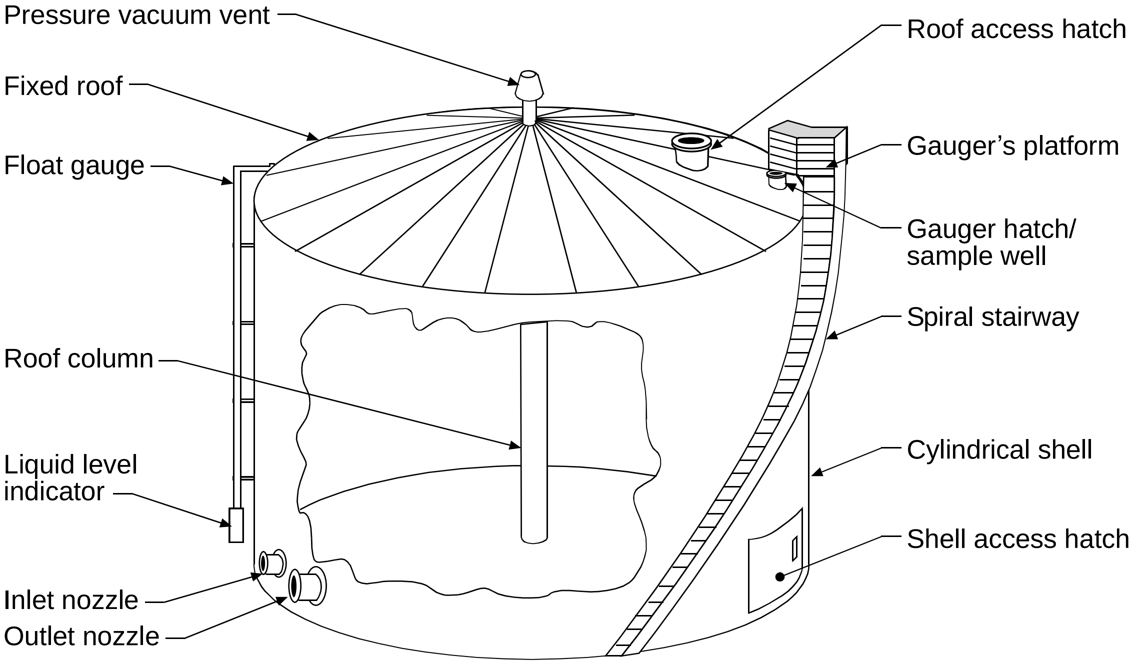


Figure 9-1. Fixed roof tank

The major types of emissions from fixed roof storage tanks are breathing and working losses. Breathing loss is the expulsion of vapor from a tank vapor space that has expanded because of changes in temperature and barometric pressure. These emissions occur in the absence of any liquid level change in the tank.

Working losses are the combination of filling and emptying losses. Filling losses occur with an increase in the liquid level in the tank. Vapors are expelled from the tank when the pressure inside exceeds the relief pressure. Emptying losses occur when air that is drawn into the tank during liquid removal saturates with organic vapor and expands, exceeding the capacity of the vapor space and exiting through the pressure-vacuum relief valve.

9.1.1.2 Internal Floating Roof Tanks

An internal floating roof tank has both a fixed roof and a roof that floats inside the tank on the liquid surface (contact roof) or is supported on pontoons several inches above the liquid surface (non-contact roof) and rises and falls with the liquid level. There are two basic types of internal floating roof tanks: tanks where the fixed roof is supported by vertical columns within the tank; and tanks with a self-supporting fixed roof. A column-supported internal floating roof tank is shown in Figure 9-2. Fixed roof tanks that have been retrofitted to employ an internal floating roof are typically of this type, while external floating roof tanks that have been converted to an internal floating roof tank typically have a self-supporting roof. Tanks initially constructed with both a fixed roof and an internal floating roof may be of either type.

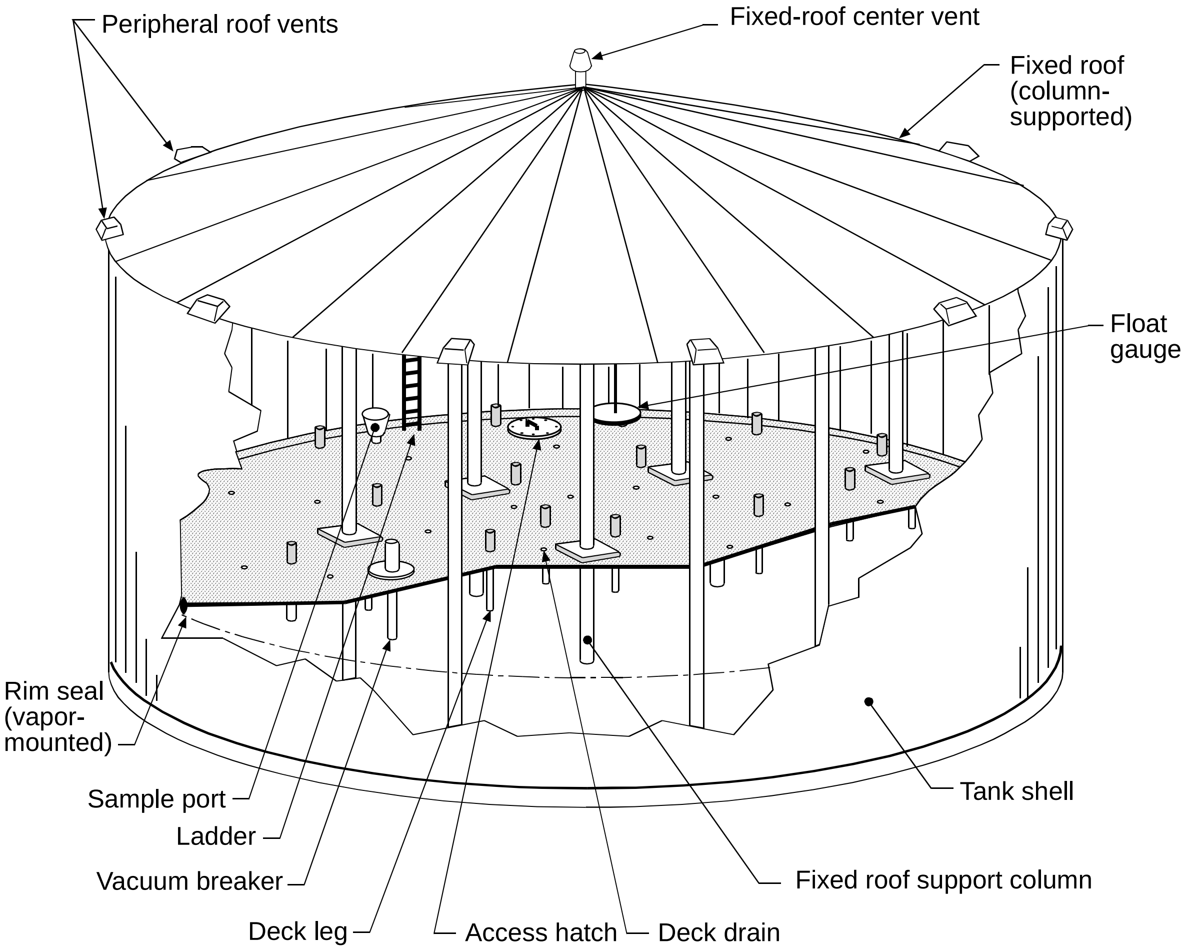


Figure 9-2. Internal floating roof tank

Usually, an internal floating roof tank is freely vented by circulation vents at the top of the fixed roof. These vents minimize the possibility of organic vapor concentrations in the tank vapor space that approach the flammable range. When circulation vents are not used, flame arrestors are provided to protect the vessel from fire or explosion. Tank venting occurs through a pressure-vacuum vent and flame arrestor.

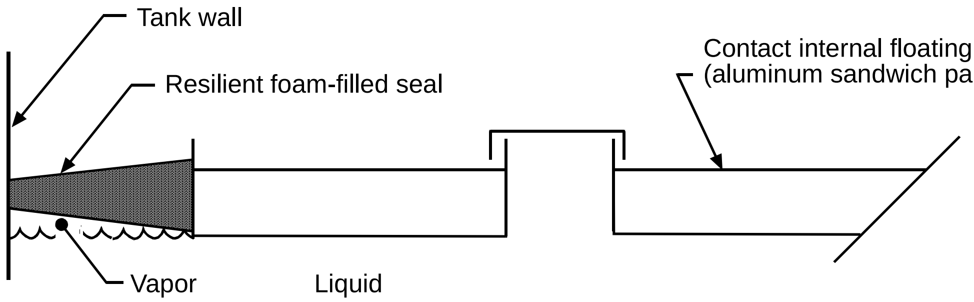
There are four common types of floating roof construction: (1) aluminum sandwich panel roofs with a honeycombed aluminum core that float in contact with the liquid; (2) an aluminum deck laid on an aluminum framework that is supported above the liquid surface by pontoons; (3) buoyant, resin-coated fiberglass reinforced polyester (FRP) panels that float in contact with the liquid; and (4) pan-type steel roofs that float in contact with the liquid with or without the help of pontoons. Steel pan roofs are constructed of welded steel sheets and, therefore, have no deck seams. Similarly, the panels of FRP roofs are butted and lapped with resin-impregnated fiberglass fabric strips and have no apparent deck seams. However, the aluminum sandwich panel sections and the sheets of aluminum decking are typically bolted together. These deck seams can be a source of VOC emissions.

Regardless of the type of roof construction, a flexible seal is used to close the annular space between the floating roof and the tank wall in order to reduce evaporative losses. These seals are designed to compensate for small irregularities in the tank shell and allow the roof to freely move up and down in the tank without binding. The two most common types are the resilient foam-filled seal and the wiper seal.

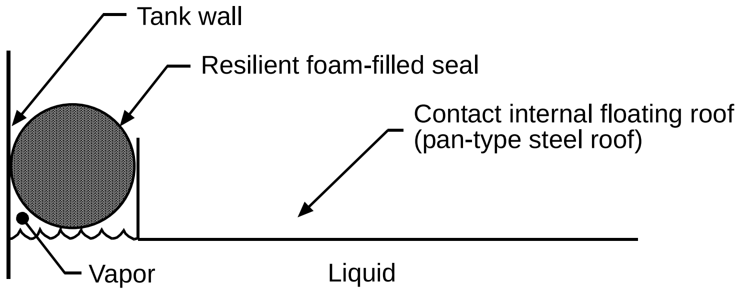
Two types of resilient foam-filled seals are shown in Figures 9-3a and 9-3b. These seals consist of a core of open-cell foam encapsulated in a coated fabric. Polyurethane-coated nylon fabric and polyurethane foam are commonly used materials. The seals are attached to a mounting on the roof perimeter and are continuous around the roof circumference. They may be mounted either in contact with the liquid surface (liquid-mounted) or several inches above the liquid surface (vapor-mounted). The expansion and contraction of the resilient material allows it to maintain contact with the tank shell while accommodating varying annular rim space widths.

Wiper seals, shown in Figure 9-3c, are commonly used as primary seals for internal floating roof tanks. Wiper seals generally consist of a continuous annular blade of flexible material that is attached to a mounting bracket on the roof perimeter and spans the annular space to contact the tank shell. The blade is flexed and its elasticity provides a sealing pressure against the tank wall. Three types of materials are commonly used to make the wipers: (1) a cellular, elastomeric material that tapers toward the end in contact with the tank wall; (2) a polyurethane foam core wrapped in a polyurethane-coated nylon fabric; and (3) a shingle-type seal that consists of overlapping segments of seal material.

a. Resilient foam-filled seal (vapor-mounted)



b. Resilient foam-filled seal (liquid-mounted)



c. Elastomeric wiper seal

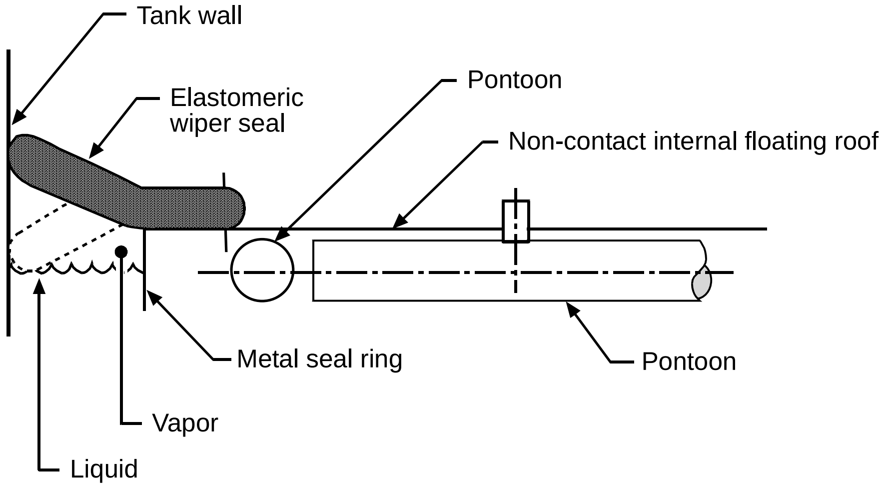


Figure 9-3. Typical flotation devices and perimeter seals for internal floating roofs

Secondary seals may be used to provide additional evaporative loss control over that achieved by the primary seal. As shown in Figure 9-4, the secondary seal is mounted on the rim of the floating roof and extends to the tank wall, completely covering the primary seal. Secondary seals can be either a resilient foam-filled seal or an elastomeric wiper seal.

Numerous fittings penetrate or are attached to an internal floating roof. These fittings serve to accommodate structural support members or to allow for operational functions. Those fittings requiring penetration through the floating roof can be a source of VOC emissions. These include column wells, roof legs, vacuum breakers, gauge-float wells, sample wells, access hatches and ladder wells.

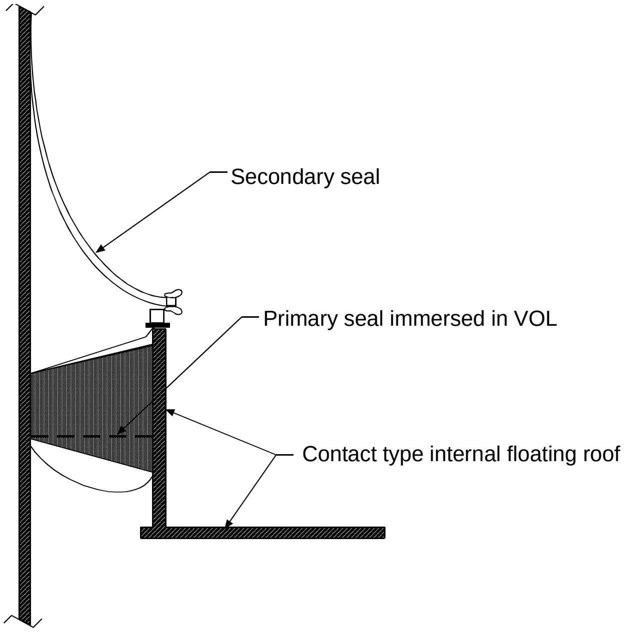


Figure 9-4. Rim-mounted secondary seal on internal floating roof

Column wells. The number of roof-support columns varies with tank diameter, ranging from a minimum of 1 to over 50 for large tanks. The columns penetrate the roof deck through a vertical peripheral well. With non-contact decks, the column wells (and all other wells) should extend down into the liquid. A sliding cover or a fabric sleeve is used to close the space between the perimeter of the well and the column.

Roof legs. To prevent damage to fittings underneath the floating roof and to allow for tank cleaning or repair, supports are provided to hold the deck at a predetermined distance off the tank bottom. These supports consist of adjustable or fixed legs attached to the floating deck as shown in Figure 9-5.

For adjustable legs, the load-carrying element passes through a well or sleeve in the deck.

Vacuum breakers. Vacuum breakers are needed to prevent damage to the floating roof during emptying or filling of the tank while the deck rests on its legs. Mechanical vacuum breakers are the most common type and act by opening a deck penetration that usually consists of a well on which a cover rests. Since the purpose of the vacuum breaker is to allow the free exchange of air or vapor, the well does not extend appreciably below the roof deck. Attached to the underside of the cover is a guide leg that is long enough to contact the tank bottom before the roof legs do. When it contacts the tank bottom, the guide leg opens the breaker by lifting the cover off the well. When the guide leg is not contacting the bottom, the penetration is closed by the cover resting on the well.

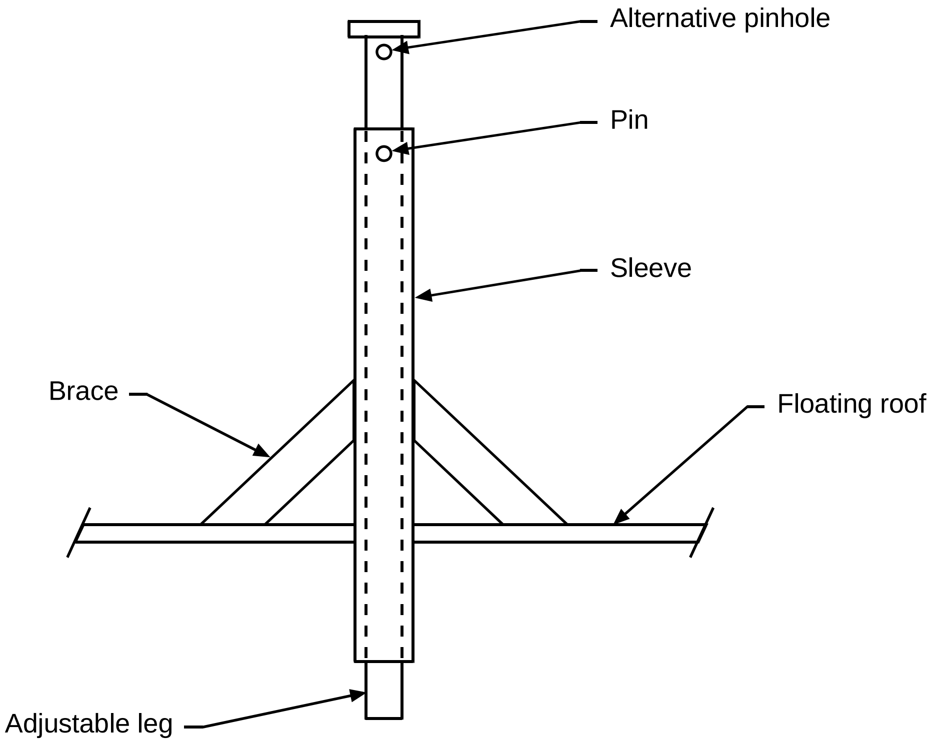


Figure 9-5. Roof leg

Gauge-float wells. Gauge floats are used to indicate the liquid level in the tank. As shown in Figure 9-6, the float rests on the liquid surface within a well that is closed by a sliding cover. A cable attaches to the float and passes through a hole in the center of the cover to an indicator on the exterior of the tank.

Sample wells. Sample wells provide access for taking samples of the liquid. Typically, the well is funnel-shaped to allow for easy entry of a sample thief. The closure is usually located at the lower end of the funnel and frequently consists of a horizontal piece of fabric slit radially to allow thief entry. Alternately, the sample well may consist of a slotted pipe extending into the liquid and equipped with a sliding cover.

Access hatches. An access hatch consists of an opening in the floating roof with a peripheral vertical well attached to the deck and a removable cover to close the opening. The hatch is typically sized to allow workers and materials to pass through the deck for construction or servicing. The cover can rest directly on the well, or a gasketed connection can be used to reduce evaporative loss. Bolting the cover to the well reduces losses further.

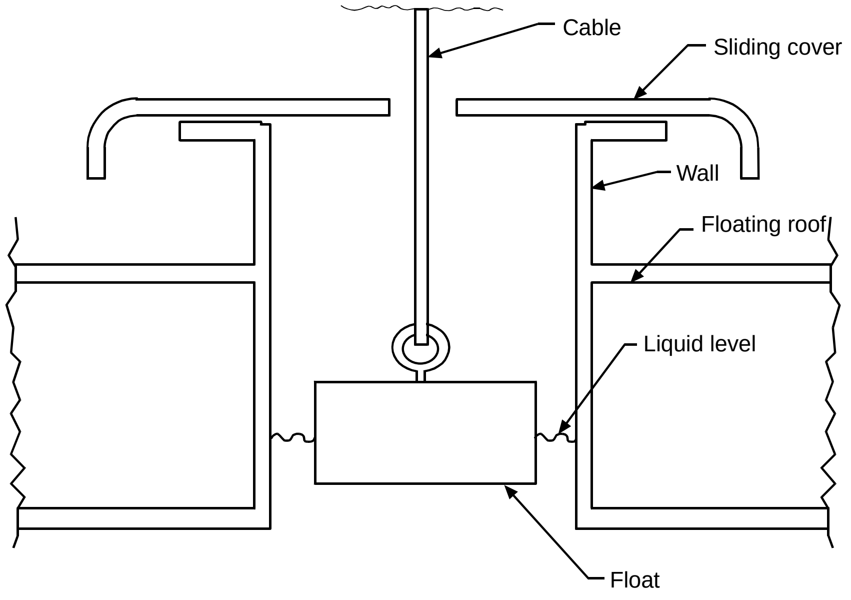


Figure 9-6. Gauge-float well

Ladder wells. Some tanks are equipped with internal ladders that extend from an access hatch in the fixed roof to the tank bottom. The deck opening through which the ladder passes is similar in construction to those for column wells.

As the wind blows over the exterior of an internal floating roof tank, air flows into the enclosed space between the fixed and floating roofs through some of the shell vents and out of the enclosed space through other vents. Any VOC vapors that have evaporated from the exposed liquid surface and that have not been contained by the floating deck will be swept out of the enclosed space. Vapors may also be expelled by the expansion of air in the enclosed space due to temperature and pressure changes.

Losses of VOC vapors from under the floating roof occur in several ways. One source is seal losses from the annular rim space around the perimeter of the floating roof. Losses also occur through the various fittings discussed above and from non-welded deck seams. Seal losses, fitting losses and deck seam losses occur during both working and free-standing periods. An additional working loss occurs when liquid is withdrawn from the tank and a wet portion of the tank wall is exposed, resulting in evaporation of the organic liquid.

9.1.1.3 External Floating Roof Tanks

An external floating roof tank consists of a cylindrical steel shell equipped with a deck or roof that floats on the surface of the stored liquid, rising and falling with the liquid level. The floating roofs are constructed of welded or riveted steel plates and are of three general types: pan, pontoon and double deck. Although numerous pan-type decks are currently in use, new tanks generally employ pontoon and double-deck floating roofs. A pontoon-type external floating roof tank is shown in Figure 9-7.

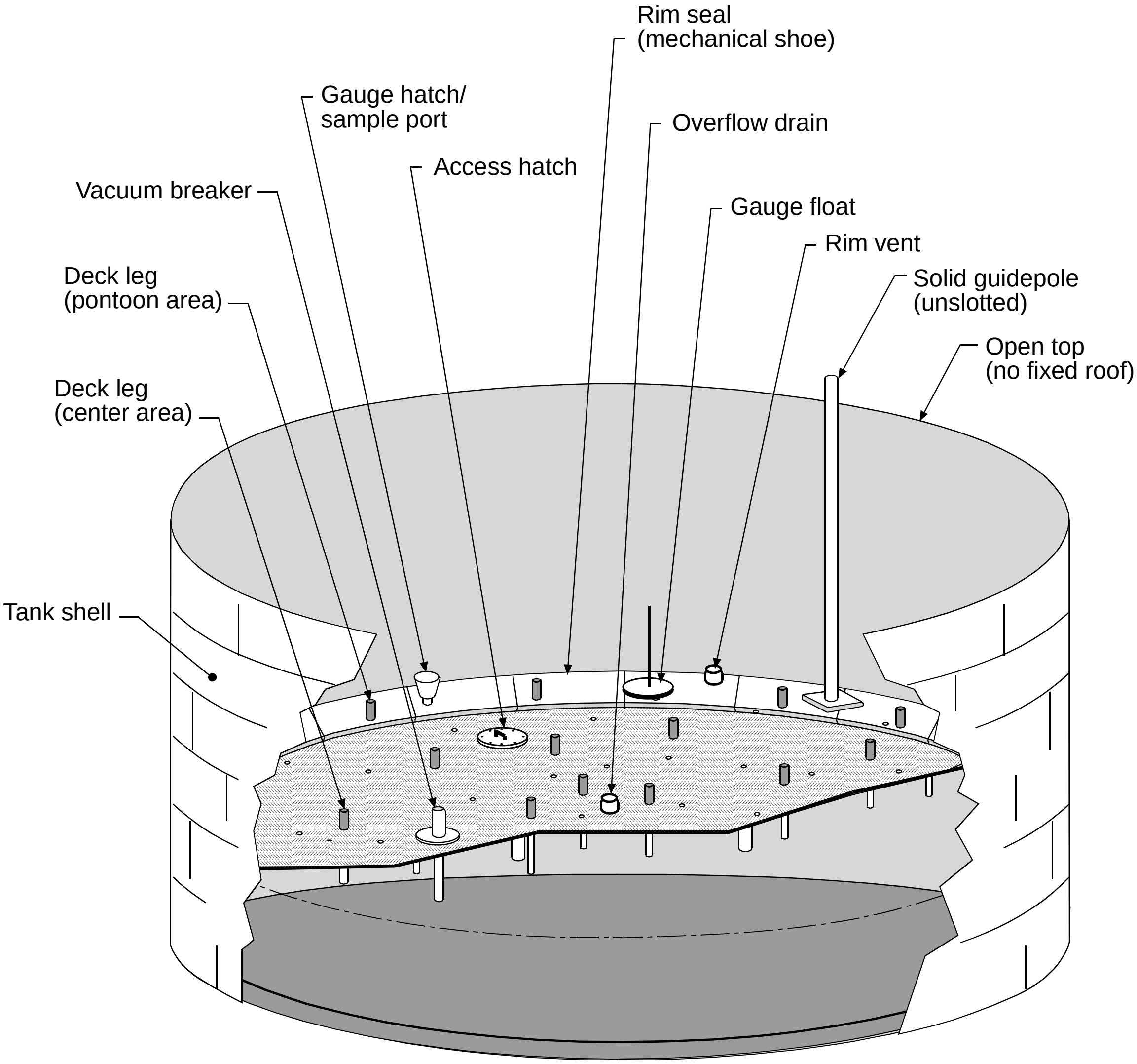
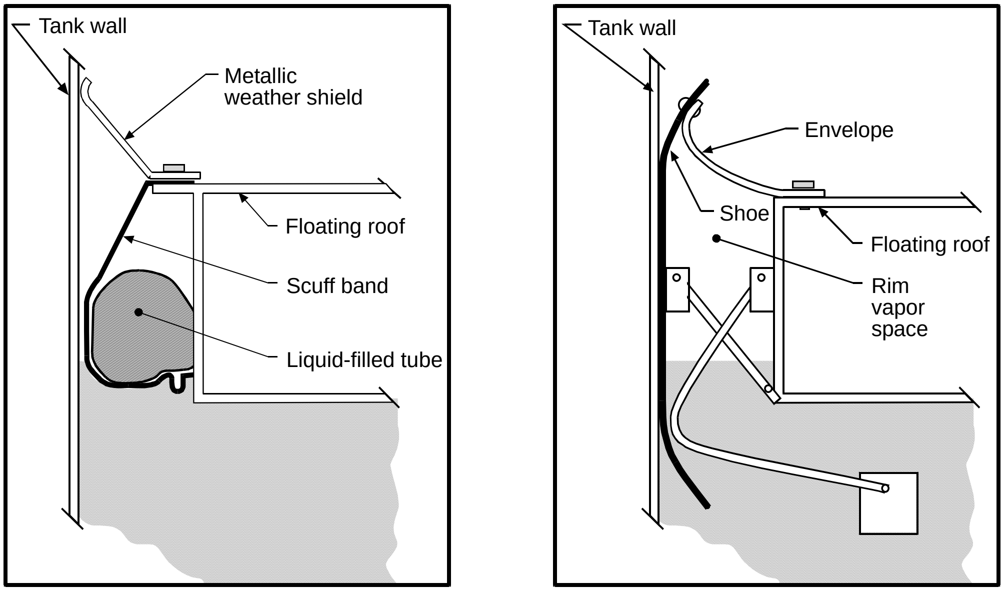


Figure 9-7. External floating roof tank

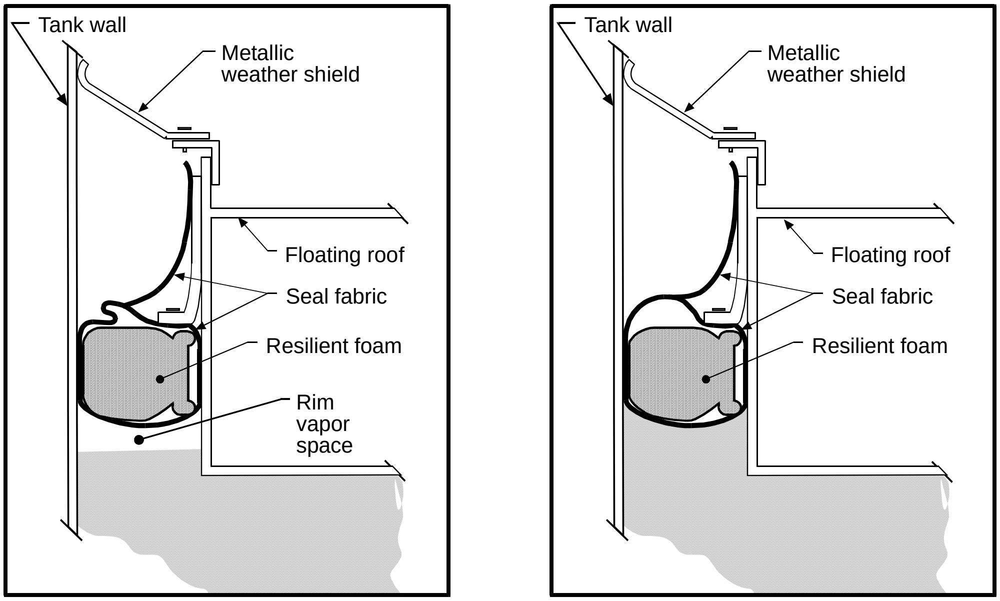
As with the internal floating roof tanks, a seal system is employed to close the annular space between the rim of the floating roof and the tank wall. The basic designs for external floating roof seals are mechanical shoe seals, liquid-filled seals, and vapor- or liquid mounted resilient foam-filled seals.

A mechanical shoe seal, shown in Figure 9-8b, consists of a metallic sheet or shoe that is held against the tank wall by springs or counter weights. Shoe heights typically range from 30-51 inches. A flexible coated fabric, the envelope, is connected from the rim of the floating roof to the shoe to form a vapor barrier over the annular space.



a. Liquid-filled seal with weather shield

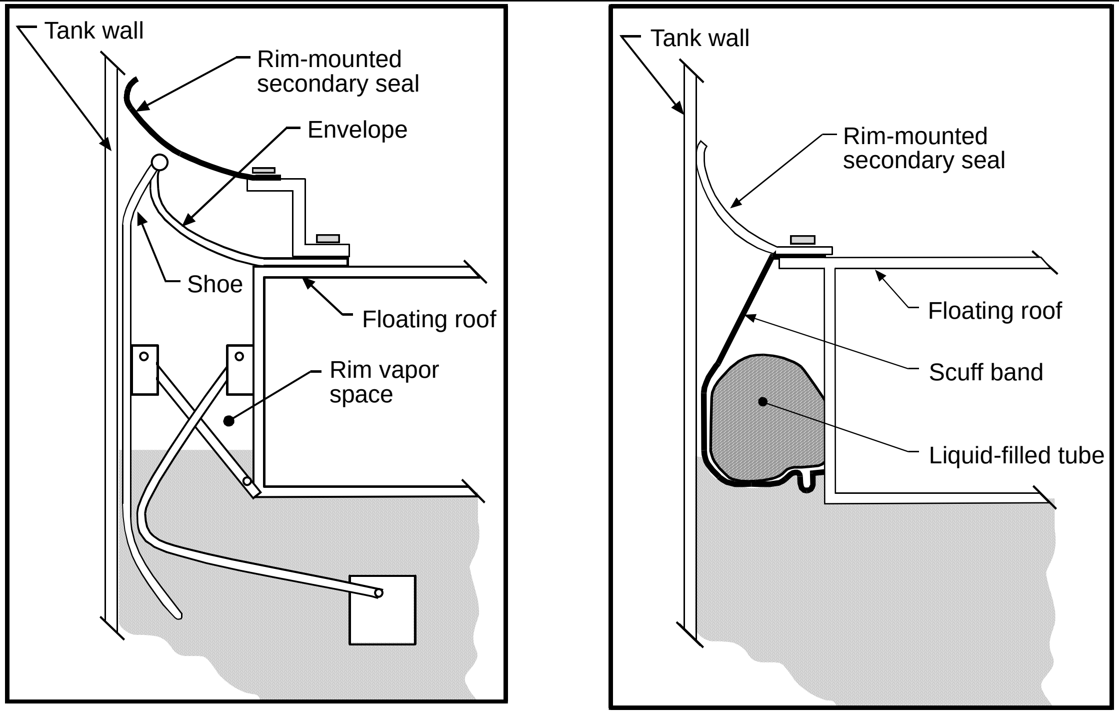
b. Metallic shoe seal



c. Vapor-mounted resilient foam-filled seal with weather shield

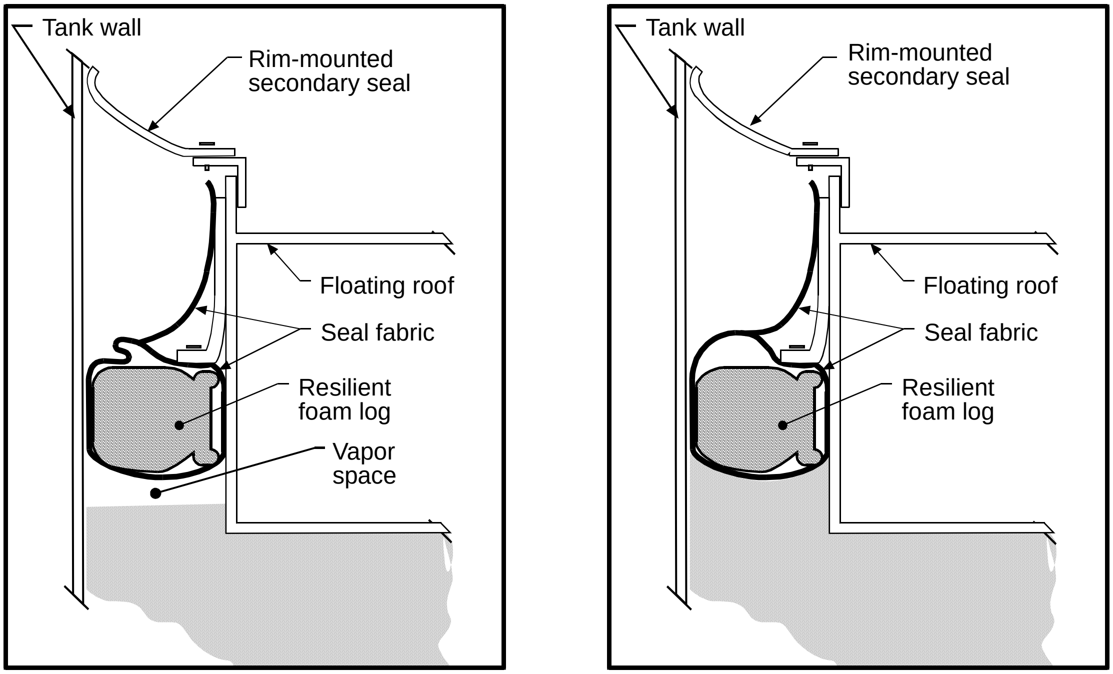
d. Liquid-mounted resilient foam-filled seal with weather shield

Figure 9-8. Primary seals



a. Shoe seal with rim-mounted secondary seal

b. Liquid-filled seal with rim-mounted secondary seal



c. Resilient foam-filled seal (vapor-mounted) with rim-rounted secondary seal

d. Resilient foam seal (liquid-mounted) with rim-rounted secondary seal

Figure 9-9. Rim-mounted secondary seals

A liquid-filled seal (Figure 9-8a) may consist of a tough fabric band or envelope filled with a liquid, or it may consist of a flexible polymeric tube filled with a liquid and sheathed with a tough fabric scuff band. The liquid is commonly a petroleum distillate or other liquid that will not contaminate the stored product if the tube ruptures. Liquid-filled seals are mounted on the liquid surface with no vapor space below the seal.

Resilient foam-filled seals consist of a core of open-cell foam encapsulated in a coated fabric. Polyurethane-coated nylon fabric and polyurethane foam are commonly used materials. The seals are attached to a mounting on the roof perimeter and are continuous around the roof circumference. They may be mounted either in contact with the liquid surface (liquid-mounted) or several inches above the liquid surface (vapor-mounted). As with the liquid-filled seals, the expansion and contraction of the resilient material allows it to maintain contact with the tank shell while accommodating varying annular rim space widths. Typical vapor-mounted and liquid mounted seals are shown in Figures 9-8c and 9-8d, respectively.

A secondary seal on an external floating roof consists of a continuous seal mounted on the rim of the floating roof and extending to the tank wall, completely covering the primary seal. Secondary seals are normally constructed of flexible polymeric materials; however, some designs incorporate a steel leaf to bridge the gap between the roof and the tank wall. The leaf acts as a compression plate to hold a polymeric wiper against the tank wall. Figure 9-9 shows several primary and secondary seal systems.

Another type of secondary seal is the shoe-mounted seal shown in Figure 9-10. A shoe-mounted seal extends from the top of the shoe to the tank wall. Since this style of secondary seal does not completely cover the primary seal, it does not provide protection against leaks in the envelope.

A weather shield (shown in Figures 9-8a, 9-8c and 9-8d) may be installed over the primary seal to protect it from deterioration caused by debris and exposure to the elements. Typically, a weather shield consists of overlapping thin metal sheets pivoted from the floating roof to ride against the tank wall. The weather shield, by the nature of its design, is not an effective vapor barrier. For this reason, it differs from the secondary seal.

As with the internal floating roof, there are numerous fittings that penetrate or are attached to an external floating roof. Those fittings requiring penetration through the floating roof, and therefore a possible source of VOC emissions, include guide-pole wells, roof legs, vacuum breakers, gauge-float wells, sample wells, access hatches, roof drains and rim vents. The roof legs, vacuum breakers, gauge-float wells and access hatches for external floating roofs are similar to those described earlier for internal floating roofs.

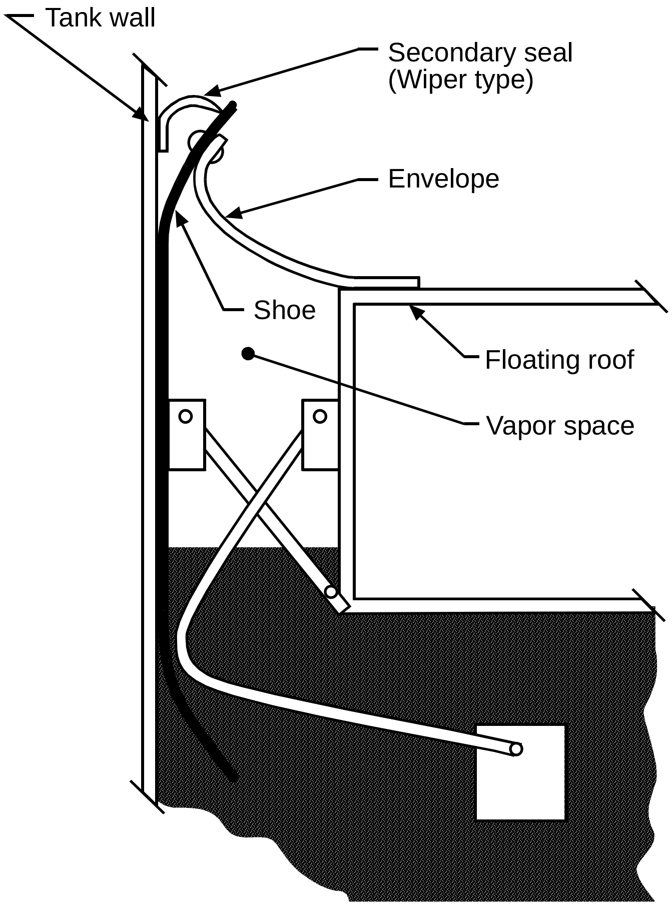
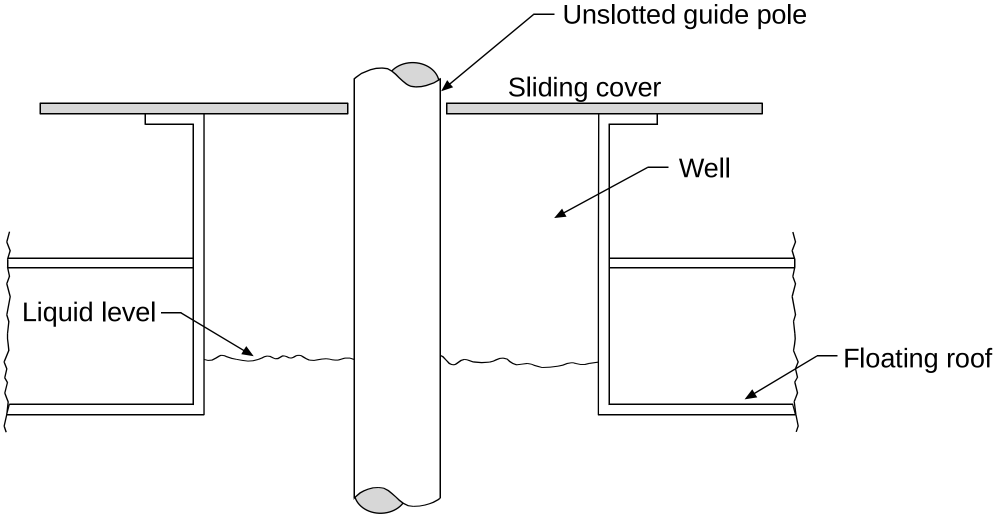


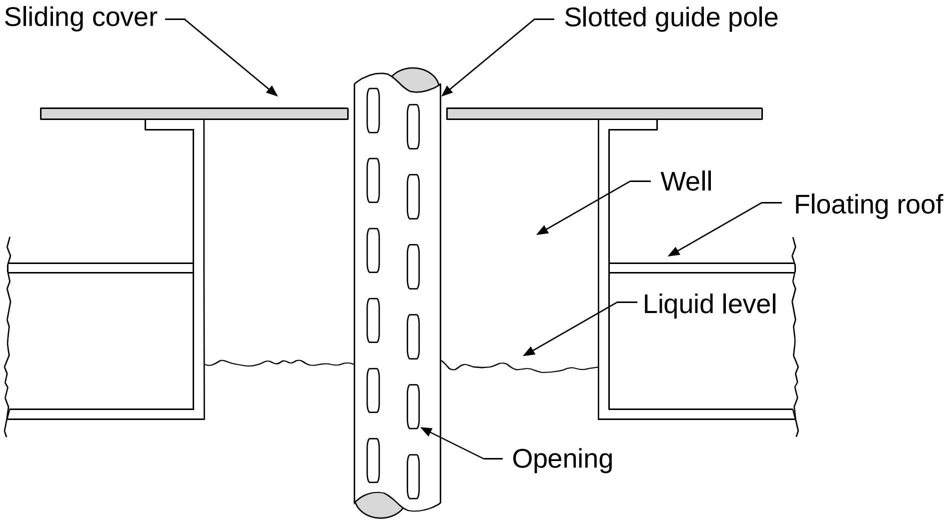
Figure 9-10. Mechanical shoe seal with shoe-mounted secondary seal

Guide-pole wells. Antirotation devices are used to prevent floating roofs from rotating and potentially damaging roof equipment and seal systems. A commonly used antirotation device is a guide pole that is fixed at the top and bottom of the tank. The guide pole passes through a well on the deck that has a sliding cover to accommodate limited radial movement of the roof, as shown in Figure 9-11. The sliding cover may be equipped with gaskets between the cover and the guide pole and between the cover and the top of the well to reduce evaporative losses. Openings at the top and bottom of the guide pole provide a means of hand-gauging the liquid level and taking bottom samples. The slotted guide pole is constructed with a series of holes or slots that allow the product to mix freely in the guide pole and thus have the same composition as the product in the tank.

Sample wells. Sample wells provide access for hand-gauging the liquid level in the tank and for taking samples of the tank contents. As shown in Figure 9-12, a sample well consists of a pipe sleeve through the deck with a self-closing gasketed cover. Sample wells are usually located under the gauger's platform, which is mounted on the top of the tank shell. The cover may have a cord attached so that it can be opened from the gauger's platform.



a. Unslotted guide-pole well



b. Slotted guide-pole well

Figure 9-11. Guide-pole wells

Roof drains. Roof drains are used to remove rainwater from the surface of the floating roof. Closed drainage systems carry rainwater from the roof to the outside of the tank through a flexible or articulated piping system or through a flexible hose system located below the deck in the product space. Since product does not enter the closed drainage system, there are no VOC emissions. Open drainage systems typically have open pipes that are flush with the top surface of the deck and extend a short distance below the bottom of the deck, allowing the rainwater to drain from the roof into the product. Overflow drains, shown in Figure 9-13, have a drain opening that is elevated above the top surface of the roof, limiting the maximum amount of rainwater that can accumulate on the floating roof. They are normally used in conjunction with a closed drainage system. Evaporative losses occur from these open drainpipes, since they are filled with product up to the liquid level in the tank.

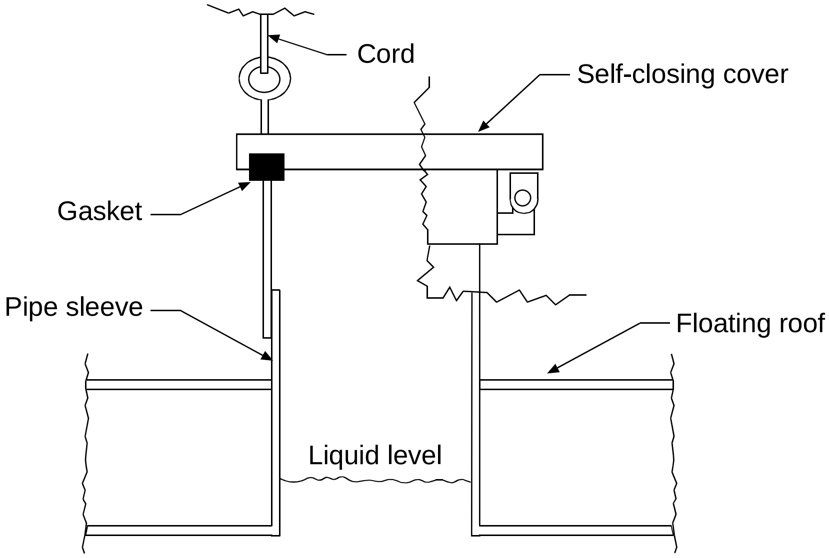


Figure 9-12. Sample well

Rim vents. Rim vents, shown in Figure 9-14, are normally supplied only on tanks equipped with a mechanical shoe primary seal. The rim vent is connected to the rim vapor space and releases any excess pressure or vacuum that is present.

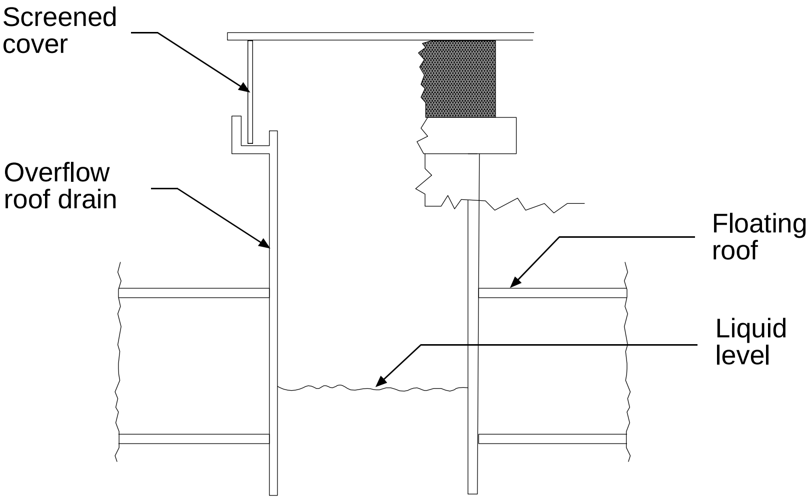


Figure 9-13. Overflow drain

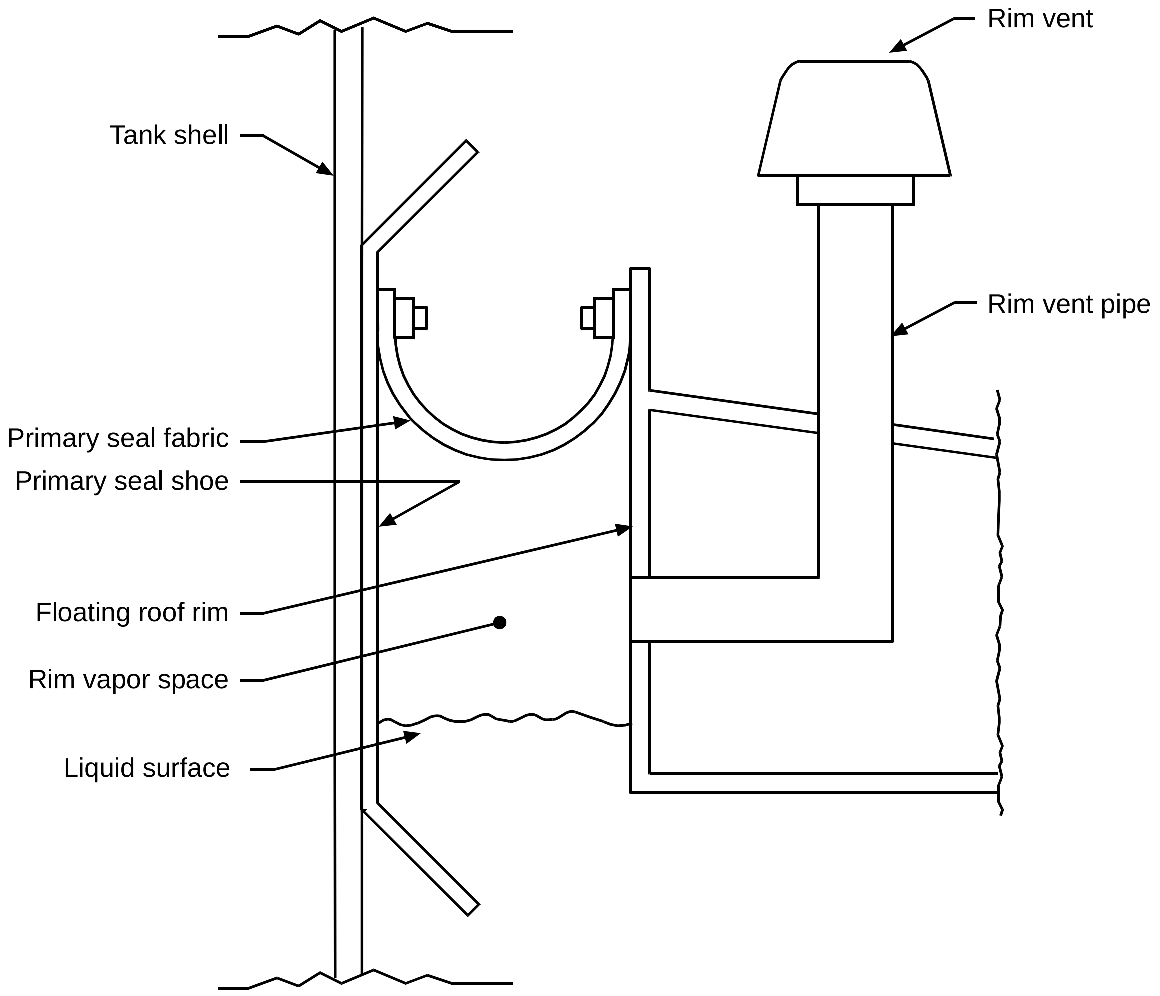


Figure 9-14. Rim vent

As the wind blows over the top of an open external floating roof tank, a differential pressure is created around the floating roof. As a result, standing storage losses, which result from causes other than a change in the liquid level, are the major source of emissions. The largest potential source of these losses is leaks from the seal in the annular rim space around the perimeter of the floating roof. Losses also occur through the various fittings discussed above. As with internal floating roof tanks, seal losses and fitting losses occur during both working and free-standing periods. Similarly, an additional working loss occurs when liquid is withdrawn from the tank and a wet portion of the tank wall is exposed, resulting in evaporation of the organic liquid.

9.1.2 Emission Control Techniques

Because of the various types of equipment that can be used to store volatile organic liquids, a general hierarchy, or ranking, of control alternatives can be developed based on emission rates. These hierarchies, in order of decreasing emission rate, are listed in Table 9-1 for fixed roof and internal floating roof tanks and in Table 9-2 for external floating roof tanks. Although other ranking scenarios could be developed, depending on the specific types of fitting used, the hierarchies presented here are meant to represent general groups of equipment alternatives.

Table 9-1.
Hierarchy of Equipment Types for Fixed Roof and Internal Floating Roof Tanks[a]

Control Option	Equipment Description
1	Fixed roof tank
2	Internal floating roof tank, bolted roof construction, vapor mounted primary seal, uncontrolled deck fittings
3	Internal floating roof tank, bolted roof construction, vapor mounted primary seal, secondary seal, controlled deck fittings
4	Internal floating roof tank, bolted roof construction, mechanical shoe or liquid mounted primary seal, secondary seal, controlled deck fittings
5	Internal floating roof tank, welded roof construction, mechanical shoe or liquid mounted primary seal, secondary seal, controlled deck fittings

[a] Listed in order of decreasing emission rate

Table 9-2.
Hierarchy of Equipment Types for External Floating Roof Tanks[a]

Control Option	Equipment Description
1	External floating roof tank, riveted roof construction, mechanical shoe primary seal, uncontrolled deck fittings
2	External floating roof tank, riveted roof construction, mechanical shoe primary seal, secondary seal, controlled deck fittings
3	External floating roof tank, welded roof construction, vapor mounted primary seal, uncontrolled deck fittings
4	External floating roof tank, welded roof construction, vapor mounted primary seal, secondary seal, controlled deck fittings
5	External floating roof tank, welded roof construction, mechanical shoe or liquid mounted primary seal, secondary seal, controlled deck fittings

[a] Listed in order of decreasing emission rate

9.1.2.1 Fixed Roof Tanks

As noted previously, a fixed roof tank is the minimum acceptable equipment for storing volatile organic liquids. One technique for reducing the working and breathing losses from these tanks is to install an internal floating roof.

The characteristics of this alternative are discussed in the next section. Losses can also be reduced by collecting the vapors and either recovering them with a carbon adsorber or refrigeration condenser or controlling them with a thermal or catalytic incinerator. The operation of these control devices is discussed in Chapter 13.

In the typical vapor recovery or control system, vapors remain in the tank until the internal pressure reaches a preset level. A pressure switch, which senses the pressure buildup in the tank, then activates blowers to collect and transfer the vapors through a closed vent system to the control device. To prevent explosive flashbacks from the control equipment, systems can be designed to operate with vapor levels above the upper explosive limit or the vapor can be enriched with natural gas to 1.2 times the upper explosive limit. Other options include blanketing with nitrogen or inert flue gas or using flame arrestors. The particular precautions employed vary widely, depending on the design of individual systems and the operating preferences of individual companies.

9.1.2.2 Internal Floating Roof Tanks

Internal floating roofs can be used directly as a control device for fixed roof tanks. Depending on the type of roof and seal system selected, the number of turnovers, the tank volume and the liquid being stored, installation of an internal floating roof reduces the emission rate by 69% to 98%. Most of this emission reduction is achieved by reducing the area of exposed liquid surface, and all floating roofs share this design benefit. The relative effectiveness of one floating roof design over another, therefore, is a function of how well the floating roof is sealed.

The most basic internal floating roof design from an emissions standpoint is the non-contact, bolted roof with a single vapor mounted wiper seal and uncontrolled fittings. The distribution of VOC losses from this design is estimated as follows:

- Rim or seal losses: 35%
- Fitting losses: 35%
- Deck seam losses: 18%
- Withdrawal losses: 12%

These percentages are based on a 16,980 ft^3 tank storing material with a vapor pressure of 1 psia. Obviously, this distribution will vary for other conditions and will depend on the tank diameter, equipment type and throughput. With the exception of withdrawal losses, which are inherent in all floating roof designs, the losses listed above can be reduced by using roofs with alternative design features.

Fitting losses occur through penetrations in the floating deck. Penetrations are needed to accommodate the various types of fittings that are required for proper operation of an internal floating roof. In general, fitting losses can be controlled with gasketing and sealing techniques or by substituting a lower-emitting fitting type that serves the same purpose. Table 9-3 lists the fitting types that contribute to emissions, along with an abbreviated description of the equipment that is considered to be representative of uncontrolled or controlled conditions.

Table 9-3.
Controlled and Uncontrolled Internal Floating Roof Deck Fittings

Deck Fitting Type	Equipment Description	
	Uncontrolled	Controlled
Access hatch	Unbolted, ungasketed cover; or unbolted gasketed cover	Bolted, gasketed cover
Gauge-float well	Unbolted, ungasketed cover; or unbolted, gasketed cover	Bolted, gasketed cover
Column well	Built-up column with sliding cover, ungasketed	Built-up column with sliding cover, gasketed; or pipe column with flexible fabric sleeve seal
Ladder well	Ungasketed sliding cover	Gasketed sliding cover
Sample well	Slotted pipe with sliding cover, ungasketed; or slotted pipe with sliding cover, gasketed	Sample thief well with slit fabric seal and 10% open area
Vacuum breaker	Weighted mechanical actuation, ungasketed	Weighted mechanical actuation, gasketed

Internal floating roof seal losses can be minimized by using liquid mounted primary seals instead of vapor mounted seals

and/or by using secondary seals in addition to primary seals. In addition, all seal systems should be designed, installed and maintained to minimize the gap between the seal and the tank shell. Data from emission tests indicate that seal losses increase rapidly when the seal gap exceeds 3 square inches per foot of tank diameter. Below this level, the effect of seal gap on seal losses is much less pronounced. The relative effectiveness of alternative roof seal systems is indicated in Table 9-4.

Table 9-4.
Internal Floating Roof Rim Seal System Control Efficiency

Seal System Description	Efficiency Relative to Baseline
Vapor mounted primary seal only	Baseline
Mechanical shoe or liquid mounted primary seal only	55%
Vapor mounted primary seal with secondary seal	63%
Mechanical shoe or liquid mounted primary seal with secondary seal	76%

Deck seam losses are inherent in several floating roof designs. Any roof constructed of sheets or panels that are connected by mechanical fasteners is expected to experience deck seam losses. These losses are considered to be a function of the length of the seams only and not the type of seam or its position relative to the liquid surface. Selecting a welded roof design eliminates deck seam losses.

9.1.2.3 External Floating Roof Tanks

The basic external floating roof is constructed of welded steel and is equipped with a mechanical shoe primary seal and uncontrolled fittings. Since these roofs do not have deck seams, losses occur during withdrawal and from fittings and the rim seal. Using the same capacity and vapor pressure used to estimate internal floating roof losses, the distribution of VOC losses from this design is estimated as follows:

- Rim or seal losses: 68%
- Fitting losses: 28%
- Withdrawal losses: 4%

Once again, this distribution will vary for other conditions and will

depend on the tank diameter, equipment type and throughput. With the exception of withdrawal losses, which are inherent in all floating roof designs, the losses listed above can be reduced by using roofs with alternative design features.

Fitting losses from external floating roof tanks occur in the same manner as fitting losses from internal floating roof tanks--through the penetrations in the floating roof deck. Similarly, fitting losses can be controlled with gasketing and sealing techniques or by substituting a lower-emitting fitting type that serves the same purpose. Table 9-5 lists the fitting types that contribute to emissions, along with an abbreviated description of the equipment that is considered to be representative of uncontrolled or controlled conditions.

Table 9-5.
Controlled and Uncontrolled External Floating Roof Deck Fittings

Deck Fitting Type	Equipment Description	
	Uncontrolled	Controlled
Access hatch	Unbolted, ungasketed cover; or unbolted gasketed cover	Bolted, gasketed cover
Gauge-float well	Unbolted, ungasketed cover; or unbolted, gasketed cover	Bolted, gasketed cover
Guide-pole well	Unslotted pipe with sliding cover, ungasketed	Unslotted pipe with sliding cover, gasketed
Sample well	Weighted mechanical actuation, ungasketed	Weighted mechanical actuation, gasketed

Vacuum breaker	Weighted mechanical actuation, ungasketed	Weighted mechanical actuation, gasketed
Roof drain	Open	90% closed
Rim vent	Weighted mechanical actuation, ungasketed	Weighted mechanical actuation, gasketed

Rim seal losses from external floating roof tanks are similar in nature to those that occur from internal floating roof tanks. The only difference is that external floating roof seal losses are believed to be dominated by wind-induced mechanisms. As with internal floating roof tanks, rim seal losses depend on the type of seal system employed. Liquid mounted seals are more effective than vapor mounted seals at reducing rim seal losses. Mechanical shoe seals, which are commonly employed on external floating roof tanks, are more effective than vapor-mounted seals, but less effective than liquid mounted seals. The relative effectiveness of alternative roof seal systems is indicated in Table 9-6.

Table 9-6.
External Floating Roof Rim Seal System Control Efficiency

Seal System Description	Efficiency Relative to Baseline
Vapor mounted primary seal only	Baseline
Vapor mounted primary seal with secondary seal	66%
Mechanical shoe primary seal only	84%
Mechanical shoe primary seal with shoe mounted secondary seal	95%
Liquid mounted primary seal only	95%
Mechanical shoe primary seal with rim mounted secondary seal	99%
Liquid mounted primary seal with rim mounted secondary seal	99%

Withdrawal losses from both internal and external floating roof tanks are entirely a function of the turnover rate and the characteristics of the tank shell. No applicable control measures have been identified to reduce withdrawal losses from floating roof tanks.

9.1.3 Emission Regulation

At the time of writing, USEPA had issued RACT recommendations for fixed roof and external floating roof tanks storing petroleum liquids, draft RACT recommendations for vessels storing volatile organic liquids, and NSPS requirements for vessels storing petroleum liquids and volatile organic liquids. There is also a MACT requirement for storage vessels at gasoline distribution facilities (40CFR63, Subpart R) that references the NSPS standard for volatile organic liquids (40CFR60, Subpart Kb). These recommended and required standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Control of Volatile Organic Emissions from Storage of Petroleum Liquids in Fixed Roof Tanks, Control Technique Guideline Document, EPA-450/2-77-036

Recommended standard:

- Install an internal floating roof equipped with a primary seal.
- Seals shall have no visible holes, tears or other openings.
- All openings except stub drains must be equipped with a cover, seal or lid that must be kept closed at all time when not in use.

The following tanks should be excluded from the guideline recommendations: vessels with capacities less than 40,000 gallons; vessels storing liquids with true vapor pressure less than 1.5 psia; and

vessels with a capacity less than 420,000 gallons storing produced crude oil and condensate prior to custody transfer.

Control of Volatile Organic Emissions from Storage of Petroleum Liquids in External Floating Roof Tanks, Control Technique Guideline Document, EPA-450/2-78-047

Recommended standard:

- Install a secondary seal that completely covers the space between the roof edge and the tank wall.
- Seals shall have no visible holes, tears or other openings.
- The area of gaps between the secondary seal and the tank wall that are larger than 0.125 inches shall not exceed 1.0 square inch per foot of tank diameter.
- Openings in the roof, except for vacuum breaker vents, rim space vents and leg sleeves, must have projections below the liquid surface and must be equipped with covers, seals or lids.

The following tanks should be excluded from the guideline recommendations: vessels with capacities less than 40,000 gallons; welded vessels storing liquids with true vapor pressure less than 4.0 psia; riveted and welded vessels with vapor mounted primary seals and storing liquids with true vapor pressure less than 1.5 psia; welded vessels with a shoe mounted secondary seal; tanks storing waxy, heavy pour crude oils; and vessels with a capacity less than 420,000 gallons storing produced crude oil and condensate prior to custody transfer.

Control of Volatile Organic Compound Emissions from Volatile Organic Liquid Storage in Floating and Fixed Roof Tanks, Control Technique Guideline Document (Draft), EPA-450/D-93-057

Recommended standard: This draft guideline applies to tanks with capacities greater than 40,000 gallons storing volatile organic liquids with vapor pressure greater than 0.75 psia.

For fixed roof tanks:

- Install the equivalent of a bolted internal floating roof equipped with vapor mounted primary seal, a secondary seal, and controlled fittings; or
- Install a vapor recovery or control system that is 95% effective by weight.

For internal floating roof tanks:

- Equip the internal floating roof with a mechanical shoe, liquid mounted or vapor mounted primary seal, a secondary seal, and controlled fittings.

For external floating roof tanks:

- Install mechanical shoe or liquid mounted primary seal, a secondary seal, and controlled fittings.

The following tanks should be excluded from the guideline recommendations: vessels at coke oven by-product plants; pressure vessels designed to operate in excess of 29.7 psia and without emissions to the atmosphere; vessels permanently attached to mobile vehicles; vessels with a capacity less than or equal to 420,000 gallons used for petroleum or condensate stored, processed or treated prior to custody transfer; vessels located at bulk gasoline plants; vessels located at gasoline service stations; and vessels used to store beverage alcohol.

Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After June 11, 1973, and Prior to May 19, 1978, 40CFR60, Subpart K

Applicability:

- Tanks storing petroleum liquids that have a capacity greater than 40,000 gallons, but not greater than 65,000 gallons, that commence construction or modification after March 8, 1974, and before May 19, 1978.
- Tanks storing petroleum liquids that have a capacity greater than 65,000 gallons that commence construction or modification after June 11, 1973, and before May 19, 1978.
- The subpart does not apply to storage vessels for petroleum or condensate stored, processed and/or treated at a drilling and production facility prior to custody transfer.

Standard:

- Vessel shall be equipped with a floating roof, a vapor recovery system or their equivalents, if the true vapor pressure at storage temperature is ≥1.5 psia but ≤11.1 psia.

- Vessel shall be equipped with a vapor recovery system or its equivalent, if the true vapor pressure at storage temperature is >11.1 psia.

Standards of Performance for Storage Vessels for Petroleum Liquids for Which Construction, Reconstruction, or Modification Commenced After May 18, 1978, and Prior to July 23, 1984, 40CFR60, Subpart Ka

Applicability:

- Tanks storing petroleum liquids that have a capacity greater than 40,000 gallons that commenced construction after May 18, 1978.

- The subpart does not apply to storage vessels with a capacity less than 420,000 gallons used for petroleum or condensate stored, processed or treated prior to custody transfer.

Standard:

If the true vapor pressure at storage temperature is ≥1.5 psia but ≤11.1 psia, the vessel shall have:

- A pontoon-type or double-deck-type external floating roof that floats on the surface of the liquid and is equipped with a primary seal and with a secondary seal that completely covers the space between the roof edge and the tank wall; or

    a. Gaps between the tank wall and a mechanical shoe or liquid mounted primary seal shall not exceed 1.5 inches and the accumulated area shall not exceed 10.0 square inches per foot of tank diameter.
    b. Gaps between the tank wall and a vapor mounted primary seal shall not exceed 0.5 inches and the accumulated area shall not exceed 1.0 square inch per foot of tank diameter.

    c. One leg of a mechanical shoe primary seal must extend into the liquid and the other end must be at least 24 inches above the liquid surface.

    d. Gaps between the tank wall and a secondary seal used in combination with a mechanical shoe or liquid mounted primary seal shall not exceed 0.5 inches and the accumulated area shall not exceed 1.0 square inch per foot of tank diameter. There shall be no gaps if the secondary seal is used in combination with a vapor mounted primary seal.

  e. There shall be no holes, tears or other openings in the primary and secondary seals.

  f. Openings in the roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface and, with the additional exception of leg sleeves, must be equipped with covers, seals or lids.

  g. Vacuum breaker vents and rim space vents must be closed when the roof is floating.

  h. Emergency roof drains must have a slotted membrane fabric cover that covers at least 90% of the area of the opening.

- A fixed roof with an internal floating roof equipped with a primary seal; or

  a. Openings in the roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface and, with the additional exceptions of stub drains and leg sleeves, must be equipped with covers, seals or lids.
  b. Vacuum breaker vents and rim space vents must be closed when the roof is floating.

- A vapor recovery or control system that is at least 95 percent efficient by weight.

If the true vapor pressure at storage temperature is >11.1 psia, the vessel shall have:

- A vapor recovery or control system that is at least 95 percent efficient by weight.

Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984, 40CFR60, Subpart Kb

Applicability:

- Tanks storing volatile organic liquids that have a capacity greater than or equal to 10,568 gallons that commenced construction after July 23, 1984.

- Tanks with a capacity less than 19,815 gallons are required to maintain records showing the dimensions of the vessel and an analysis of the capacity of the vessel. They are exempt from other provisions of the subpart.

- Tanks with a capacity greater than 39,894 gallons storing material with a true vapor pressure <u><</u>0.5 psia, or tanks with a capacity greater than or equal to 19,815 gallons but less than 39,894 gallons storing material with a true vapor pressure <u><</u>2.2 pisa, are required to maintain records showing the dimensions of the vessel, an analysis of the capacity of the vessel, the volatile organic liquid stored, the period of storage and the maximum true vapor pressure during the storage period. They are exempt from other provisions of the subpart.

- The subpart does not apply to vessels at coke oven by-product plants; pressure vessels designed to operate in excess of 29.7 psia and without emissions to the atmosphere; vessels permanently attached to mobile vehicles; vessels with a capacity less than or equal to 420,000 gallons used for petroleum or condensate stored, processed or treated prior to custody transfer; vessels located at bulk gasoline plants; vessels located at gasoline service stations; and vessels used to store beverage alcohol.

Standard:

For a tank capacity ≥39,894 gallons, if the true vapor pressure at storage temperature is ≥0.75 psia but <11.1 psia, or a tank capacity ≥19,815 gallons but <39,894 gallons, if the true vapor pressure at storage temperature is ≥4.0 psia but <11.1 psia, the vessel shall have:

- A pontoon-type or double-deck-type external floating roof that floats on the surface of the liquid and is equipped with a mechanical shoe or liquid mounted primary seal and with a secondary seal that completely covers the space between the roof edge and the tank wall; or

    a. Gaps between the tank wall and the mechanical shoe or liquid mounted primary seal shall not exceed 1.5 inches and the accumulated area shall not exceed 10.0 square inches per foot of tank diameter.
    b. One leg of a mechanical shoe primary seal must extend into the liquid and the other end must be at least 24 inches above the liquid surface.

    c. Gaps between the tank wall and the secondary seal shall not exceed 0.5 inches and the accumulated area shall not exceed 1.0 square inch per foot of tank diameter.

    d. There shall be no holes, tears or other openings in the primary and secondary seals.

e. Openings in a non-contact roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface.

f. Openings in the roof, except for vacuum breaker vents, rim space vents, roof drains and leg sleeves, must be equipped with gasketed covers, seals or lids.

g. Vacuum breaker vents and rim space vents are to be gasketed and must be closed when the roof is floating.

h. Emergency roof drains must have a slotted membrane fabric cover that covers at least 90% of the area of the opening.

- A fixed roof with an internal floating roof equipped with a mechanical shoe or liquid mounted primary seal or with both primary and secondary seals; or

  a. Openings in a non-contact roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface
  b. Openings in the roof, except for vacuum breaker vents, rim space vents, stub drains, leg sleeves, column wells, ladder wells and sample wells, must be equipped with gasketed covers or lids.

  c. Covers on access hatches and gauge-float wells must be bolted except when they are in use.

  d. Vacuum breaker vents and rim space vents are to be gasketed and must be closed when the roof is floating.

  e. Openings in the roof for sampling must be a sample well with a slit fabric cover that covers at least 90% of the opening.

  f. Openings in the roof for columns supporting the fixed roof must have a flexible fabric seal or a gasketed sliding cover.

  g. Openings in the roof for ladders must have a gasketed sliding cover.

- A closed vent system and control device.

  a. The closed vent system must operate with no detectable emissions as indicated by an instrument reading of less than 500 ppm above background.
  b. The control device must be at least 95 percent efficient by weight.

For a tank capacity $\geq$19,815 gallons, if the true vapor pressure at storage temperature is >11.1 psia, the vessel shall have:

- A closed vent system and control device.

  a. The closed vent system must operate with no detectable emissions as indicated by an instrument reading of less than 500 ppm above background.

  b. The control device must be at least 95 percent efficient by weight.

9.1.4 Process Inspection

There should be two goals in any field inspection. First is to evaluate the source's compliance with any rule-specific monitoring and recordkeeping requirements and with the provisions of the Title V permit. In addition, changes in operating conditions or parameters that could result in increased emissions should be evaluated. With storage tanks, increased emissions usually result from leaks in the rim space and fitting seals. Recommended general inspection items include the following:

- ***Review records maintained by the source.*** Three types of data should be reviewed: design information, operational information and maintenance information. The design data should be evaluated to determine the capacity of the tank and to confirm that control techniques appropriate to RACT, NSPS or MACT requirements have been implemented. This would include the type of floating roof used and the types of rim space seals and roof penetration seals employed. Operational information should be compared to the operating permit and to the provisions of the RACT, NSPS or MACT regulations. These parameters would include the liquid stored, the period of storage and the maximum true vapor pressure during the storage period. Maintenance information should include the results of required inspections and the repair or replacement records.

- ***Observe the condition of the tank.*** The general condition of the tank should be evaluated. The tank shell should be checked for evidence of corrosion, and inspection hatches should be checked for liquid or vapor leaks. On fixed roof tanks, the condition of pressure-vacuum relief valves should be checked.

- ***Observe the floating roof.*** Observations of internal floating roofs should be conducted from inspection hatches on the roof. Evaluations of external floating roofs can be conducted from the ladder platform or, if safe to do so, on the surface of the roof itself. Visually determine the general condition of the roof, whether the roof is floating on the surface of the liquid, and whether any liquid is accumulated on it. Check the condition of the rim space seals and look for any gaps. Check the roof penetrations and the methods use to seal them.

- ***Measure rim seal gap areas.*** On external floating roof tanks, if it is safe to do so, quantitatively determine the gap areas in the primary and secondary seals.

9.2 Petroleum Product Distribution

Many petroleum products are distributed from refineries to customers in drums and railroad cars, generally resulting in minimal VOC emissions. However, gasoline, diesel fuel, jet fuel and heating oil are generally distributed through a series of intermediate storage and transfer facilities, resulting in a much greater potential for VOC losses. As an example of this distribution network, this section will focus on the delivery of gasoline from the refinery to the final user, the automobile.

9.2.1 Process Description

Figure 9-15 shows a schematic of the typical arrangement of the gasoline marketing system. Gasoline is transferred from the refinery by ship, barge or pipeline to large storage facilities called bulk terminals. Facilities handling more than 20,000 gallons of gasoline per day are considered bulk terminals; however, the daily throughput at the average bulk terminal is about 250,000 gallons, and some large facilities have throughputs greater than 1 million gallons per day.

Gasoline is delivered from bulk terminals to bulk plants using large tank trucks that have a capacity of 8,000-10,000 gallons. Facilities handling less than 20,000 gallons of gasoline per day are considered bulk plants; however, the daily throughput at the average bulk plant is about 5,000 gallons. Bulk plants are intermediate storage facilities that provide gasoline to service stations, commercial accounts and farms. The gasoline is delivered to these customers using smaller trucks, called bobtail trucks or tank wagons, that have a capacity of 1,500-3,000 gallons.

Small tank trucks deliver the gasoline to service stations and commercial fuel-dispensing facilities. The gasoline is stored in underground tanks and then pumped into the vehicle's fuel tank. Daily throughput at the average service station is about 2,000 gallons.

When gasoline flows into a receiving container, it displaces vapors in the vapor space of that container into the atmosphere. Emissions caused by displacement occur at (1) bulk terminals when gasoline is loaded into tank trucks; (2) at bulk plants when the gasoline is unloaded from large tank trucks into the storage tanks, and then again when it is loaded from the storage tanks into smaller tank trucks; and (3) at service stations when gasoline is unloaded into the underground storage tanks, and then again when the gasoline is dispensed into the vehicle's fuel tank. Additionally, vapors are emitted from leaks and spills during transfers.

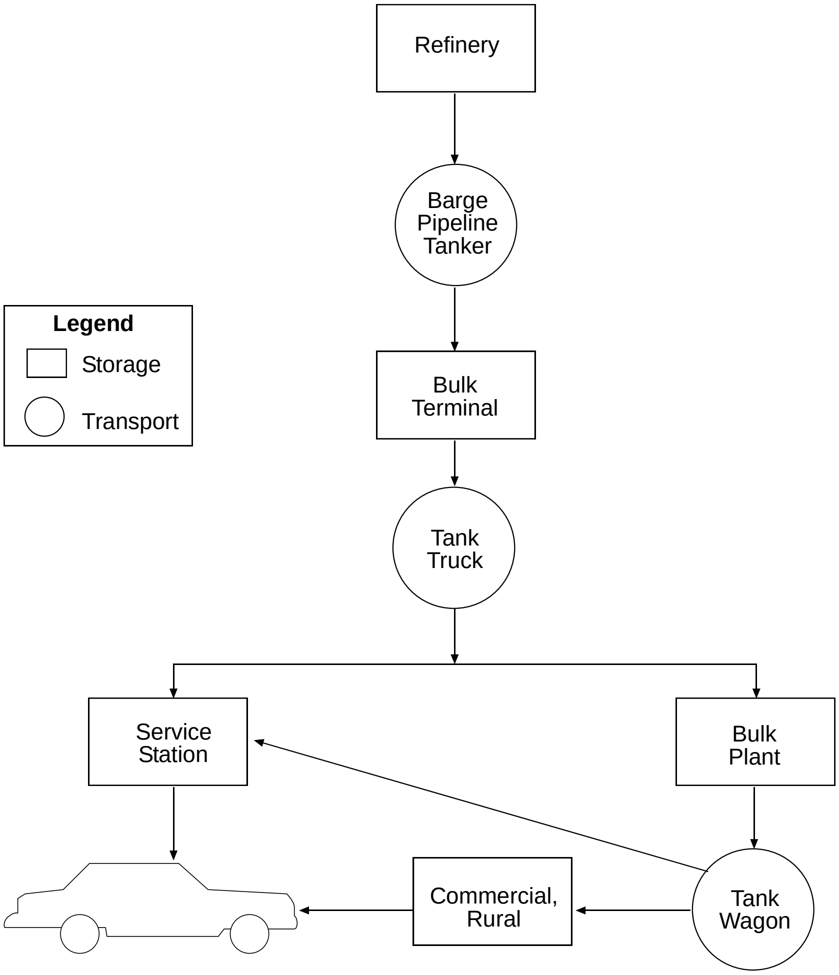


Figure 9-15. Gasoline marketing system

9.2.2 Emission Control Techniques

Vapor collection and processing equipment has been installed and operated for over 20 years at gasoline marketing emission sources. The basic strategy has been to collect the vapors emitted at the end of the gasoline marketing chain (service stations and bulk plants) and transport them back to the beginning of the chain (bulk terminals) for recovery or destruction. To accomplish this, equipment for collection of the vapors is needed at each facility, as well as on the tank truck.

9.2.2.1 Tank Trucks

The tank trucks used to deliver gasoline to bulk plants and services stations are an integral part of the vapor collection system. In addition to being equipped with vapor return piping, the tank and vapor collection hoses must be free of any significant leaks. This can be demonstrated by passing an annual pressure-vacuum decay test and by periodic monitoring for leaks with a portable gas detector. The decay test requires that the tank and vapor collection hoses not sustain a pressure change of more than a set value when pressurized or evacuated to specified pressures.

9.2.2.2 Bulk Terminals

Figure 9-16 shows a typical arrangement of vapor collection and processing equipment at a bulk terminal. As gasoline is pumped from the storage tank into the tank truck, the vapors are displaced through a vapor-collection system of pipes and hoses to a vapor processor for either recovery or destruction. Refrigeration condensation units and carbon adsorbers are the most common vapor recovery devices installed at bulk terminals, and ground flares and thermal oxidizers are the most common types of destruction devices. The operation of these control devices is discussed in Chapter 13.

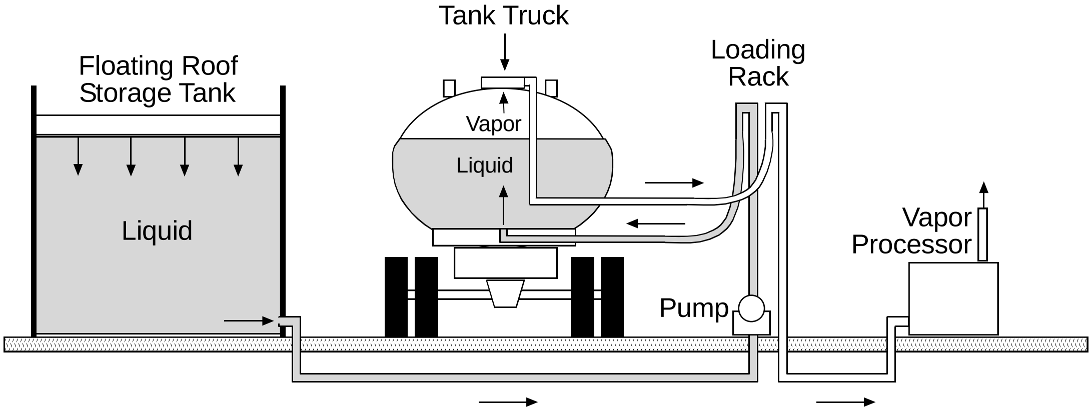


Figure 9-16. Bulk terminal with vapor collection and processor

9.2.2.3 Bulk Plants

At bulk plants and service stations, the primary method for controlling emissions caused by displacement during loading and unloading operations is to transfer the vapors being displaced from the receiving container back to the dispensing container. This method is called vapor balancing. Figure 9-

17 shows an example of vapor balancing at bulk plants. Gasoline unloaded from large tank trucks into the bulk plant's storage tank displaces the vapors inside the storage tank through vapor piping to the tank truck's vapor-collection system and then into the truck tank. The collected vapors in the tank truck are then transported back to the bulk terminal, where they are collected and processed. In reverse, vapors displaced by liquid loaded into the small tank trucks are routed through the vapor collection system on the tank truck to the vapor piping at the plant and then into the storage tank vapor space. The control efficiency of vapor balance systems ranges from 93% to 100%.

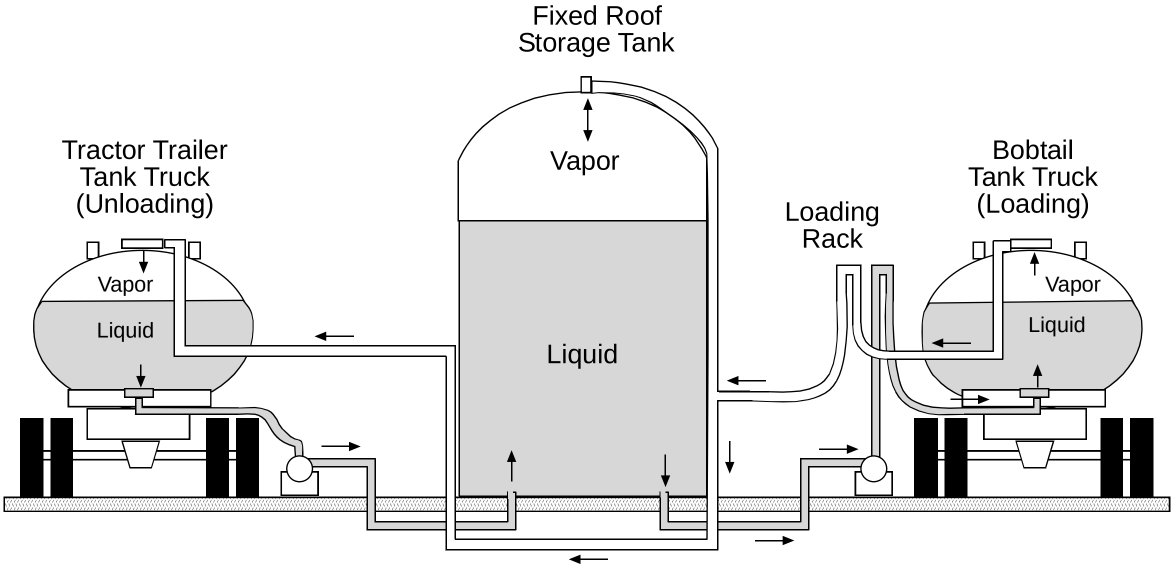


Figure 9-17. Bulk plant with vapor balance system

9.2.2.4 Service Stations

Figure 9-18 illustrates vapor balancing during storage tank loading at a service station. Vapor balancing the displaced vapors from the underground storage tank to the tank truck is commonly called Stage I controls. Controlling emissions from vehicle refueling operations is called Stage II controls and is based on conveying the vapors displaced from the vehicle fuel tank to the underground storage tank through the use of a special hose and nozzle.

In the vapor balance Stage II system shown in Figure 9-19, the vapors are conveyed from the vehicle fuel tank to the storage tank by the natural pressure differential created during refueling. For these systems to be effective, it is necessary to maintain a good seal between the fueling nozzle and the fuel tank fill pipe. Newer Stage II designs use vacuum assist to create a slight negative pressure at the nozzle-fill pipe interface, increasing vapor recovery. Since these systems create extra volume, they must either vent the excess vapors to the atmosphere or direct them to a vapor processor. Hybrid systems combine vapor balance and vacuum assist. They enhance vapor recovery at the nozzle-fill pipe interface with vacuum, while keeping the vacuum low enough to minimize the volume returned to the vapor-recovery system.

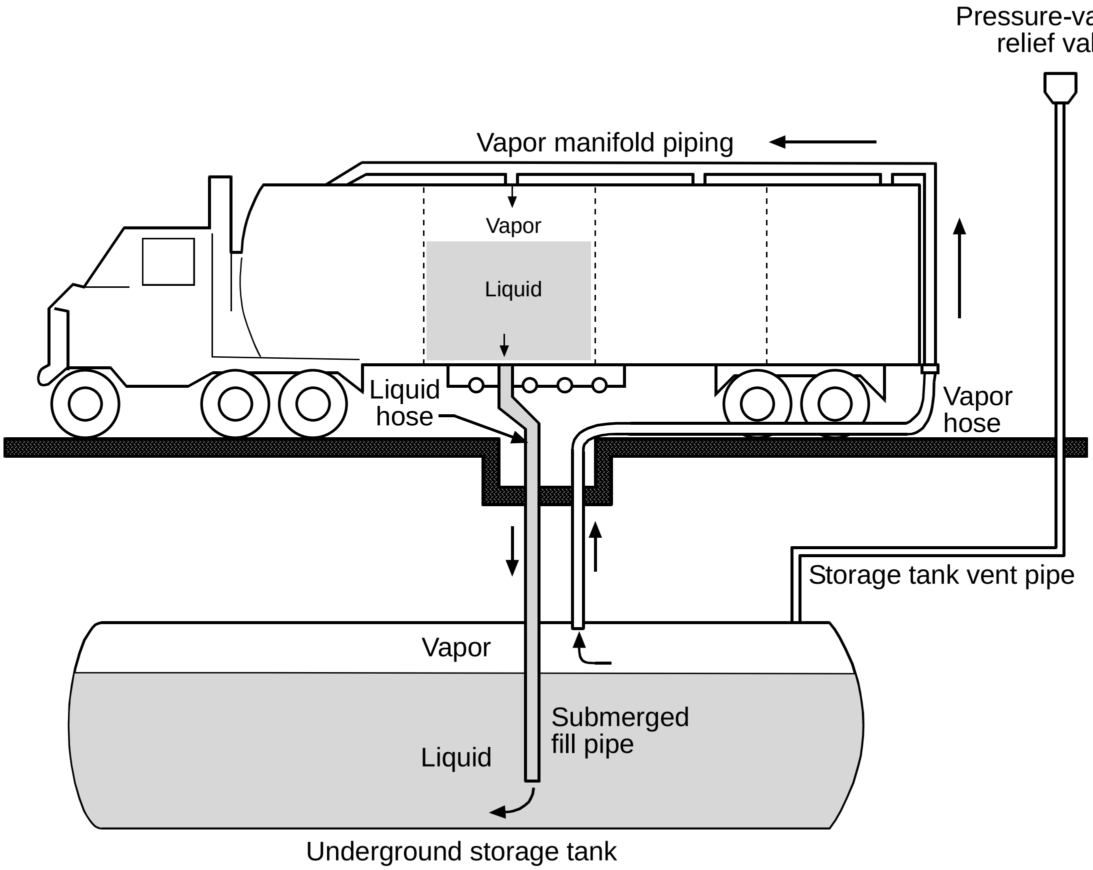


Figure 9-18. Service station underground storage tank fueling (Stage I controls)

Another vehicle refueling control technique is to use an onboard system. Onboard refueling systems use a vapor seal in the vehicle fill pipe that forces the displaced vapors to a carbon adsorber on the vehicle. When the vehicle is in operation, the carbon is regenerated by a reverse-direction, warm air flow through the carbon canister. The recovered vapors are directed into the engine's air intake and burned. Onboard systems have been demonstrated to achieve 94% efficiency.

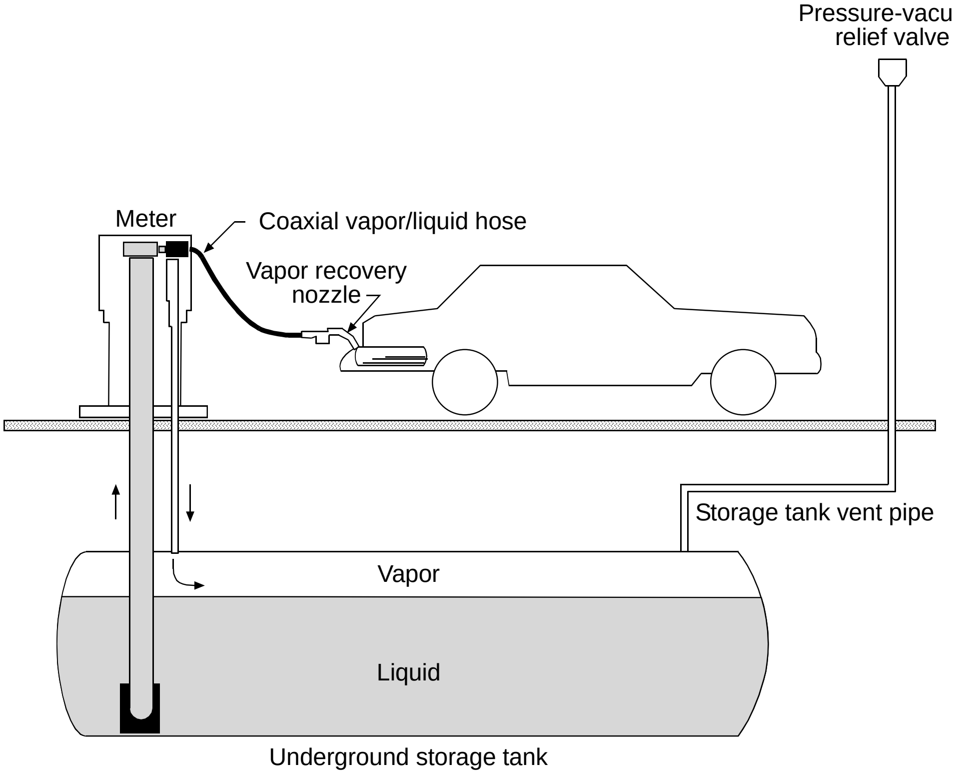


Figure 9-19. Service station vehicle refueling (Stage II controls)

9.2.3 Emission Regulation

At the time of writing, USEPA had issued RACT recommendations for gasoline tank trucks, gasoline loading terminals, bulk gasoline plants and service stations, NSPS requirements for bulk gasoline terminals, and MACT requirements for gasoline distribution facilities. These recommended and required standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Control of Volatile Organic Compound Leaks from Gasoline Tank Trucks and Vapor Collection Systems, Control Technique Guideline Document, EPA-450/2-78-051

Recommended standard:

- Gasoline tank trucks and their vapor collection systems shall not sustain a pressure change of more than 3 inches of H_2O in 5 minutes when pressurized to 18 inches of H_2O or evacuated to 6 inches of H_2O.

- These shall be no avoidable visible liquid leaks. Invariably, there will be a few drops of liquid from disconnection of dry breaks in liquid lines even when well maintained; these few drops shall be allowed (There are approximately 20-30 drops per milliliter; thus a "few drops" is roughly 0.2 milliliter.).

Control of Hydrocarbons from Tank Truck Gasoline Loading Terminals, Control Technique Guideline Document, EPA-450/2-77-026

Recommended standard:

- The bulk gasoline terminal must be equipped with a vapor collection system that is at least 90% efficient by weight.

- Emissions to the atmosphere must not exceed 0.67 pounds per 1,000 gallons of gasoline loaded.

- All displaced vapors must be vented only to the vapor control system.

- All loading and vapor lines are to be equipped with fittings which make vapor-tight connections and which close automatically when disconnected.

- The pressure in the vapor collection system shall not exceed the tank truck relief settings.

- No gasoline may be spilled, discarded in sewers, stored in open containers or handled in any manner that would result in evaporation.

Control of Volatile Organic Emissions from Bulk Gasoline Plants, Control Technique Guideline Document, EPA-450/2-77-035

Recommended standard:

- A vapor balance system, or equivalent, shall be used to control vapors displaced during the loading of storage tanks from large tank trucks and the loading of small tank trucks from storage tanks.

- The fill pipe is to extend within 6 inches of the bottom of tank trucks and storage tanks during top submerged filling and is to be flush with the tank bottom during bottom filling.

- There must be no leaks in tank truck pressure-vacuum relief valves and hatch covers, or in truck tanks, storage tanks, or associated vapor return lines, during loading or unloading operations.

- Hatches of tank trucks are not to be opened at any time during loading operations.

- Pressure relief valves on storage tanks and tank trucks are to be set to release at the highest possible pressure.

- No gasoline may be spilled, discarded in sewers, stored in open containers or handled in any manner that would result in evaporation.

Small, independent bulk plants handling less than 4,000 gallons per day may be exempted from vapor balancing during the loading of small tank trucks.

Design Criteria for Stage I Vapor Control Systems—Gasoline Service Stations, USEPA, Office of Air Quality Planning and Standards, November 1975

Recommended standard:

- A vapor balance system shall be used to control vapors displaced during the loading of underground storage tanks.

- The fill pipe is to extend within 6 inches of the bottom of the storage tank.

- All loading and vapor lines are to be equipped with fittings which make vapor-tight connections and which close automatically when disconnected.

- There must be no leaks in tank truck or storage tank pressure-vacuum relief valves or in associated vapor return lines during loading operations.

Standards of Performance for Bulk Gasoline Terminals, 40CFR60, Subpart XX

Applicability Date: December 17, 1980

Standard:

- Each facility shall be equipped with a vapor collection system to collect vapors displaced from tank trucks during product loading.

- Emissions to the atmosphere from the vapor collection system shall not exceed 0.29 pounds per 1,000 gallons of gasoline loaded.

- For existing vapor recovery systems, emissions to the atmosphere from the vapor collection system shall not exceed 0.67 pounds per 1,000 gallons of gasoline loaded.
- Vapors collected at one loading rack shall not be passed to another loading rack.
- Gasoline tank truck shall be vapor tight.
- Pressure in the vapor collection system and liquid loading equipment shall not exceed 17.7 inches of H_2O during product loading.
- No pressure-vacuum vent in the vapor collection system shall begin to open at a system pressure less than 17.7 inches of H_2O.
- The vapor collection system, the vapor processing system, and each loading rack shall be inspected each calendar month for liquid or vapor leaks.

National Emission Standards for Gasoline Distribution Facilities (Bulk Gasoline Terminals and Pipeline Breakout Stations), 40CFR63, Subpart R

Applicability: Each new and existing bulk gasoline terminal and pipeline breakout station with an emissions screening factor greater than 1.0 and that is a major source of hazardous air pollutants.

Standard:

For loading racks:

- Each facility shall be equipped with a vapor collection system to collect vapors displaced from tank trucks during product loading.
- Emissions to the atmosphere from the vapor collection system shall not exceed 0.08 pounds per 1,000 gallons of gasoline loaded.
- Vapors collected at one loading rack shall not be passed to another loading rack.
- Gasoline tank truck shall be vapor tight.
- Pressure in the vapor collection system and liquid loading equipment shall not exceed 17.7 inches of H_2O during product loading.
- No pressure-vacuum vent in the vapor collection system shall begin to open at a system pressure less than 17.7 inches of H_2O.

For storage vessels:

For a tank capacity ≥19,815 gallons, the vessel shall have:

- A pontoon-type or double-deck-type external floating roof that floats on the surface of the liquid and is equipped with a mechanical shoe or liquid mounted primary seal and with a secondary seal that completely covers the space between the roof edge and the tank wall; or

  a. Gaps between the tank wall and the mechanical shoe or liquid mounted primary seal shall not exceed 1.5 inches and the accumulated area shall not exceed 10.0 square inches per foot of tank diameter.

  b. One leg of a mechanical shoe primary seal must extend into the liquid and the other end must be at least 24 inches above the liquid surface.

  c. Gaps between the tank wall and the secondary seal shall not exceed 0.5 inches and the accumulated area shall not exceed 1.0 square inch per foot of tank diameter.

  d. There shall be no holes, tears or other openings in the primary and secondary seals.

  e. Openings in a non-contact roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface.

  f. Openings in the roof, except for vacuum breaker vents, rim space vents, roof drains and leg sleeves, must be equipped with gasketed covers, seals or lids.

  g. Vacuum breaker vents and rim space vents are to be gasketed and must be closed when the roof is floating.

  h. Emergency roof drains must have a slotted membrane fabric cover that covers at least 90% of the area of the opening.

- A fixed roof with an internal floating roof equipped with a mechanical shoe or liquid mounted primary seal or with both primary and secondary seals; or

  a. Openings in a non-contact roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface.

- A closed vent system and control device.

  a. The closed vent system must operate with no detectable emissions as indicated by an instrument reading of less than 500 ppm above background.

  b. The control device must be at least 95 percent efficient by weight.

For equipment leaks:

- Perform a monthly leak inspection of all equipment in gasoline service during the loading of a tank truck. Detection methods incorporating sight, sound and smell are acceptable, but instrumental detection may also be used.
- An initial attempt to repair a leak shall be made no later than 5 days after the leak is detected. Repair or replacement of leaking equipment shall be complete within 15 days after the leak is detected.
- Gasoline shall not be handled in a manner that would result in vapor releases to the atmosphere for extended periods of time.

9.2.4 Process Inspection

There should be two goals in any field inspection. First is to evaluate the source's compliance with any rule-specific monitoring and recordkeeping requirements and with the provisions of the Title V permit. In addition,

changes in operating conditions or parameters that could result in increased emissions should be evaluated. In gasoline distribution, increased emissions usually result from leaks in the tank truck, the product delivery system, the vapor collection system and the vapor balance system. Recommended general inspection items include the following:

- ***Obtain source information.*** Determine the method of refueling the facility and the daily maximum and annual total throughput. Determine the number and location of loading stations and what materials are loaded at each one. Determine the method of controlling VOC emissions. If a vapor recovery and control system is used, determine if it runs continuously during loading or if it uses a vapor accumulator and runs intermittently. Review maintenance records for the facility.

- ***Check tank truck and storage tank equipment.*** Determine if the tank truck and storage tank are properly equipped for vapor recovery. Determine if tank truck has a valid leak-tightness certification. Verify that the tank truck and storage tank use submerged filling.

- ***Observe operating procedures.*** Verify that the vapor return line is connected during filling. Verify that unconnected vapor return lines at other interconnected loading stations are closed off. Verify that the overfill sensor is connected to the pump and that the umbilical cord is not bypassed. Verify that relief valves do not open during filling and that the tank is not overfilled. If a top-loading nozzle is used, verify that the grommet is not cracked or damaged and that a good seal is maintained as the truck settles during loading. Verify that loading of distillate fuel into trucks previously containing gasoline is not being done at loading stations not connected to the vapor recovery system.

- ***Check for vapor leaks.*** Check piping and hoses, line connections, hatch covers and relief valves for vapor leaks.

- ***Check for liquid leaks.*** Check piping and hoses, line connections, access hatches and tank shell for liquid leaks. Verify that no spills or excessive drips occur when the lines are disconnected.

- ***Check vapor recovery and control system operation.*** Verify that the vapor recovery system is operating during loading or when the vapor accumulator is full. If the vapor recovery system is not operating, verify that the accumulator level indicator is rising during filling. Verify that the accumulator pressure relief valve is not stuck open.

The inspection of carbon adsorbers, condensers, and catalytic and thermal incin-erators used in vapor recovery and control systems is covered in APTI Course 455, Inspection of Gas Control Devices and Selected Industries. The reader is referred to this course for guidance.

Review Questions

1. What type of vessel is not commonly used to store volatile organic liquids?
   a. Fixed roof tanks
   b. Internal floating roof tanks
   c. External floating roof tanks
   d. Pressure tanks

2. What type of tank is generally considered the minimum acceptable equipment for storing volatile organic liquids?
   a. Fixed roof tanks
   b. Internal floating roof tanks
   c. External floating roof tanks
   d. Pressure tanks

3. What are the major types of emissions from fixed roof storage tanks? Select all that apply.
   a. Isobaric losses
   b. Breathing losses
   c. Rim seal losses
   d. Working losses

4. Which type of floating roof construction can be a source of VOC emissions? Select all that apply.
   a. Pan-type steel roofs
   b. Aluminum sandwich panel roofs
   c. Aluminum deck roofs
   d. Resin-coated FRP roofs

5. Which type of primary rim seal is not used on floating roofs?
   a. Foam-filled cells
   b. Liquid-filled cells
   c. Gas-filled cells

6. Which type of fitting requires the penetration of an internal floating roof? Select all that apply.
   a. Fixed roof support columns
   b. Floating roof legs
   c. Vacuum breakers
   d. Ladders

7. Which type of floating roof primary rim seal is the least effective?
   a. Vapor mounted foam-filled cell
   b. Liquid mounted foam-filled cell
   c. Mechanical shoe
   d. Liquid mounted liquid-filled cell

8. Which of the following is not considered a floating roof secondary rim seal?
   a. A flexible polymeric wiper mounted between the roof rim and the tank wall
   b. A metallic weather shield mounted between the roof rim and the tank wall
   c. A flexible polymeric wiper mounted between a mechanical shoe and the tank wall

9. Which type of fitting requires the penetration of an external floating roof? Select all that apply.
   a. Guide pole
   b. Roof legs
   c. Vacuum breakers
   d. Ladders

10. Which type of external floating roof drain is not usually a source of VOC emissions?
    a. Open drain
    b. Closed drain
    c. Overflow drain
    d. Stub drain

11. What control method can be used to reduce the emissions from fixed roof storage tanks? Select all that apply.
    a. Nitrogen blanketing
    b. Internal floating roof
    c. Vapor recovery and control system
    d. Flame arrestors

12. Which of the following are sources of VOC emissions from the most basic internal floating roof design? Select all that apply.
    a. Rim seal losses
    b. Fitting losses
    c. Deck seam losses
    d. Withdrawal losses

13. Which of the following are sources of VOC emissions from the most basic external floating roof design? Select all that apply.
    a. Rim seal losses
    b. Fitting losses
    c. Deck seam losses
    d. Withdrawal losses

14. What control techniques are used to reduce VOC emissions from floating roof fittings? Select all that apply.
    a. Wells that penetrate into the liquid
    b. Cover, lids or seals
    c. Substitution of a lower-emitting fitting type

d. Reverse pressure blanketing

15. What control techniques are used to reduce withdrawal losses from internal and external floating roof tanks? Select all that apply.
    a. Flexible wipers
    b. Cover, lids or seals
    c. Spray-wash systems
    d. None

16. Which of the following should be elements in the inspection of storage tanks? Select all that apply.
    a. Review records maintained by the source
    b. Inspect the top of the floating roof and its seals and fittings
    c. Inspect the bottom of the floating roof if the tank is empty and ventilated
    d. Check condition of pressure-vacuum relief valves on fixed roof tanks

17. What are the sources of VOC emissions during gasoline distribution? Select all that apply.
    a. Filling storage tanks and loading tank trucks at bulk terminals
    b. Filling storage tanks and loading tank trucks at bulk plants
    c. Filling storage tanks and fueling vehicles at service stations
    d. Leaks and spills during transfers

18. What is the most common technique used to control VOC emissions at bulk plants?
    a. Vapor balance
    b. Vapor recovery and control systems
    c. Inert gas blanketing
    d. Pressure-vacuum relief valves

19. What techniques are used to control VOC emissions from vehicle fueling? Select all that apply.
    a. Stage I vapor recovery
    b. Vapor balance Stage II vapor recovery
    c. Vacuum assist Stage II vapor recovery
    d. Onboard vapor recovery system

20. Which of the following should be elements in the inspection of bulk plants? Select all that apply.
    a. Check pressure settings of pressure-vacuum relief valves
    b. Verify that the vapor return line is connected during filling
    c. Check for liquid and vapor leaks
    d. Check filling rate

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Review Answers

1. What type of vessel is not commonly used to store volatile organic liquids?
   d. Pressure tanks

2. What type of tank is generally considered the minimum acceptable equipment for storing volatile organic liquids?
   a. Fixed roof tanks

3. What are the major types of emissions from fixed roof storage tanks? Select all that apply.
   b. Breathing losses
   d. Working losses

4. Which type of floating roof construction can be a source of VOC emissions? Select all that apply.
   b. Aluminum sandwich panel roofs
   c. Aluminum deck roofs

5. Which type of primary rim seal is not used on floating roofs?
   c. Gas-filled cells

6. Which type of fitting requires the penetration of an internal floating roof? Select all that apply.
   a. Fixed roof support columns
   b. Floating roof legs
   c. Vacuum breakers
   d. Ladders

7. Which type of floating roof primary rim seal is the least effective?
   a. Vapor mounted foam-filled cell

8. Which of the following is not considered a floating roof secondary rim seal?
   b. A metallic weather shield mounted between the roof rim and the tank wall

9. Which type of fitting requires the penetration of an external floating roof? Select all that apply.
   a. Guide pole
   b. Roof legs
   c. Vacuum breakers

10. Which type of external floating roof drain is not usually a source of VOC emissions?
    b. Closed drain

11. What control method can be used to reduce the emissions from fixed roof storage tanks? Select all that apply.
    b. Internal floating roof
    c. Vapor recovery and control system

12. Which of the following are sources of VOC emissions from the most basic internal floating roof design? Select all that apply.
    a. Rim seal losses
    b. Fitting losses
    c. Deck seam losses
    d. Withdrawal losses

13. Which of the following are sources of VOC emissions from the most basic external floating roof design? Select all that apply.
    a. Rim seal losses
    b. Fitting losses
    d. Withdrawal losses

14. What control techniques are used to reduce VOC emissions from floating roof fittings? Select all that apply.
    a. Wells that penetrate into the liquid
    b. Cover, lids or seals
    c. Substitution of a lower-emitting fitting type

15. What control techniques are used to reduce withdrawal losses from internal and external floating roof tanks? Select all that apply.
    d. None

16. Which of the following should be elements in the inspection of storage tanks? Select all that apply.
    a. Review records maintained by the source
    b. Inspect the top of the floating roof and its seals and fittings
    d. Check condition of pressure-vacuum relief valves on fixed roof tanks

17. What are the sources of VOC emissions during gasoline distribution? Select all that apply.
    a. Filling storage tanks and loading tank trucks at bulk terminals
    b. Filling storage tanks and loading tank trucks at bulk plants
    c. Filling storage tanks and fueling vehicles at service stations
    d. Leaks and spills during transfers

18. What is the most common technique used to control VOC emissions at bulk plants?
    a. Vapor balance

19. What techniques are used to control VOC emissions from vehicle fueling? Select all that apply.
    - **b.** Vapor balance Stage II vapor recovery
    - **c.** Vacuum assist Stage II vapor recovery
    - **d.** Onboard vapor recovery system

20. Which of the following should be elements in the inspection of bulk plants? Select all that apply.
    - **a.** Check pressure settings of pressure-vacuum relief valves
    - **b.** Verify that the vapor return line is connected during filling
    - **c.** Check for liquid and vapor leaks

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10 Degreasing

Degreasers, or organic solvent cleaners, use organic solvents or their vapors to remove grease, oil, wax, tar, carbon deposits and fluxes from metal, plastic, printed circuit boards, and other surfaces. This cleaning is typically done prior to such processes as painting, plating, heat treating and machining, or as part of maintenance operations.

The three basic types of degreasing equipment are cold cleaners, open top vapor cleaners, and in-line or conveyorized cleaners. In-line cleaners can be either cold cleaners or vapor cleaners. Data on the number of cleaners in use is limited. However, using information from a 1974 survey of all cleaners and a 1987 survey of halogenated solvent cleaners, it is estimated that there are approximately 2,000,000 cold cleaners, 35,000 open top vapor cleaners and 6,000 in-line cleaners.

The primary solvents used in cold cleaners are mineral spirits, Stoddard solvents and alcohols. Cold cleaners that use halogenated solvent are of a type called carburetor cleaners. The solvent used is typically methylene chloride that has been blended with other solvents and additives to reduce flammability and increase cleaning power. The majority of halogenated solvent use is in vapor cleaners, both open top and in-line. The most commonly used solvents have been methylene chloride, carbon tetrachloride, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane (methyl chloroform) and trichlorotrifluoroethane (CFC-113). However, since production of carbon tetrachloride, methyl chloroform and CFC-113 has been phased out under the stratospheric ozone protection provisions (Title VI) of the Clean Air Act Amendments of 1990, many facilities have switched to hydrochlorofluorocarbons (HCFCs). Their production phase-out date extends until 2030.

10.1 PROCESS DESCRIPTION

This section describes the equipment and operating procedures used in cold cleaning, open top vapor cleaning and in-line cleaning. Sources of air emissions from these operations, and the parameters that influence them, will also be discussed.

10.1.1 Cold Cleaners

Cold cleaners are used for both maintenance and manufacturing degreasing. Maintenance cleaners are more numerous and are usually simpler, smaller and less expensive than manufacturing cleaners. One type of maintenance cold cleaner is the carburetor cleaner mentioned earlier and shown in Figure 10-1. Small parts to be cleaned are placed in the basket and then immersed in the solvent. An air motor is used to agitate the basket to improve the cleaning action.

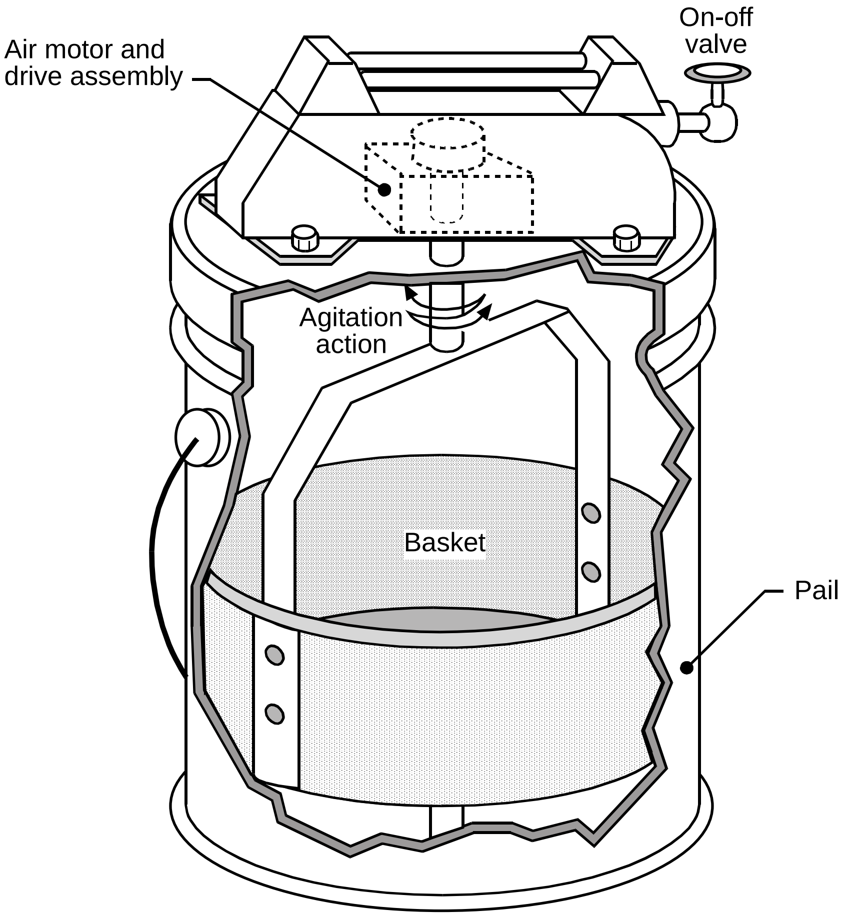

Figure 10-1. Carburetor cleaner

Another type of maintenance cold cleaner is the spray sink shown in Figure 10-2. As the name implies, the spray sink is simply a basin that sits on top of the solvent drum. A submersible pump delivers the solvent to the sink through a spray nozzle. There is no access to the solvent bath. Instead, parts are cleaned by hand brushing and spraying.

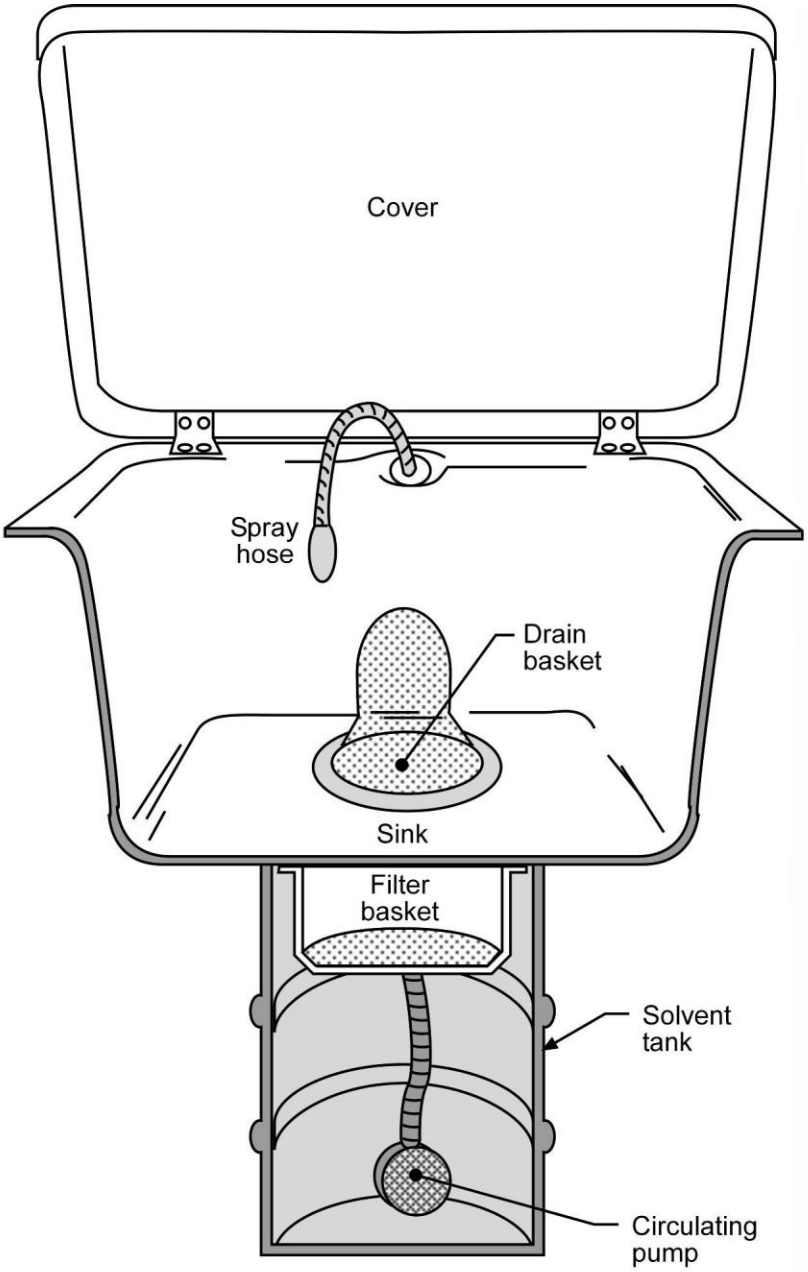

Figure 10-2. Spray sink

When larger parts have to be maintenance cleaned, or when a higher degree of cleanliness is needed, or when cleaning is done as part of a manufacturing operation, the larger dip-tank style of cold cleaner, shown in Figure 10-3, is used. Although the number of these types of cold cleaners is much smaller, they tend to emit more solvent per cleaner because of their larger size and workload. Here, the parts are either placed in a basket or secured by a holder so they can be lowered into the solvent bath. To improve cleaning action, the solvent bath may be agitated by compressed air bubbles or ultrasonic vibration, or the parts themselves may be agitated. After the parts are removed from the bath, additional cleaning may be done by hand brushing and spraying. After the cleaning is completed, solvent that may be trapped in cavities is poured off and the parts are placed on a rack, usually internal, for 15 to 30 seconds or until they are dry.

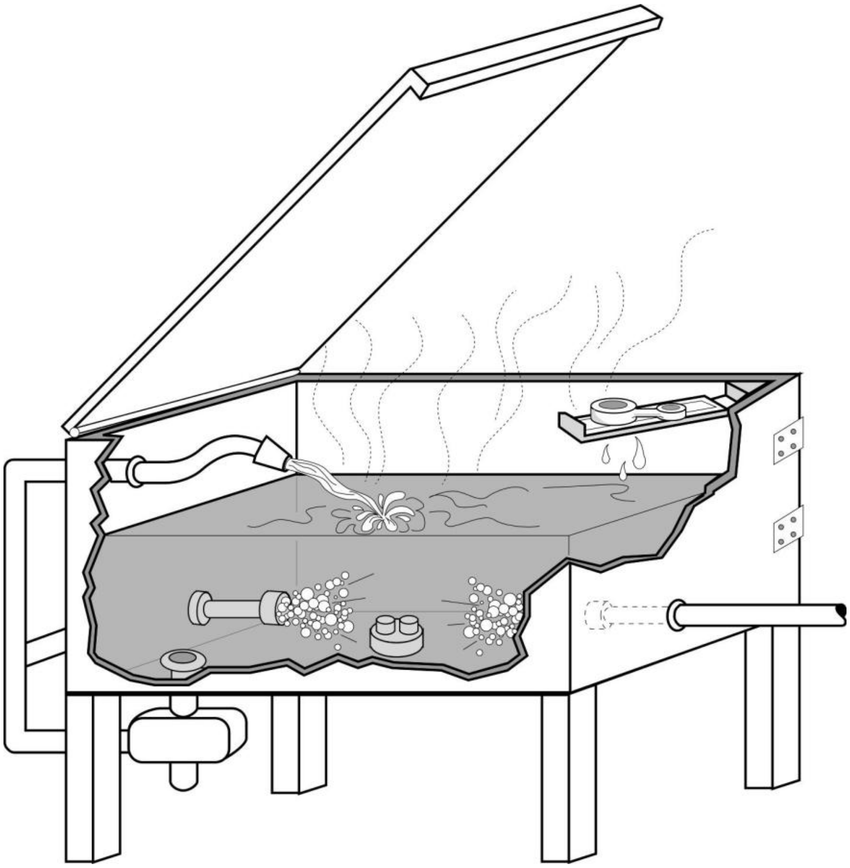

Figure 10-3. Cold cleaner

Aside from leaks, there are three potential sources of air emissions from cold cleaners: waste solvent disposal, solvent carryout and bath evaporation. If not done properly, waste solvent disposal is by far the greatest of these. However, if the waste solvent is conveyed to a responsible waste handler or if it is distilled on-site in an environmentally responsible manner, this source is minimal. The next greatest potential source of air emissions is solvent carryout. Removing parts from the cleaner that have trapped solvent or are not yet dry can result in significant losses to the atmosphere. However, the use of non-porous holders, pouring off trapped solvent, and allowing the parts to dry before they are removed from the cleaner result in minimal emissions.

Assuming the two other potential sources are properly handled, the greatest actual source of emissions from cold cleaners is bath evaporation. Obviously, bath evaporation is greatest when the cover on the cleaner is open. Bath emissions also increase when air currents across the open tank are high and when agitation is employed. Interestingly, agitation of low volatility solvents causes a greater increase in emissions than agitation of high volatility solvents. The losses from high volatility solvents are already so great that agitation does not increase them as much. Bath losses also increase when spraying is done above the tank top and when high-pressure, fine-atomizing nozzles are used. Methods for reducing these emissions will be discussed in the following section on emission control techniques.

10.1.2 Open Top Vapor Cleaners

Open top vapor cleaners are used primarily in metalworking and other manufacturing operations. The basic cleaner, shown in Figure 10-4, is a tank equipped with a heating system to boil the liquid solvent. As the solvent boils, dense vapors rise to the level of the primary condensing coils. Coolant, usually chilled water, is circulated through the coils in order to condense the rising solvent vapors and create a controlled vapor zone that reduces losses from the tank. In addition, there may be a coolant jacket around the outside of the tank at the level of the primary condensing coils. The walls of the tank are heated by conduction from the boiling solvent. Vapor near the walls is warmed by convection and, being less dense, tends to flow up the walls and out of the tank. The coolant jacket is used to cool the tank wall in order to reduce this loss.

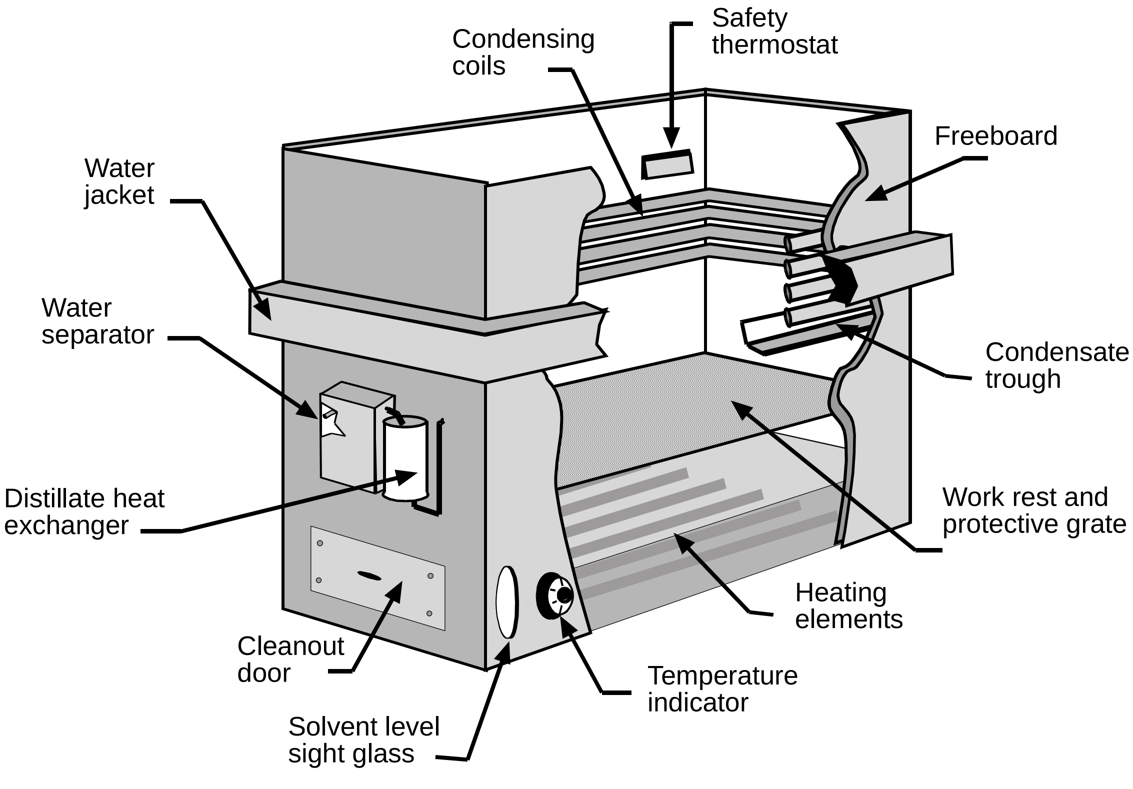

Figure 10-4. Open top vapor cleaner

Condensate from the primary coils is a mixture of halogenated solvent and water. This mixture forms a low boiling azeotrope, which, if returned directly to the boiling chamber, would result in increased emissions. Consequently, condensate from the primary coils is captured and directed to a water separator. The water separator is simply a container in which the water phase separates from the solvent phase because of differences in density. The less dense water is removed from the top of the separator and sent to disposal, and the solvent is returned to the cleaner. Some machines use a canister of dessicant, such as a molecular sieve, to further reduce water contamination or to replace the water separator.

In vapor cleaning, the parts are either placed in a basket or secured by a holder and then lowered into the solvent vapor. Condensing solvent dissolves some contaminants and flushes both dissolved and undissolved soils from the parts. Where more intense cleaning is desired, the parts may be first immersed in the solvent, then cleaned in the vapor zone, and finally sprayed with solvent. After the cleaning is completed, solvent that may be trapped in cavities is poured off and the parts are allowed to dry inside the unit before being removed.

As with cold cleaners, the three potential sources of air emissions from open top vapor cleaners are waste solvent disposal, solvent carryout and bath losses. If the waste solvent is properly handled, non-porous holders are used, and the parts allowed to dry before being removed from the cleaner, the first two potential sources again become minimal, leaving bath losses as the most significant actual source. Bath emissions increase when air currents across the open tank are high, when spraying is done above the vapor zone, and when high-pressure, fine-atomizing nozzles are used.

Bath losses are also influenced by the size and mass of the parts being cleaned and by the rate at which they are introduced and withdrawn from the vapor zone. Parts with a cross-sectional area greater than about half the cross-sectional area of the tank create a piston effect that tends to push vapor out of the tank. Likewise, rapid introduction and removal of parts increases emissions by pushing or dragging vapor out of the tank. Massive parts may draw so much heat out of the vapor zone that it collapses. As the vapor zone rebuilds, any solvent vapor that is above the zone will be pushed out of the cleaner. Methods for reducing these emissions will be discussed in the following section on emission control techniques.

10.1.3 In-Line Cleaners

In-line, or conveyorized, cleaners operate on a continuous basis and are most often found in plants where there is a constant stream of parts to be cleaned. Except for entrance and exit openings, the cleaners are nearly always totally enclosed to help control solvent losses from the system. Although in-line units can operate as either cold or vapor cleaners, the majority of in-line machines using halogenated solvent are vapor cleaners. The same cleaning techniques are used, but typically on a larger scale than with batch units.

The three most common types of in-line cleaners are cross-rod, monorail and mesh belt. The cross-rod cleaner, shown in Figure 10-5, gets its name from the rods from which parts containers are suspended as they are conveyed through the machine. Parts are contained in pendant baskets or in perforated or wire mesh cylinders that may be rotated within the liquid solvent and/or vapor zone. This type of equipment is well suited to handling small parts that need to be immersed in solvent for satisfactory cleaning or that require tumbling to drain solvent from cavities.

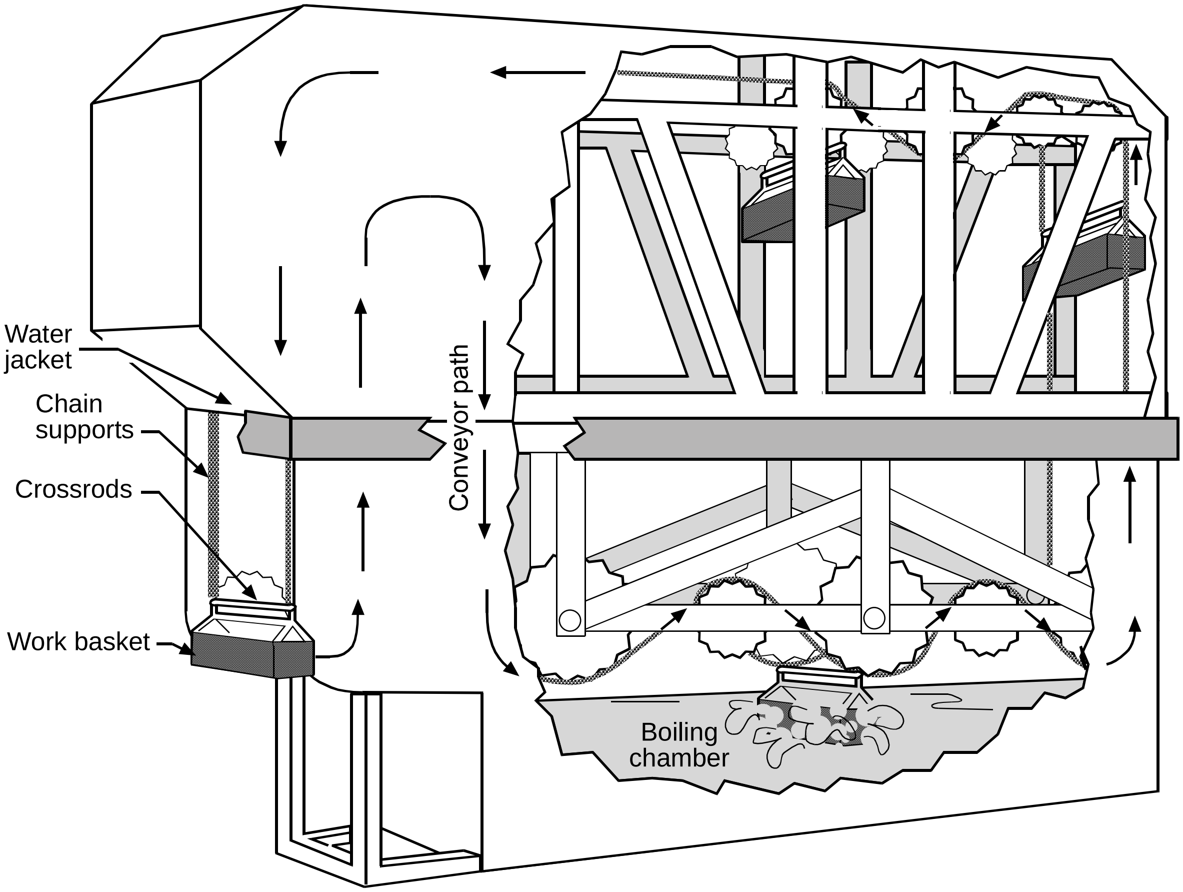

Figure 10-5. Cross-rod in-line cleaner

The monorail cleaner, shown in Figure 10-6, is usually chosen when parts are being conveyed between manufacturing operations on a monorail conveyor and is well suited to automatic cleaning with solvent spray and vapor. It may be of the straight-through design illustrated or may incorporate a U-turn within the machine so that parts exit through an opening parallel to the entrance. The U-turn monorail cleaner has lower vapor loss because the design eliminates the possibility of drafts through the machine.

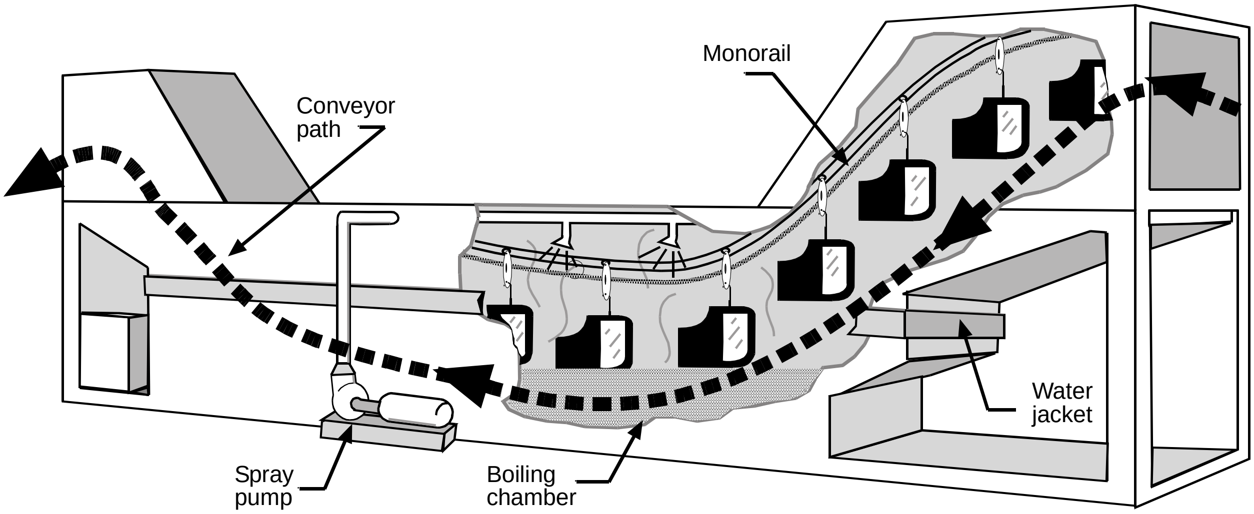

Figure 10-6. Monorail in-line cleaner

The mesh belt cleaner, shown in Figure 10-7, is designed to allow simple and rapid loading and unloading of parts. It conveys those parts through a long, narrow boiling chamber, cleaning them either by condensing vapor or by immersion in the solvent or by both. A related cleaner is the strip cleaner. The strip cleaner is similar to the belt cleaner except that the strip itself is the material being cleaned.

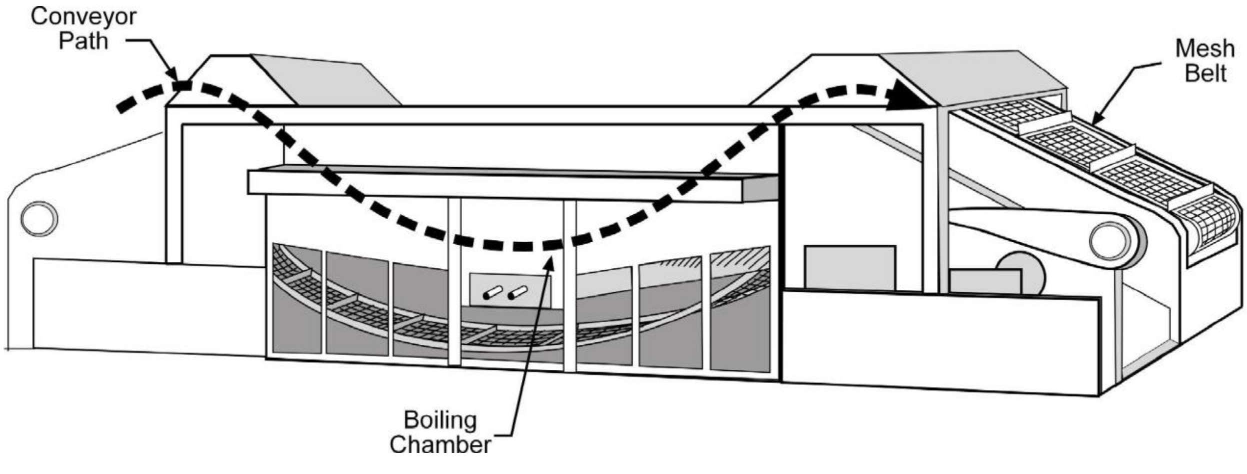

Figure 10-7. Mesh belt in-line cleaner

Production of printed circuit boards is a common application of the mesh belt cleaner. The circuit pattern is produced by projecting ultraviolet rays through an artwork film onto a copper sheet covered with resist, causing the exposed areas to harden. A developer, such as 1,1,1-trichloroethane, is used to dissolve the unexposed resist, and then an acid is used to remove the copper not covered by the hardened resist. Next, a stripping agent, such as methylene chloride, is used to remove the hardened resist, exposing the circuit pattern. Finally, molten solder is bonded to the copper circuit and a defluxer, often a CFC, is used to dissolve the solder flux. In many facilities, aqueous and semi-aqueous materials are being used to replace the organic developers, strippers and defluxers.

The sources of emissions for in-line cleaners and the parameters that influence them are the same as for the batch cleaners. Because in-line cleaners are automated, the losses are less on a per-part basis than for a manually operated cleaner. However, because of the larger volume of parts cleaned, overall emissions are typically higher. Idling losses would likely be lower, however, since the enclosed design makes the units less subject to drafts.

10.2 EMISSION CONTROL TECHNIQUES

Almost all of the emission control techniques that apply to organic solvent cleaners involve equipment design features and operating practices, usually applied in combination. The following sections briefly describe the various emission reduction techniques that can be applied to cold cleaners, open top vapor cleaners and in-line cleaners.

10.2.1 Cold Cleaners

Bath losses from cold cleaners are usually controlled by combinations of covers, increased freeboard ratio, reduced room drafts, refrigerated primary condensers, carbon adsorption, and selected operation and maintenance practices. These techniques are also employed in open top vapor cleaners and are discussed more fully below. If halogenated solvents are being used, effective emission reduction can be achieved by placing a layer of water over the solvent.

10.2.2 Open Top Vapor Cleaners

Bath losses from open top vapor cleaners are usually controlled by combinations of covers, refrigerated freeboard devices, refrigerated primary condensers, increased freeboard ratio, reduced room drafts, enclosed designs, mechanically assisted parts handling, carbon adsorbers and selected operation and maintenance practices.

10.2.2.1 Covers

Manual or powered covers are used to eliminate drafts within the freeboard area and thereby reduce evaporative losses. The freeboard area is that area between the top of the vapor zone and the top of the cleaner. Hinged covers are not recommended because opening and closing them can disturb the air-vapor interface. Preferred are roll-top or biparting covers that close horizontally. Biparting covers can be constructed to close around the cables holding parts baskets when the basket is inside the cleaner.

10.2.2.2 Refrigerated Freeboard Devices

Freeboard refrigeration devices consist of a second set of cooling coils located above the primary condenser. These secondary coils cool the air immediately above the vapor zone, creating a temperature inversion that reduces the mixing of air and solvent vapors. Above freezing units operate at a temperature of about 40°F, while below freezing units operate within a temperature range of -5°F to -25°F. Below freezing units are defrosted on a timed cycle to remove accumulated solvent-water ice.

10.2.2.3 Refrigerated Primary Condensers

Evaporative losses can be reduced by using a refrigerated primary condenser that operates at a temperature of 40°F to 50°F. In addition to condensing the solvent vapor, the colder primary condenser temperatures also cool the air above the vapor interface in a way similar to freeboard refrigeration devices.

10.2.2.4 Increased Freeboard Ratio

Higher freeboard zones reduce evaporative losses by diminishing the effects of air currents and by lengthening the distance the vapor must travel to escape the cleaner. Freeboard ratio is defined as the height of the cleaner above the vapor zone (above the liquid level, for cold cleaners) divided by the interior width (the smaller of the plan dimensions) of the cleaner. As the cleaner width increases, its susceptibility to room drafts increases, unless the freeboard height is increased proportionally.

10.2.2.5 Reduced Room Draft

Air currents across the top of the cleaner affect the solvent emission rate by carrying away solvent vapors that have diffused into the freeboard area and by creating turbulence. Reducing room drafts to calm conditions can greatly reduce emission rates.

10.2.2.6 Enclosed Designs

Completely enclosing the cleaner, except for a single opening through which parts enter and exit, reduces losses by creating a still air environment within the machine that limits solvent evaporation. The opening for the parts may be in the side of the unit, above the freeboard, or in the top of the unit, with a sliding cover that closes once the parts are in the cleaner.

10.2.2.7 Mechanically Assisted Parts Handling

Rapid introduction and removal of parts increases emissions by pushing or dragging vapor out of the tank and by increasing turbulence at the air-vapor interface. A human operator is generally unable to move parts at or below the maximum speed required in many state and USEPA regulations. Use of a mechanically assisted parts handling system can reduce emissions by consistently moving parts in and out of the cleaner at appropriate rates.

10.2.2.8 Carbon Adsorption

Carbon adsorption is used in conjunction with a lip exhaust system. The lip exhaust draws in the solvent vapors evaporating from the bath and from cleaned parts and directs them through an activated carbon adsorber. The solvent vapors are removed from the gas stream and then recovered during the desorption cycle. These systems are most commonly used on large cleaners where the value of the recovered solvent helps to offset the high capital equipment costs.

10.2.2.9 Operation and Maintenance

Additional operation and maintenance practices that help reduce emissions include the following:

- If using a spray system, spray within the vapor zone at a downward angle. Use a low pressure, coarse-atomizing nozzle.
- On start-up, start the condenser coolant flow prior to starting the solvent sump heater. Reverse the process on shutdown.
- During downtime, operate a sump cooler to reduce solvent vapor pressure or pump the solvent to an airtight storage container.
- Allow sufficient parts drainage time above the vapor zone before removing parts from the cleaner.
- Repair visible leaks and replace or repair cracked gaskets, malfunctioning pumps, water separators, and steam traps promptly.
- Perform solvent transfer in a closed system using submerged fill piping.
- Utilize control safety switches, including vapor level control thermostat, sump thermostat, liquid solvent level control, spray pump control switch and secondary heater switch.

10.2.3 In-Line Cleaners

Bath losses from in-line cleaners are usually controlled by combinations of minimizing entrance and exit openings, refrigerated freeboard devices, drying tunnels, rotating baskets, carbon adsorbers, hot vapor recycle or superheated vapor, and selected operation and maintenance practices.

10.2.3.1 Minimizing Entrance and Exit Openings

A reduction in the area of entrance and exit openings reduces evaporative losses by minimizing air currents inside the machine. Machines that use U-turn designs virtually eliminate the problem of air currents, and monorail cleaners can utilize internal baffles to control the effect of airflow through the machine. When the cleaner is not in use, covers should be used to reduce downtime emissions.

10.2.3.2 Refrigerated Freeboard Devices

The refrigerated freeboard device on an in-line vapor cleaner functions in the same manner as one on an open top vapor cleaner.

10.2.3.3 Drying Tunnels

A drying tunnel is an enclosure that extends the exit area of the cleaner. The tunnel allows solvent from cleaned parts to evaporate in an enclosed area where it can be recovered back into the cleaner or into a carbon adsorption system.

10.2.3.4 Rotating Baskets

A rotating basket is a perforated cylinder containing parts to be cleaned that slowly rotates during the cleaning process. The rotation prevents trapping of solvent on the parts, reducing carryout emissions.

10.2.3.5 Carbon Adsorbers

Carbon adsorption is a major emission control technology for in-line cleaners. The enclosure around in-line cleaners makes it easier to capture and direct emissions to a control device.

10.2.3.6 Hot Vapor Recycle or Superheated Vapor

Hot vapor recycle and superheated vapor are technologies that reduce solvent carryout emissions. In both systems, cleaned parts are warmed and solvent evaporated by passing them through a superheated solvent vapor zone within the vapor layer before they are removed from the cleaner. The vapor recycle process continuously recirculates solvent vapor from the vapor zone through a heater and back to the vapor zone, while the superheated vapor process utilizes heating coils in the vapor zone. Hot vapor recycle is applicable to in-line cleaners because an enclosure is needed for effective recirculation of the vapors. Superheated vapor technology can be applied to both in-line and open top vapor cleaners.

10.2.3.7 Operation and Maintenance

The operation and maintenance practices described for open top vapor cleaners also apply to in-line cleaners.

10.3 EMISSION REGULATION

At the time of writing, USEPA had issued RACT recommendations for degreasers that use both halogenated and non-halogenated solvents and MACT requirements for degreasers that use halogenated solvents. These recommended and required standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Solvent Metal Cleaning, Control Technique Guideline Document, EPA-450/2-77-022

Recommended standard:

RACT guidelines for degreasers are divided into two levels of control. Control System A consists of operating practices and simple, inexpensive control equipment. Control System B consists of System A plus additional requirements to improve control effectiveness. Facilities emitting less than 100 tons per year are expected to apply System A. Facilities emitting more than 100 tons per year or that are located in urban non-attainment areas greater than 200,000 population are expected to apply System B.

<u>For cold cleaners</u>

System A:

- Cover
- Facility for draining cleaned parts
- Label summarizing operating requirements
    a. Proper disposal of waste solvent
    b. Close degreaser when not handling parts
    c. Drain cleaned parts for 15 seconds or until dripping stops

System B:

- Cover (must be able to operate with one hand if solvent vapor pressure is greater than 0.3 psi at 100°F or solvent is agitated)
- Facility for draining cleaned parts (must be internal if solvent vapor pressure is greater than 0.6 psi at 100°F)
- Solid spray at pressure minimizing splashing
- Major control device (if solvent vapor pressure is greater than 0.6 psi at 100°F or solvent temperature is over 120°F)
    a. Freeboard ratio greater than 0.7
    b. Water cover
    c. Other equivalent control (refrigerated chiller, adsorber)

<u>For open top vapor cleaners</u>

System A:

- Cover, closed except when processing
- Minimize solvent carryout
    a. Rack parts for drainage
    b. Move parts in and out at less than 11 ft/min
    c. Degrease for 30 seconds or until condensation stops
    d. Tip out pools of solvent
    e. Dry parts within degreaser for 15 seconds or until visually dry
- No porous or absorbent materials
- Work load not over half of open top area
- Vapor level drop should be less than 4 inches when parts enter
- Never spray above vapor level
- Repair leaks immediately
- Dispose of waste solvent properly
- Exhaust ventilation less than 65 cfm/ft^2
- No water in solvent exiting separator

System B:

- Powered cover if degreaser opening is greater than 10 ft^2
- Safety switches
    a. Condenser flow switch and thermostat (shuts off sump heat if condenser coolant is not circulating or is too warm)
    b. Spray safety switch (shuts off spray pump if the vapor level drops excessively)
- Major control device
    a. Freeboard ratio greater than 0.75
    b. Refrigerated chiller
    c. Enclosed design
    d. Carbon adsorption system or equivalent, with ventilation less than 50 cfm/ft^2 and exhausting less than 25 ppm
- Label summarizing operating procedures

<u>For in-line cleaners</u>

System A:

- Exhaust ventilation less than 65 cfm/ft^2
- Minimize solvent carryout
    a. Rack parts for drainage
    b. Move parts in and out at less than 11 ft/min

- Dispose of waste solvent properly
- Repair leaks immediately
- No water in solvent exiting separator

System B:

- Major control device
    - a. Refrigerated chiller
    - b. Carbon adsorption system or equivalent, with ventilation less than 50 cfm/ft^2 and exhausting less than 25 ppm
- Drying tunnel or other means to prevent solvent carryout
- Safety switches
    - a. Condenser flow switch and thermostat (shuts off sump heat if condenser coolant is not circulating or is too warm)
    - b. Spray safety switch (shuts off spray pump or conveyor if the vapor level drops excessively)
    - c. Vapor level control thermostat (shuts off sump heat if vapor level rises too high)
- Minimize entrance and exit openings
- Down-time covers that are installed immediately after shutdown and removed just before start-up

Open top vapor degreasers with an area less than 10.76 ft^2 and in-line cleaners with an air-vapor interface less than 21.53 ft^2 should be exempted from the requirement of a major control device. Exemptions should also be approved for facilities located in rural non-attainment areas that emit less than 100 tons per year.

National Emission Standards for Halogenated Solvent Cleaning, 40 CFR 63, Subpart T

Applicability:

Batch vapor, in-line vapor, in-line cold and batch cold cleaning machines that contain methylene chloride, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride or chloroform or any combination thereof in a total concentration greater than 5 percent by weight.

Standard:

For batch cold cleaning machines:

- Employ a tight fitting cover and a water layer at least 1 inch thick; or employ a tight fitting cover and a freeboard ratio of 0.75 or greater.
- Collect and store waste solvent in closed containers.
- Spray only within the freeboard area.

- Drain parts for 15 seconds or until dripping stops. Tip or rotate parts having cavities.
- Solvent level shall not exceed the fill line.
- Use agitation that produces a rolling action with no observable splashing.
- Do not expose machine to drafts greater than 132 fpm when the cover is open.
- Wipe up spills immediately.

For batch vapor and in-line cleaning machines:

- Employ an idling and downtime mode cover or a reduced room draft (50 fpm).
- Have a freeboard ratio of 0.75 or greater.
- Use automated system to move parts in and out at 11 fpm or less.
- Employ device that shuts off sump heat if solvent level drops to the heater coils.
- Employ device that shuts off sump heat if vapor level rises above primary condenser.
- Employ a primary condenser.
- Spray within the vapor zone.
- Parts shall not occupy more than half of the machine cross-sectional area unless they are introduced at 3 fpm or less.
- Orient parts so that solvent drains freely. Do not remove from machine until dripping stops.
- Employ one of the control combinations listed in Tables 10-1 through 10-4 or demonstrate idling emissions less than 0.045 pounds per hour per square foot for a batch vapor machine or less than 0.020 pounds per hour per square foot for an in-line machine.

Table 10-1.
Control Combinations for Batch Vapor Machines Less Than 13 ft^2 in Area

Option	Control Combination
1	Working-mode cover, freeboard ratio of 1.0, superheated vapor
2	Freeboard refrigeration device, superheated vapor
3	Working-mode cover, freeboard refrigeration device
4	Reduced room draft, freeboard ratio of 1.0, superheated vapor
5	Freeboard refrigeration device, reduced room draft
6	Freeboard refrigeration device, freeboard ratio of 1.0
7	Freeboard refrigeration device, dwell*
8	Reduced room draft, dwell, freeboard ratio of 1.0
9	Freeboard refrigeration device, carbon adsorber
10	Freeboard ratio of 1.0, superheated vapor, carbon adsorber

*Dwell is holding parts in the freeboard area above the vapor zone for drainage. Dwell time is calculated as 35% of the time required for parts in the vapor zone to stop dripping.

Table 10-2.
Control Combinations for Batch Vapor Machines Greater Than 13 ft^2 in Area

Option	Control Combination
1	Freeboard refrigeration device, freeboard ratio of 1.0, superheated vapor
2	Dwell, freeboard refrigeration device, reduced room draft
3	Working-mode cover, freeboard refrigeration device, superheated vapor
4	Freeboard ratio of 1.0, reduced room draft, superheated vapor
5	Freeboard refrigeration device, reduced room draft, superheated vapor
6	Freeboard refrigeration device, reduced room draft, freeboard ratio of 1.0
7	Freeboard refrigeration device, superheated vapor, carbon adsorber

Table 10-3.
Control Combinations for Existing In-Line Machines

Option	Control Combination
1	Superheated vapor, freeboard ratio of 1.0
2	Freeboard refrigeration device, freeboard ratio of 1.0
3	Dwell, freeboard refrigeration device
4	Dwell, carbon adsorber

Table 10-4.
Control Combinations for New In-Line Machines

Option	Control Combination
1	Superheated vapor, freeboard refrigeration device
2	Freeboard refrigeration device, carbon adsorber
3	Superheated vapor, carbon adsorber

10.4 PROCESS INSPECTION

There should be two goals in any field inspection. First is to evaluate the source's compliance with any rule-specific monitoring and recordkeeping requirements and with the provisions of the Title V permit. In addition, changes in operating conditions or parameters that could result in increased emissions should be evaluated. In degreasing systems, increased emissions usually result from failure to follow proper operating procedures, equipment failures, improper waste solvent disposal, and leaks. Recommended general inspection items include the following:

- ***Review records maintained by the source.*** Three types of data should be reviewed: design information, operational information and maintenance information. The design data should be evaluated to determine compliance with RACT or MACT requirements. This would include such items as degreaser dimensions, solvent type, cover design, type of drainage facility, types of safety switches, hoist design speed, conveyor design speed, exhaust ventilation rate, and types of add-on control equipment. Operational information should be compared to the operating permit and to the provisions of the RACT or MACT regulations. These parameters would include solvent use, operating frequency, quantity and types of parts being cleaned, and the use of bath and downtime covers. Maintenance information should include repair or replacement records, calibration records for temperature sensors, and general observations regarding the condition of the equipment.
- ***Check equipment operation.*** Observe the condition and integrity of the operating equipment. Check to determine if all the equipment items called for in the permit and regulations are present and in good operating condition. If possible, compare the solvent temperature, coolant temperature and flow rate, hoist speed, conveyor speed, and actual ventilation rates with the regulatory requirements and the baseline values.
- ***Observe operating procedures.*** Check the procedures being followed to be sure that actual practice conforms to the regulatory requirements.
- ***Observe work area.*** Check for ventilation ducts, floor fans, and airflow baffles around the degreaser that may affect the solvent evaporation rate.

- ***Check for liquid leaks.*** Look for drips and puddles around the degreaser tank and around hose and pipe connections and fittings, valves, pumps, storage containers, water separators, and distillation units.
- ***Review waste solvent disposal procedures.*** Determine that acceptable methods are being followed for the disposal of the waste solvent.

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Review Questions

1. What are the three basic types of degreasing equipment?
    a. Cross-rod, monorail and mesh belt cleaners
    b. Cold, open top vapor and in-line cleaners
    c. Carburetor, spray sink and cold cleaners

2. What type of solvent is typically used in cold cleaners?
    a. Halogenated solvents
    b. Aqueous solvents
    c. Petroleum solvents

3. What type of solvent is typically used in vapor cleaners?
    a. Halogenated solvents
    b. Aqueous solvents
    c. Petroleum solvents

4. What type of cold cleaner typically uses halogenated solvent?
    a. Spray sink
    b. Carburetor cleaner
    c. Monorail cleaner

5. What is the greatest potential source of emissions from degreasing operations?
    a. Waste solvent disposal
    b. Solvent carryout
    c. Bath losses

6. What is usually the greatest actual source of emissions from degreasing operations?
    a. Waste solvent disposal
    b. Solvent carryout
    c. Bath losses

7. Which of the following increase emissions from cold cleaners? Select all that apply.
    a. Covers
    b. High air currents
    c. Solvent agitation
    d. High pressure sprays

8. Which of the following decrease emissions from cold cleaners? Select all that apply.
    a. Covers
    b. Reduced air currents
    c. Reduced freeboard
    d. Low pressure sprays

9. Which of the following increase emissions from vapor cleaners? Select all that apply.
    a. Rapid introduction of parts
    b. Reduced air currents
    c. Large, massive parts
    d. Spraying within vapor zone

10. Which of the following decrease emissions from vapor cleaners? Select all that apply.
    a. Reduced room currents
    b. Increased freeboard
    c. Refrigerated freeboard devices
    d. Covers

11. Which of the following decrease emissions from in-line vapor cleaners. Select all that apply.
    a. Minimizing entrance and exit openings
    b. Refrigerated freeboard devices
    c. Drying tunnels
    d. Water cover

12. What is freeboard ratio in a vapor cleaner?
    a. Height of the cleaner above the liquid level divided by the interior width
    b. Height of the cleaner above the vapor level divided by the interior width
    c. Height of the cleaner above the vapor level divided by the interior length
    d. Interior length of the cleaner divided by the interior height

13. What is freeboard ratio in a cold cleaner?
    a. Height of the cleaner above the liquid level divided by the interior width
    b. Height of the cleaner above the vapor level divided by the interior width
    c. Height of the cleaner above the vapor level divided by the interior length
    d. Interior length of the cleaner divided by the interior height

14. How does superheated vapor reduce emissions from vapor cleaners?
    a. Increases vapor density
    b. Reduces solvent carryout
    c. Captures spray droplets

15. What is the most common add-on control device for vapor degreasers?
    a. Wet scrubber
    b. Thermal incinerator
    c. Catalytic incinerator
    d. Carbon adsorber

16. What types of recommended and required standards has USEPA issued for degreasers using petroleum solvents? Select all that apply.

a. RACT recommendations
b. NSPS requirements
c. MACT requirements

17. What types of recommended and required standards has USEPA issued for degreasers using halogenated solvents? Select all that apply.

a. RACT recommendations
b. NSPS requirements
c. MACT requirements

18. Which of the following should be included in a general inspection of a degreasing facility?

a. Review records
b. Observe operating procedures
c. Check for liquid leaks
d. All of the above

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Review Answers

1. What are the three basic types of degreasing equipment?
   b. Cold, open top vapor and in-line cleaners

2. What type of solvents are typically used in cold cleaners?
   c. Petroleum solvents

3. What type of solvents are typically used in vapor cleaners?
   a. Halogenated solvents

4. What type of cold cleaner typically uses halogenated solvent?
   b. Carburetor cleaner

5. What is the greatest potential source of emissions from degreasing operations?
   a. Waste solvent disposal

6. What is usually the greatest actual source of emissions from degreasing operations?
   c. Bath losses

7. Which of the following increase emissions from cold cleaners? Select all that apply.
   b. High air currents
   c. Solvent agitation
   d. High pressure sprays

8. Which of the following decrease emissions from cold cleaners? Select all that apply.
   a. Covers
   b. Reduced air currents
   d. Low pressure sprays

9. Which of the following increase emissions from vapor cleaners? Select all that apply.
   a. Rapid introduction of parts
   c. Large, massive parts

10. Which of the following decrease emissions from vapor cleaners? Select all that apply.
   a. Reduced room currents
   b. Increased freeboard
   c. Refrigerated freeboard devices
   d. Covers

11. Which of the following decrease emissions from in-line vapor cleaners. Select all that apply.

a. Minimizing entrance and exit openings
b. Refrigerated freeboard devices
c. Drying tunnels

12. What is freeboard ratio in a vapor cleaner?

b. Height of the cleaner above the vapor level divided by the interior width

13. What is freeboard ratio in a cold cleaner?

a. Height of the cleaner above the liquid level divided by the interior width

14. How does superheated vapor reduce emissions from vapor cleaners?

b. Reduces solvent carryout

15. What is the most common add-on control device for vapor degreasers?

d. Carbon adsorber

16. What types of recommended and required standards has USEPA issued for degreasers using petroleum solvents? Select all that apply.

a. RACT recommendations

17. What types of recommended and required standards has USEPA issued for degreasers using halogenated solvents? Select all that apply.

a. RACT recommendations
c. MACT requirements

18. Which of the following should be included in a general inspection of a degreasing facility?

d. All of the above

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Allen, R.D., Inspection Source Test Manual for Solvent Metal Cleaning (Degreasers), EPA 340/1-79-008, June 1979.

Turner, M.B. and R.V. Crume, "Evaporative Loss Sources: Organic Solvent Cleaning (Degreasing)", Air Pollution Engineering Manual, Chapter 9, A.J. Buonicore and W.T. Davie, eds., Van Nostrand Reinhold, New York, 1992.

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11 Dry Cleaning

Dry cleaning is the process of cleaning fabrics by washing them in a non-aqueous solvent. Like aqueous cleaning, this process is performed in three steps. The first step, *washing*, is done by agitating the items to be cleaned in a solvent bath. In the next step, *extraction*, excess solvent is removed in a spin cycle by using centrifugal force. The third step, *drying*, is conducted by tumbling the items in a warm air stream in order to vaporize and remove the solvent.

There are two solvents in common use by the dry cleaning industry. The most common solvent is perchloroethylene, which is used by about 75% to 80% of dry cleaning facilities. Next in importance are the petroleum solvents, which represent about 20% to 25% of solvent usage. These include Stoddard solvent, 140-F solvent, odorless solvent and low-end-point solvent. The most common of these is Stoddard solvent. 140-F solvent has a higher flash point than Stoddard solvent, which makes it safer to use but slower to dry. Low-end-point solvent has a lower flash point than Stoddard solvent in order to reduce the time and energy needed for drying. Odorless solvent is Stoddard solvent that has been formulated to have minimum odor. The percentage distribution of solvent use has likely changed in recent years because of Title III regulations.

The dry cleaning industry can be divided into three types of facilities: commercial, industrial and coin operated. The most common type is the commercial dry cleaner, which offers dry cleaning services to the general public. Industrial dry cleaners are the largest facilities and are usually operated in conjunction with a service that rents uniforms and other items to commercial, industrial or institutional clients. Coin operated facilities are used directly by the consumer.

The steps involved in the dry cleaning process may be conducted in one, two or three machines. Processes that use more than one piece of equipment to complete the steps are called *transfer processes*. When older equipment or petroleum solvents are used, washing and extraction are performed in one machine and the items are transferred to a second machine for drying. In some older industrial dry cleaners that use petroleum solvents, separate machines are used for each step. When one machine is used for all three steps, it is called a *dry-to-dry process*. Coin operated facilities typically use the dry-to-dry process, as do newer facilities that use non-petroleum solvents.

11.1 PROCESS DESCRIPTION

A number of equipment items are used in the dry cleaning process, in addition to those employed for washing, extraction and drying. These include tanks and pumps for holding and recirculating the solvent, solvent filters, distillation units with condensers and separators to clean and collect the used solvent, and muck cookers to reclaim solvent from the filtered solids. Other equipment includes boilers, steam coils, fans and ducts for generating and moving the warm air used for drying, lint filters, and condensers and separators to recover the solvent removed during drying. In addition to this processing equipment, facilities usually employ some type of air pollution control equipment to prevent the release of vapors to the atmosphere.

11.1.1 Washing and Extraction

A schematic of the washing cycle of the dry cleaning process is shown in Figure 11-1. Although dry cleaning is essentially the laundering of items in a non-aqueous solvent, it is necessary to add a small amount of detergent to the solvent to improve cleaning. Primarily, the detergent is used to carry small amounts of water in the solvent to the fabric for removal of water-soluble soils. Because moisture enters with the fabrics, it is not usually necessary to add water.

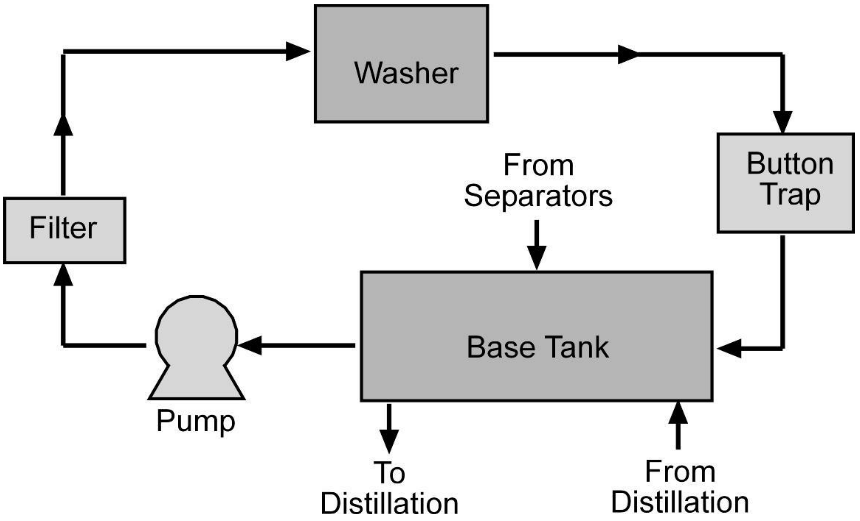

Figure 11-1. Diagram of the washing process

The primary part of a washer is the perforated cylinder into which the fabrics to be cleaned are placed. This cylinder rotates inside a liquid- and vapor-tight enclosure to prevent the escape of the solvent or its vapors. The fabrics are tumbled for 15 to 40 minutes, depending on their weight, the tightness of their weave and the degree of soiling. In the more common bath process, the solvent is continuously circulated through the cylinder, through the button trap and into the base tank, where it is recirculated through the filter and back into the cylinder. Variations on this procedure include the batch process, in which the same solvent remains in the cylinder throughout the washing cycle, and the batch-bath process. In the batch-bath process, the fabrics are first tumbled in a batch of solvent that is not circulated. This solvent is then pumped to the distillation unit and the washer refilled with solvent from the base tank. This solvent is circulated during the final portion of the washing cycle.

At the completion of the washing cycle, the solvent is drained from the cylinder, through the button trap and into the base tank. In machines that wash and extract in the same unit, the cylinder rotational speed is increased to about 10 times that used during washing. The excess solvent is removed from the fabrics by centrifugal force and is drained through the button trap and into the base tank. In a small number of older facilities, the wet fabrics are transferred to a separate unit for extraction. The recovered solvent again drains through the button trap and into the base tank.

Direct release of solvent vapors during the washing and extraction steps only occurs at facilities that transfer the damp fabrics from the washer/extractor to the dryer or from the washer to the extractor to the dryer. To reduce this loss, air is pulled through the cylinder as the door is opened and sent to the air pollution control device before being discharged to the atmosphere. Fugitive emissions from both transfer and dry-to-dry processes can occur from fittings and seals around the cylinder door, button trap, base tank, recirculating pump and filter housing.

11.1.2 Drying

The next step in the dry cleaning process is drying the fabrics that have been washed and extracted. This step, whether done in a separate unit or as part of a dry-to-dry process, usually involves recovery of the evaporated solvent from a heated, recirculated air stream, followed by aeration and cool-down with once-through ambient air. It is this last portion of the drying cycle that results in a direct release of solvent vapors from the dryer. In some older dryers that are used to remove petroleum solvents, heated outside air is drawn through the cylinder and exhausted to the atmosphere without recovery. This is done because of the explosivity of petroleum solvents and because, at the time the units were designed, the solvents were not expensive. In this section, only recovery-type or reclaimer dryers will be discussed.

A schematic of the drying cycle of the dry cleaning process is shown in Figure 11-2. At facilities that use perchloroethylene as the cleaning solvent, recirculated air is heated to about 180°F to 190°F by passing it over steam or electric heating coils. The heated air stream passes through the rotating cylinder to evaporate solvent and moisture in the fabric and exits the dryer at about 120°F to 140°F. It is this exit temperature that is used to control the inlet temperature to the dryer. The exiting air stream passes through a lint filter and then enters a water- or refrigerant-cooled condenser that reduces the temperature to about 85°F to 90°F, causing the moisture and solvent in the air stream to condense. The condensate flows to a separator. Perchloroethylene is heavier than water and will not mix with it. The recovered solvent is drained from the bottom of the separator and returned to the base tank. The cooled air stream passes over the heating coils and begins another circuit. Average drying time is about 20 minutes, but this may vary depending on the weight and weave of the fabric.

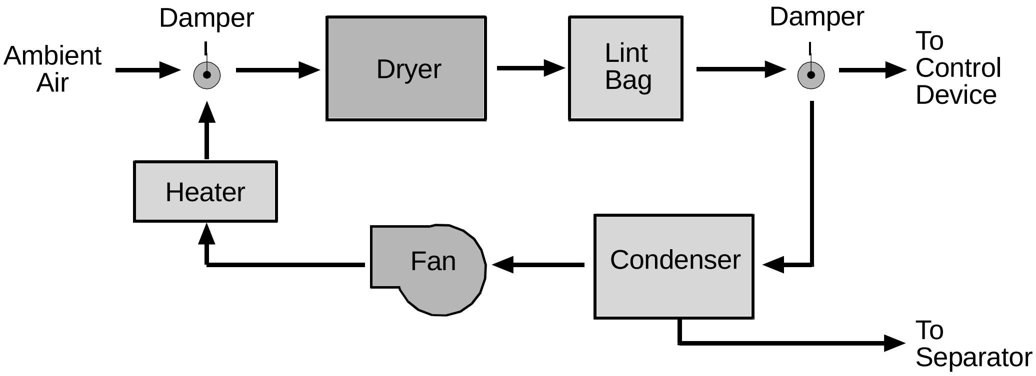

Figure 11-2. Diagram of the drying process.

When petroleum solvents are used, the drying cycle is similar to that employed with perchloroethylene. In order to prevent the formation of explosive concentrations of solvent vapors, the petroleum recovery dryer has a greater airflow than the perchloroethylene unit. Also, since petroleum solvents are less volatile, higher temperatures and longer cycle times are used. The air stream typically enters the dryer at about 212°F and exits at about 140°F to 150°F, and the drying cycle lasts between 15 and 50 minutes, depending on the weight and weave of the fabric. Finally, since petroleum solvents are lighter than water, they are removed from the top of the separator.

Recovery dryers have dampers on the inlet and outlet of the recirculation ductwork. Closed during drying, these dampers are opened during aeration and cool-down, after drying is completed. Aeration usually lasts about 5 minutes. When these dampers are opened, ambient air is pulled through the cylinder and exhausted from the dryer to an air pollution control device.

The amount of solvent vapors that could be released to the atmosphere during the drying cycle depends on the type of dryer being used. Dry-to-dry machines and recovery dryers used in transfer processes release solvent vapors only during aeration and cool-down or when the door is opened to remove the cleaned fabrics. Older non-recovery petroleum dryers release solvent vapors throughout drying, aeration and cool-down, as well as when the door is opened to remove the cleaned fabrics. The cleaned fabrics will continue to release small amounts of the dry cleaning solvent for extended periods.

11.1.3 Solvent Filtering

Filters are installed on all dry cleaning processes to remove suspended and dissolved materials from the solvent. The two types most commonly employed are powder filters and cartridge filters.

Powder filters are a commonly used older type of filter. They typically use diatomaceous earth deposited on a tubular or flat-plate element of cloth, woven metal fabric or metal screening. They may also use a pre-coat of activated carbon and/or activated clay. Activated carbon is added to remove color and activated clay is used to remove some non-volatile residues. The filtering material is removed and replaced when the accumulated contaminants cause the pressure drop across the filter to reach a predetermined level. The removed material, called *muck*, is cooked in the distillation unit to vaporize and recover the solvent for reuse. Solvent vapors are released during removal and replacement of the filter material and when the muck is processed to recover the solvent.

Cartridge filters are constructed of folded elements and are manufactured in three types: carbon core, all carbon and all paper. Cartridge filters eliminate the need for muck cooking, since the entire cartridge is disposed of when the pressure across the filter reaches the predetermined level. Also, since the cartridges are usually dried in place, the release of solvent vapors during filter changing is minimized.

11.1.4 Solvent Distillation

Distillation units are used to clean used solvents of dissolved oils, waxes and grease, solvent-soluble dyes and insoluble soils. Stills for perchloroethylene operate at atmospheric pressure and can be either batch or continuous units. Petroleum solvent stills operate under vacuum and are usually continuous units.

Distillation units have four basic parts: a boiling chamber, a condenser, a gravimetric separator and a moisture separator. Spent solvent enters the boiling chamber where steam coils volatilize the solvent and water, leaving the still residue. Still residue is composed of oils, grease and dirt and a small amount of solvent. The solvent and water vapors enter a water-cooled condenser and are condensed. The condensate is pumped to a gravimetric separator where the solvent and water are separated by differences in their density. The recovered solvent is then pumped to a tank containing rags or salt pellets that remove any remaining moisture.

Distillation of petroleum solvents typically takes place under a vacuum of 22 to 27 in. Hg, in order to lower the boiling point to 225°F to 235°F. Perchloroethylene solvents are distilled at atmospheric pressure with stills operated at 250°F.

All stills must be boiled-down on a periodic basis in order to remove accumulated material from the boiling chamber. During boil-down, the steam flow to the still is increased to the maximum rate and the still residues are allowed to boil for up to 30 minutes. Steam or air sweeping may be employed at the end of the boil-down operation to increase solvent recovery. The remaining still residues are removed and disposed of.

Releases of solvents occur during disposal of still residues and from the vacuum pump used on petroleum solvent stills. Releases can also occur during steam or air sweeping, if the sweeping rate is greater than the condenser can handle.

11.2 EMISSION CONTROL TECHNIQUES

Techniques for the control of solvent emissions from dry cleaning processes include add-on control devices, dry cleaning equipment design, and operating procedures. Also of importance for the control of fugitive emissions is proper maintenance of gaskets, seals, valves, and piping and ductwork connections.

11.2.1 Carbon Adsorption

Activated carbon adsorption can be used to control emissions from washer and dryer loading and unloading, from room floor vents, from the distillation unit and from the dryer aeration cycle. Efficiencies are generally greater than 95%.

11.2.2 Condensation

Refrigerated condensers provide a level of control comparable to carbon adsorption for washer and dryer loading and unloading, for the distillation unit and for the dryer aeration cycle. Floor vents are not usually vented to a refrigeration unit because of difficulties in maintaining sufficiently low temperatures with the larger amount of warm ambient air entering the system.

11.2.3 Azeotropic Vapor Recovery

Azeotropic vapor recovery units operate only during the aeration cycle and take advantage of the fact that, when water is combined with chlorinated solvents, the resulting mixture evaporates at a lower temperature than the pure solvent. A typical azeotropic recovery system is shown in Figure 11-3. When the dryer cycles to aeration, the air drawn from the dryer passes through the lint filter and condenser, and then to a water bubbler, where it is saturated with moisture. The saturated air stream is circulated back to the dryer, where it forms a low-boiling azeotrope with the solvent in the fabric. The cycle repeats itself until aeration is complete. There is no venting to the atmosphere when this type of recovery is employed.

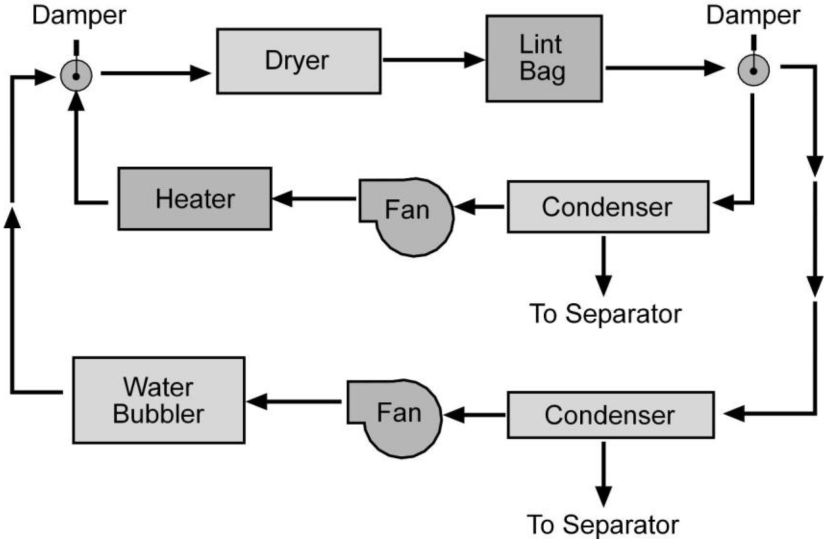

Figure 11-3. Diagram of the azeotropic drying process

11.2.4 Fugitive Emission Control

Fugitive emissions in the form of liquid or vapor losses result from poor maintenance or housekeeping. Liquid losses can be detected by sight; vapor losses, if significant, can be detected by smell. Sources of liquid leaks include machine door gaskets, hose connections, button traps, valves, filter gaskets, pump seals, base tanks, storage containers and distillation units. Vapor leaks can come from aeration damper seals, open lint filters and button traps, holes in ductwork, open storage containers and removal of articles that have not completely dried.

The most efficient way to reduce these emissions is an effective program of maintenance and training. Equipment operators and maintenance personnel should be taught to inspect and identify solvent liquid and vapor leaks and to repair these leaks immediately. Operators should also be trained to close containers of solvent when they are not being used and to keep washer and dryer doors closed whenever garments are not being loaded or unloaded.

11.3 EMISSION REGULATION

At the time of writing, USEPA had issued RACT recommendations for perchloroethylene and petroleum solvent dry cleaners, NSPS requirements for petroleum solvent dry cleaners and MACT requirements for perchloroethylene dry cleaners. These recommended and required standards are summarized below. The student is referred to the applicable document for additional information on testing methods and procedures and reporting and recordkeeping requirements.

Perchloroethylene Dry Cleaning Systems Control Technique Guideline Document, EPA-450/2-78-047

Recommended standard:

- Vent dryer exhaust through a carbon adsorber or equivalent device with an outlet concentration ≤100 ppmv (Coin operated dry cleaners are exempt.).
- Reduce filter residue to ≤25% perchloroethylene and still residue to ≤60% perchloroethylene.
- Drain filter cartridges for ≥24 hours or until dry before disposal.
- Immediately repair liquid and vapor leaks.

Large Petroleum Dry Cleaners Control Technique Guideline Document, EPA-450-3-82-009

Recommended standard:

- Use a solvent recovery dryer to reduce emissions by 81%.
- Use a cartridge filter.
- Improve operation of distillation unit.
- Repair liquid and vapor leaks within 3 working days.

Standards of Performance for Petroleum Dry Cleaners, 40CFR60, Subpart JJJ

Applicability Date: December 14, 1982

Applicability Size: ≥84 pound capacity

Standard:

- Use a solvent recovery dryer.
- Use a cartridge filter. Drain in sealed housing for at least 8 hours prior to removal.
- Inspect every 15 days and repair all vapor and liquid leaks within the subsequent 15 day period.

National Perchloroethylene Air Emission Standards for Dry Cleaning Facilities, 40 CFR 63, Subpart M

Applicability: Each dry cleaning facility that uses perchloroethylene, except coin-operated machines. An existing transfer plant that was installed before December 9, 1991, or a new plant that was installed between December 9, 1991, and September 22, 1993, is exempt from all but recordkeeping and maintenance requirements if it uses less than 200 gallons of perchloroethylene per year. An existing dry-to-dry plant, or a new plant that was installed between December 9, 1991, and September 22, 1993, is similarly exempted if it uses less than 140 gallons of perchloroethylene per year.

Standard:

<u>For existing systems</u>:

- Route gas stream within dry cleaning machine through a refrigerated condenser or equivalent control device or through a carbon adsorber installed prior to September 22, 1993.
- Contain transfer machines located at a major source in a room enclosure under negative pressure.

<u>For new systems</u>:

- Route gas stream within dry cleaning machine through a refrigerated condenser or equivalent control device.
- Eliminate emissions during transfer of articles between washer and dryer.
- If at a major source, route gas stream within dry cleaning machine through a carbon adsorber or equivalent device before or as the door is opened.

<u>For each refrigerated condenser on a dry-to-dry machine, dryer or reclaimer</u>:

- Shall not release gas stream within machine while machine drum is rotating.
- Shall have an outlet temperature less than 45°F.
- Shall have a diverter valve that prevents air drawn in when the door is open from passing through the refrigerated condenser.

<u>For each refrigerated condenser on a washer</u>:

- Shall not vent gas stream within machine until door opens.
- Shall have a temperature drop of at least 20°F.
- Shall not use the same condenser coil that is used by a dry-to-dry machine, dryer or reclaimer.

<u>For each carbon adsorber</u>:

- Shall not be bypassed.
- If used on an existing machine or on a new machine immediately upon door opening, outlet concentration at the end of the last cycle before regeneration must be equal to or less than 100 ppmv.
- If used on a new machine prior to door opening, the concentration inside the drum at the end of the cycle must be equal to or less than 300 ppmv.

<u>For each room enclosure</u>:

- Shall vent all air through a carbon adsorber or equivalent control device.
- Carbon adsorber can not be the same one used for the dry cleaning machine.

<u>Additional requirements</u>:

- Use a cartridge filter. Drain in sealed housing for at least 24 hours prior to removal.

- Inspect system weekly and repair leaks within 24 hours.

11.4 PROCESS INSPECTION

There should be two goals in any field inspection. The first is to evaluate the sources compliance with any rule-specific monitoring and recordkeeping requirements and with the provisions of the Title V permit. In addition, changes in operating conditions or parameters that could result in increased emissions should be evaluated. In dry cleaning systems, increased emissions usually result from increased solvent use, from liquid and vapor leaks, or from reduced performance of the air pollution control device. Recommended general inspection items include the following:

- ***Review records maintained by the source.*** These may include solvent purchases, the results of internal inspection audits, the results of monitoring checks, and the date and description of repairs.
- ***Check for vapor leaks.*** Observe the condition and integrity of the ductwork, fans and dampers. If possible, check suspect areas with a vapor detector.
- ***Check for liquid leaks.*** Look for drips and puddles around door gaskets, hose and pipe connections and fittings, valves, pumps, solvent tanks and storage containers, water separators, distillation units, and the filter housing.

The inspection of carbon adsorbers and condensers is covered in APTI Course 455, Inspection of Gas Control Devices and Selected Industries. The reader is referred to this course for guidance.

Review Questions

1. What is the most common dry cleaning solvent?
   a. 140-F solvent
   b. Perchloroethylene
   c. CFC-113
   d. Methylene chloride

2. What is the most common type of dry cleaning facility?
   a. Coin-operated
   b. Industrial
   c. Commercial

3. What are the steps involved in dry cleaning? Select all that apply.
   a. Steam purging
   b. Washing and extraction
   c. Fumigation
   d. Drying

4. Machines that are not unloaded until the dry cleaning process is complete are called _______?
   a. dry-to-dry
   b. azeotropic
   c. transfer

5. Other than leaks, when are solvent vapors emitted from a transfer washer/extractor? Select all that apply.
   a. During the tumble cycle
   b. During the extraction cycle
   c. When the door is opened
   d. When the recycler vents

6. Other than leaks, when are solvent vapors emitted from a vented dry-to-dry machine? Select all that apply.
   a. During the tumble cycle
   b. During the aeration cycle
   c. When the lint bag purges
   d. When the door is opened

7. What are the two most common solvent filters?
   a. Powder filters
   b. Osmosis filters
   c. Activated carbon filters
   d. Cartridge filters

8. Which type of solvent filter allows the least emissions to the atmosphere?
   a. Powder filters
   b. Osmosis filters
   c. Activated carbon filters
   d. Cartridge filters

9. What are the sources of emissions from solvent distillation?
   a. During disposal of still residues
   b. From the vacuum pump used with petroleum solvents
   c. During steam or air sweeping
   d. All of the above

10. What are the most common techniques used to control emissions of solvent vapors? Select all that apply.
   a. Refrigerated condenser
   b. Solvent absorber
   c. Carbon adsorber
   d. Catalytic incinerator

11. What types of recommended and required standards has USEPA issued for perchloroethylene dry cleaners? Select all that apply.
   a. RACT recommendations
   b. NSPS requirements
   c. MACT requirements

12. Which of the following should be included in a general inspection of a dry cleaning facility?
   a. Review records
   b. Check for vapor leaks
   c. Check for liquid leaks
   d. All of the above

Review Answers

1. What is the most common dry cleaning solvent?
   b. Perchloroethylene

2. What is the most common type of dry cleaning facility?
   c. Commercial

3. What are the steps involved in dry cleaning? Select all that apply.
   b. Washing and extraction
   d. Drying

4. Machines that are not unloaded until the dry cleaning process is complete are called _______?
   a. dry-to-dry

5. Other than leaks, when are solvent vapors emitted from a transfer washer/extractor? Select all that apply.
   c. When the door is opened

6. Other than leaks, when are solvent vapors emitted from a vented dry-to-dry machine? Select all that apply.
   b. During the aeration cycle
   d. When the door is opened

7. What are the two most common solvent filters?
   a. Powder filters
   d. Cartridge filters

8. Which type of solvent filter allows the least emissions to the atmosphere?
   d. Cartridge filters

9. What are the sources of emissions from solvent distillation?
   d. All of the above

10. What are the most common techniques used to control emissions of solvent vapors? Select all that apply.
    a. Refrigerated condenser
    c. Carbon adsorber

11. What types of recommended and required standards has USEPA issued for perchloroethylene dry cleaners? Select all that apply.
    a. RACT recommendations
    c. MACT requirements

12. Which of the following should be included in a general inspection of a dry cleaning facility?
    d. All of the above

References

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12 Liquid Asphalt

Asphalt cement is classified as a semi-solid at ambient temperature. However, it can be liquefied by heating it to 275°F to 325°F, by blending it with petroleum distillates or solvents, or by emulsifying it with water. These latter two methods of liquefying produce what are referred to, respectively, as *cutback asphalt* and *emulsified asphalt*. All types of liquefied asphalt are used to produce paving materials. In addition, cutback and emulsified asphalt may be used as prime coats over soil prior to laying the final surface, as a bonding layer between surfaces, as sealants or as a mulch treatment to control vegetation growth.

12.1 HOT MIX ASPHALT

Hot mix is the most durable of the asphalt paving materials and is produced by mixing aggregate with heated asphalt cement. In the traditional batch process, the aggregate is dried in a rotary dryer to reduce the surface moisture and to heat the stone so that the asphalt cement can coat it properly. The heated and dried aggregate is conveyed to the top of a mixing tower, as shown in Figure 12-1. Here, the aggregate is screened and segregated by size into several hot bins. The aggregate is discharged from the bins into a weigh hopper in the size proportions specified for the paving material. The proportioned aggregate is dumped into a pug mill, where it is mixed with about 5% by weight of heated asphalt cement. The hot mix asphalt is then loaded into trucks that pull directly underneath the pug mill.

Hot mix is also produced in drum mix plants, as shown in Figure 12-2. In this process, aggregate of various sizes is accurately metered from cold bins onto a conveyor leading to the dryer. The aggregate is heated and dried in the initial portions of the dryer. Heated asphalt cement is spayed onto the aggregate from an injection pipe that extends into the lower end of the dryer. The hot mix produced in the drum mixer is conveyed to a heated storage silo and loaded into trucks that pull underneath it.

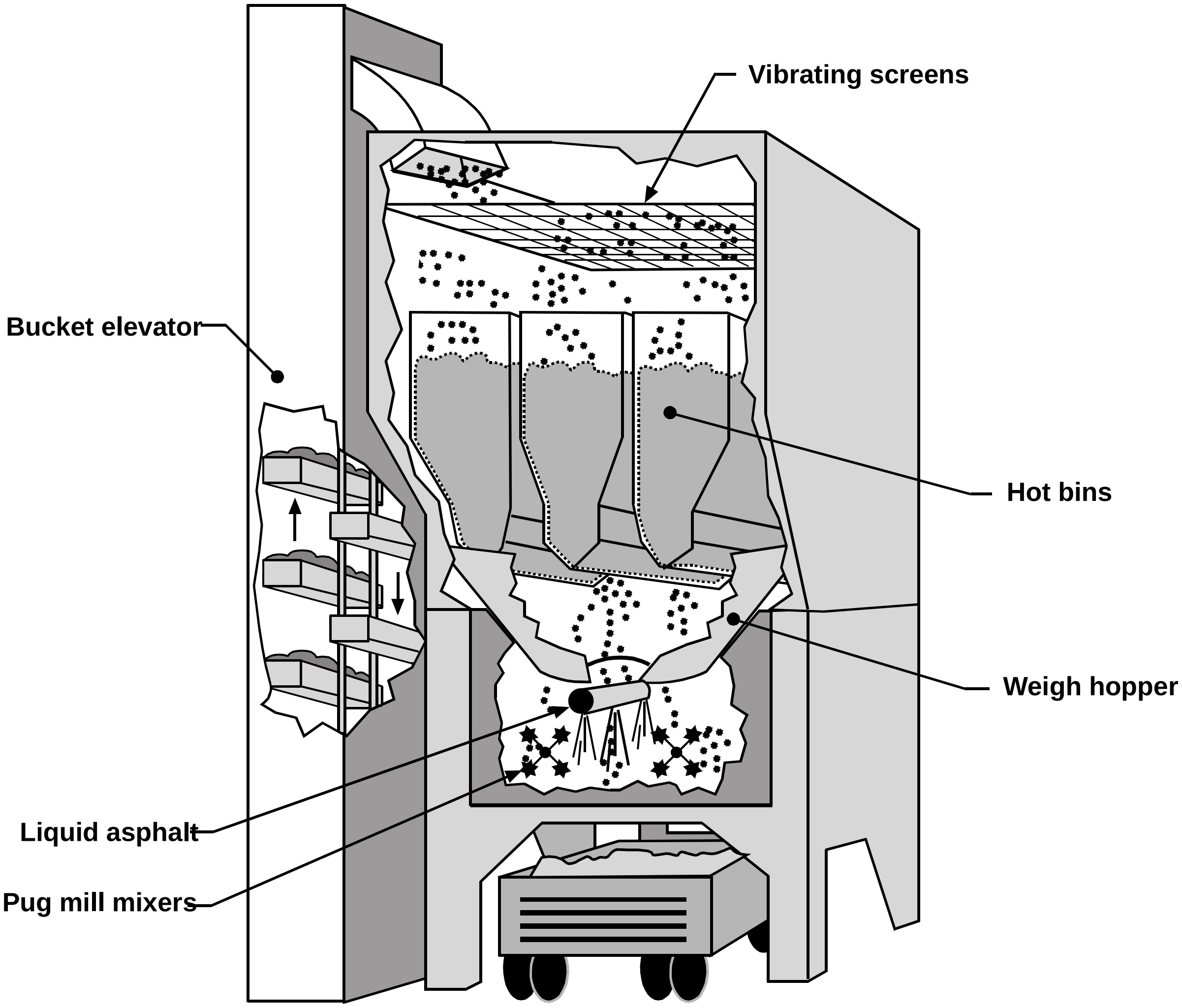

Figure 12-1. Hot mix plant weigh bins, screens, and pug mill

Information on VOC emissions from conventional and drum mix asphalt plants is very limited; but, in general, indicates relatively low values. USEPA's *Compilation of Air Pollutant Emission Factors* (AP-42) gives a value of 0.028 pounds per ton of asphalt concrete produced in a conventional asphalt plant. A study on drum mix plants by the Maryland Air Management Administration found an average VOC emission rate of 0.429 pounds per ton of asphalt cement. Since asphalt concrete is approximately 5% asphalt cement, this study gives a value similar to that from USEPA.

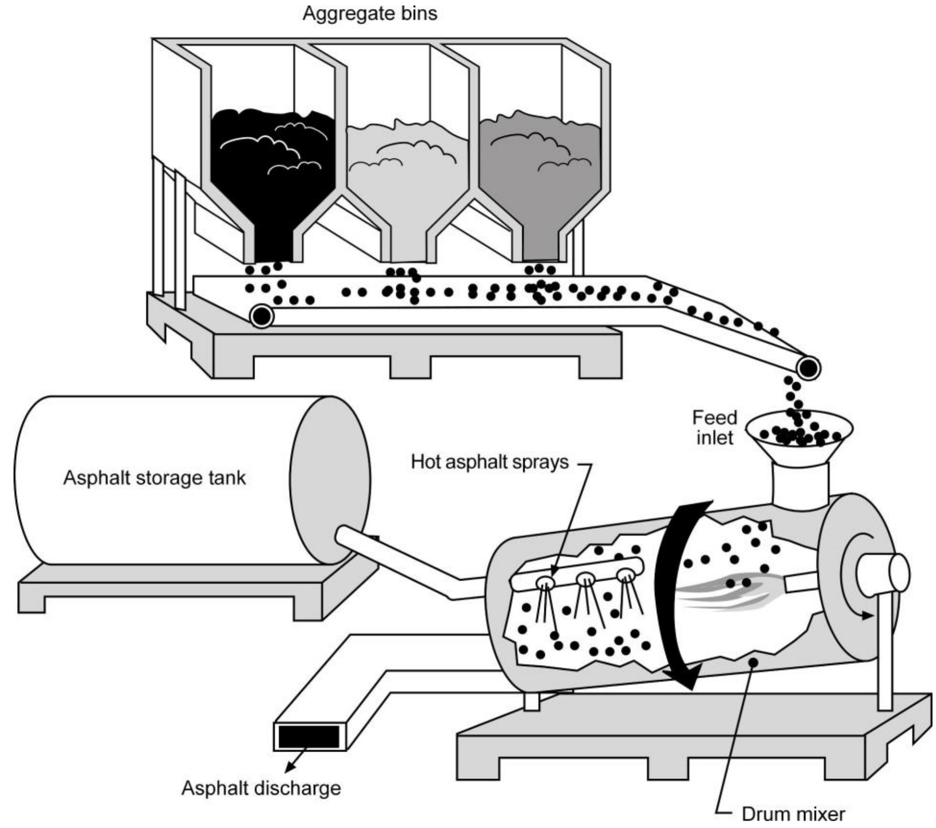

Figure 12-2. Drum mix type asphalt plant

12.2 CUTBACK ASPHALT

Asphalt cement can be blended or cut back with petroleum distillates or solvents to make it usable for direct spraying or for mixing with aggregate. The blend is approximately two-thirds asphalt cement to one-third solvent. Paving material referred to as *cold patch* is produced by mixing the cutback asphalt with aggregate in a simple open pug mill or revolving drum. Cold patch does not possess the strength properties of hot mix, but its longer curing time results in a more workable product. It is typically used for low traffic volume secondary roads, for small patch work, and for hand spreading in small areas.

There are three types of cutback asphalt and four or five different grades for each type. The most durable is Rapid Cure, or RC, which is produced by blending the asphalt cement with gasoline or naptha. These solvents evaporate quickly and leave a hard, viscous asphalt base in a curing time of about two or three hours. Medium Cure, or MC, is produced by using kerosene, which is less volatile than gasoline or naptha. The slower solvent evaporation rate leaves a base of medium hardness in a curing time of about two or three days. Slow Cure, or SC, contains a low volatility fuel oil solvent. Sometimes referred to as road oils, they leave a soft low viscosity asphalt on the aggregate. Curing time is more difficult to estimate, but could be on the order of two or three weeks.

Obviously, the problem with cutback asphalt is that VOCs are released to the atmosphere as it cures. However, unlike other VOC-containing materials, not all of the organic is lost. Rapid Cure loses about 80% of its solvent, Medium Cure about 70%, and Slow Cure about 25%.

12.3 EMULSIFIED ASPHALT

Instead of using cutback solvents, liquid asphalt can be made as an emulsion. Emulsified asphalt consists of sheared asphalt cement suspended in water that contains an emulsifying agent. The mixture is typically one-third liquid and two-thirds asphalt cement, and the liquid fraction is usually 98% water and 2% emulsifying agent. The emulsifying agent is some type of fatty acid, usually a wood product derivative such as tall oil, rosin and lignin. Some solvent may be added to give certain coating properties.

Like cutback asphalt, emulsified asphalt is produced in three basic types: Rapid Setting (RS), Medium Setting (MS) and Slow Setting (SS). Each type has properties and curing times similar to the comparable cutback asphalt and generally does not require a change in equipment or application procedures.

Although low in VOC content, emulsified asphalt is not usually VOC free. It may contain from 1% to 12% VOC, and some part of this would be lost to the atmosphere during curing. An offset allowance at a Hampton Roads, Virginia, refinery in the 1970s assumed a 5% solvent content in the replacement emulsified asphalt and that 50% of this would evaporate.

12.4 EMISSION REGULATION

At the time of writing, USEPA had issued an NSPS standard for hot mix asphalt plants (40 CFR 60, Subpart I); however, it addresses only particulate emissions. RACT guidance recommends substituting emulsified asphalt for cutback asphalt. Exceptions to this recommendation include:

- When cutback asphalt is applied in cold weather (less than 50°F).
- When emulsified asphalt is stored for longer than a month. This would allow adding some solvent to keep it from setting up.
- When cutback asphalt is used as a prime coat to prepare soil for road construction.
- When it can be demonstrated that there are no VOC emissions from the cutback asphalt. This could be done using distillation data or by heating the asphalt to 500°F with less than 5% solvent loss.

Review Questions

1. What is the most durable asphalt paving material?
   a. Hot mix asphalt
   b. Cutback asphalt
   c. Emulsified asphalt

2. Which asphalt paving material has the highest VOC emissions?
   a. Hot mix asphalt
   b. Cutback asphalt
   c. Emulsified asphalt

3. Which liquid asphalt has the lowest VOC emissions?
   a. Hot mix asphalt
   b. Cutback asphalt
   c. Emulsified asphalt

4. What is the NSPS limit for VOC emissions from hot mix asphalt plants?
   a. 0.028 lbs per ton of asphalt concrete
   b. 0.429 lbs per ton of asphalt cement
   c. There is no VOC limit

5. What is the RACT recommendation concerning the use of cutback asphalt?
   a. Use no more than 30% solvent in the cutback asphalt
   b. Replace with emulsified asphalt
   c. Use cutback asphalt only in warm weather

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Review Answers

1. What is the most durable asphalt paving material?
   a. Hot mix asphalt

2. Which asphalt paving material has the highest VOC emissions?
   b. Cutback asphalt

3. Which liquid asphalt has the lowest VOC emissions?
   c. Emulsified asphalt

4. What is the NSPS limit for VOC emissions from hot mix asphalt plants?
   c. There is no VOC limit

5. What is the RACT recommendation concerning the use of cutback asphalt?
   b. Replace with emulsified asphalt

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13 Introduction to Control Technology

The control of gaseous contaminants from industrial sources began with efforts to recover useful raw materials and products contained in gas streams. Many of the control techniques in use today had their origins in the 1940s and 1950s as collectors used for process control. In the 1950s and 1960s, control equipment for gaseous contaminants began to be applied for environmental purposes. In this chapter you will be introduced to some of the technologies being used to control VOC emissions. For more extensive treatments of this subject, the student is referred to APTI Course 415, Control of Gaseous Emissions, and APTI Course 455, Advanced Inspection Techniques.

13.1 Carbon Adsorption

Adsorption processes have been used since the early 1950s for high efficiency collection of a wide variety of organic vapors and several types of inorganic gases. Their use has been expanding recently due to innovations in the designs of the systems and because of the development of improved adsorbents.

In adsorption processes, gaseous contaminants are removed from a gas stream by transferring them to the surface of a solid adsorbent. These adsorbent materials include silica gel, activated alumina, molecular sieves, polymers and activated carbon. The most common material for the adsorption of organic pollutants is activated carbon. A properly designed activated carbon system is generally capable of removing 95% to more than 98% of an organic contaminant.

Activated carbon, like the other adsorbents, has a total surface area on the order of millions of square feet per pound. It can be produced from a variety of raw materials, including coal, wood, nutshells and petroleum-based products. The activation process takes place in two steps. First, the raw material is heated in the absence of oxygen to about 1,100°F in order to drive off all volatile material. The remaining carbon is then "activated" by using steam, air or carbon dioxide to attack the carbon and increase the pore structure, thereby increasing the surface area. The temperature used, the amount of oxygen present and the type of raw material used affect the properties of the activated carbon.

13.1.1 Types of Adsorption Processes

There are two types of adsorption processes: chemical adsorption, or chemisorption, and physical adsorption. In chemical adsorption, the contaminant molecule is held to a site on the adsorbent surface by a bond formed through chemical reaction, either with the adsorbent itself or with something that has been impregnated into the adsorbent. Since a chemical bond is formed, it is very difficult to regenerate the adsorbent for reuse. Because of this, chemical adsorption is not often used in air pollution control systems. It is used, however, in the sampling of gaseous contaminants. For example, mercury vapors are sampled by collecting them on activated carbon that has been impregnated with iodine.

In physical adsorption, the contaminant molecule is lightly held to the surface of the adsorbent by weak intermolecular forces known as van der Waals' forces. These are the same forces that occur in condensation and result from an electrostatic attraction between the molecules of the adsorbent and the molecules of the contaminant. This electrostatic attraction is greatest when the polarities of the respective molecules are the same. Since most organic molecules are non-polar, because of their symmetry, they are generally collected using activated carbon, which is also non-polar. Because the contaminant molecules are only lightly held to the activated carbon surface, the adsorbent material can easily be regenerated for reuse.

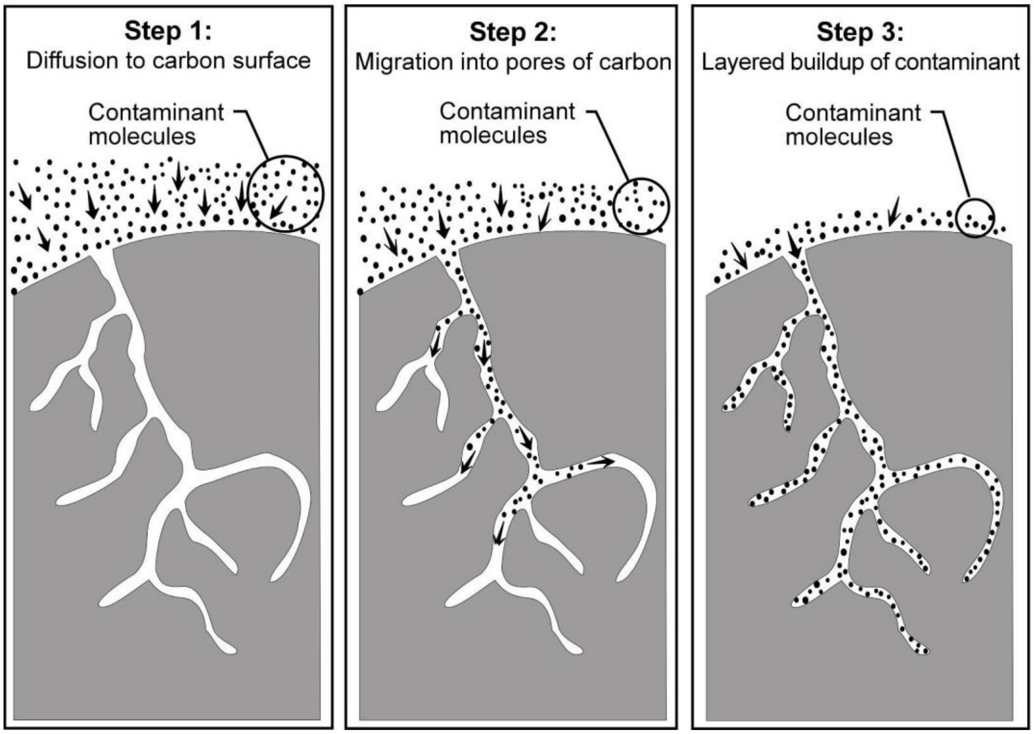


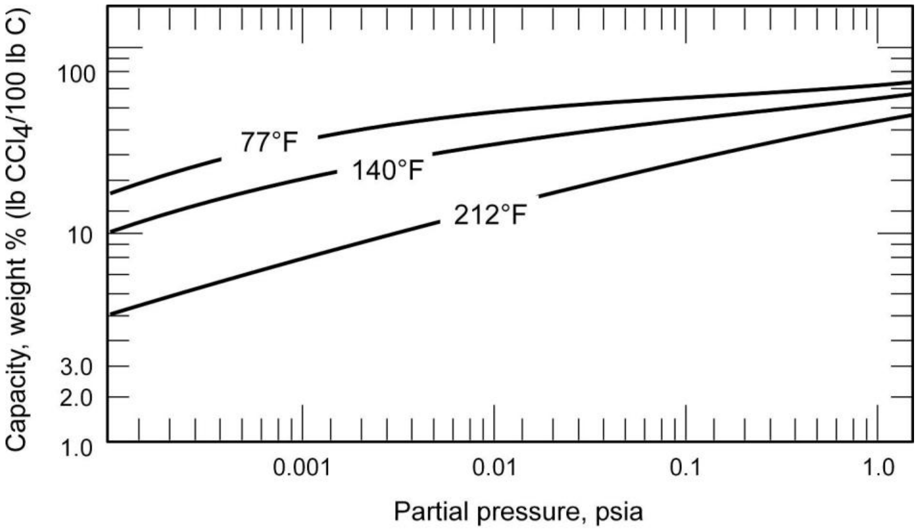
Figure 13-1. Adsorption steps

The activated carbon used in most air pollution control systems is in the form of granules smaller than the end of your little finger. As shown in Figure 13-1, most of the surface area is in an internal pore structure formed by the activation process. To reach this surface area, the contaminant molecules must diffuse from the turbulently mixed gas stream outside the granules into macropores that are typically larger than 4,000 nm in diameter. From the macropores, the molecules diffuse into transitional pores that are 400 to 4,000 nm in diameter and finally into the micropores that are less than 400 nm in diameter.

Physical adsorption is a dynamic process. That is, the contaminant molecules are in constant motion, adsorbing and desorbing and moving over the surface of the activated carbon. For this reason, one does not have to worry, in multi-contaminant systems, about a larger contaminant molecule blocking access to a micropore that could be entered by a smaller contaminant molecule. This may happen momentarily, but eventually the larger molecule will move, allowing access to the smaller molecule.

Since the electrostatic force between the contaminant molecule and the adsorbent also occurs between the contaminant molecules themselves, it is possible to build up layers of adsorbed material, increasing the capacity. Related to this phenomenon is the process of condensation. In micropores about the diameter of two molecular dimensions, a line of molecules on one side of the pore will be attracted to molecules on the other side, causing them to condense in the pore. This condensed material can be difficult to remove during regeneration.

13.1.2 Adsorption Capacity



Source: Adapted from Technical Bulletin, Calgon Corp.

Figure 13-2. Adsorption isotherm for carbon tetrachloride on activated carbon

The amount of material adsorbed by activated carbon is termed its *retention* and is expressed in weight percent or as the ratio of pounds of organic contaminant adsorbed per 100 pounds of carbon. Saturated activated carbon will generally hold 20 to 40 pounds of contaminant per 100 pounds of carbon. The most common method of expressing saturation capacity data is the *isotherm*. The isotherm is a constant temperature plot of the adsorbent capacity at saturation versus the concentration of the contaminant in the gas stream, usually expressed in partial pressure. Figure 13-2 is an example isotherm for carbon tetrachloride adsorption onto activated carbon.

The ability of activated carbon to retain organic contaminants is influenced by a number of parameters. One of these is temperature. At lower temperatures, because of the lower vibrational frequency of the molecules, the retention is high. As temperature increases, it becomes increasingly difficult to keep the contaminant molecules on the surface and retention goes down. Because of this, carbon adsorbers are usually operated at temperatures no higher than about 125°F.

Retention is also influenced by the absolute pressure of the system. At higher pressures, retention is higher because the molecules in the gas stream are more closely spaced, making it more difficult for contaminant molecules to escape from the surface and move back into the gas stream. As the pressure is reduced, the wider spacing of the gas stream molecules makes it more difficult to keep contaminant molecules on the surface, and retention goes down.

Similarly, the concentration or *partial pressure* of the contaminant molecules in the gas stream also influences the retention. At higher concentrations, more contaminant molecules are moving toward the surface, making it more difficult for molecules on the surface to escape, and retention is increased. Likewise, at lower concentrations it is easier for molecules on the surface to escape and retention is reduced. Even though retention is higher for higher concentration gas streams, this does not mean that less carbon is needed. At higher concentrations, there is more material to be collected, generally requiring larger amounts of carbon.

Retention is affected by the molecular weight of contaminant molecules, because of variations in their vibrational frequency. Small molecules with high vibrational frequencies are difficult to retain on the carbon surface. Generally, molecules with molecular weights less than about 45 are not good candidates for adsorption. As the molecular weight of molecules increases, retention increases. However, molecules with a molecular weight greater than about 200 are also not good candidates for adsorption. Although they are readily retained by the activated carbon, they are more difficult to remove during regeneration. Also, contaminants that can react with the surface, like organic acids, aldehydes and some ketones, are not good candidates for carbon adsorption.

Moisture in the gas stream can also affect retention. Although water molecules are polar, they will adsorb onto activated carbon, competing with the organic contaminant for adsorption sites. This generally becomes a concern when the relative humidity of the gas stream is greater than about 50%. The designer usually counteracts this effect by using more total carbon when the relative humidity is high.

Adsorption is also affected by the presence of liquid or solid particles in the gas stream. As the gas stream wiggles through the bed of carbon granules, any particles in the gas stream would be collected on the surface of the granules, blocking access to the high surface area in the internal pore structure. Accumulated particulate matter can also cause poor flow distribution, reducing collection efficiency. As a result, any particulate matter in the gas stream must be removed before entering the adsorber.

13.1.3 Types of Adsorption Systems

There are two types of activated carbon systems: those that regenerate on site and those that do not. Systems that do not regenerate on site typically use ½-inch to 4-inch thick carbon beds that are formed into pleated or folded panels or into cylinders. Examples of these are shown in Figure 13-3. These systems are generally used to remove trace concentrations of contaminants from a gas stream. Service life for these systems is usually six months to two years.

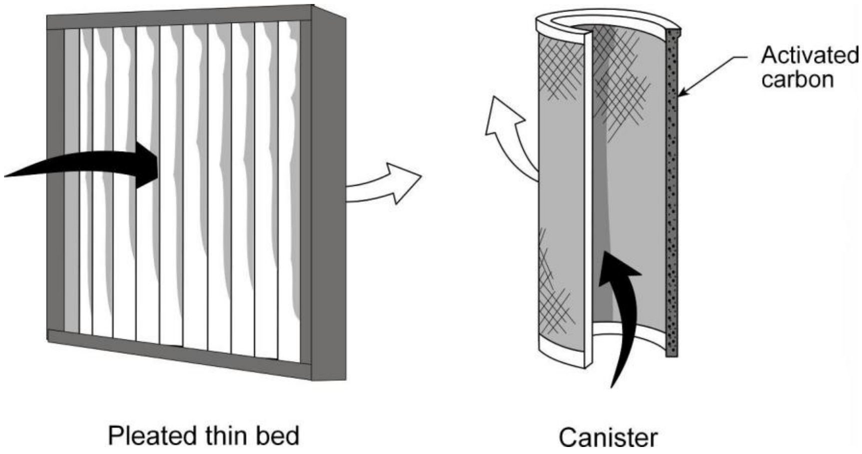


Figure 13-3. Nonregenerative adsorbers

Another type of system that is not regenerated on site is essentially a 55-gallon drum containing about 100 to 150 pounds of activated carbon, shown in Figure 13-4. Although these have thick carbon beds and are capable of handling high concentrations of contaminants, they are typically used in temporary applications where on-site regeneration is not practical. With both of these designs, the carbon would be returned to the supplier for regeneration or transferred to a waste handler for regeneration or destruction.

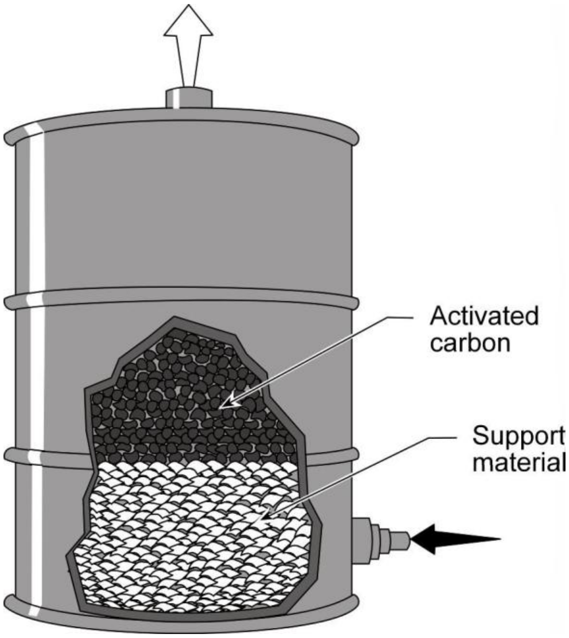


Figure 13-4. Nonregenerative canister adsorber

The most common industrial adsorber is the fixed-bed design that regenerates on site. An example of this collector is shown in Figure 13-5. The activated carbon will be contained in two or more vessels or modules, so that one of them can be taken off line for regeneration while the others continue to collect the contaminants. The carbon beds in these modules are typically 1.5 to 4 feet thick. The lower dimension is set to reduce channelization of the gas flow that can occur in thinner beds. The upper dimension is set because of the energy required to move the gas stream through thicker beds. The contaminated gas stream flows down through the operating modules to mitigate fines formed from attrition of the carbon being introduced into the cleaned gas stream.

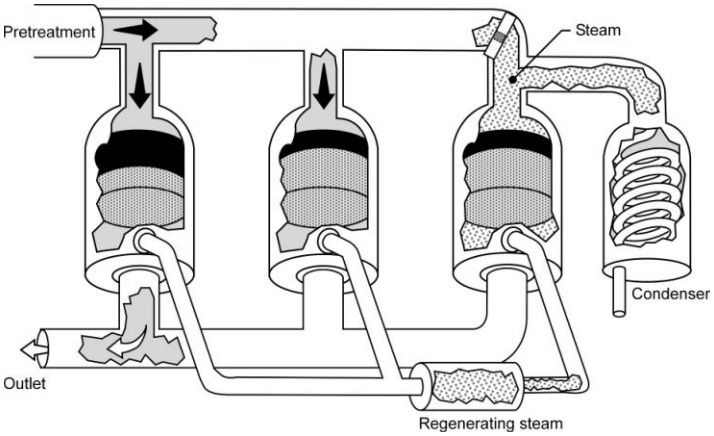


Figure 13-5. Three-bed regenerative system

When a module is put back on line after regeneration, the carbon will contain a small quantity of contaminant that was not practical to remove during regeneration. This is called the *heel* and is generally 3 to 5 weight percent or 3 to 5 pounds of contaminant per 100 pounds of carbon. Since regeneration is conducted with an upward flow, this heel is left as an essentially saturated layer at the top of the carbon bed.

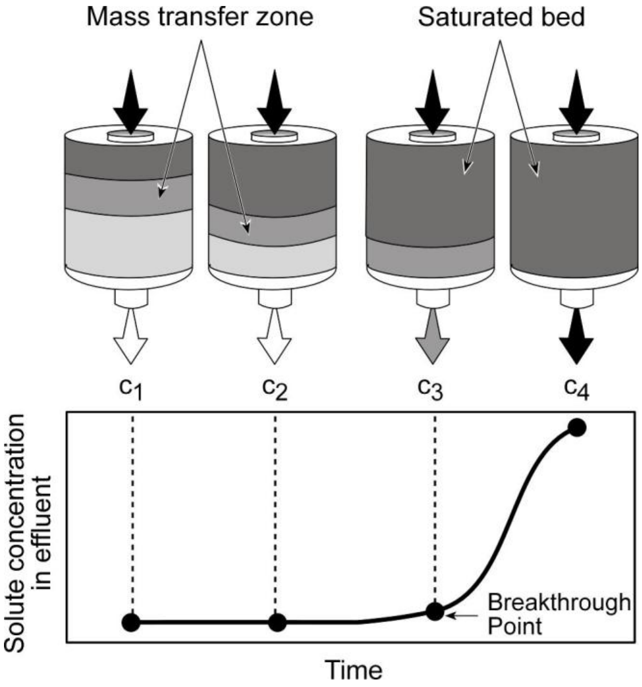


Figure 13-6. Mass transfer zone movement

When the gas flow enters this vessel, a *mass transfer zone*, or MTZ, is formed (see Figure 13-6). This is the zone of active adsorption and is generally 2 to 4 inches thick. As adsorption proceeds, the MTZ moves down the bed, leaving behind it saturated carbon. When the MTZ reaches the end of the bed, the module is taken off line for regeneration. If the MTZ is allowed to exit the bed, a condition called *breakthrough* occurs and the outlet concentration rises rapidly.

The quantity of organic material that can be retained by the carbon bed during each adsorption cycle is the difference between the capacity at breakthrough and the heel capacity. This is termed *working capacity* and is conservatively estimated to be about half of the saturation capacity or, typically, about 10 to 20 pounds of contaminant per 100 pounds of carbon.

There are two ways to decide when to take a module off line for regeneration. The most effective way is to use an analyzer in the outlet gas stream that takes the module off line when breakthrough occurs. This allows for full utilization of the carbon bed, but requires the purchase, operation and calibration of an analyzer. It is the most expensive option.

A lower-cost option is to use mechanical or electronic timers. The breakthrough curve for the adsorption process can be obtained from the carbon supplier, and the source can use scale-up calculations to predict the time that breakthrough should occur. This time can then be refined in the field using a portable analyzer. Although this is a lower-cost option, it does not usually provide for full utilization of the carbon bed. For conservancy, the MTZ is generally just inside the bed when the module is taken off line. Obviously, the use of timers is not an acceptable option when the gas flow rate or contaminant concentration or both vary in a random manner.

13.1.4 Regeneration Methods

There are two methods for regenerating an activated carbon bed: *thermal swing*, where the temperature is increased, or *pressure swing*, where the pressure is reduced. The most common technique is thermal swing using low quality stream as the heating fluid, illustrated in Figure 13-7. Since the product of the regeneration is a mixed fluid of condensed contaminant and water, it is generally not used in systems where the contaminant has any significant solubility in water.

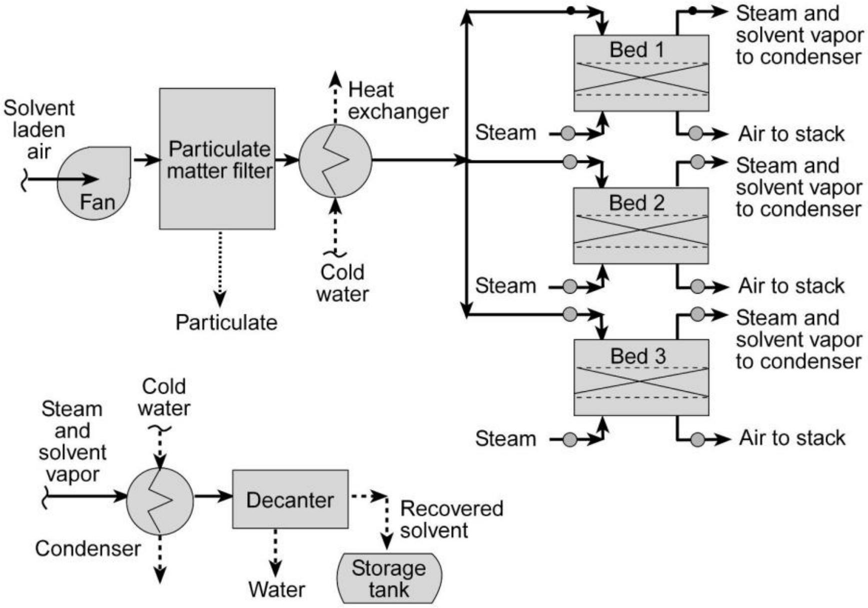


Figure 13-7. Steam regeneration

After the module is taken off line, steam is introduced in an upward flow through the bed. There is an initial delay in desorption as the bed and vessel heat up. As desorption proceeds, the steam flow sweeps the contaminants out of the bed to a condenser. A decanter is used to separate the condensate and recover the organic contaminant. The recovered organic may be returned to the process or used as all or part of the fuel in the steam generator. Contaminant that does not condense is returned to the inlet of the operating modules.

Once desorption is completed, the carbon bed is hot and wet and it is not a good adsorber for both reasons. To cool the bed down and dry it out, a purge flow is taken from the outlet of the operating modules and directed upward through the desorbed bed. The regeneration process–from the time the module is taken off line for regeneration until it is ready to be returned to service–typically takes 1 to 1.5 hours.

Where water contamination is a problem, thermal swing can be accomplished using a hot gas, such as nitrogen. The desorption process is the same as when steam is used, except that when desorption is completed the carbon bed is hot but not wet. A purge flow is again taken from the outlet of the operating modules and directed upward through the desorbed bed for cooling. The regeneration process–from the time the module is taken off line for regeneration until it is ready to be returned to service–typically takes only 45 minutes to 1 hour.

The other method for regeneration uses a change in pressure, rather than heating. Most carbon adsorbers used for air pollution control operate at atmospheric pressure. After the module is taken off line, a vacuum pump is used to reduce the pressure in the vessel to about 50 mm Hg and to provide the gas movement to sweep the desorbed contaminants out of the bed to a condenser. If explosive concentrations are possible, a blanketing gas such as nitrogen is used. Once desorption is completed, it is only necessary to return the module to atmospheric pressure before returning it to service. The regeneration process–from the time the module is taken off line for regeneration until it is ready to be returned to service–typically takes 15 to 30 minutes. Because of the cost of operating and maintaining the vacuum generation equipment, this technique is usually only applied to small sources, such as gasoline marketing.

13.1.5 Other Adsorber Designs

There are many variations in adsorber system design, most of them directed toward reducing what is called *idle carbon*. In the conventional fixed-bed system, adsorption occurs only in the relatively thin mass transfer zone. The rest of the carbon is idle, contributing only to the energy required to move the gases through the system. In some designs, the activated carbon is held between concentric cylinders, as shown in Figure 13-8. The unit slowly rotates from an adsorption station, to a desorption station and finally to a purging station before returning to the adsorption station. In other designs, the activated carbon flows down and across several perforated plates mounted in a tower, similar to a tray absorber, as the contaminated gas flows upward through the perforations (see Figure 13-9). The spent carbon is either regenerated by indirect heating and cooling sections below the trays or is directed to another perforated-plate tower that uses hot gas for regeneration. The regenerated carbon is returned to the top of the adsorption tower.

Newer adsorption systems make use of recently developed carbon fiber material. The carbon fiber is a thin-layer material with micropores leading directly from the adsorbent surface. The carbon fibers may be formed into cylindrical units, similar to fabric filter bags, or into a rotating honeycomb element. Regeneration is accomplished using steam or a hot gas. An example of a carbon fiber system is shown in Figure 13-10.

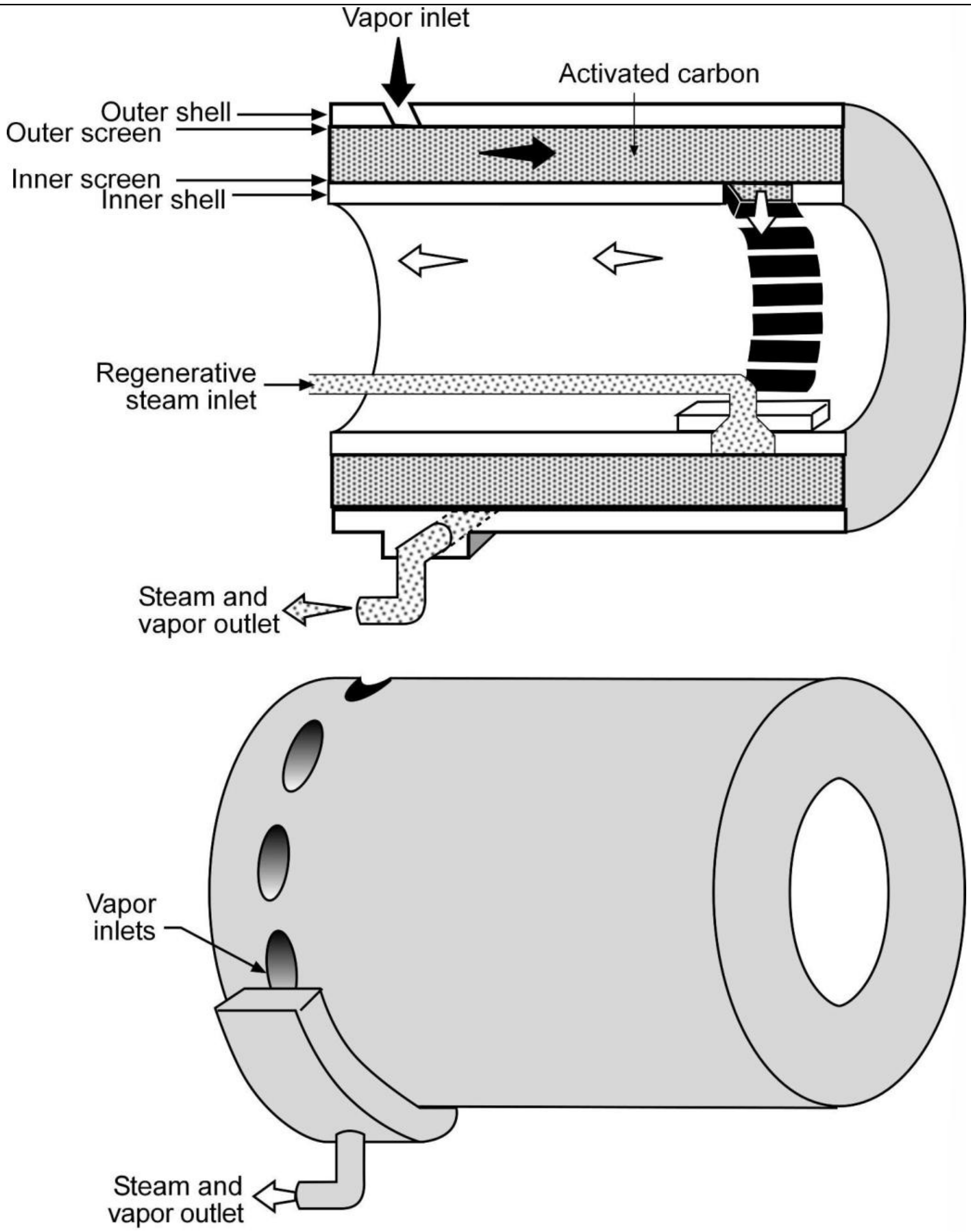


Figure 13-8. Rotary bed system

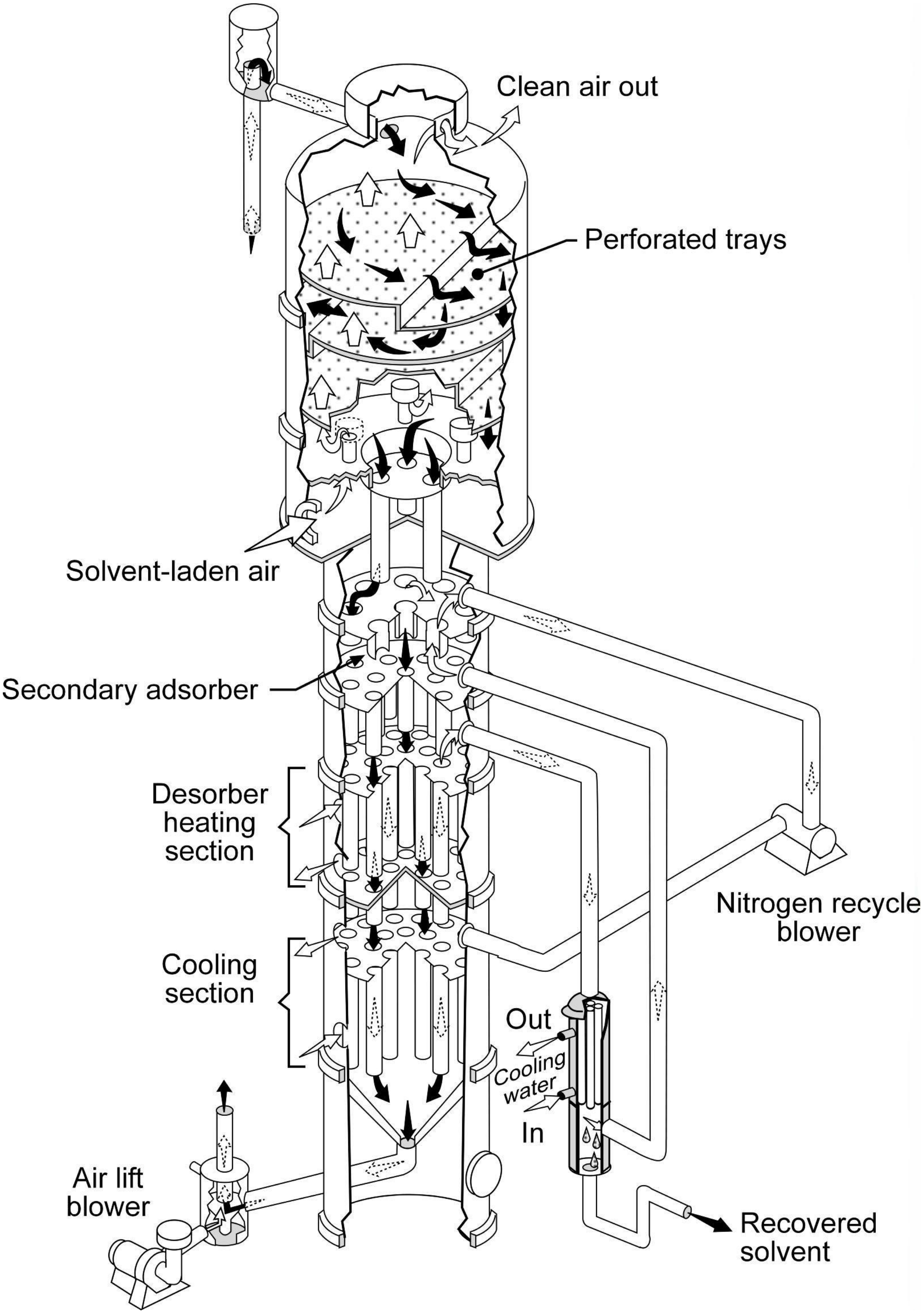


Figure 13-9. Fluidized bed adsorber

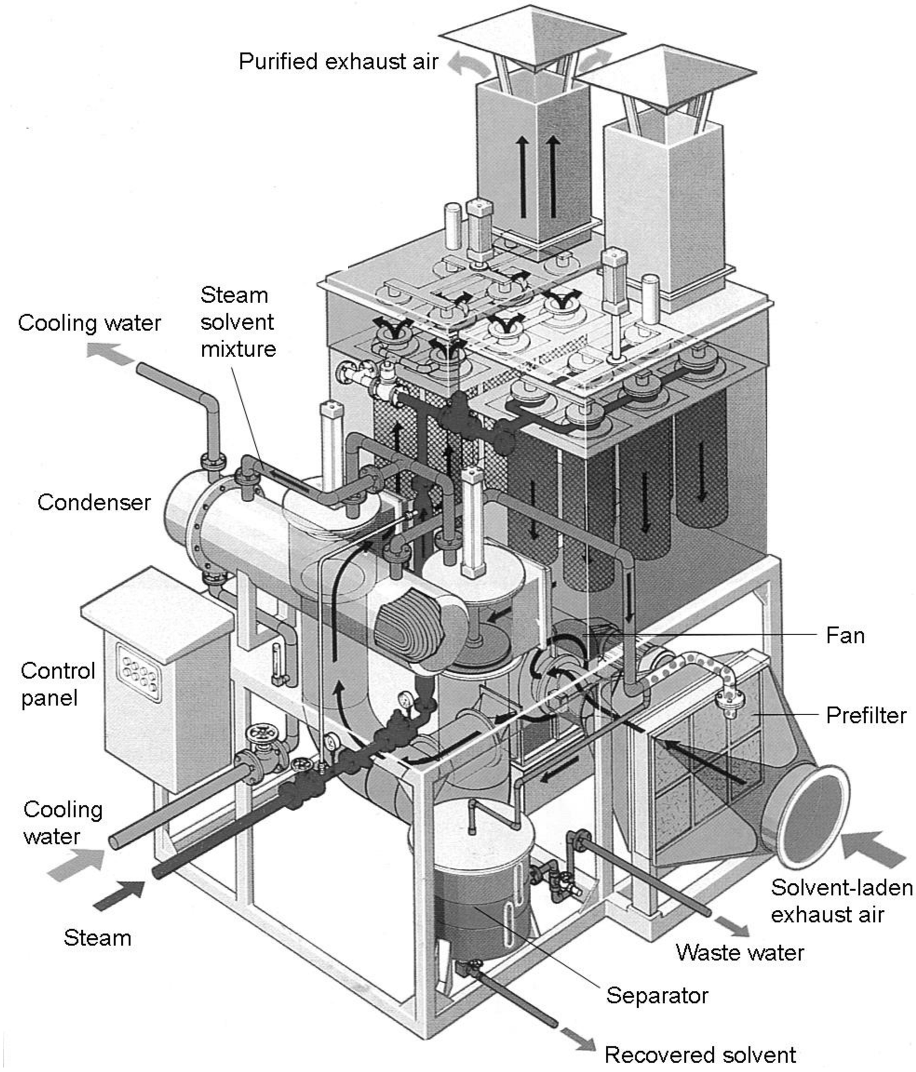


Figure 13-10. Carbon fiber system

(Reprinted courtesy of Durr Industries, Inc., Plymouth, Michigan)

13.2 Incineration

In vapor incineration processes, organic contaminants are removed from a gas stream by oxidizing them to other compounds. If the organic compounds are composed of carbon and hydrogen, then the products of that oxidation are carbon dioxide and water vapor. However, if the organic materials contain chlorine, fluorine or sulfur, then hydrochloric acid vapor, hydrofluoric acid vapor, sulfur dioxide or other compounds may be formed, requiring absorbers downstream of the incinerator in order to reduce the emission of these compounds. In general, incinerators are capable of destruction efficiencies greater than 95%. Some incinerator designs have destruction efficiencies greater than 99%.

There are three common types of incineration processes: flares, thermal oxidizers and catalytic oxidizers. Flares are usually used for gas streams that have an organic vapor concentration greater than two to three times the lower explosive limit. The *lower explosive limit*, or LEL, is the level of organic vapor concentration at which oxidation will be self-supporting if a source of ignition is provided. Thermal oxidizers are used for contaminated gas streams that have an organic vapor concentration that is generally less than 50% of the LEL and usually less than 25%. Catalytic oxidizers are used for gas streams that have concentrations less than 25% of the LEL.

13.2.1 Flares

A typical flare consists of a system that first collects the waste gases and then passes them through a knockout drum to remove any liquids before entering the flare stack. Flame arrestors are placed between the knockout drum and the flare stack to prevent flashback of flames into the collection system. The flare stack is a hollow pipe that may extend to heights above 150 feet. The flare tip is at the top of the stack, where the waste gases are ignited by pilot flames. If the gases do not have sufficient heat content, fuel will be added to the gas stream. This is called a *fired* or *endothermic flare*.

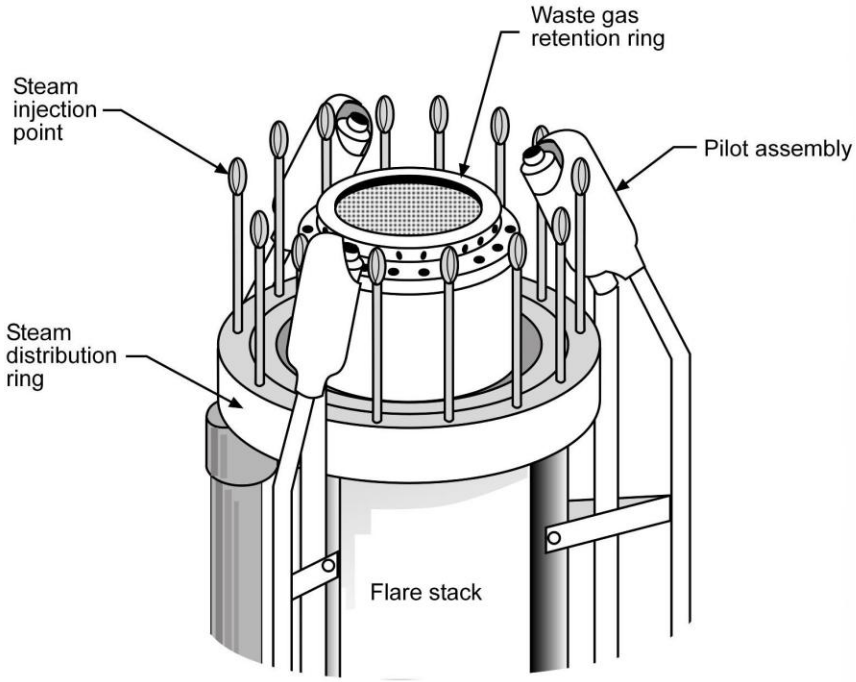


Figure 13-11. Flare tip

The flare tip is designed to provide good mixing characteristics over a range of gas flow rates, while maintaining smokeless combustion. Steam jets are one of the most effective ways to mix air with the waste gases. An example of a flare tip with steam injection is shown in Figure 13-11. In addition to increasing turbulence, steam injection reduces the partial pressure of the contaminant gases, reducing polymerization of higher molecular weight organic compounds in the waste gas stream. The steam also reacts with the waste gases to produce oxygenated compounds that burn at lower temperatures. For these reasons, steam is often used for waste gases that are difficult to burn. Compounds with a hydrogen-to-carbon ratio less than 0.3 will usually require steam injection.

In order to reduce the noise, light and safety concerns inherent with an open flame, the flare may be enclosed and located at ground level. Ground flares consist of multiple burners enclosed in a refractory-lined shell. The waste gases are introduced through a jet or venturi to provide turbulent mixing, and the combusted gases are discharged through a stack. Some plants incorporate both designs: a ground flare for normal operation and an elevated flare for emergency releases.

13.2.2 Thermal Oxidizers

The thermal oxidizer consists of a refractory-brick lined chamber that has one or more gas- or oil-fired burners. The contaminated gas stream does not usually pass through the burner itself, unless a portion of the gas stream is used to provide the oxygen needed to support combustion of the fuel. Instead, the burners are used to heat the gas stream to the temperature necessary to oxidize the organic contaminants. That temperature is based primarily on the autoignition temperature of the most difficult-to-destroy compound in the gas stream.

Autoignition temperatures for most organic compounds range from 750°F to 1,000°F. Operation at temperatures near the autoignition value will result in destruction of the contaminants; however, the carbon in the compounds will be left primarily as CO, even if sufficient oxygen is available. To fully oxidize the carbon to CO_2, incineration should be conducted at a minimum temperature of 1,300°F. Most thermal oxidizers operate at temperatures of 1,300°F to 1,800°F.

The combustion chamber is sized to provide sufficient residence time to complete the oxidation reactions. The time needed for destruction depends on the temperature and mixing within the chamber, with shorter times required at higher temperatures. Typical residence times are 0.3 to 0.5 seconds, but may exceed 1 second. Residence time is typically calculated by dividing the volume of the combustion chamber by the actual volumetric flow rate through the combustion chamber. However, it should be recognized that not all of the combustion chamber may be at the effective oxidation temperature. Thus, residence times calculated in this manner should be somewhat higher than the minimum desired value.

13.2.2.1 Recuperative Thermal Oxidizers

Because of fuel costs, most incinerators use heat exchangers to recover some of the heat from the treated gas stream. That heat is usually used to pre-heat the contaminated gas stream before it enters the incinerator. One type of heat exchanger is the *recuperator*, and incinerators that use them are sometimes called *recuperative thermal oxidizers*. The most common recuperator is shell-and-tube heat exchanger. These devices have a shell that encloses numerous small tubes. The contaminated gas stream flows through these tubes, while the treated gas stream flows through the shell across the tubes. Approximately 50% to 60% of the heat from the treated gas stream is transferred through the tubes to the waste gas stream. An example of a recuperative thermal oxidizer is shown in Figure 13-12.

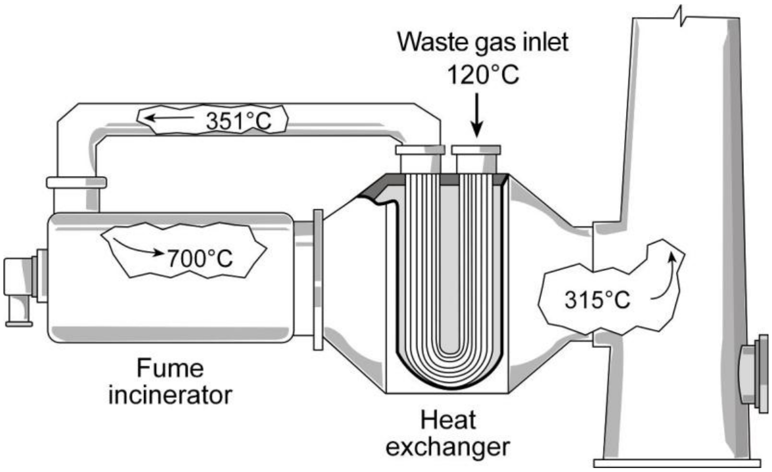


Figure 13-12. Double pass recuperative heat exchanger

Because of the presence of the heat exchanger, particle concentrations in the inlet gas stream must be minimized. Particulate matter can foul the inside surfaces of the tubes, reducing the thermal efficiency. It can also increase the resistance to flow through the heat exchanger, reducing the fan’s ability to move volume through the system, potentially causing fugitive emissions at the source. Some recuperative units include clean-out ports and access hatches to facilitate cleaning.

13.2.2.2 Regenerative Thermal Oxidizers

Another type of heat exchanger is the regenerator, and incinerators that use them are sometimes called *regenerative thermal oxidizers*. A regenerator consists of a set of refractory beds that store heat. Heat recovery is achieved by passing the waste gas stream through a packed ceramic bed at the inlet to the incinerator that was previously heated with the gases exiting the incinerator. It is common to use at least three beds in a regenerative system. One bed is used to pre-heat the waste gas stream, one bed is used to store heat from the treated gas stream, and one bed is in a purge cycle. The purge cycle is needed to prevent emission spikes each time the gas flow is reversed. A set of gas flow dampers is used to switch the inlet, outlet and purge gas streams to the appropriate beds. An example of a regenerative thermal oxidizer is shown in Figure 13-13. This unit has three parallel beds with an overhead refractory-lined combustion chamber equipped with two gas-fired burners.

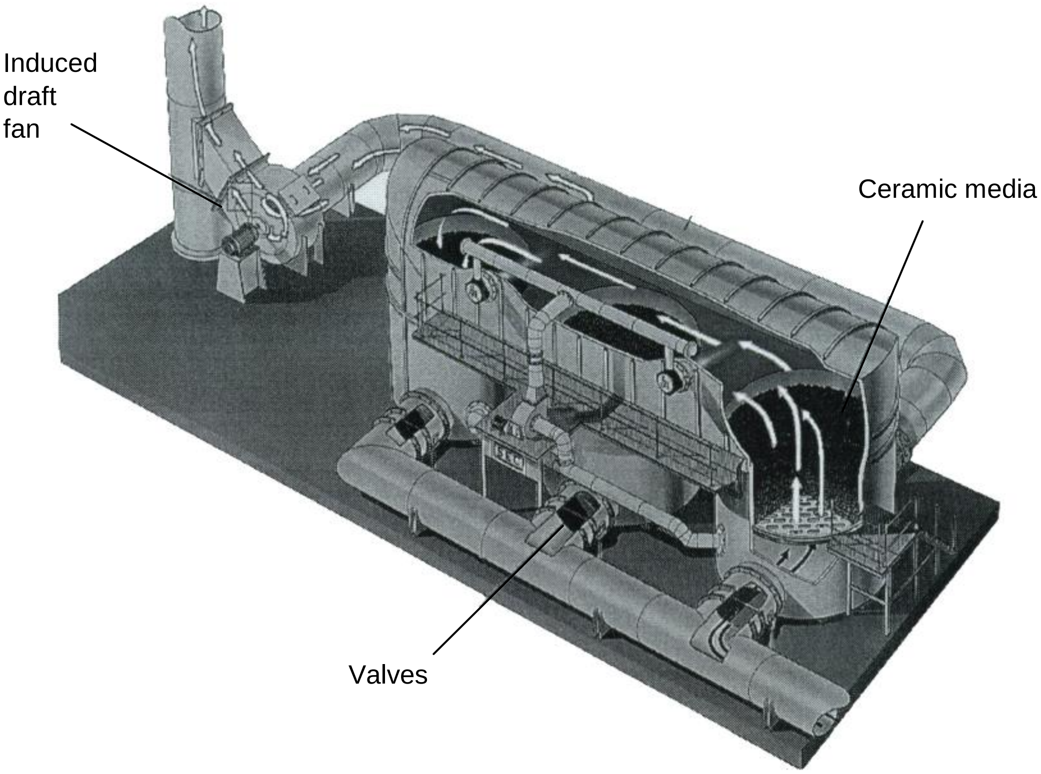


Figure 13-13. Regenerative thermal oxidizer
(Reprinted courtesy of Smith Engineering Co., Ontario, California)

Regenerative heat exchangers have much higher heat recovery efficiencies than recuperative units, recovering as much as 95% of the heat from the treated gas stream. Because of the high inlet gas temperatures created by the heat recovery, burner fuel is typically required only if the organic vapor concentration is very low. At moderate-to-high concentrations, the heating value of the organic compounds may be sufficient to maintain the necessary temperatures.

Another type of regenerative thermal oxidizer is shown in Figure 13-14. This unit is called a *flameless oxidizer*, since the burner is used only for preheating the packed bed prior to the introduction of the contaminated gas stream. In some designs, preheating is done with electrical resistance heaters. The packed bed is a proprietary design that has high heat recovery and storage capabilities, allowing the bed to be maintained at appropriate incineration temperatures using only the heat from the oxidation of the organic compounds. Also, since the burner only operates for a short time, NO_x generation rates are low.

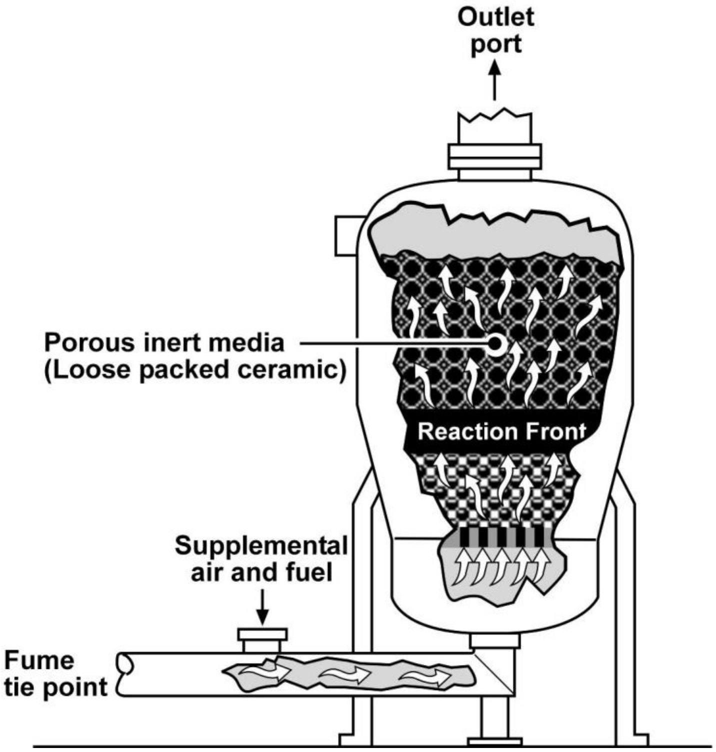


Figure 13-14. Flameless thermal oxidizer
(Reprinted courtesy of Thermatrix, Inc., San Jose, California)

13.2.2.3 Process Heaters and Boilers

An alternative to installing a thermal oxidizer is to incinerate the contaminated gas stream in a process heater or boiler. This avoids the capital cost of new equipment. The contaminated gas stream is typically injected close to the main burners, or it may be used as part of the combustion air supplied to the burners. Process heaters and boilers are normally designed to operate with combustion chamber temperatures greater than 1,800°F and flue gas residence times in excess of 1 to 2 seconds. These conditions are similar to those of conventional thermal oxidizers.

There are some limitations in the use of a process heater or boiler as an incinerator. The boiler must operate within about 40% to 100% of the design load in order to provide the temperatures necessary for organic vapor destruction. The waste gas stream should be only a small portion of the total gas flow through the unit. If the volume of additional gas is large, maximum recommended velocities through the unit would be exceeded, potentially lowering the destruction efficiency of the system. Finally, there should be nothing in the waste gas stream or its combustion products that would present a corrosion problem or cause deposits on heat transfer surfaces.

13.2.3 Catalytic Oxidizers

In order to minimize fuel consumption, catalytic oxidizers are designed with both recuperative and regenerative heat exchangers. Since the advantages and limitations of the recuperators and regenerators are identical to those used on thermal oxidizers, this section will discuss only the characteristics of catalytic oxidation.

A catalyst is a substance that accelerates a chemical reaction without undergoing a change itself. The typical catalysts used in incineration are noble metal oxides of platinum, palladium or rhodium that are deposited as a thin layer on a high surface area material, such as alumina, that is bonded to a support structure. Base metal oxides, such as vanadium pentaoxide, titanium dioxide or manganese dioxide, may also be used. The support structure is arranged in a matrix that provides high geometric surface area, low pressure drop and uniform flow. Structures providing these characteristics include honeycombs, grids and mesh pads.

An example of a catalytic oxidizer is shown in Figure 13-15. After passing through the heat transfer section, the contaminated gas stream is heated to the required temperature by a gas-fired burner and then passed through the catalyst material, called the bed. The catalyst causes the oxidation reaction to occur at much lower temperatures than would be required for thermal oxidation. This is the principal advantage of catalytic oxidation. Because of the lower operating temperature, less fuel is required for heating, and refractory-lined combustion chambers are usually not needed. In some cases, it is possible for the catalytic oxidizer to operate without supplemental fuel, except during start-up.

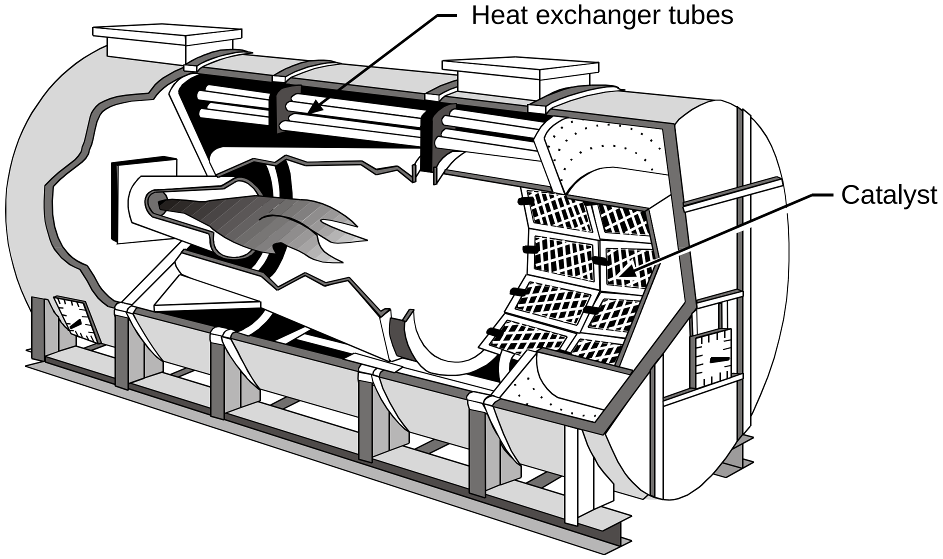


Figure 13-15. Cutaway of a catalytic oxidizer

The inlet temperature to the catalyst bed is generally about 100°F above the catalytic autoignition temperature of the most difficult-to-destroy compound in the gas stream. Most organic compounds have catalytic autoignition temperatures of about 400°F to 500°F, giving a typical minimum inlet temperature of about 500°F to 600°F. For each 1% LEL concentration that is oxidized in the catalyst bed, the gas stream temperature will increase about 27°F. For a 25% LEL gas stream concentration, the total temperature increase would be about 675°F, bringing the outlet temperature from the catalyst bed to about 1,175°F to 1,275°F. This is very close to the temperature that can cause damage to most catalyst materials. For this reason, catalytic oxidizers are usually used only on gas streams with an organic vapor concentration less than 25% of the LEL.

The quantity of catalyst is often described in terms of the *space velocity*. Space velocity is calculated by dividing the standard volumetric flow rate by catalyst bed volume and is essentially the reciprocal of residence time at standard conditions. Typical space velocities for noble metal catalysts are 30,000 to 40,000 per hour. For the less active base metal catalyst, space velocities are typically 10,000 to 15,000 per hour.

The primary disadvantages of catalytic oxidizers are the cost of the catalyst and performance problems related to physical and chemical deterioration of the catalyst material. Catalytic oxidizers usually cannot be used effectively on waste gas streams with high concentrations of liquid or solid particles. These particles deposit on the catalyst surface, blocking access for the organic compounds. This is termed *fouling*. When low concentrations of particles are present, periodically cleaning the catalyst can restore more than 90% of its activity.

Certain metals can react or alloy with the catalyst, permanently deactivating it. This is called *catalyst poisoning*. Fast acting poisons include mercury, phosphorus, arsenic, antimony and bismuth. Slow acting poisons include lead, zinc and tin. At temperatures above about 1,000°F, even copper and iron are capable of alloying with platinum, reducing its activity.

Some materials, principally sulfur and halogen compounds, have a high adsorptive affinity for some catalytic surfaces, reducing the active sites available to the organic compounds. This is termed *masking*. Although removing the masking agent will return catalyst activity to normal, the better approach is to use a catalyst that is not masked by compounds in the gas stream. Vanadium pentaoxide and titanium dioxide, for example, are not masked by sulfur compounds.

High temperatures can also result in catalyst deactivation. Loss of activity because of high temperature is called *thermal aging*. This results in a rapid loss of catalyst activity and is caused primarily by the sintering of the catalyst support material. Sintering involves the merging of the support material ridges. As this occurs, catalyst is trapped below the surface of the support material and is no longer available to the organic compounds. Extremely high temperatures can cause volatilization of the catalyst material.

13.3 Condensation

In condensation processes, gaseous contaminants are removed from a gas stream by causing them to change to a liquid. In general, this can be accomplished by increasing the pressure or reducing the temperature or by a combination of both. However, because of the cost of operating and maintaining compression equipment, most condensers for air pollution control use temperature reduction.

The ultimate efficiency of a condenser depends on the operating temperature. As a vapor-laden gas stream is cooled, the molecules slow down and crowd together so closely that weak electrostatic forces between the molecules cause them to condense. The point at which this occurs is termed the *dew point temperature*. With further reduction in temperature, the vapor pressure of the condensing compound decreases. The lower the vapor pressure, the lower the concentration of the contaminant in the gas stream. Condensation systems generally operate at efficiencies greater than 90%.

Three types of condensers are used for air pollution control: conventional systems, refrigeration systems and cryogenic systems. They are typically applied to sources where the recovered organic compounds have a significant value. Since it would be difficult to separate a large number of compounds in the condensate, there are usually only one or two organic compounds in the gas stream being treated. Also, since particles can cause fouling problems in most of the equipment types, condensers are typically used only on gas streams that have little or no particulate contamination.

13.3.1 Conventional Systems

Conventional systems are relatively simple devices that usually use air or water to reduce the gas stream temperature to as low as about 40°F. Temperatures as low as 0°F can be achieved using brine coolants. There are two categories of conventional systems: direct contact condensers and surface condensers. In a direct contact condenser, the coolant and the gas stream physically contact one another. The coolant and the condensed material leave the unit in a single mixed stream. In a surface condenser, the coolant and the gas stream are separated by a heat transfer surface. The coolant and the condensed material leave the unit in separate streams.

13.3.1.1 Direct Contact Condensers

Direct contact condensers are essentially wet scrubbing equipment, like spray towers, tray towers or ejectors. These devices directly contact the gas stream with a chilled liquid, usually water, as illustrated in Figure 13-16. If the vapor is soluble in the coolant, absorption will also occur, increasing the amount of contaminant that can be removed.

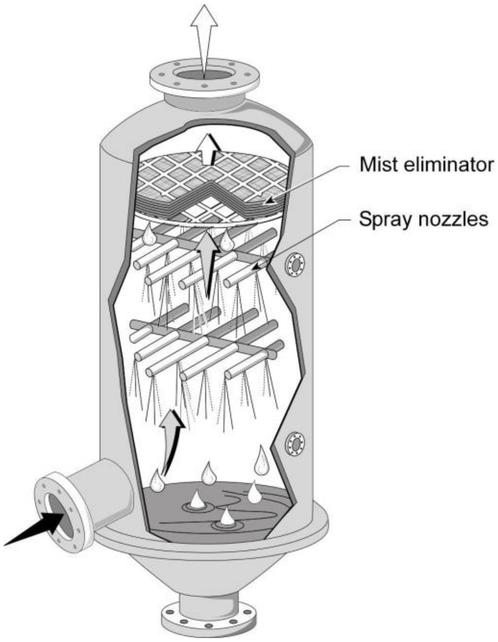


Figure 13-16. Direct contact condenser

An ejector condenser is shown in Figure 13-17. Ejectors use high-pressure liquid coolant sprays to create suction that pulls the contaminated gas stream from the source. As the gas stream moves through the throat of the ejector, it directly contacts the coolant, causing condensation. Absorption can also occur, if the contaminant is soluble in the coolant.

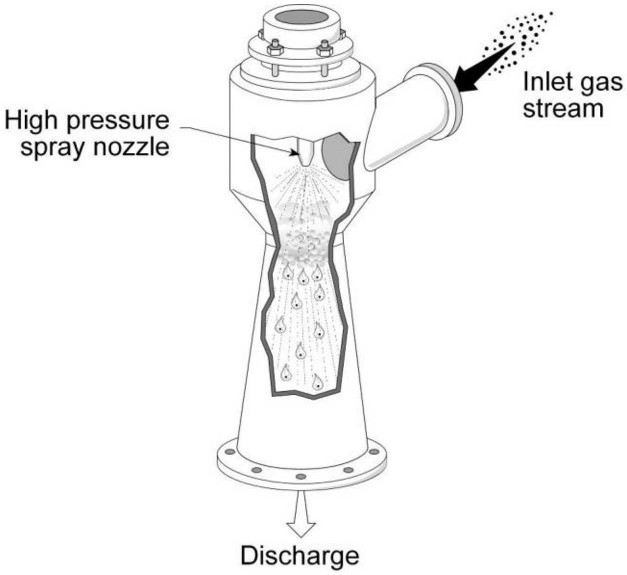


Figure 13-17. Ejector condenser

The main advantages of contact condensers are their simplicity and low cost. The main disadvantage is the mixing of the condensed contaminants with the water, which increases wastewater treatment or contaminant recovery costs.

13.3.1.2 Surface Condensers

The typical surface condenser is the shell-and-tube heat exchanger illustrated in Figure 13-18. These devices have a cylindrical shell that encloses numerous small tubes that run parallel to the cylindrical axis. The coolant, usually chilled water or brine, flows through these tubes, while the gas stream flows through the shell, outside the tubes. Heat from the gas stream is transferred through the tubes to the coolant, reducing the gas stream temperature and causing the contaminant to condense.

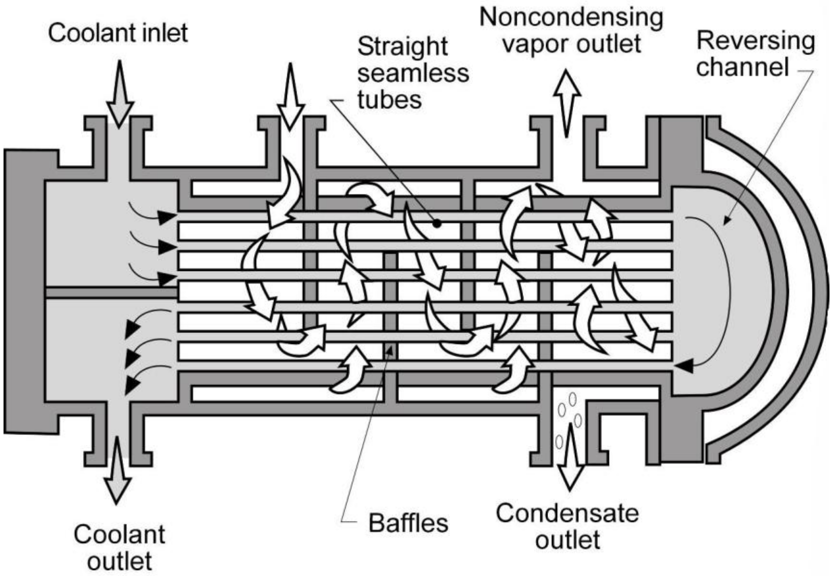


Figure 13-18. Multipass shell-and-tube condenser

In order to increase the heat transfer efficiency, baffles are typically used to cause the gas stream to make several passes across the tube bundle, and reversing chambers are used to cause the coolant to make several passes. Also, the condensate flow is usually restricted to cause flooding of the lower portion of the tube bundle. This lowers the temperature of the condensate in order to reduce evaporation when the material exits the unit.

Another surface condenser is the tube-and-fin heat exchanger shown in Figure 13-19. In these devices, the contaminated gas stream flows through tubes that have several fins along their outside surface. Heat from the gas stream is transferred through the tubes and fins to an air stream that is blown across their surface, again causing the contaminant to condense.

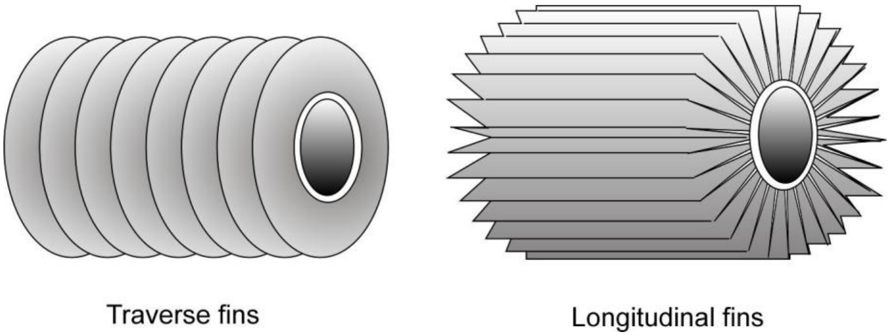


Figure 13-19. Tube-and-fin condenser elements

Surface condensers are more expensive to construct and to maintain than contact condensers. The temperature difference between the gas stream and the coolant causes the shell to expand and contract at a different rate than the tube bundle. To avoid damaging the condenser, floating head construction is used. In a floating head, one end of the tube bundle is mounted on a sliding seal that allows it to move independent of the shell. This seal is prone to deterioration and leakage. Offsetting the costs of construction and maintenance is the higher heat transfer efficiency and the recovery of contaminant that is not mixed with the cooling fluid.

13.3.2 Refrigeration Systems

Refrigeration systems use compressed coolants and operate at temperatures as low as -150°F. The most common coolants are chlorinated fluorocarbons, or CFCs, although this is changing in response to the Clean Air Act Amendments of 1990. A simplified schematic of a refrigeration system is shown in Figure 13-20. The refrigerated liquid, flowing through tubes in a shell-and-tube heat exchanger, absorbs heat from the gas stream flowing on the shell side, reducing the gas stream temperature and causing the contaminant to condense. The absorbed heat causes the refrigerant liquid to change to a vapor. The refrigerant vapor is compressed and passed through a tube-and-fin heat exchanger, where the heat is transferred to air blown over the fins, converting the refrigerant back to a liquid. The compressed refrigerant liquid flows through an expansion valve to reduce its pressure and then returns to the condenser.

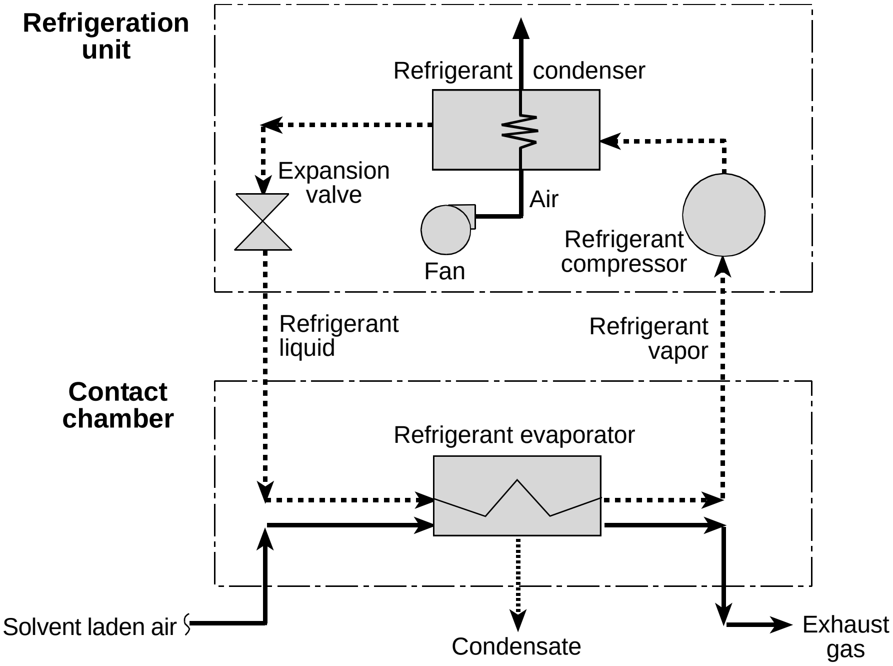


Figure 13-20. Basic refrigeration system

To prevent the accumulation of ice, the gas stream usually passes through a condenser maintained at about 40°F to condense any moisture before it enters the low-temperature condenser (see Figure 13-21). In order to achieve extremely low temperatures in the main chamber, cascade systems are typically used. Cascade systems are interconnected refrigeration systems where one unit is used to expel the heat from another unit. Different coolants may be used in the interconnected units, depending on their operating temperature.

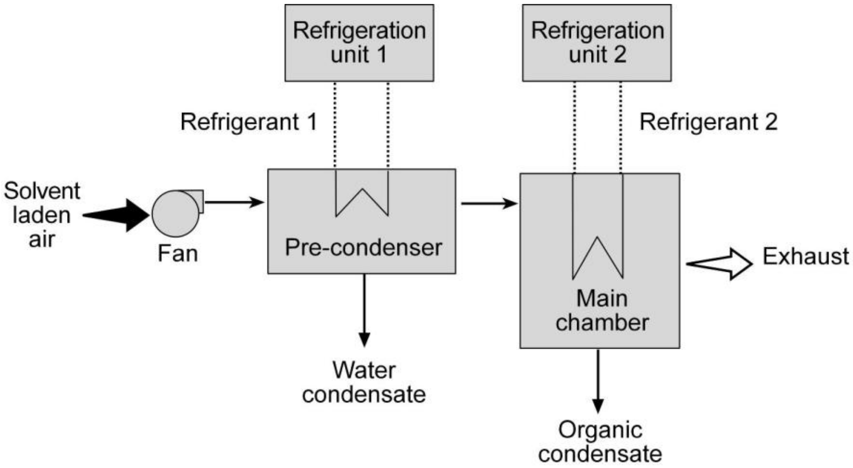


Figure 13-21. Simplified flowchart of a refrigeration system.

13.3.3 Cryogenic Systems

Cryogenic control systems use liquefied gases, such as nitrogen and carbon dioxide, to obtain temperatures as low as -320°F. These systems are relatively simple, since no refrigeration unit is needed and the coolant is vented to the atmosphere. In the simplest cryogenic system, illustrated in Figure 13-22, the liquefied gas, flowing through tubes in a shell-and-tube heat exchanger, absorbs heat from the gas stream flowing on the shell side, reducing the gas stream temperature and causing the contaminant to condense. The absorbed heat causes the liquefied coolant to change to a gas, which is discharged to the atmosphere.

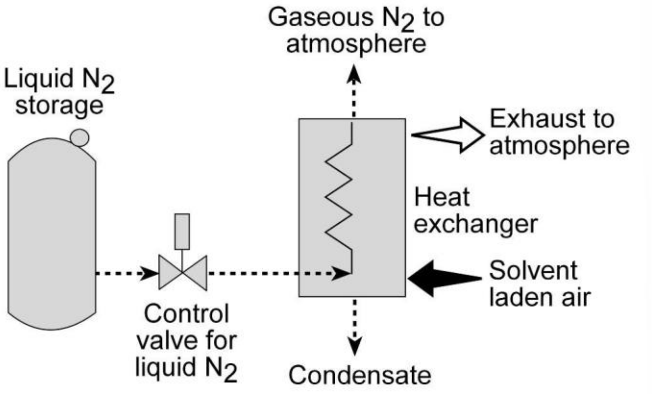


Figure 13-22. Single heat exchanger, indirect contact cryogenic system

At these extremely low temperatures, it is possible for the contaminant to accumulate as frost on the exterior surfaces of the tubes. To avoid this problem, it may be necessary to operate a parallel heat exchanger. One heat exchanger would be defrosting, while the other is in service. Another solution is a dual heat exchanger system shown in Figure 13-22. In the first heat exchanger, the liquefied gas is used to cool a circulating heat exchange fluid to a temperature just above the freezing point of the contaminants. This fluid flows to a second heat exchanger, where it is used to condense the contaminants, and then returns to the first heat exchanger.

Liquefied gases can also be used in direct contact systems. These systems also avoid the frosting problem, since there are no surfaces at extremely cold temperatures. The liquefied gas is injected through spray nozzles into an open chamber, where it directly contacts the contaminated gas stream. The chamber is insulated to keep the temperature as low as possible. Strip-heaters may be mounted on the exterior of the chamber walls for the occasional removal of any accumulated frost from the interior surfaces.

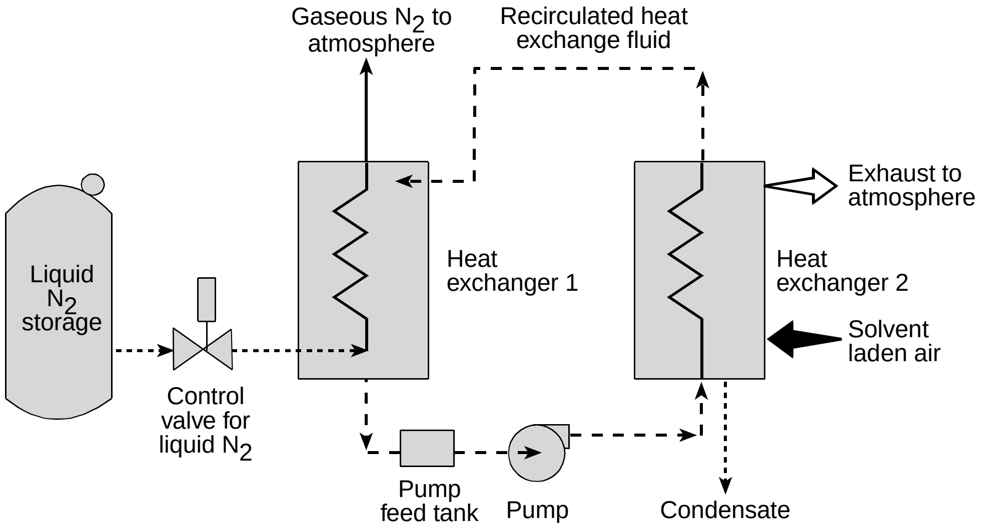


Figure 13-23. Dual heat exchange cryogenic system

13.4 Bioreactors

Bioreaction systems are sorption processes that use aerobic microorganisms to consume the organic compounds. They are used primarily for gas streams with a low organic vapor concentration and where the compounds are soluble in water and biodegradable. The main classes of bioreactors are biofilters, biotrickling filters and bioscrubbers. The classes of compounds that can be removed in these systems include alcohols, aldehydes, esters, ketones and many aromatic hydrocarbons. Removal efficiencies range from 60% to more than 99%.

13.4.1 Biofilters

Biofilters use a fixed microbial population in a stationary water phase, as illustrated in Figure 13-24. The microorganisms grow in a biofilm on the surface of a medium, or they are suspended in the water phase surrounding the medium. The filter medium consists of relatively inert materials, such as compost and peat, which provide a large surface area and additional nutrient supply. As the gas stream passes through the bed, the contaminants sorb into the biofilm and onto the filter medium, where they are degraded.

Biofilter beds are 3 to 5 feet deep and have a void volume of about 50% and water content of about 60% by weight. They usually have some sort of water addition to control moisture and add nutrients. Often, this involves only humidification of the gas stream before it enters the biofilter. However, if humidification proves inadequate, direct irrigation of the bed may be necessary. The operating temperature of the bed is 60°F to 85°F and the pH of the support material is typically 6 to 8. Compounds containing sulfur or nitrogen can generate acidic byproducts during biodegradation, requiring alkali addition to maintain the pH level. Gas stream residence time in the bed ranges from 15 to 60 seconds.

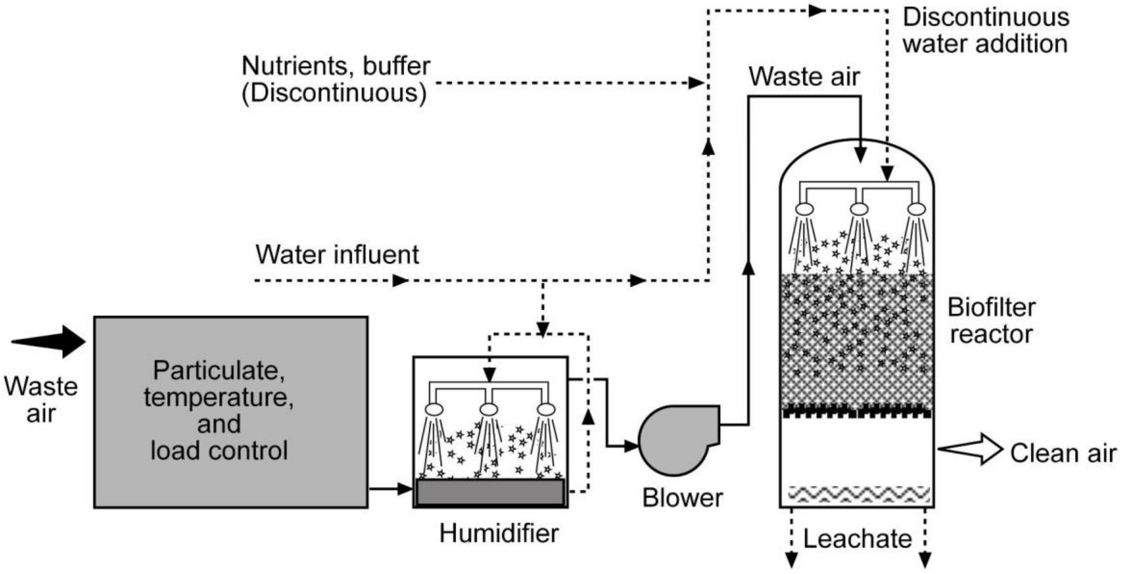


Figure 13-24. Biofilter system

Biofilters are relatively inexpensive to construct and to operate, they have a low pressure drop, and they produce no further waste streams. However, they have a large space requirement, the moisture and pH can be difficult to control, and particulate matter may clog the medium.

13.4.2 Biotrickling Filters

Biotrickling filters have a fixed microbial population in a flowing water phase, as illustrated in Figure 13-25. Prior to biodegradation, the contaminants are absorbed from the gas stream into a water phase that flows over an inorganic packing material. Microbes fixed to the packing and suspended in the water degrade the absorbed contaminants as they pass through the reactor. Biotrickling filters can be operated co-currently or counter-currently and are governed by many of the same operating conditions as biofilters. Nutrients, acids or bases may be added to the recirculated water to regulate the environment for optimal pollutant removal.

Biotrickling filters are more complex and expensive to construct and operate than biofilters, but they are better able to treat acid-producing contaminants. They are prone to clogging by biomass and produce a waste stream that requires further processing.

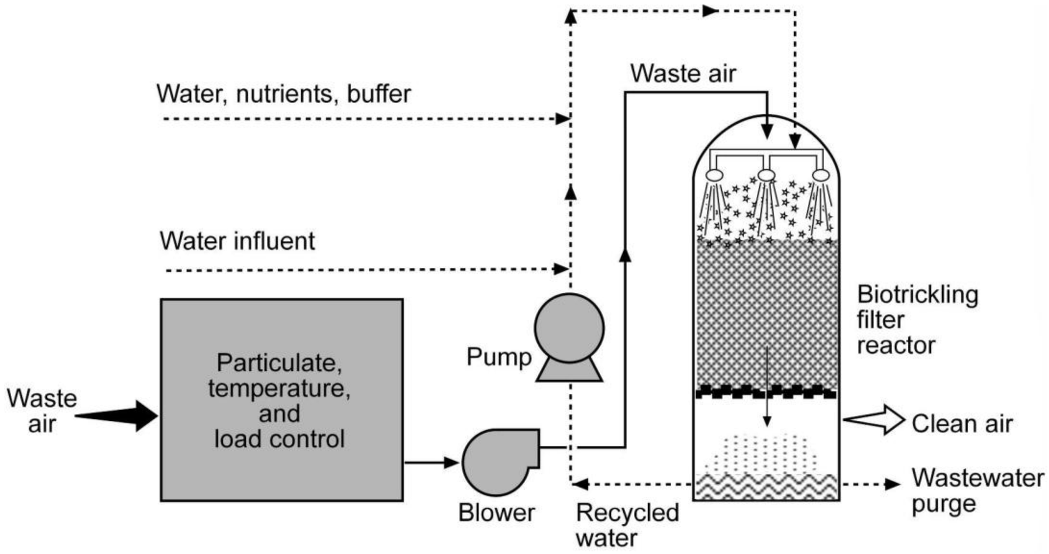


Figure 13-25. Biotrickling filter system

13.4.3 Bioscrubbers

Bioscrubbers have a suspended microbial population in a flowing water phase, as illustrated in Figure 13-26. Absorption takes place in typical wet scrubbing equipment, such as spray towers, plate towers or packed beds. The effluent from the wet scrubber is then transferred to a separate aerated vessel, where degradation of the contaminants is performed by suspended microbes. As with the biotrickling filter, the recirculated water allows nutrients, acids or bases to be added to maintain an environment conducive to optimal pollutant removal. They are less prone to clogging by biomass, but do produce a waste stream that requires further processing.

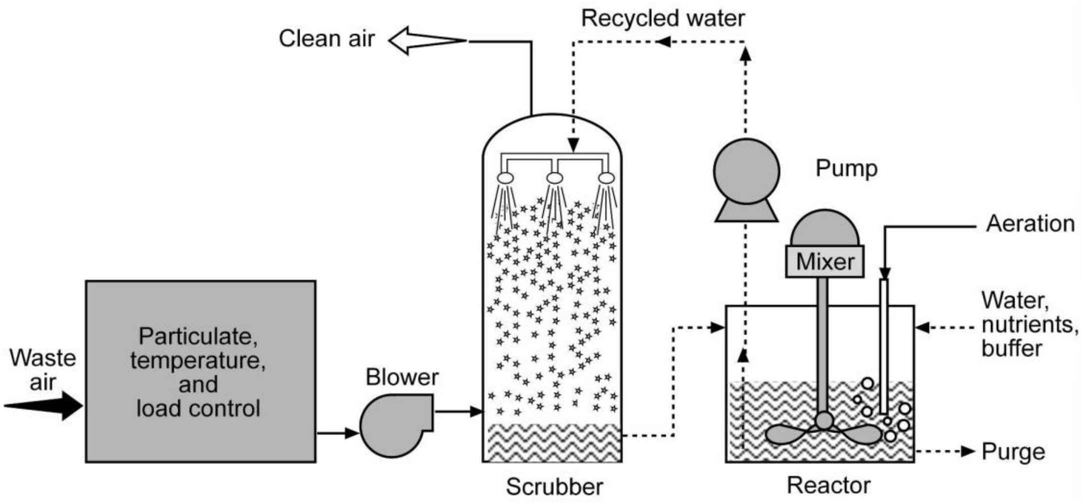


Figure 13-26. Bioscrubber system

Review Questions

Adsorption

1. What is the most common adsorbent used in adsorption systems?
   a. Activated alumina
   b. Molecular sieves
   c. Activated carbon
   d. Silica gel

2. What type of adsorption mechanism is used in regenerative systems?
   a. Physical
   b. Chemical
   c. Biological
   d. Ionic

3. The capacity of an adsorbent increases with ________. Select all that apply.
   a. low gas stream temperature
   b. high gas stream pressure
   c. high contaminant concentration
   d. low contaminant molecular weight

4. How is the capacity of an adsorbent affected by increased gas stream humidity?
   a. It increases
   b. It decreases
   c. It is not affected

5. Why are high molecular weight compounds not good candidates for regenerative adsorption?
   a. They are not adsorbed efficiently
   b. They are difficult to desorb
   c. They are difficult to condense

6. Which type of capacity is available for each adsorption cycle?
   a. Breakthrough capacity
   b. Saturation capacity
   c. Working capacity
   d. Heel capacity

7. What methods are used to regenerate an activated carbon adsorber? Select all that apply.
   a. Chemical displacement
   b. Thermal swing
   c. Incineration
   d. Pressure swing

8. What solvent recovery equipment is needed for an activated carbon adsorber that is collecting water-insoluble organic compounds and using low pressure steam for regeneration?
   a. Condenser and decanter
   b. Distillation column
   c. Stripping column
   d. Molecular sieve

Incineration

9. What type of incinerator is typically used to oxidize an organic contaminant that is at a concentration of 25% to 50% of the LEL?
   a. Flare
   b. Thermal oxidizer
   c. Catalytic oxidizer

10. Why is steam sometimes used in flare incineration? Select all that apply.
    a. It helps reduce noise
    b. Its injection increases turbulent mixing
    c. It reduces polymerization
    d. It aids in burning

11. What is the typical operating temperature range of a thermal oxidizer?
    a. 1,300°F to 1,800°F
    b. 750°F to 1,000°F
    c. 1,300°C to 1,800°C
    d. 1,000°F to 1,200°F

12. What is the residence time for a thermal oxidizer?
    a. 0.1-0.2 seconds
    b. 2-3 seconds
    c. 0.3-0.5 seconds
    d. It depends on the temperature and the contaminant

13. What is the typical inlet temperature range for a catalytic oxidizer?
    a. 300°F to 500°F
    b. 500°F to 700°F
    c. 700°F to 900°F
    d. 900°F to 1,00°F

14. Which of the following can permanently reduce the activity of a catalyst? Select all that apply.
    a. Physical deterioration
    b. Masking
    c. Exposure to excessively high temperatures
    d. Poisoning

15. Regenerative heat exchangers are composed of _______.
   a. packed beds of ceramic material
   b. tube banks
   c. tubes with fins
   d. activated carbon

Condensation

16. The gas stream exiting a condensation system has an organic vapor concentration _______.
   a. equal to 10% of the inlet concentration
   b. equal to 10% of the vapor pressure at the exit temperature
   c. equal to the vapor pressure at the exit temperature
   d. equal to zero

17. What is the exiting temperature of a shell-and-tube condenser using water or brine as the coolant?
   a. 0°F to 40°F
   b. Less than 0°F
   c. Less than -10°F
   d. Greater than 100°F

18. Which of the following are types of direct contact condensers? Select all that apply.
   a. Spray towers
   b. Venturi ejectors
   c. Tray towers
   d. Cooling towers

19. What exit temperature are refrigeration systems capable of?
   a. 32°F
   b. 0°F
   c. -150°F
   d. -320°F

20. What exit temperature are cryogenic systems capable of?
   a. 32°F
   b. 0°F
   c. -150°F
   d. -320°F

21. What coolants are used in cryogenic systems? Select all that apply.
   a. Liquid helium
   b. Liquid carbon dioxide
   c. Liquid oxygen
   d. Liquid nitrogen

22. Why are precondensers used in refrigeration systems? Select all that apply.
   - a. To prevent frost accumulation in the main condensing chamber
   - b. To minimize water-organic separation problems
   - c. To reduce the organic concentration entering the main chamber
   - d. To reduce the temperature at the inlet to the main chamber

Bioreactors

23. Which of the following is true regarding bioreactors? Select all that apply.
   - a. The organic compounds must be soluble in water
   - b. The organic compounds must be biodegradable
   - c. The organic compound must be at high concentration

24. Which bioreactor does not have a liquid discharge that requires further treatment?
   - a. Biofilters
   - b. Biotrickling filters
   - c. Bioscrubbers

25. What is the typical operating temperature and pH of a bioreactor?
   - a. 85°F to 100°F and pH of 6 to 8
   - b. 60°F to 85°F and pH of 8 to 10
   - c. 60°F to 85°F and pH of 6 to 8
   - d. 85°F to 100°F and pH of 8 to 10

Review Answers

Adsorption

1. What is the most common adsorbent used in adsorption systems?
   c. Activated carbon

2. What type of adsorption mechanism is used in regenerative systems?
   a. Physical

3. The capacity of an adsorbent increases with _______. Select all that apply.
   a. Low gas stream temperature
   b. High gas stream pressure
   c. High contaminant concentration.

4. How is the capacity of an adsorbent affected by increased gas stream humidity?
   b. It decreases

5. Why are high molecular weight compounds not good candidates for regenerative adsorption?
   b. They are difficult to desorb

6. Which type of capacity is available for each adsorption cycle?
   c. Working capacity

7. What methods are used to regenerate an activated carbon adsorber? Select all that apply.
   b. Thermal swing
   d. Pressure swing

8. What solvent recovery equipment is needed for an activated carbon adsorber that is collecting water-insoluble organic compounds and using low pressure steam for regeneration?
   a. Condenser and decanter

Incineration

9. What type of incinerator is typically used to oxidize an organic contaminant that is at a concentration of 25% to 50% of the LEL?
   b. Thermal oxidizer

10. Why is steam sometimes used in flare incineration? Select all that apply.
    b. Its injection increases turbulent mixing
    c. It reduces polymerization
    d. It aids in burning

11. What is the typical operating temperature range of a thermal oxidizer?
    a. 1,300°F to 1,800°F

12. What is the residence time for a thermal oxidizer?
    d. It depends on the temperature and the contaminant

13. What is the typical inlet temperature range for a catalytic oxidizer?
    b. 500°F to 700°F

14. Which of the following can permanently reduce the activity of a catalyst? Select all that apply.
    a. Physical deterioration
    c. Exposure to excessively high temperatures
    d. Poisoning

15. Regenerative heat exchangers are composed of _______.
    a. packed beds of ceramic material

Condensation

16. The gas stream exiting a condensation system has an organic vapor concentration _______.
    c. equal to the vapor pressure at the exit temperature

17. What is the exiting temperature of a shell-and-tube condenser using water or brine as the coolant?
    a. 0°F to 40°F

18. Which of the following are types of direct contact condensers? Select all that apply.
    a. Spray towers
    b. Venturi ejectors
    c. Tray towers

19. What exit temperature are refrigeration systems capable of?
    c. -150°F

20. What exit temperature are cryogenic systems capable of?
    d. -320°F

21. What coolants are used in cryogenic systems? Select all that apply.
    b. Liquid carbon dioxide
    d. Liquid nitrogen

22. Why are precondensers used in refrigeration systems? Select all that apply.
    a. To prevent frost accumulation in the main condensing chamber

Bioreactors

23. Which of the following is true regarding bioreactors? Select all that apply.
    a. The organic compounds must be soluble in water
    b. The organic compounds must be biodegradable

24. Which bioreactor does not have a liquid discharge that requires further treatment?
    a. Biofilters

25. What is the typical operating temperature and pH of a bioreactor?
    c. 60°F to 85°F and pH of 6 to 8

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