Sources and Control of Volatile Organic Air Pollutants

APTI Course 482

Student Workbook

June, 2025

By: William Franek; Ph.D., P.E., DEE & Louis DeRose; J.D., M.S., P.E.

Course 482

Sources and Control of Volatile Organic Air Pollutants

June 16 – 20, 2025

AGENDA

LOCATION	**MODERATOR**
On-Line (CenSARA)	William J. Franek; Ph.D., P.E., DEE

DAY & TIME	SUBJECT	SPEAKER
Monday, June 16 (Central Time)		
9:00	Course Overview	W. Franek
9:15	Properties and Fundamentals	W. Franek
11:00	BREAK	
11:15	Properties and Fundamentals (cont’d)	W. Franek
12:15	Properties of Organic Vapors	L. DeRose
1:15	ADJOURN	
Tuesday, June 17		
9:00	Source Measurement Techniques	W. Franek
10:15	National Sources and the Regulatory Approach	L. DeRose
11:00	BREAK	
11:15	National Sources and the Regulatory Approach (cont’d)	L. DeRose
12:15	Surface Coating	W. Franek
1:15	ADJOURN	
Wednesday, June 18		
9:00	Surface Coating (cont’d)	W. Franek
9:15	Graphic Arts	W. Franek
10:45	Calculating VOC Content of Coatings and Inks	W. Franek
11:00	BREAK	
11:15	Calculating VOC Content of Coatings and Inks (cont’d)	W. Franek
1:00	Petroleum Refining	W, Franek
1:15	ADJOURN	
Thursday, June 19		
9:00	Petroleum Refining	W. Franek
9:45	Petroleum Product Storage and Distribution	L. DeRose
11:00	BREAK	
11:15	Petroleum Product Storage and Distribution (Cont.)	L. DeRose
12:15	Degreasing & Drycleaning	W. Franek
1:30	ADJOURN	

DAY & TIME	SUBJECT	SPEAKER
Friday, June 20		
9:00	Batch Process VOM/HAP Calculations for Chemical Mfg.	W. Franek
10:30	Intro to VOC Control Technology	L. DeRose
11:00	BREAK	
11:15	Intro to VOC Control Technology (cont.)	DeRose & Franek
1:30	ADJOURN	

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APTI Course 482

Sources and Control of Volatile Organic Air Pollutants

Volatile Organic Compound (VOC)

"…any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity…"

---40CFR51.100

Course Objective

- Provide information on sources of VOCs and techniques for controlling their emission
- Focus is on reduction of VOCs for attaining or maintaining ozone NAAQS

Course Topics

Topic	Chapter
Properties and Fundamentals	2
Source Measurement Techniques	3
National Sources and the Regulatory Approach	4
Surface Coating	5
Graphic Arts	6
Calculating the VOC Content of Paints and Inks	7

Course Topics

Topic	Chapter
Batch Process VOM/HAP Calculation for Chemical Mfg. Industry	7B
Petroleum Refining	8
Petroleum Product Storage and Distribution	9
Degreasing	10
Dry Cleaning	11
Introduction to Control Technology	13

Chapter 2
Sources and Control of Volatile
Organic Air Pollutants

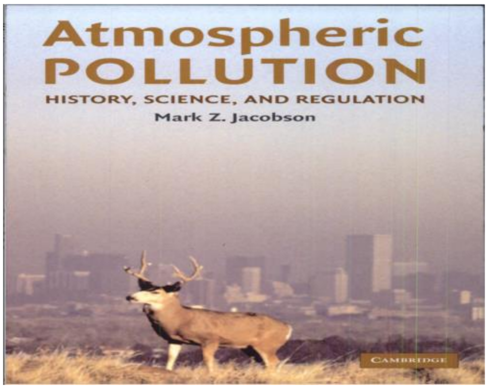
"Properties and Fundamentals"

Importance of Organic Compounds (in Air Pollution Reactants)

- Volatile compounds contribute to the formation of ozone and photochemical oxidants
- Compounds can have toxic effects on plants and animals

Topics Covered

- Review of organic chemistry
- Formation of ozone and photochemical smog
- Properties of organic vapors



Atmospheric
POLLUTION
HISTORY, SCIENCE, AND REGULATION
Mark Z. Jacobson
CAMBRIDGE

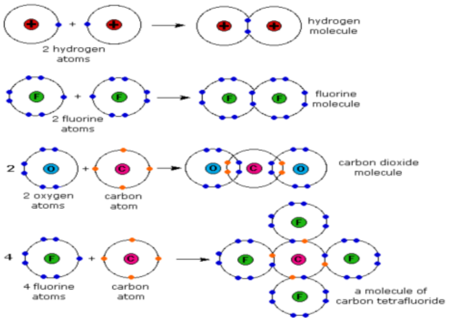
Review of Organic Chemistry

- Chemistry of the compounds of carbon
- Number of organic compounds exceeds 10 million
- Number of inorganic compounds is about 300,000

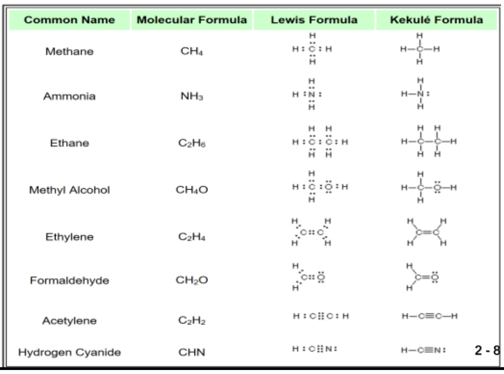
Characteristics of the Carbon Atom

- Atomic number = 6
- Atomic weight = 12
- Total electrons = 6
- Valence electrons = 4
- Forms covalent bonds
  - Single
  - Double
  - Triple

Lewis Formula Covalent Bonds Diagrams

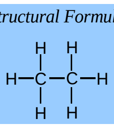


Structural Formulas Table

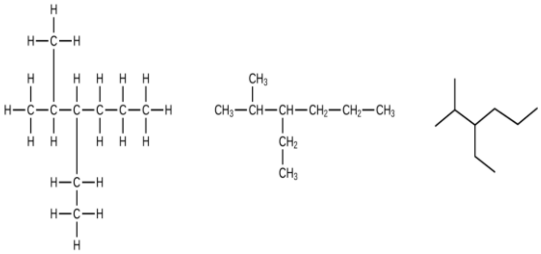


Common Name	Molecular Formula	Lewis Formula	Kekulé Formula
Methane	CH_4	H : C : H	H—C—H
Ammonia	NH_3	H : N :	H—N :
Ethane	C_2H_6	H : C : C : H	H—C—C—H
Methyl Alcohol	CH_4O	H : C : O : H	H—C—O—H
Ethylene	C_2H_4	C :: C	C=C
Formaldehyde	CH_2O	C :: O	C=O
Acetylene	C_2H_2	H : C ⋮⋮ C : H	H—C≡C—H
Hydrogen Cyanide	CHN	H : C ⋮⋮ N :	H—C≡N :

Molecular, Structural and Semi-Structural Formulas

Molecular Formula	*Structural Formula*	*Semi-structural Formula*
C_2H_6	 $H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$	$CH_3—CH_3$

Chemical Structure Represented Three Different Ways



Expanded formula   Condensed formula   Skeletal structure

Hydrocarbons

Compounds formed only from carbon and hydrogen

- Alkanes
- Alkenes
- Alkynes
- Cyclic compounds

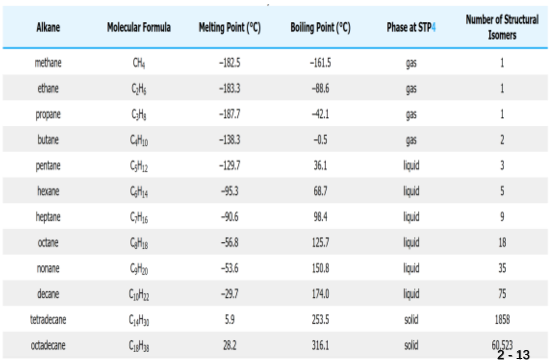
Alkanes

Carbon atoms linked only by single bonds

General formula: C_nH_{2n+2}

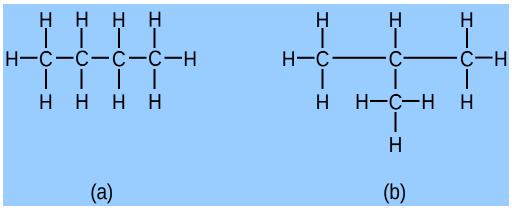
Methane (CH_4)
Ethane (C_2H_6)
Propane (C_3H_8)
Butane (C_4H_{10})
Pentane (C_5H_{12})

Properties of Some Alkanes



Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[4]	Number of Structural Isomers
methane	CH_4	−182.5	−161.5	gas	1
ethane	C_2H_6	−183.3	−88.6	gas	1
propane	C_3H_8	−187.7	−42.1	gas	1
butane	C_4H_{10}	−138.3	−0.5	gas	2
pentane	C_5H_{12}	−129.7	36.1	liquid	3
hexane	C_6H_{14}	−95.3	68.7	liquid	5
heptane	C_7H_{16}	−90.6	98.4	liquid	9
octane	C_8H_{18}	−56.8	125.7	liquid	18
nonane	C_9H_{20}	−53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	−29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Isomers of Butane



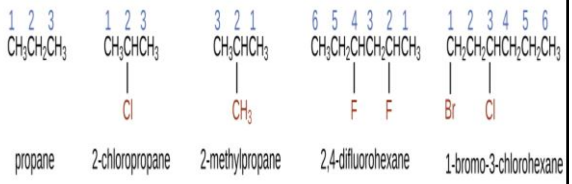
n-butane

i-butane

Isomers

- Compounds with the same molecular formulas, but with different structures
- All alkanes with four or more carbon atoms exist as isomers
- Alkanes with five or more carbon atoms exist as more than two isomers

Naming Alkanes



IUPAC Rules (uiuc.edu)

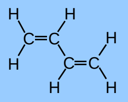
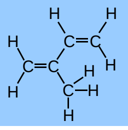
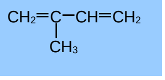
Alkenes

Hydrocarbons that contain one double bond

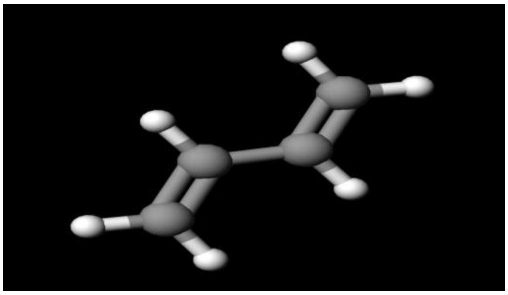
General formula: C_nH_{2n}

Ethylene (C_2H_4)
Propylene (C_3H_6)
Butylene (C_4H_8)
Pentylene (C_5H_{10})

Diolefin Compounds

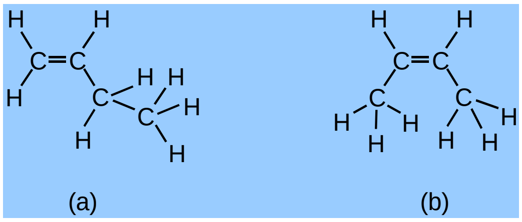
Molecular Formula	*Name*	*Structural Formula*	*Semi-structural Formula*
C_4H_6	butadiene		$CH_2=CH-CH=CH_2$
C_5H_8	2-methyl butadiene		 $CH_2=C(CH_3)-CH=CH_2$

3-D Structure for 1,3-Butadiene



https://webbook.nist.gov/chemistry/name-ser/

Butylene Isomers



Alkynes

Hydrocarbons that contain one triple bond

General formula: C_nH_{2n-2}

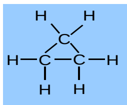
Ethyne (C_2H_2)
Propyne (C_3H_4)
Butyne (C_4H_6)
Pentyne (C_5H_8)

Cyclic Compounds

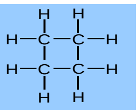
- Cycloparaffins
- Aromatic hydrocarbons

Unprecedented" Control – Scientists Twist Chemical Bonds Beyond Their Limits (scitechdaily.com)

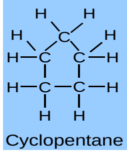
Examples of Cycloparaffin Compounds



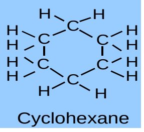
Cyclopropane



Cyclobutane

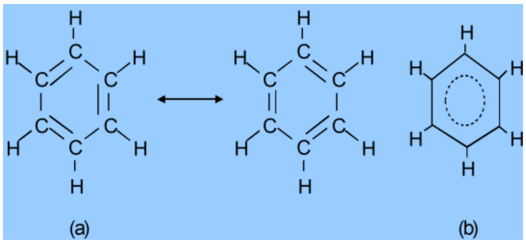


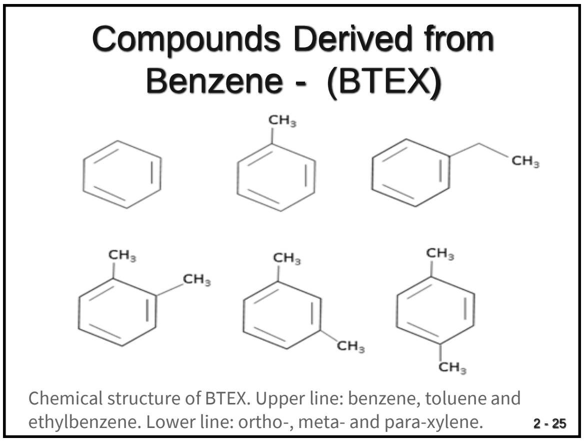
Cyclopentane



Cyclohexane

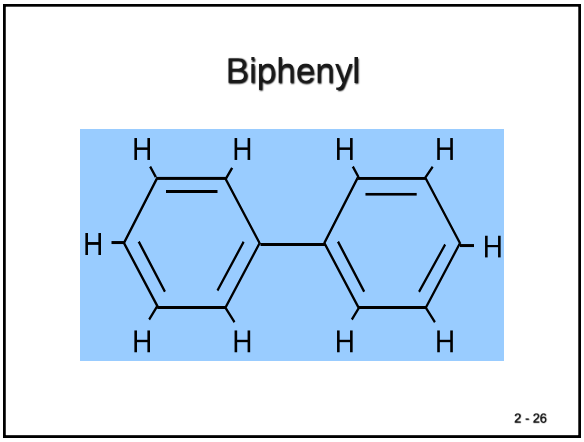
Benzene Structure



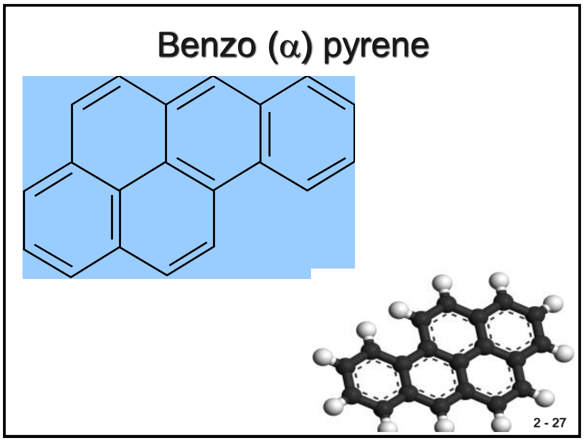


Compounds Derived from Benzene - (BTEX)

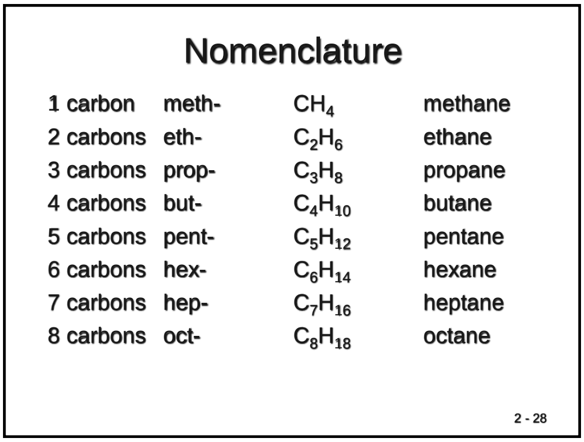
Chemical structure of BTEX. Upper line: benzene, toluene and ethylbenzene. Lower line: ortho-, meta- and para-xylene.



Biphenyl

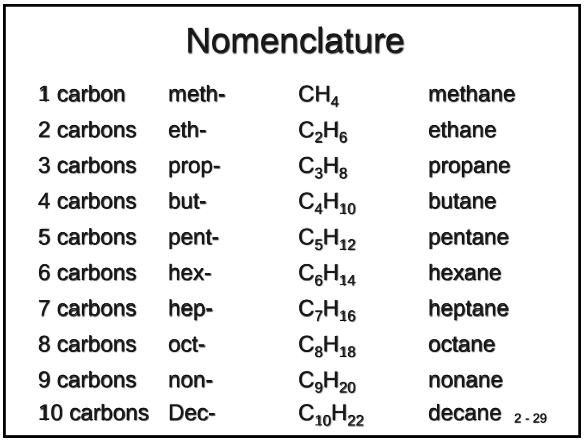


Benzo (α) pyrene



Nomenclature

1 carbon	meth-	CH_4	methane
2 carbons	eth-	C_2H_6	ethane
3 carbons	prop-	C_3H_8	propane
4 carbons	but-	C_4H_{10}	butane
5 carbons	pent-	C_5H_{12}	pentane
6 carbons	hex-	C_6H_{14}	hexane
7 carbons	hep-	C_7H_{16}	heptane
8 carbons	oct-	C_8H_{18}	octane



Nomenclature

1 carbon	meth-	CH_4	methane
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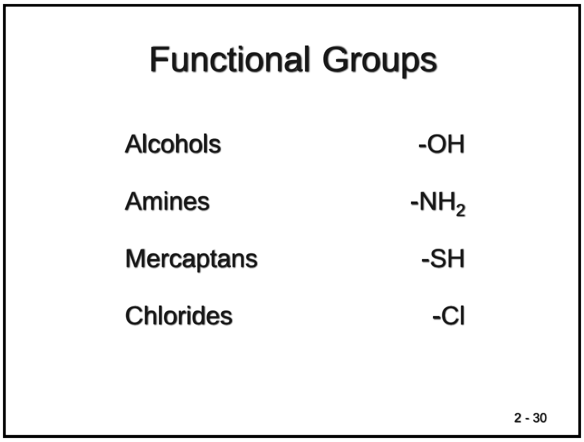
4 carbons	but-	C_4H_{10}	butane
5 carbons	pent-	C_5H_{12}	pentane
6 carbons	hex-	C_6H_{14}	hexane
7 carbons	hep-	C_7H_{16}	heptane
8 carbons	oct-	C_8H_{18}	octane
9 carbons	non-	C_9H_{20}	nonane
10 carbons	Dec-	$C_{10}H_{22}$	decane

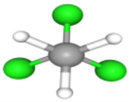


Functional Groups

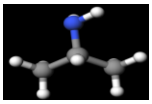
Alcohols	-OH
Amines	$-NH_2$
Mercaptans	-SH
Chlorides	-Cl

Location of Substitution

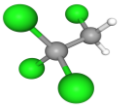
1,1,1-trichloroethane $C_2H_3Cl_3$



2-propylamine C_3H_9N

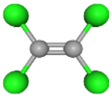


1,1,2,2 Tetrachloroethane $C_2H_2Cl_4$

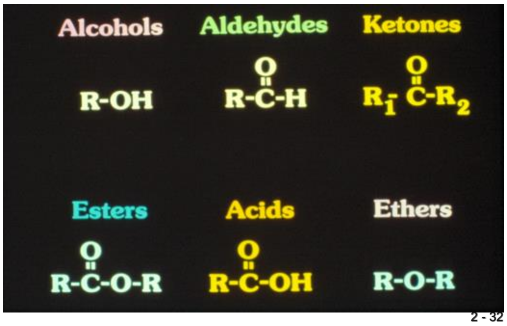


Perchloroethylene C_2Cl_4

(1,1,2,2-tetrachloroethylene)



Functional Groups Containing Oxygen



Alcohols

R-OH

Aldehydes

$\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-H}$

Ketones

$\text{R}_1\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R}_2$

Esters

$\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-R}$

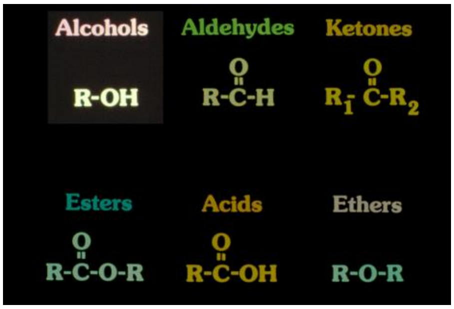
Acids

$\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH}$

Ethers

R-O-R

Functional Groups Containing Oxygen



Alcohols

R-OH

Aldehydes

$\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-H}$

Ketones

$\text{R}_1\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R}_2$

Esters

$\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-R}$

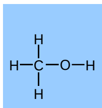
Acids

$\text{R-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH}$

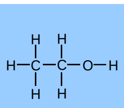
Ethers

R-O-R

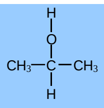
Common Alcohols



Methyl alcohol



Ethyl alcohol

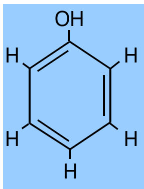


Isopropyl alcohol (Isopropanol)

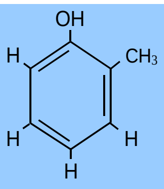
$CH_3-CH_2-CH_2-O-H$

n-propyl alcohol

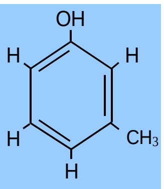
Phenols



Phenol

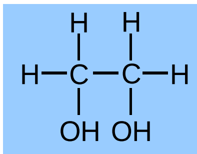


Ortho-cresol (o-cresol)

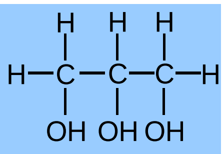


Meta-cresol (m-cresol)

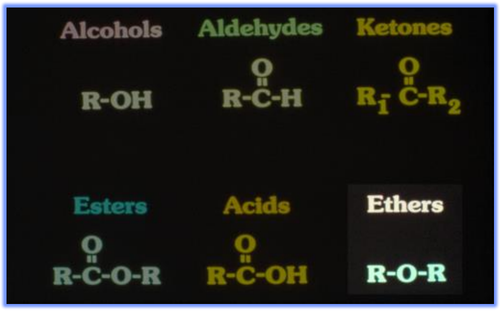
Polyhydric Alcohols



Ethylene glycol



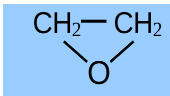
Glycerol



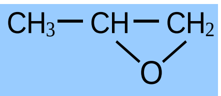
Ether Compounds

- Diethyl ether
  $CH_3CH_2\text{-}O\text{-}CH_2CH_3$
- Methyl ethyl ether
  $CH_3\text{-}O\text{-}CH_2CH_3$

Cyclic Ethers

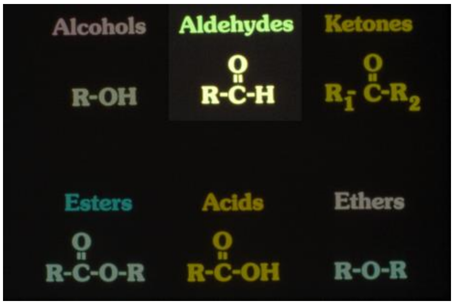


Ethylene oxide



Propylene oxide

15.5: Esters - Structures and Names - Chemistry LibreTexts



Alcohols

R-OH

Aldehydes

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

Ketones

$R_1-\overset{O}{\overset{\|}{C}}-R_2$

Esters

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

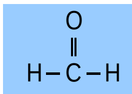
Acids

$R-\overset{O}{\overset{\|}{C}}-OH$

Ethers

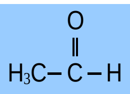
R-O-R

Aldehydes



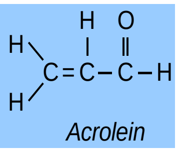
$H-\overset{O}{\overset{\|}{C}}-H$

Formaldehyde

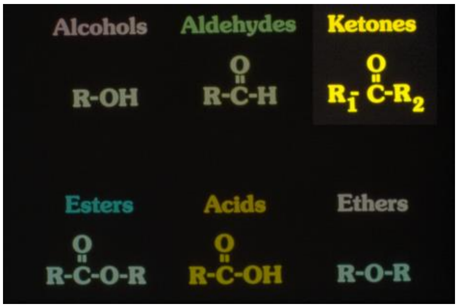


$H_3C-\overset{O}{\overset{\|}{C}}-H$

Acetaldehyde



Acrolein



Alcohols

R-OH

Aldehydes

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

Ketones

$R_1-\overset{O}{\overset{\|}{C}}-R_2$

Esters

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

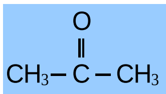
Acids

$R-\overset{O}{\overset{\|}{C}}-OH$

Ethers

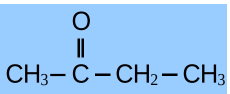
R-O-R

Ketones



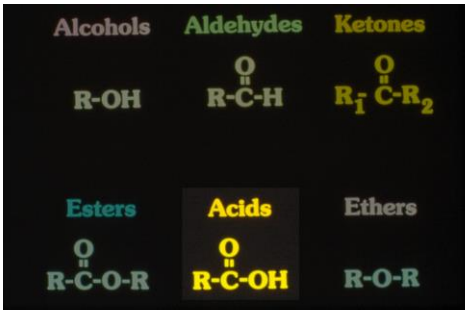
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Acetone



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

Methyl ethyl ketone (MEK)



Alcohols

R-OH

Aldehydes

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

Ketones

$R_1-\overset{O}{\overset{\|}{C}}-R_2$

Esters

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

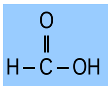
Acids

$R-\overset{O}{\overset{\|}{C}}-OH$

Ethers

R-O-R

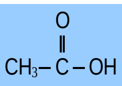
Acids



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

Formic acid

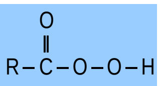
(a)



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

Acetic acid

(b)

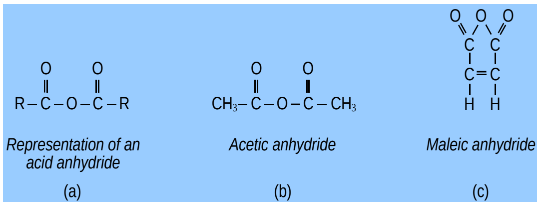


$R-\overset{O}{\overset{\|}{C}}-O-O-H$

Peroxyacids

(c)

Acid Anhydrides



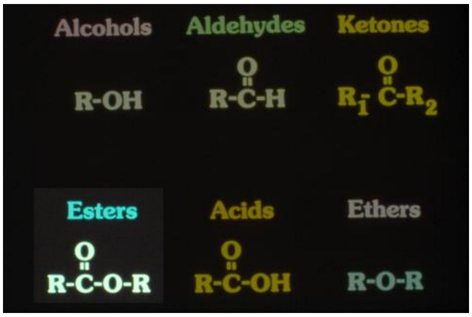
$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$

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

Representation of an acid anhydride
(a)

Acetic anhydride
(b)

Maleic anhydride
(c)



Alcohols
$R-OH$

Aldehydes
$R-\overset{\overset{O}{\|}}{C}-H$

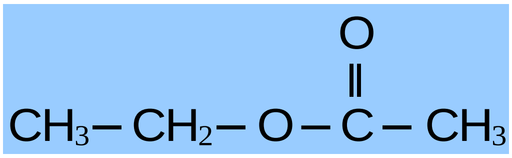
Ketones
$R_1-\overset{\overset{O}{\|}}{C}-R_2$

Esters
$R-\overset{\overset{O}{\|}}{C}-O-R$

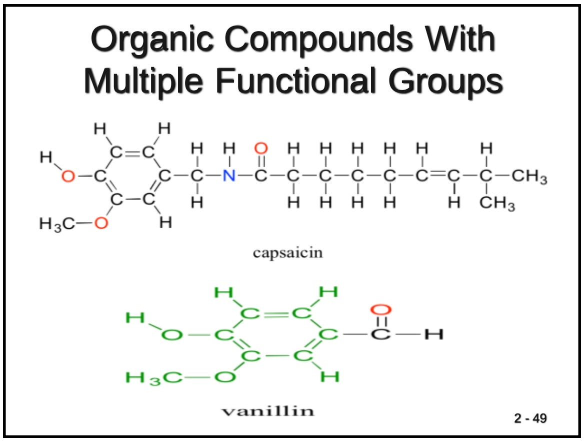
Acids
$R-\overset{\overset{O}{\|}}{C}-OH$

Ethers
$R-O-R$

Ethyl Acetate



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

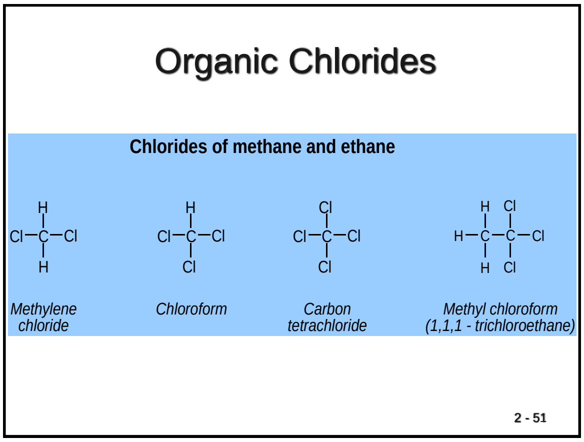


Organic Compounds With Multiple Functional Groups

capsaicin

vanillin

Organic Compounds Containing Halides



Organic Chlorides

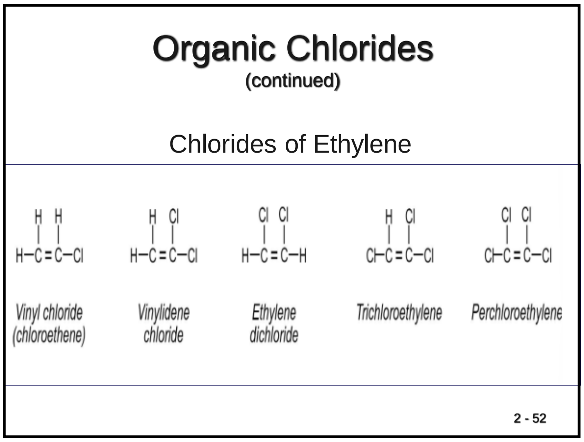
Chlorides of methane and ethane

Methylene chloride

Chloroform

Carbon tetrachloride

Methyl chloroform (1,1,1 - trichloroethane)



Organic Chlorides

(continued)

Chlorides of Ethylene

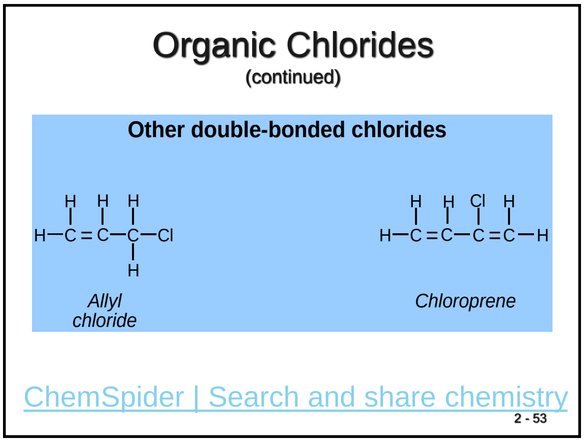
Vinyl chloride (chloroethene)

Vinylidene chloride

Ethylene dichloride

Trichloroethylene

Perchloroethylene



Organic Chlorides

(continued)

Other double-bonded chlorides

Allyl chloride

Chloroprene

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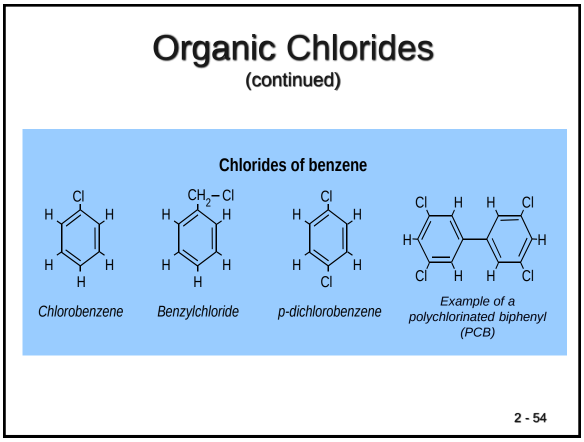


Organic Chlorides

(continued)

Chlorides of benzene

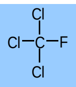
Chlorobenzene

Benzylchloride

p-dichlorobenzene

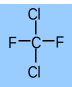
Example of a polychlorinated biphenyl (PCB)

Chlorofluorocarbons



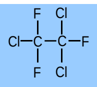
CCl_3F

Trichlorofluormethane (Freon 11)



CCl_2F_2

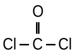
Dichlorodifluoromethane (Freon 12)



$CCl_2F\text{-}CClF_2$

Trichlorotrifluoroethane (Freon 13)

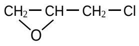
Compounds Containing Both Oxygen and Chlorine



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

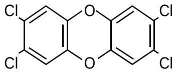
Phosgene

(a)



Epichlorohydrin

(b)

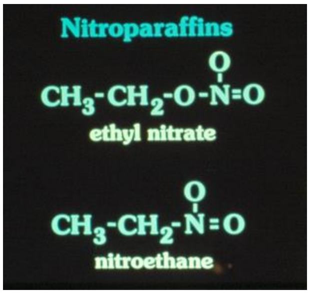


Dioxin (TCDD)
2,3,7,8, tetrachlorodibenzo-p-dioxin

(c)

PubChem (nih.gov)

Organic Compounds Containing Nitrogen



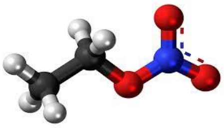
Nitroparaffins

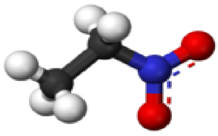
$CH_3\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{|}{N}}{=}O$

ethyl nitrate

$CH_3\text{-}CH_2\text{-}\overset{O}{\overset{|}{N}}{=}O$

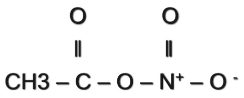
nitroethane



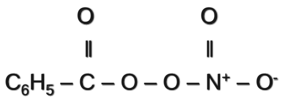


NITROETHANE | CAMEO Chemicals | NOAA

PAN and PBN Compounds



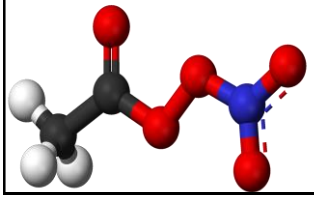
$$\mathrm{CH3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{N^{+}}-O^{-}}$$

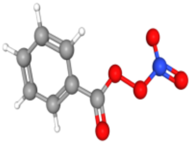


$$\mathrm{C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{N^{+}}-O^{-}}$$

- Peroxyacetyl nitrate

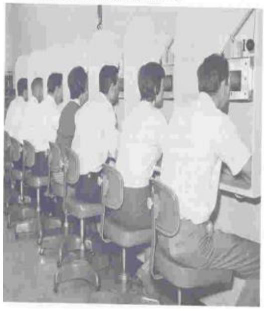
Peroxybenzoyl nitrate





Smog Chamber

Figure 1. Eye irritation test is the primary method used in the Smog Chamber to evaluate contribution to photochemical smog.



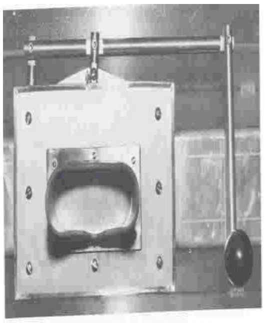
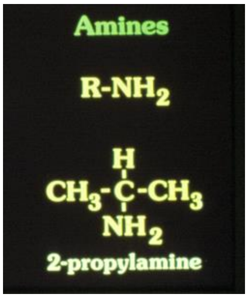


Figure 3. Smog Chamber eye port

Two Smog Researchers Use A Plastic Helmet And Suit:

Organic Compounds Containing Nitrogen



Amines

$R\text{-}NH_2$

$$CH_3\text{-}\overset{H}{\underset{NH_2}{C}}\text{-}CH_3$$

2-propylamine

Amine Compounds

- Primary amine: RNH_2

  CH_3NH_2

- Secondary amine: R_2NH

  $CH_3NHC_2H_5$

- Tertiary amine: R_3N

  $(C_2H_5)_3N$

Organic Compounds Containing Sulfur

- Methyl mercaptan

  CH_3SH

- Dimethyl sulfide

  CH_3SCH_3

Formation of Ozone and Photochemical Smog

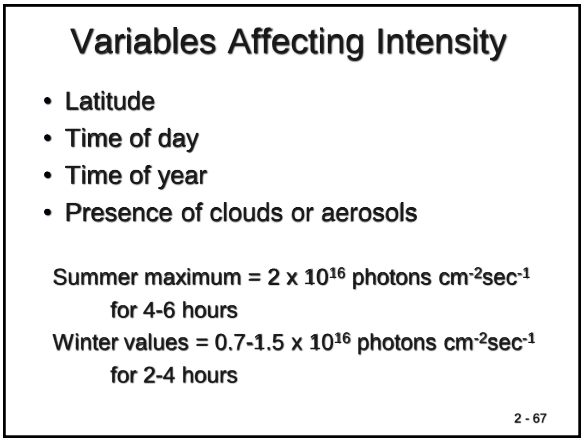
Smog in Los Angeles, California

Photochemical Reactions

$$A \xrightarrow{h\nu} A^*$$

$$A^* \rightarrow B + C + \ldots$$

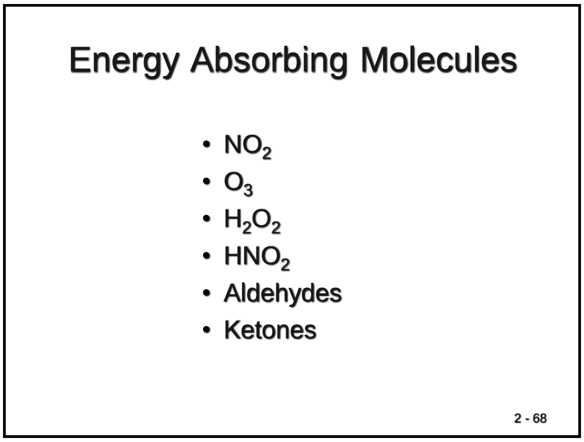
Wavelengths of interest are 280 nm to 730 nm



Variables Affecting Intensity

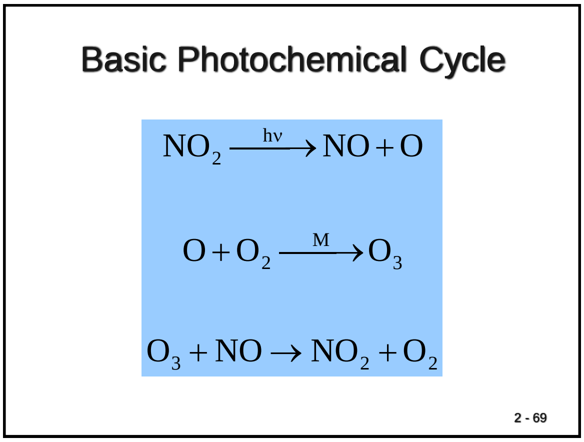
- Latitude
- Time of day
- Time of year
- Presence of clouds or aerosols

Summer maximum = 2 x 10^{16} photons $cm^{-2}sec^{-1}$
for 4-6 hours
Winter values = 0.7-1.5 x 10^{16} photons $cm^{-2}sec^{-1}$
for 2-4 hours



Energy Absorbing Molecules

- NO_2
- O_3
- H_2O_2
- HNO_2
- Aldehydes
- Ketones



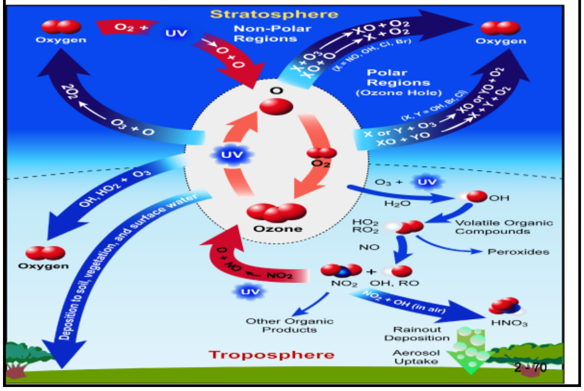
Basic Photochemical Cycle

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \xrightarrow{M} O_3$$

$$O_3 + NO \rightarrow NO_2 + O_2$$

Schematic overview of photochemical processes influencing stratospheric and tropospheric ozone



Role of VOCs

$$O_3 \xrightarrow{h\nu} O^* + O_2$$

$$O^* + H_2O \rightarrow 2OH\cdot$$

Understanding OH· reactions is key

Reactions of Formaldehyde

Photolysis:

$$HCHO \xrightarrow{h\nu} H\cdot + HCO\cdot$$

Reaction with OH:

$$HCHO + OH\cdot \rightarrow HCO\cdot + H_2O$$

Reactions of Formaldehyde (cont'd)

$$H\cdot + O_2 \xrightarrow{M} HO_2\cdot$$

$$HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$$

Reactions of Formaldehyde (cont'd)

$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$$

$$OH\cdot + NO_2 \rightarrow HNO_3$$

Reactions of Acetaldehyde

Photolysis:

$$CH_3CHO \xrightarrow{hv} CH_3\cdot + HCO\cdot$$

Reaction with OH:

$$CH_3CHO + OH\cdot \rightarrow CH_3CO\cdot + H_2O$$

Reactions of Acetaldehyde (cont'd)

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$$

$$CH_3O_2\cdot + NO \rightarrow NO_2 + CH_3O\cdot$$

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot$$

Reactions of Acetaldehyde (cont'd)

$$CH_3CO\cdot + O_2 \rightarrow CH_3COO_2\cdot$$

$$CH_3COO_2\cdot + NO \rightarrow NO_2 + CH_3COO\cdot$$

$$CH_3COO\cdot + O_2 \rightarrow CH_3O_2\cdot + CO_2$$

$$CH_3COO_2\cdot + NO_2 \rightarrow CH_3COO_2NO_2$$

Reactions of Hydrocarbons

$$RH + OH\cdot \rightarrow R\cdot + H_2O$$

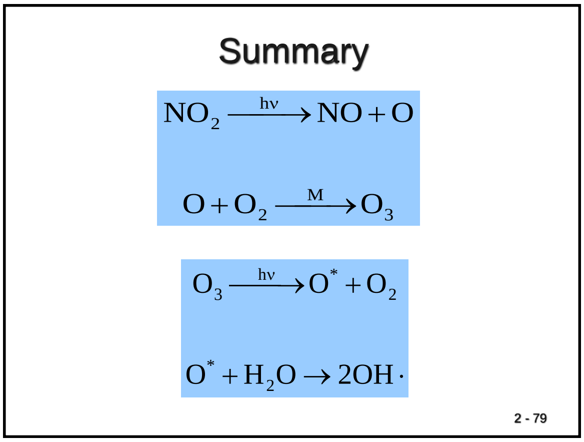
$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot$$

$$RO_2\cdot + NO \rightarrow RONO_2$$

$$RO\cdot + O_2 \rightarrow HO_2\cdot + RCHO$$

$$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$$



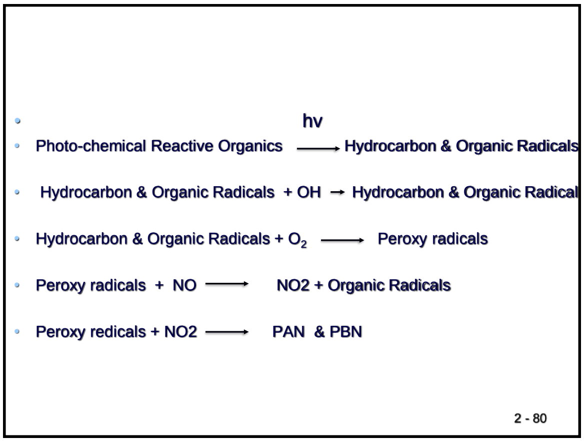
Summary

$$NO_2 \xrightarrow{h\nu} NO + O$$

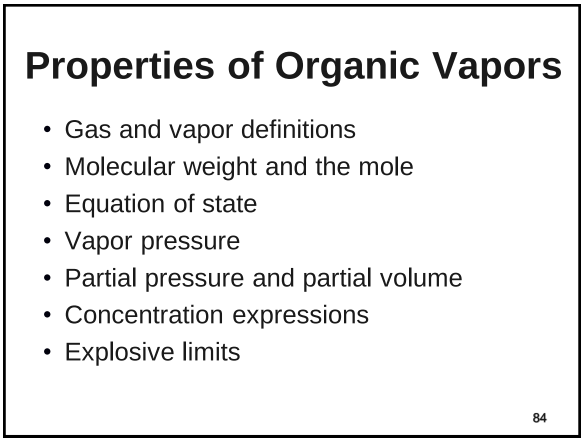
$$O + O_2 \xrightarrow{M} O_3$$

$$O_3 \xrightarrow{h\nu} O^* + O_2$$

$$O^* + H_2O \rightarrow 2OH\cdot$$



- Photo-chemical Reactive Organics $\xrightarrow{hv}$ Hydrocarbon & Organic Radicals
- Hydrocarbon & Organic Radicals + OH → Hydrocarbon & Organic Radical
- Hydrocarbon & Organic Radicals + O_2 ⟶ Peroxy radicals
- Peroxy radicals + NO ⟶ NO2 + Organic Radicals
- Peroxy redicals + NO2 ⟶ PAN & PBN



Properties of Organic Vapors

- Gas and vapor definitions
- Molecular weight and the mole
- Equation of state
- Vapor pressure
- Partial pressure and partial volume
- Concentration expressions
- Explosive limits

Gas and Vapor Definitions

- The **critical temperature** is the highest temperature at which a pure component liquid and vapor can exist in equilibrium.
- A gaseous material below its critical temperature is a **vapor**. (Compressing a vapor at constant temperature will cause it to condense.)
- A gaseous material above its critical temperature is a **gas**. (Compressing a gas at constant temperature will not cause it to condense).

The Mole

A mole is a mass of material that contains a certain number of molecules. It is numerically equal to the molecular weight.

*The mass of one **mole** of a substance is equal to that substance's **molecular weight**.* For example, oxygen (O_2) has an atomic weight of 16 with 2 atoms of oxygen (O_2) in the molecule. Therefore, the molecular weight of O_2 is (16 x 2) = 32, and as a result there are 32 grams per gram-mole, 32 kilograms per kilogram-mole, and 32 pounds per-pound mole (of oxygen).

Molecular Weight

Molecular weight is the sum of the *atomic weights* of all atoms in a molecule

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:

$$MW_{mixture} = \sum_{i=1}^{n} \chi_i MW_i$$

χ_i = mole fraction of component i

MW_i = molecular weight of component i

Example

Calculate the average molecular weight of air at EPA standard conditions. Consider air to be composed of 21 mole% oxygen and 79 mole% nitrogen.

$$MW_{mixture} = \sum_{i=1}^{n} \chi_i MW_i$$

$$MW_{air} = 0.21\left(32\, {}^{g}\!/\!{}_{mole}\right) + 0.79(28\, {}^{g}\!/\!{}_{mole}) = 29\, {}^{g}\!/\!{}_{mole}$$

MW = 29 g/mole

Equation of State

The ideal gas law:

PV = nRT

P = absolute pressure

V = gas volume

n = number of moles

R = constant

T = absolute temperature

Values for R:

10.73 psia-ft^3/lb-mole-°R

0.73 atm-ft^3/lb-mole-°R

82.06 atm-cm^3/g-mole-K

8.31 x 10^3 kPa-m^3/kg-mole-K

Absolute Pressure

$$P = P_b + P_g$$

where

P = absolute pressure

P_b = barometric pressure or atmospheric pressure

P_g = gauge (or static) pressure

Standard Pressure

Units	Value
Atmosphere (atm)	1
Pounds force per square inch (psi)	14.70
Inches of mercury (in Hg)	29.92
Millimeters of mercury (mm Hg)	760
Feet of water column (ft WC)	33.92
Inches of water column (in WC)	407
Kilopascals (kPa)	101.3
Millibars (mb)	1013

Standard barometric pressure is the average atmospheric pressure at sea level, 45°N latitude, and at 35°F.

Standard Temperature

Group	T_{std}
USEPA (General)	68°F (20°C)
USEPA (Air monitoring)	77°F (25°C)
Industrial hygiene	70°F (21.1°C)
Combustion	60°F (15.6°C)
Science	32°F (0°C)

Volume Correction

$$\frac{PV}{T} = nR = \text{CONSTANT (if } n = \text{CONSTANT)}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad V_1 = V_2\left(\frac{P_2}{P_1}\right)\left(\frac{T_1}{T_2}\right)$$

$$\text{SCFM} = \text{ACFM}\left(\frac{P_{act}}{P_{std}}\right)\left(\frac{T_{std}}{T_{act}}\right)$$

$$\text{ACFM} = \text{SCFM}\left(\frac{P_{std}}{P_{act}}\right)\left(\frac{T_{act}}{T_{std}}\right)$$

Example

A particulate control system consists of a hood, ductwork, fabric filter, fan, and stack. The total gas flow entering the fabric filter is 8,640 scfm. The gas temperature in the inlet duct is 320°F and the static pressure is -10 in WC. The barometric pressure is 28.30 in Hg.

If the inlet duct has inside dimensions of 3 feet by 4 feet, what is the velocity into the fabric filter?

$V = Q_{acfm}/\text{area}$

$$\text{ACFM} = \text{SCFM}\left(\frac{P_{std}}{P_{actual}}\right)\left(\frac{T_{actual}}{T_{std}}\right)$$

Convert the static pressure to absolute pressure:

$$P = 28.30\ \text{in Hg}\left(\frac{407\ \text{in WC}}{29.92\ \text{in Hg}}\right) + (-10\ \text{in WC}) = 375\ \text{in WC}$$

$P = P_b + P_g$

And then…

Convert the gas temperature to absolute temperature:

$$T_{actual} = 320°\text{F} + 460° = 780°\text{R}$$

Convert the inlet flow rate to actual conditions:

$$Q_{actual} = 8{,}640\ \text{scfm}\left(\frac{780°\text{R}}{528°\text{R}}\right)\left(\frac{407\ \text{in WC}}{375\ \text{in WC}}\right) = 13{,}853\ \text{acfm}$$

Calculate the velocity:

$$V = \frac{13{,}853\ \text{ft}^3/\text{min}}{3\text{ft}\cdot 4\text{ft}} = 1{,}154\ \text{ft}/\text{min}$$

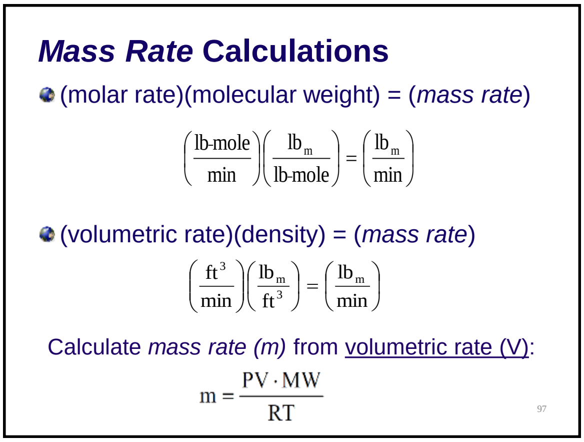
Molar Volume

$$\frac{V}{n} = \frac{RT}{P}$$

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

At 68°F and 1 atm. (EPA Standard conditions):

$$= \frac{\left(0.73\,\frac{atm - ft^3}{lb - mole\cdot°R}\right)(528°R)}{1\,atm} = 385.4\,\frac{ft^3}{lb - mole}$$



Mass Rate Calculations

- (molar rate)(molecular weight) = (*mass rate*)

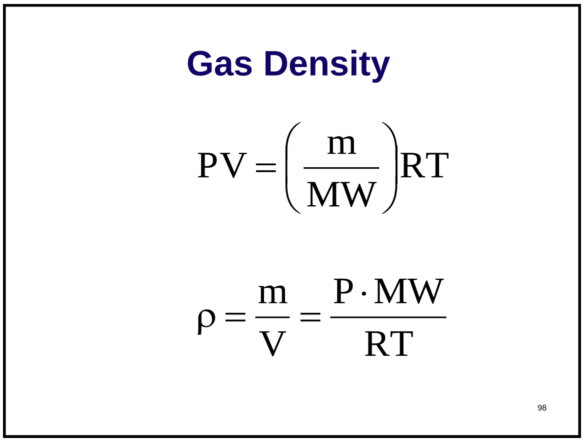
$$\left(\frac{\text{lb-mole}}{\text{min}}\right)\left(\frac{\text{lb}_m}{\text{lb-mole}}\right)=\left(\frac{\text{lb}_m}{\text{min}}\right)$$

- (volumetric rate)(density) = (*mass rate*)

$$\left(\frac{\text{ft}^3}{\text{min}}\right)\left(\frac{\text{lb}_m}{\text{ft}^3}\right)=\left(\frac{\text{lb}_m}{\text{min}}\right)$$

Calculate *mass rate (m)* from volumetric rate (V):

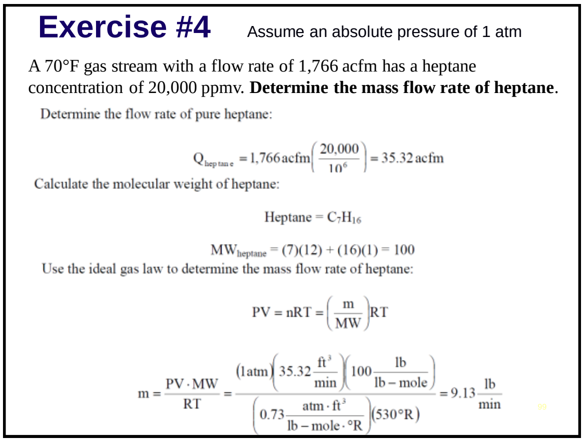
$$\text{m}=\frac{\text{PV}\cdot\text{MW}}{\text{RT}}$$



Gas Density

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

$$\rho=\frac{\text{m}}{\text{V}}=\frac{\text{P}\cdot\text{MW}}{\text{RT}}$$



Exercise #4

Assume an absolute pressure of 1 atm

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:

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

Calculate the molecular weight of heptane:

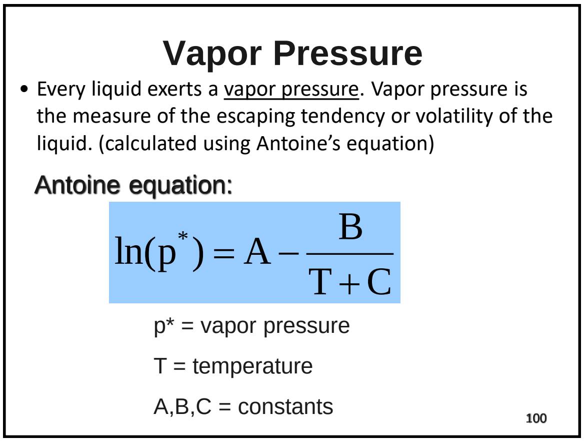
$$\text{Heptane}=\text{C}_7\text{H}_{16}$$

$$\text{MW}_{\text{heptane}}=(7)(12)+(16)(1)=100$$

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

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

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



Vapor Pressure

- Every liquid exerts a vapor pressure. Vapor pressure is the measure of the escaping tendency or volatility of the liquid. (calculated using Antoine's equation)

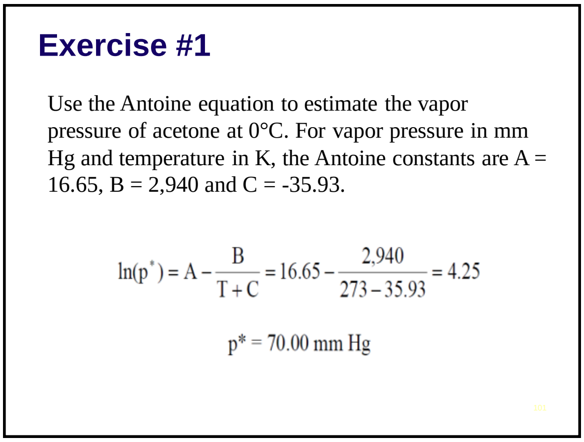
Antoine equation:

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

p* = vapor pressure

T = temperature

A,B,C = constants

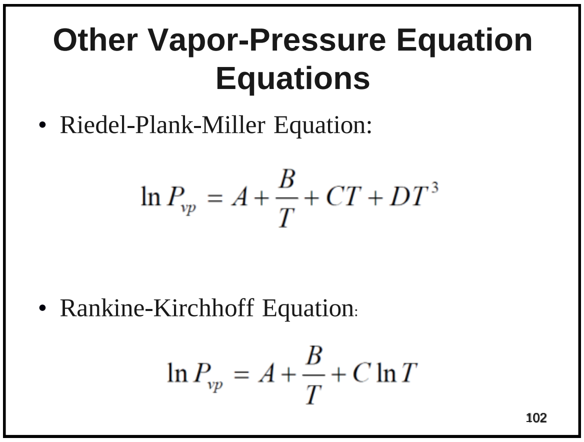


Exercise #1

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.

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

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



Other Vapor-Pressure Equation Equations

- Riedel-Plank-Miller Equation:

$$\ln P_{vp} = A + \frac{B}{T} + CT + DT^3$$

- Rankine-Kirchhoff Equation:

$$\ln P_{vp} = A + \frac{B}{T} + C \ln T$$

Partial Pressure

- Partial pressure is the pressure exerted by a single gas as if it occupied the entire volume by itself.
- *Dalton's law* of partial pressures for non-reacting gases (at constant temperature & volume):
- Equation: $\mathbf{p_{ag} + p_{bg} = P_t}$
  - $\mathbf{p_{ag}}$ = partial pressure of "a" in gas phase
  - $\mathbf{p_{bg}}$ = partial pressure of "b" in gas phase
  - $\mathbf{P_t}$ = total gas pressure

Partial Pressure

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:

$$\frac{p_i}{P_T} = \frac{n_i}{n_T}$$

Partial Volume

Amagat's law (analogous to Dalton's law) states that the total volume of a gas mixture is the sum of the individual volumes of each non-reactive gas at constant temperature and total pressure.

$$V_T = V_{ag} + V_{bg} + \ldots$$

Again, using the ideal gas at constant temperature and total pressure, you get:

$$\frac{v_i}{V_T} = \frac{n_i}{n_T}$$

Combining the prior two equations gives

$$\frac{p_i}{P_T} = \frac{n_i}{n_T} = \frac{v_i}{V_T}$$

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 yi.

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.
- Partial pressure
- Parts per million by volume (ppmv)

$$\text{ppmv}_i = \left(\frac{v_i}{V_T}\right) x10^6$$

- Mass per unit volume

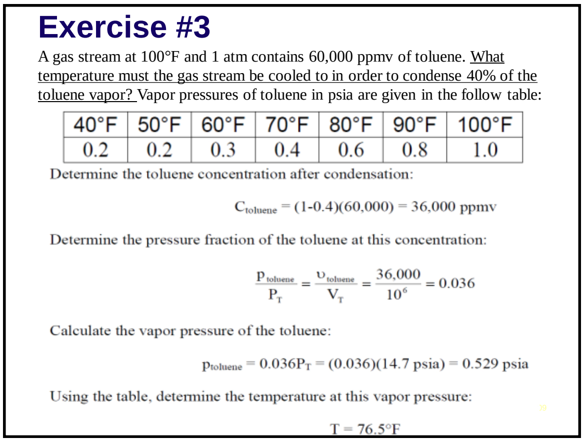
Exercise #2

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.

Solution: From an earlier slide, the pressure fraction equals the mole fraction ($Y_{acetone}$): $p_i/P_T = v_i/V_T = n_i/n_T$

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

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



Exercise #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

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:

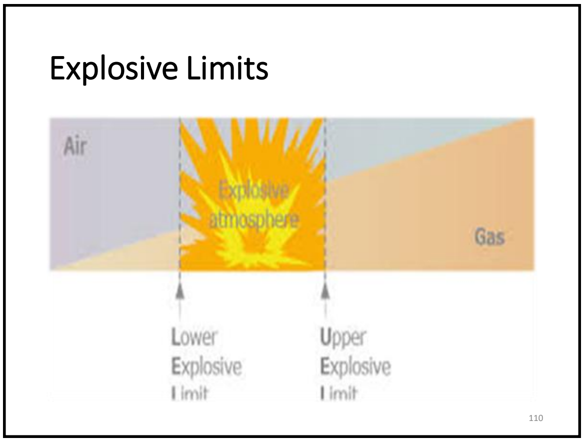
$$\frac{P_{toluene}}{P_T} = \frac{\upsilon_{toluene}}{V_T} = \frac{36,000}{10^6} = 0.036$$

Calculate the vapor pressure of the toluene:

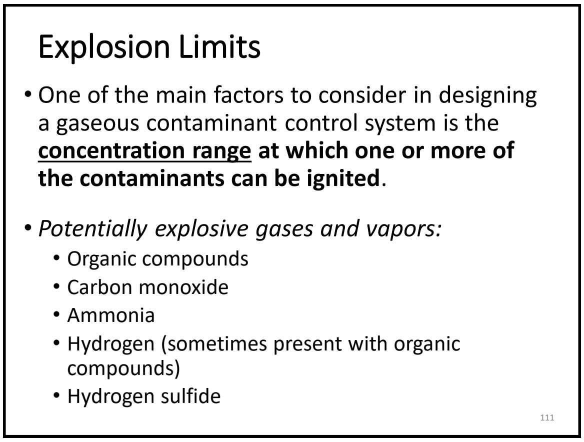
$$p_{toluene} = 0.036P_T = (0.036)(14.7 \text{ psia}) = 0.529 \text{ psia}$$

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

$$T = 76.5°F$$

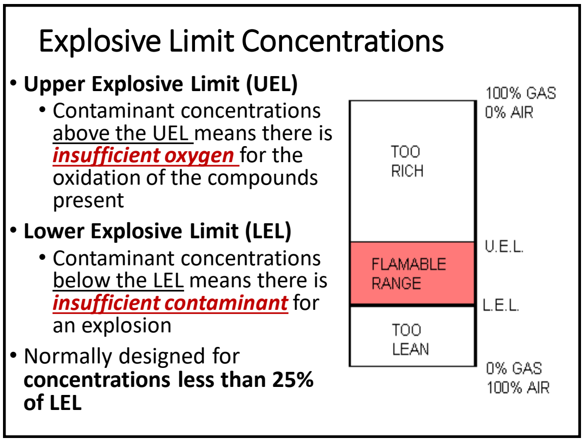


Explosive Limits



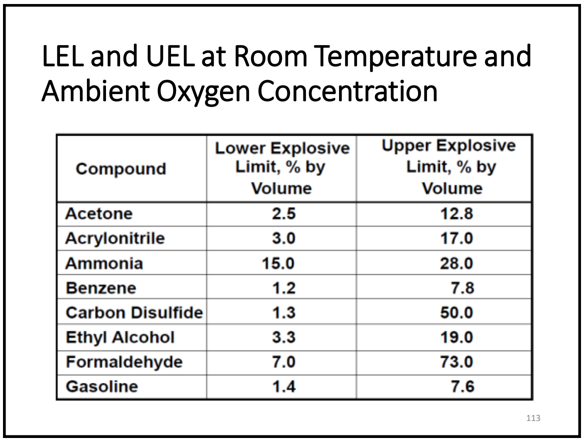
Explosion Limits

- One of the main factors to consider in designing a gaseous contaminant control system is the **<u>concentration range</u> at which one or more of the contaminants can be ignited**.
- *Potentially explosive gases and vapors:*
  - Organic compounds
  - Carbon monoxide
  - Ammonia
  - Hydrogen (sometimes present with organic compounds)
  - Hydrogen sulfide



Explosive Limit Concentrations

- **Upper Explosive Limit (UEL)**
  - Contaminant concentrations above the UEL means there is ***insufficient oxygen*** for the oxidation of the compounds present
- **Lower Explosive Limit (LEL)**
  - Contaminant concentrations below the LEL means there is ***insufficient contaminant*** for an explosion
- Normally designed for **concentrations less than 25% of LEL**



LEL and UEL at Room Temperature and Ambient Oxygen Concentration

Compound	Lower Explosive Limit, % by Volume	Upper Explosive Limit, % by Volume
Acetone	2.5	12.8
Acrylonitrile	3.0	17.0
Ammonia	15.0	28.0
Benzene	1.2	7.8
Carbon Disulfide	1.3	50.0
Ethyl Alcohol	3.3	19.0
Formaldehyde	7.0	73.0
Gasoline	1.4	7.6

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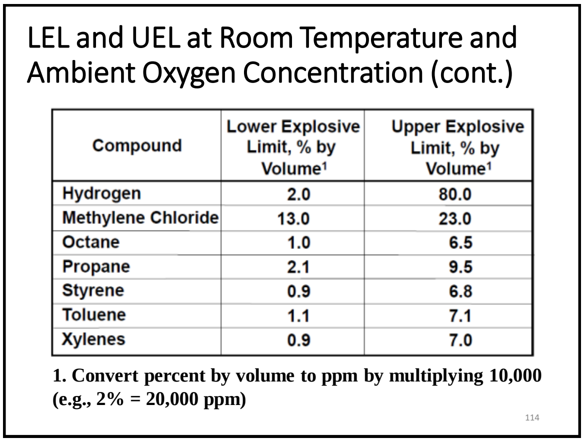

LEL and UEL at Room Temperature and Ambient Oxygen Concentration (cont.)

Compound	Lower Explosive Limit, % by Volume[1]	Upper Explosive Limit, % by Volume[1]
Hydrogen	2.0	80.0
Methylene Chloride	13.0	23.0
Octane	1.0	6.5
Propane	2.1	9.5
Styrene	0.9	6.8
Toluene	1.1	7.1
Xylenes	0.9	7.0

1. Convert percent by volume to ppm by multiplying 10,000 (e.g., 2% = 20,000 ppm)

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Percentages & Concentrations

- 1% = 10,000 ppm
- 0.1% = 1000 ppm
- 0.01% = 100 ppm
- 0.001% = 10 ppm
- 0.0001% = 1 ppm = 1000 ppb
- 0.000001% = 0.1 ppm = 100 ppb
- 0.0000001% = 0.01ppm = 10 ppb
- 0.00000001% = 0.001 ppm = 1 ppb = 1000 ppt (parts per trillion)

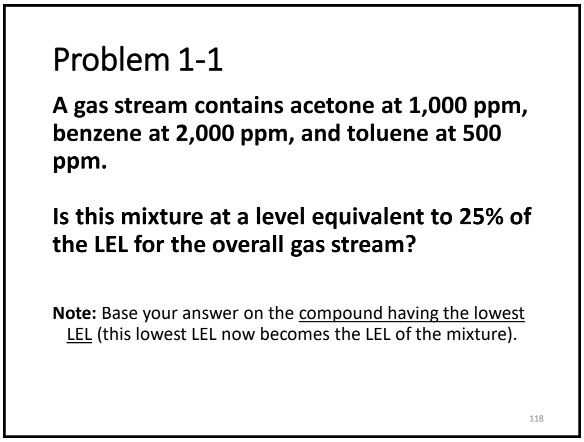
Additional LEL & UEL Considerations

- A gas stream having **contaminants with a large explosive range requires extreme caution** in control system design and operation

- Additional LEL and UEL concentrations for specific compounds **can be found in *Material Data Safety Sheets*** or other references

LEL of Mixtures

- Estimation of mixture LEL (**two methods**)
  1. Assume that **LEL of all contaminants equal to lowest LEL of any single contaminant** –most conservative approach (Problem 1-1)
  2. Use **LeChatelier equations** based on weighted average of LEL of each component (Problem 1-2)
- One of the best approaches is to have a qualified laboratory measure the LEL & UEL

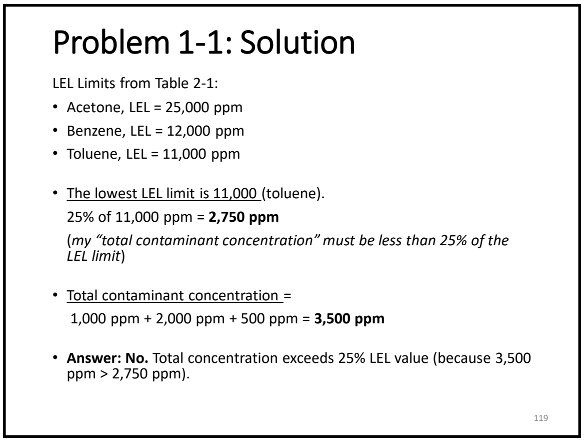


Problem 1-1

A gas stream contains acetone at 1,000 ppm, benzene at 2,000 ppm, and toluene at 500 ppm.

Is this mixture at a level equivalent to 25% of the LEL for the overall gas stream?

Note: Base your answer on the compound having the lowest LEL (this lowest LEL now becomes the LEL of the mixture).



Problem 1-1: Solution

LEL Limits from Table 2-1:

- Acetone, LEL = 25,000 ppm
- Benzene, LEL = 12,000 ppm
- Toluene, LEL = 11,000 ppm

- The lowest LEL limit is 11,000 (toluene).

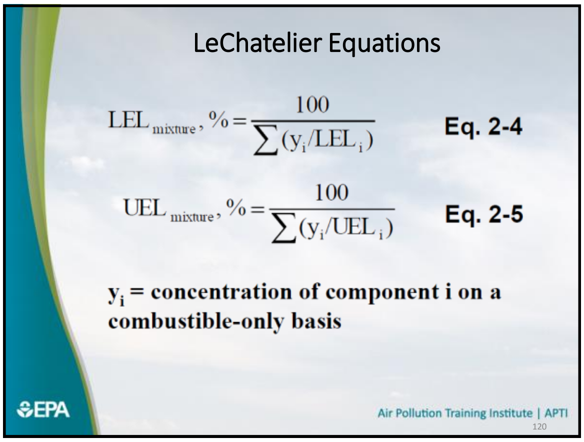
  25% of 11,000 ppm = **2,750 ppm**

  (*my "total contaminant concentration" must be less than 25% of the LEL limit*)

- Total contaminant concentration =

  1,000 ppm + 2,000 ppm + 500 ppm = **3,500 ppm**

- **Answer: No.** Total concentration exceeds 25% LEL value (because 3,500 ppm > 2,750 ppm).



LeChatelier Equations

$$\text{LEL}_{\text{mixture}}, \% = \frac{100}{\sum (y_i/\text{LEL}_i)} \quad \textbf{Eq. 2-4}$$

$$\text{UEL}_{\text{mixture}}, \% = \frac{100}{\sum (y_i/\text{UEL}_i)} \quad \textbf{Eq. 2-5}$$

y_i = concentration of component i on a combustible-only basis

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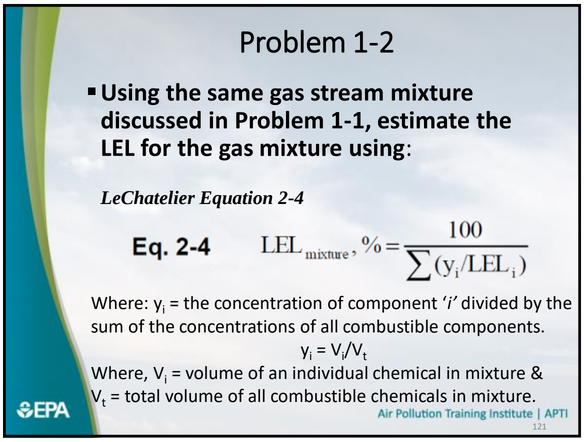


Problem 1-2

- **Using the same gas stream mixture discussed in Problem 1-1, estimate the LEL for the gas mixture using**:

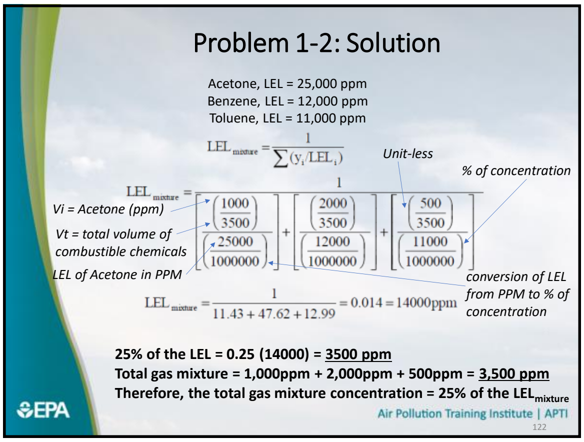
LeChatelier Equation 2-4

Eq. 2-4 $$\text{LEL}_{\text{mixture}},\% = \frac{100}{\sum (y_i/\text{LEL}_i)}$$

Where: y_i = the concentration of component '*i*' divided by the sum of the concentrations of all combustible components.

$y_i = V_i/V_t$

Where, V_i = volume of an individual chemical in mixture & V_t = total volume of all combustible chemicals in mixture.



Problem 1-2: Solution

Acetone, LEL = 25,000 ppm
Benzene, LEL = 12,000 ppm
Toluene, LEL = 11,000 ppm

$$\text{LEL}_{\text{mixture}} = \frac{1}{\sum (y_i/\text{LEL}_i)}$$

$$\text{LEL}_{\text{mixture}} = \frac{1}{\left[\dfrac{\left(\dfrac{1000}{3500}\right)}{\left(\dfrac{25000}{1000000}\right)}\right] + \left[\dfrac{\left(\dfrac{2000}{3500}\right)}{\left(\dfrac{12000}{1000000}\right)}\right] + \left[\dfrac{\left(\dfrac{500}{3500}\right)}{\left(\dfrac{11000}{1000000}\right)}\right]}$$

Unit-less

% of concentration

Vi = Acetone (ppm)

Vt = total volume of combustible chemicals

LEL of Acetone in PPM

conversion of LEL from PPM to % of concentration

$$\text{LEL}_{\text{mixture}} = \frac{1}{11.43 + 47.62 + 12.99} = 0.014 = 14000\text{ppm}$$

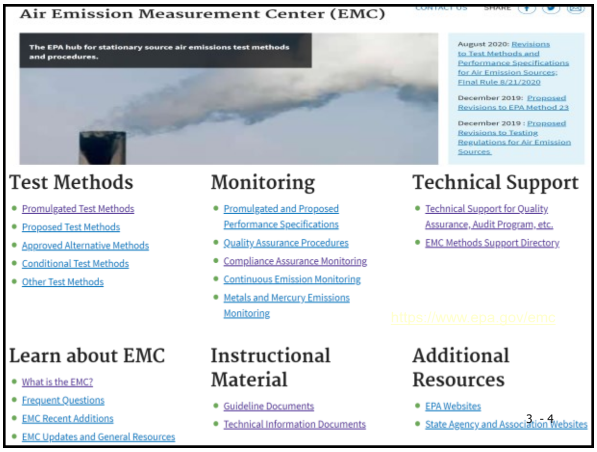
25% of the LEL = 0.25 (14000) = <u>3500 ppm</u>
Total gas mixture = 1,000ppm + 2,000ppm + 500ppm = <u>3,500 ppm</u>
Therefore, the total gas mixture concentration = 25% of the LEL$_{\text{mixture}}$

Chapter 3

Source Measurement Techniques for VOC’s

Sampling At a Landfill Enclosed Flare

Sampling At A Potato Chip Fryer



Air Emission Measurement Center (EMC)

CONTACT US SHARE

The EPA hub for stationary source air emissions test methods and procedures.

August 2020: Revisions to Test Methods and Performance Specifications for Air Emission Sources; Final Rule 8/21/2020

December 2019: Proposed Revisions to EPA Method 23

December 2019 : Proposed Revisions to Testing Regulations for Air Emission Sources

Test Methods

- Promulgated Test Methods
- Proposed Test Methods
- Approved Alternative Methods
- Conditional Test Methods
- Other Test Methods

Monitoring

- Promulgated and Proposed Performance Specifications
- Quality Assurance Procedures
- Compliance Assurance Monitoring
- Continuous Emission Monitoring
- Metals and Mercury Emissions Monitoring

Technical Support

- Technical Support for Quality Assurance, Audit Program, etc.
- EMC Methods Support Directory

https://www.epa.gov/emc

Learn about EMC

- What is the EMC?
- Frequent Questions
- EMC Recent Additions
- EMC Updates and General Resources

Instructional Material

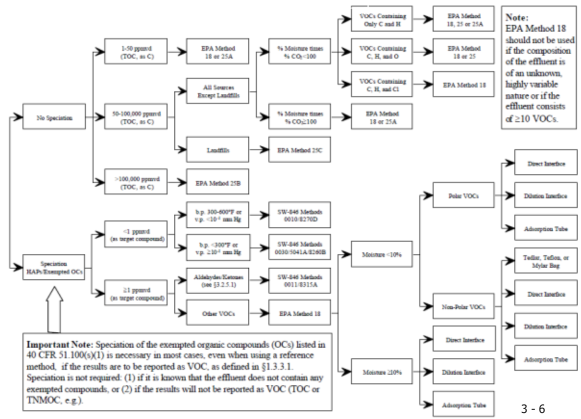
- Guideline Documents
- Technical Information Documents

Additional Resources

- EPA Websites
- State Agency and Association Websites

Selection of VOC Test Methods

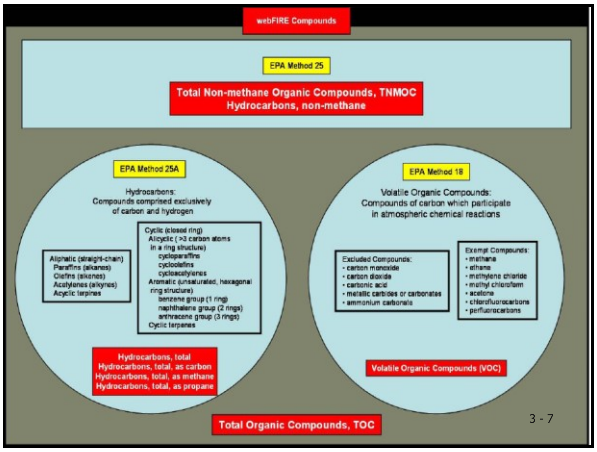
- Pennsylvania Department of Environmental Protection, "*Source Testing Manual"* (Revision 3.3), provides a general scheme for the selection of a VOC test method.
- The selection scheme does not address all of the possibilities.
- Scheme follows 2 different paths:
  - Speciated VOCs
  - Non-speciated VOCs



Note: EPA Method 18 should not be used if the composition of the effluent is of an unknown, highly variable nature or if the effluent consists of ≥10 VOCs.

Important Note: Speciation of the exempted organic compounds (OCs) listed in 40 CFR 51.100(s)(1) is necessary in most cases, even when using a reference method, if the results are to be reported as VOC, as defined in §1.3.3.1. Speciation is not required: (1) if it is known that the effluent does not contain any exempted compounds, or (2) if the results will not be reported as VOC (TOC or TNMOC, e.g.).

https://www.dep.pa.gov/Business/Air/BAQ/BusinessTopics/SourceTesting/Pages/default.aspx



Speciation VOC Methods

- Method 18 (VOC by gas chromatograph (GC)): Based on separating components of a gas mixture in a GC column and measuring separated components with suitable detector (i.e., Flame Ionization Detector (FID).

  Applicable to VOC concentrations greater than 1ppm in the sampled gas.
- Method 25 (non-methane organic compounds) applies to the measurement of VOCs as total gaseous non-methane organics, condensable and non-condensable, as carbon in source emissions. (All compounds are converted to methane before measuring with a FID.)

Non-Speciation VOC Methods

- Method 25A (organic concentration using a FID): This method is applicable to total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or aromatic hydrocarbons.
  - Results are expressed in terms of volume concentration of propane (or other appropriate organic calibration gas) or in terms of carbon.
- Method 25B (organic concentration using an infrared analyzer)
- Method 25C (non-methane organic compounds from landfills).

Measurement Methods

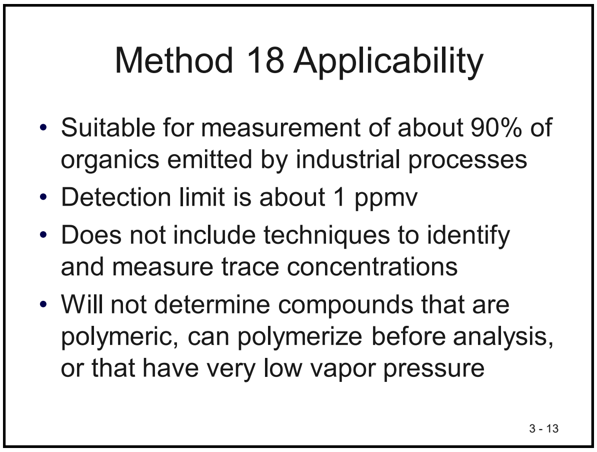
- Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography
- Method 25, Determination of Total Gaseous Non-Methane Organic Emissions as Carbon
- Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer
- **Method 320, Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive FTIR Spectroscopy**

Federal Reference Method 18

General GC Methodology

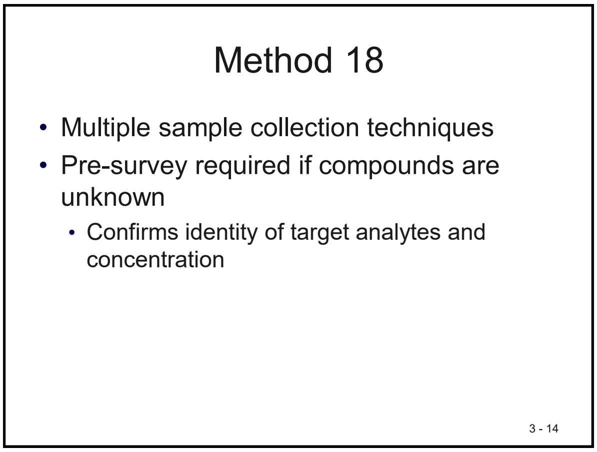
Method 18

- Gas Chromatography (GC)
- Generic GC method
- Determines the concentration of discrete organic compounds in the sample
- Applies to the analysis of approximately 90% of total gaseous organics emitted from an industrial source



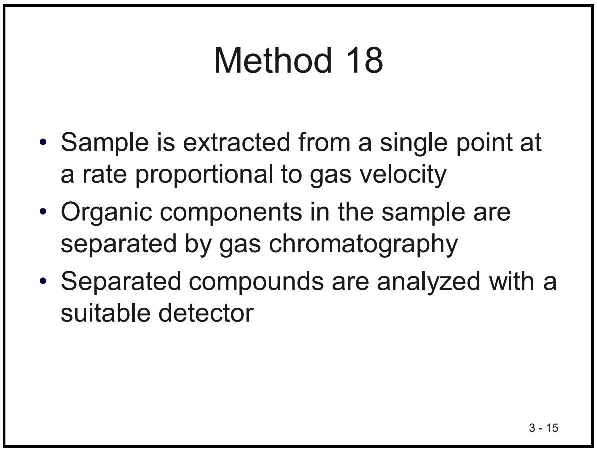
Method 18 Applicability

- Suitable for measurement of about 90% of organics emitted by industrial processes
- Detection limit is about 1 ppmv
- Does not include techniques to identify and measure trace concentrations
- Will not determine compounds that are polymeric, can polymerize before analysis, or that have very low vapor pressure



Method 18

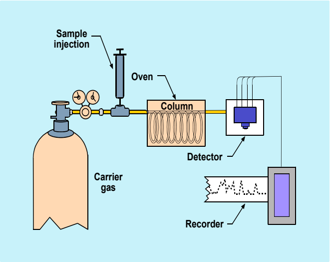
- Multiple sample collection techniques
- Pre-survey required if compounds are unknown
  - Confirms identity of target analytes and concentration



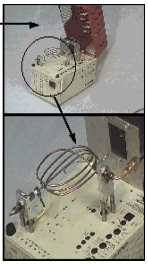
Method 18

- Sample is extracted from a single point at a rate proportional to gas velocity
- Organic components in the sample are separated by gas chromatography
- Separated compounds are analyzed with a suitable detector

Method 18



"Virtual Oven" shown mounted on 110 chassis. Column is connected to heated injector and detector blocks for higher temperature samples.

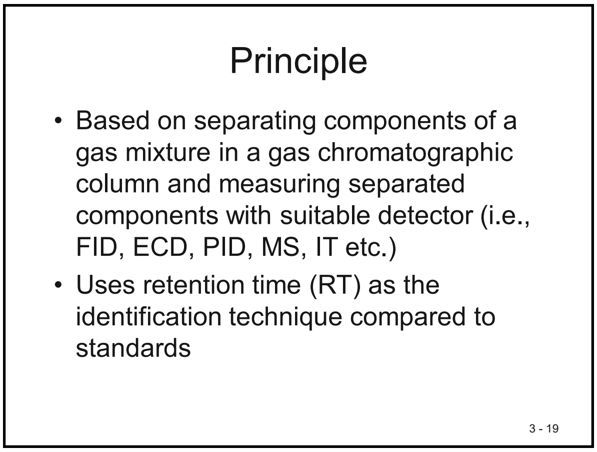


Applicability

- FRM 18 is a generic method which is wide open for quantifying speciated organic compounds
- FRM 18 is a “self-certifying” method…..”performance-base” method! Most all other VOC methods are “procedure-base!”
- “Regulatory science” vs. “measurement science!”

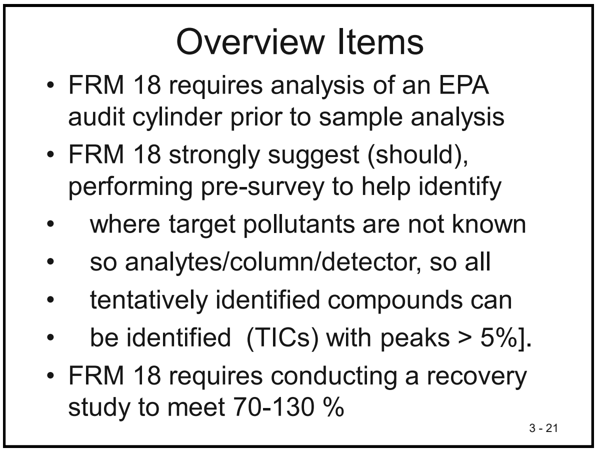
Applicability

- FRM 18 will not determine compounds that are
  - Polymeric (high molecular weight)
  - Analytes that can polymerize before analysis
  - Analytes that have very low vapor pressure at stack or instrument conditions (< 10^{-3} mm Hg)



Principle

- Based on separating components of a gas mixture in a gas chromatographic column and measuring separated components with suitable detector (i.e., FID, ECD, PID, MS, IT etc.)
- Uses retention time (RT) as the identification technique compared to standards



Overview Items

- FRM 18 requires analysis of an EPA audit cylinder prior to sample analysis
- FRM 18 strongly suggest (should), performing pre-survey to help identify
- where target pollutants are not known
- so analytes/column/detector, so all
- tentatively identified compounds can
- be identified (TICs) with peaks > 5%].
- FRM 18 requires conducting a recovery study to meet 70-130 %

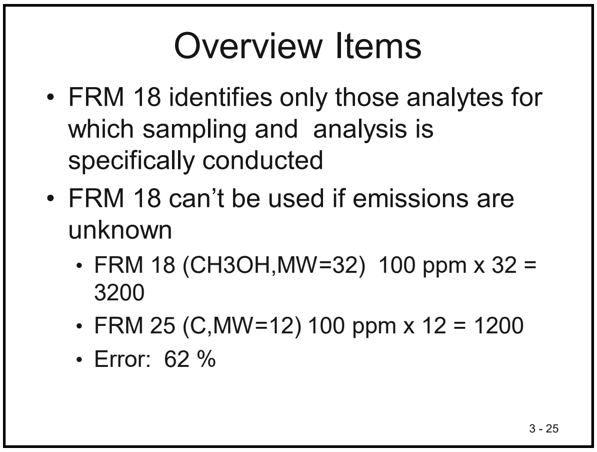
Pre-Survey Sampling Techniques

- Evacuated or purged glass sampling flasks
- Flexible bags
- Adsorption tubes
- Canisters

Survey Canister Sampling

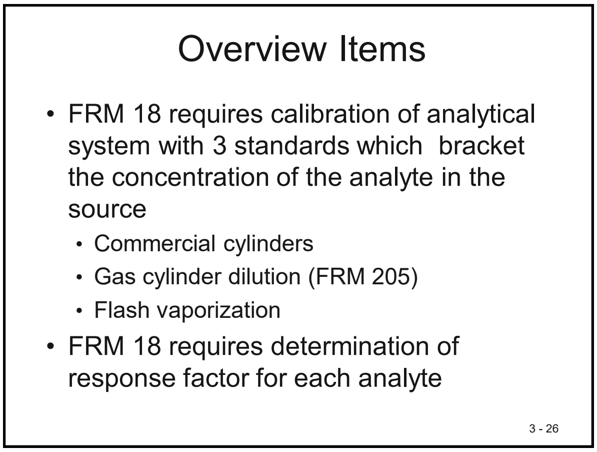
Overview Items

- FRM 18 provides concentration (usually in terms of “ppm”) for speciated organics
- Mass emission rate can be provided as long as FRM 1 and 2 are incorporated into the monitoring program



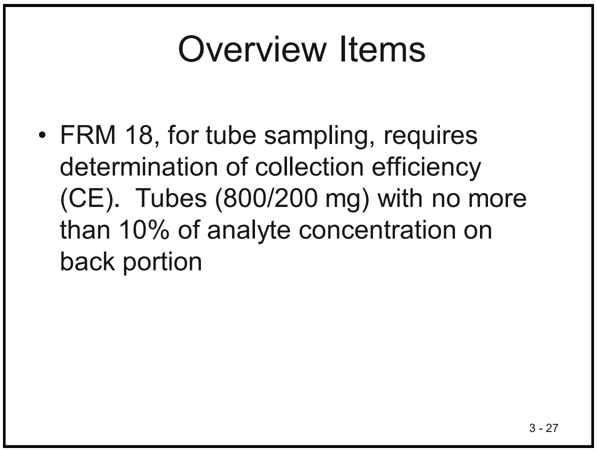
Overview Items

- FRM 18 identifies only those analytes for which sampling and analysis is specifically conducted
- FRM 18 can't be used if emissions are unknown
  - FRM 18 (CH3OH,MW=32) 100 ppm x 32 = 3200
  - FRM 25 (C,MW=12) 100 ppm x 12 = 1200
  - Error: 62 %



Overview Items

- FRM 18 requires calibration of analytical system with 3 standards which bracket the concentration of the analyte in the source
  - Commercial cylinders
  - Gas cylinder dilution (FRM 205)
  - Flash vaporization
- FRM 18 requires determination of response factor for each analyte



Overview Items

- FRM 18, for tube sampling, requires determination of collection efficiency (CE). Tubes (800/200 mg) with no more than 10% of analyte concentration on back portion

Overview Items

- FRM 18 pushes you to using direct injection, Tedlar bags or adsorbents as sampling options
- FRM 18 allows correction of emissions to “Recovery Study” results: Reported emissions = FRM 18 Conc./R
- For solid adsorbent, no more than 10% of analyte found on back tube

Overview Items

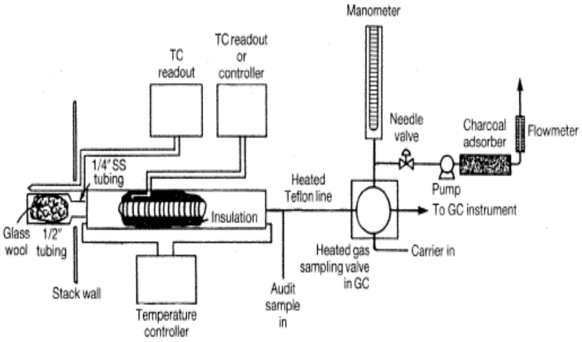
- All tubing used in the sampling train must be Teflon…no Tygon tubing allowed
- Aluminized Mylar bags are recommended for low concentration bag sampling because of low permeation rate
- Canister sampling can only be used during survey, not for compliance application

RM 18 Sampling Techniques

- Direct Injection
- Integrated bag
- Glass sampling flask
- Adsorbent tubes
  - Charcoal
  - Silica Gel
  - Florisil®
  - CarboTrap® 300
  - Tenax® TA
- (Must perform recovery study for each sampling approach)

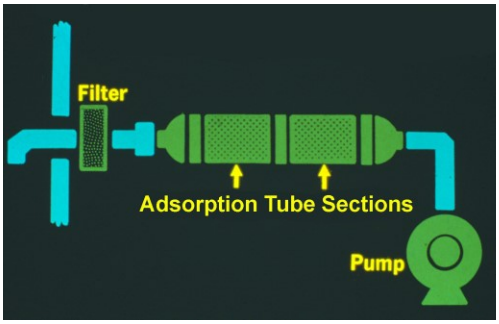
Direct or Dilution Interface Sampling

- Strengths
  - No loss or alteration of compounds
  - Method of choice when temperature is below 100°C and VOC concentrations are suitable
- Weaknesses
  - GC must be located at sampling site
  - Cannot sample proportionally or obtain time integrated sample



Method 18 Direct Interface Sampling

Adsorption Tube Sampling



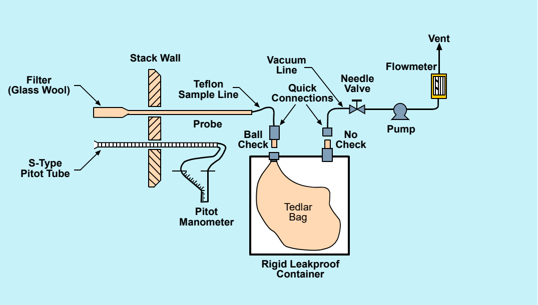
Adsorbent Media

- Activated carbon
- Silica gel
- Tenax
- XAD resin
- **Carbopack C/Carbopack B**

Adsorption Tube Sampling

- Strengths
  - Samples are compact and easy to handle
  - Samples returned to lab for analysis
  - Can be stored up to a week at 0°C
- Weaknesses
  - Breakthrough capacity must be known
  - Effect of moisture must be known
  - Quantitative recovery of compounds must be known
  - Samples must be collected at a constant rate

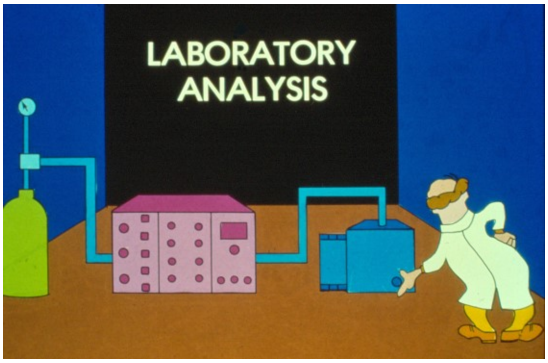
Flexible Bag Sampling

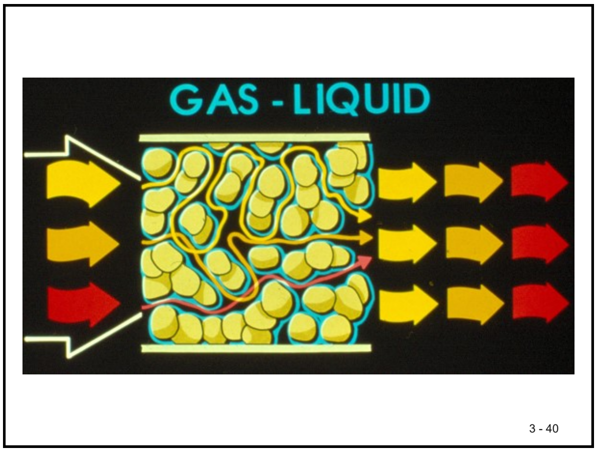


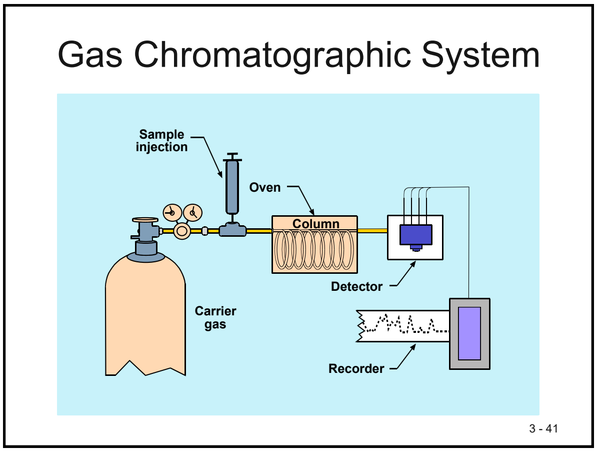
Flexible Bag Sampling

- Strengths
  - Samples approximate form in stack
  - Samples are returned to lab for analysis
  - Samples may be collected proportionally
- Weaknesses
  - Bags are awkward and bulky and prone to leaks
  - Compounds may adsorb onto bag surface
  - Compounds may react with bag surface or with each other
  - Storage time is generally less than 24 hours

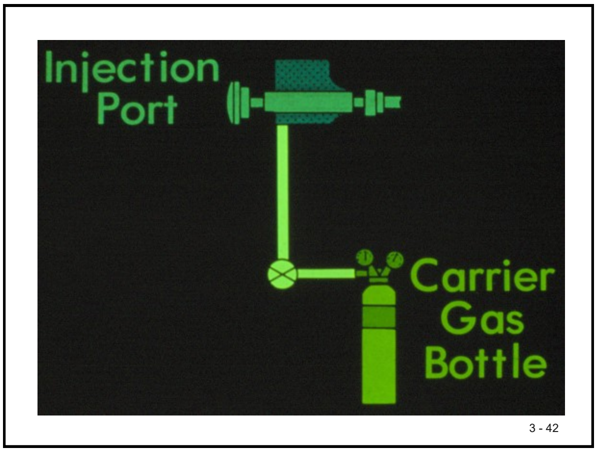
Flexible Bag Sampling

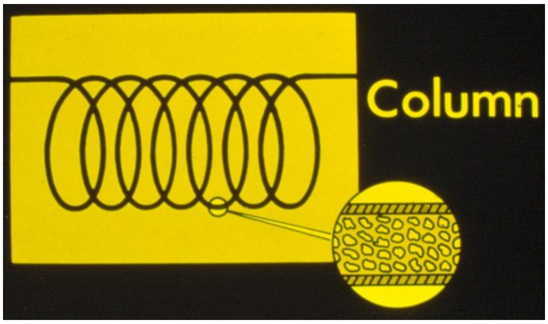


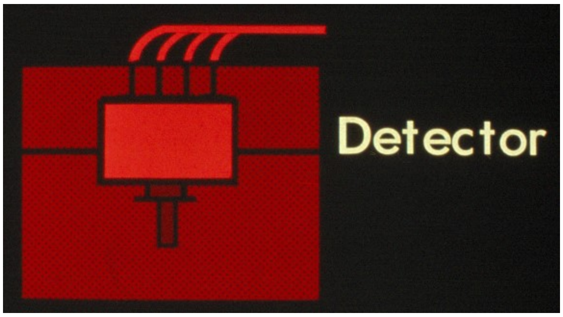




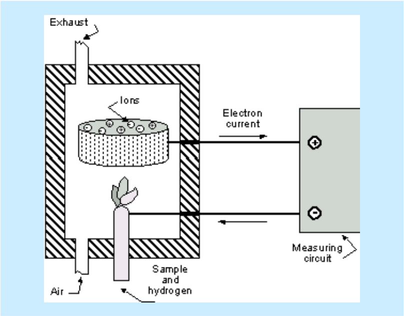
Gas Chromatographic System



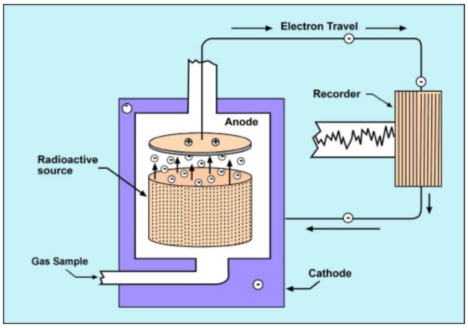


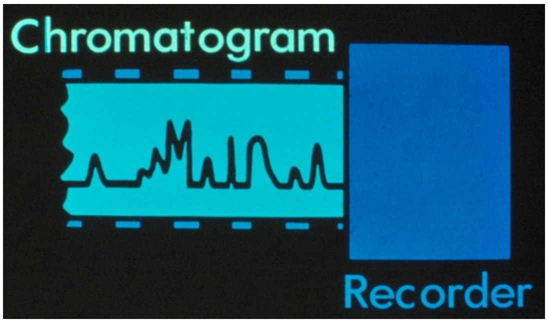


Flame Ionization Detector

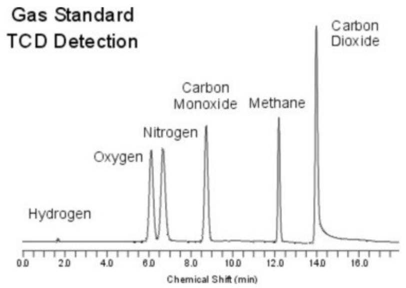


Electron Capture Detector





Standard Chromatogram of a Mixture of Gases



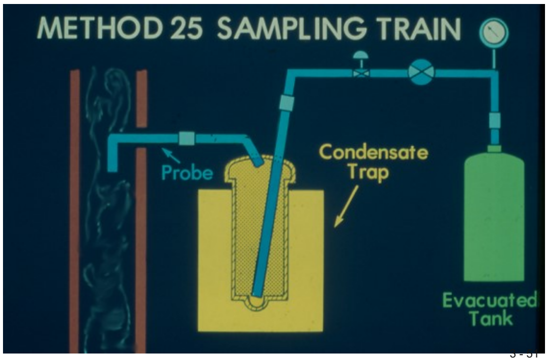
Regulations Specifying Method 18

- **§ 60.780 Standards—Control devices.**
- (a) For each control device used to comply with the provisions in §§ 60.774, 60.775, and 60.779 of this subpart, the owner or operator shall operate and maintain the control device or combination of control devices in accordance with the requirements of paragraphs (b) through (g) of this section, unless otherwise specified in this subpart.
- (b) Whenever organic VOC emissions are vented to a control device used to comply with the provisions of this subpart, such control device shall be operating.
- (c) The control device shall be designed and operated in accordance with paragraph (c)(1), (c)(2), (c)(3), (c)(4), or (c)(5) of this section.
- (1) An enclosed combustion device (including but not limited to a vapor incinerator, boiler, or process heater) shall meet the conditions in paragraph (c)(1)(i), (c)(1)(ii), or (c)(1)(iii) of this section, alone or in combination with other control devices.

Regulations Specifying Method 18

- If a boiler or process heater is used as the control device, then the vent stream shall be introduced into the flame zone of the boiler or process heater.
- (i) Reduce the total organic compound emissions, less methane and ethane, or total VOC emissions vented to the control device by 95 percent by weight or greater; (ii) Achieve an outlet total organic compound concentration, less methane and ethane, or total VOC concentration of 20 parts per million by volume on a dry basis corrected to 3 percent oxygen.
- The owner or operator shall use either Method 18, 40 CFR part 60, appendix A, or any other method or data that hasbeen validated according to the applicable procedures in Method 301, 40 CFR part 63, appendix A; or (iii) Provide a minimum residence time of 0.5 seconds at a minimum temperature of 760° C.

Method 25



Method 25

- Sample is extracted from a single point at a rate proportional to gas velocity
- Sample is separated into condensable and non-condensable fractions
- Analysis yields total gaseous non-methane organic emissions as carbon

Method 25 Applicability

- Organic compounds which are a gas or have significant vapor pressure at or below 250°F
- Sources with concentrations of 50 ppmv to 5% by volume
- High concentrations of CO_2 and water vapor can cause interference at low concentrations

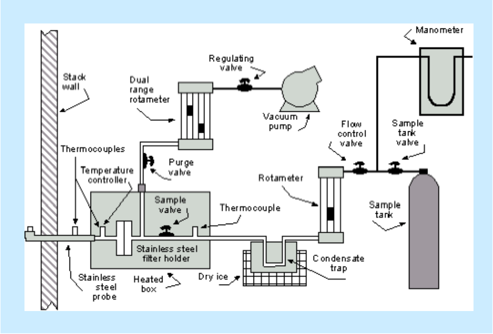
Method 25 Applicability

- Not Applicable
  - For measuring concentrations of VOCs or mass emissions of VOCs from sources whose concentrations are < 50 ppm
  - Possible bias when:
    - $\% \; CO_2 \times \% \; H_2O > 100$
  - As water freezes in the trap, CO_2 is trapped out prematurely. The CO_2, when reduced to methane, is counted as VOCs in the analytical system

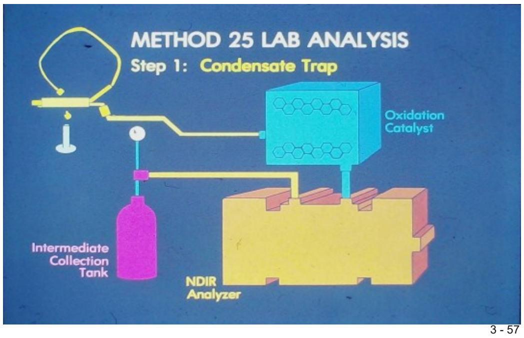
Method 25 Applicability

- Not Applicable
  - For measuring emissions from sources whose principle solvents are chlorinated hydrocarbons
  - Generally, for any situation, where a simpler procedure is more accurate
  - For sources with VOC emissions typically < 50 ppm

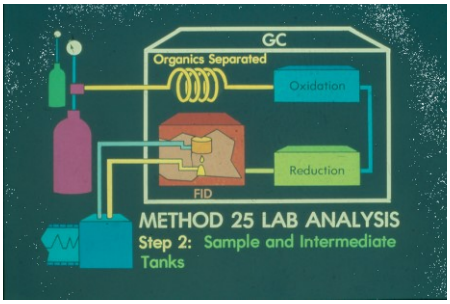
Method 25 Sampling Train



Method 25 Lab Analysis

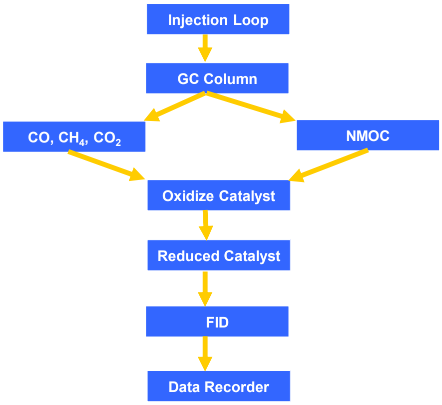


Method 25 Lab Analysis



Method 25 Analysis

- Condensate trap is purged with zero air and purged gas is collected in the sample tank
- Condensed VOCs are volatilized, oxidized to CO_2, and collected in a second tank
- VOCs in the sample tank are separated with GC, oxidized to CO_2, reduced to methane and measured by FID
- CO_2 peak in second tank is measured and counted as VOCs
- Total VOCs is the sum of both analyses



Injection Loop

GC Column

CO, CH_4, CO_2

NMOC

Oxidize Catalyst

Reduced Catalyst

FID

Data Recorder

Method 25 Advantages

- Advantage
  - Gives constant results from source to source whether sample composition is known or not
  - Sample train does require heated probe and filter, but is less complicated than FRM 5 hardware advantage

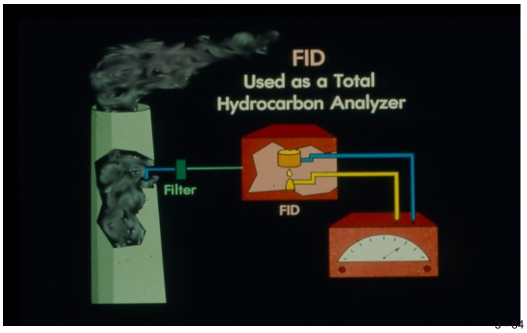
Method 25 Disadvantages

- Disadvantage
  - Will not yield true mass emission rate nor instantaneous results
  - No real time data (sample must be returned to laboratory for analysis)
  - High moisture and CO_2 together can cause interference
  - $(\%CO_2)(\%H_2O)>100$ gives potential high bias (EPA Guidelines)

Method 25 Disadvantages

- Disadvantage
  - No on-site data
  - QA/QC of the sampling train is only done prior to testing
  - No final leak check
  - Results sent out for analysis
  - Has a synergistic effects in high moisture and CO2 atmospheres
  - Detection limit 50 ppm as Carbon

Method 25A



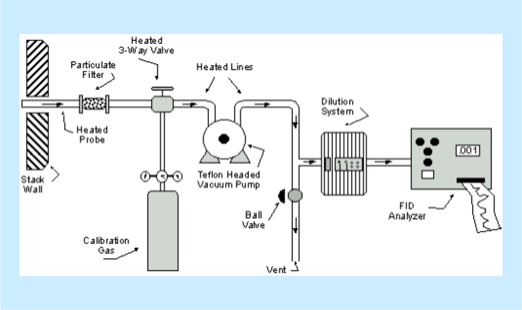
Method 25A

- Measures total organic concentration on a continuous, real-time basis using an FID
- Method is best applied to the measurement of vapors consisting primarily of alkanes, alkenes or aromatic hydrocarbons
- Gives reduced response to compounds that are highly substituted or chlorinated

Method 25A Basic Theory

- Sample is introduced into an ionization chamber and burned
- Process separates free ions
- Free ions are attracted to a collecting electrode
- Collection of the ions results in an increased current which is proportional to the concentration of the compound
- By-products are H_2O and CO_2

Method 25A Sampling Train



Method 25A Inlet/Outlet Testing At A Thermal Oxidizer Test

Method 25A

Advantages

- Wide dynamic and linear range (0-10,000 ppm)
- Highly sensitive to hydrocarbon vapors
- Very stable and repeatable
- Unaffected by ambient levels of CO, CO_2 and water vapor

Method 25A

- Disadvantages
  - Requires oxygen > 16% to operate
  - Total hydrocarbon detector - not specific
  - Value report in terms of calibration
  - Under estimates long chain, halogenated and oxygenated hydrocarbons

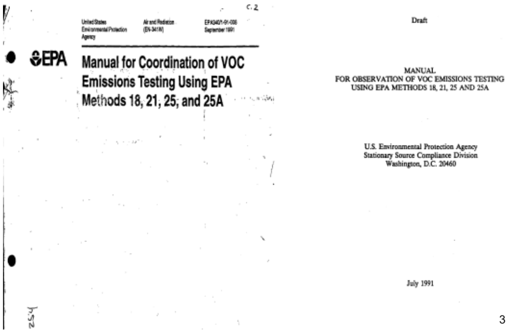
Method 25A

- The use of Method 25A usually must be justified to regulatory agencies instead of using Method 25.
- Key points would be:
  - Expected concentration < 50 ppm
  - VOCs known to consist of C and H

Applicability of Methods

	FRM 18	**FRM 25**	**FRM 25A**
Measures…	**VOCs**	**TGNMO**	**THC**
Principle…	**GC/MD**	**GC/FID**	**FID**
Carbon Resp…	**1:1**	**1:1**	**Var.**
Results Exp As..	**VOC**	**As C**	**Cal Gas**

Methods 18, 21, 25 ,25A Sampling Documents



c. 2

United States Environmental Protection Agency | Air and Radiation (EN-341W) | EPA340/1-91-008 September 1991

EPA

Manual for Coordination of VOC Emissions Testing Using EPA Methods 18, 21, 25, and 25A

Draft

MANUAL
FOR OBSERVATION OF VOC EMISSIONS TESTING
USING EPA METHODS 18, 21, 25 AND 25A

U.S. Environmental Protection Agency
Stationary Source Compliance Division
Washington, D.C. 20460

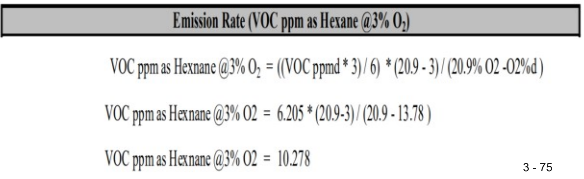
July 1991

Example of NMOC Calculation For An Enclosed Flare

A control system designed and operated to reduce NMOC by 98 weight percent, or, when an enclosed combustion device is used for control, to either reduce NMOC by 98 weight percent or reduce the outlet NMOC concentration to less than 20 parts per million by volume, dry basis as hexane at 3 percent oxygen. The reduction efficiency or parts per million by volume must be established by an initial performance test to be completed no later than 180 days after the initial startup of the approved control system using the test methods specified in § 60.764(d).

Example

- $$ppm_{corr} = ppm_{methane} \times \frac{\text{1 carbon in methane}}{\text{6 carbons in hexane}} \times (20.9 - 3\ \%\ O_2) \times \frac{1}{1 - \%\ \text{Moisture}}$$



Emission Rate (VOC ppm as Hexane @3% O_2)

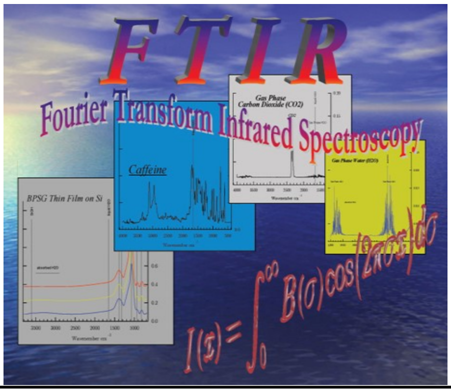
VOC ppm as Hexnane @3% O_2 = ((VOC ppmd * 3) / 6) * (20.9 - 3) / (20.9% O2 -O2%d)

VOC ppm as Hexnane @3% O2 = 6.205 * (20.9-3) / (20.9 - 13.78)

VOC ppm as Hexnane @3% O2 = 10.278

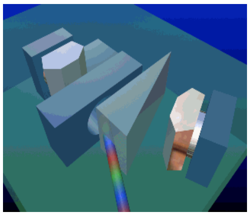
Method 320

- Sample is extracted from the gas steam
- IR absorption spectra determined by directing IR beam through sample cell to a detector
- Compounds determined by matching to known spectra
- Concentrations determined by reference samples



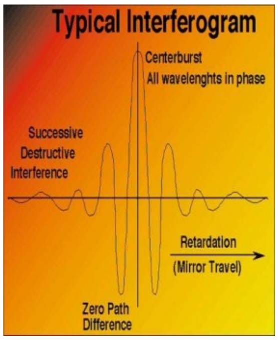
FTIR

- Wavelength of light absorbed is characteristic of the chemical bond
- FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint"



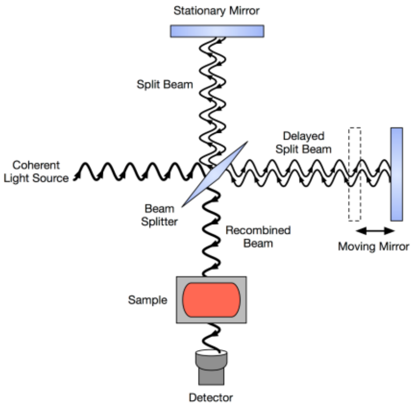
FTIR Theory and Instrumentation

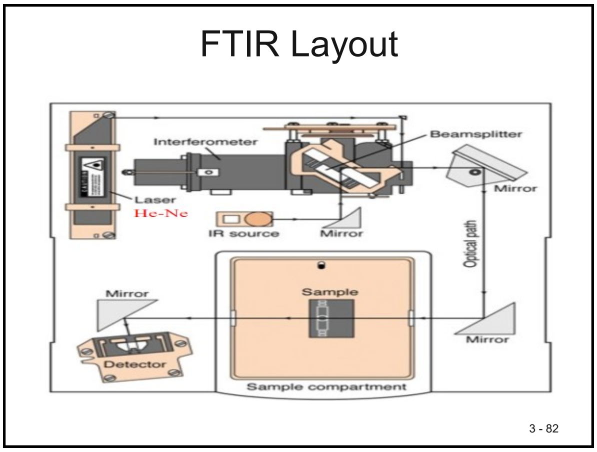
- The heart of the system is the interferometer in which the light from the source is divided into two beams.
- Beams pass through the sample cell and then recombine resulting in a signal.
- All information required to identify and quantify the gases in the sample is present in the interferogram.
- Interferogram signal is converted to a frequency spectrum by a mathematical technique called Fourier Transformation.



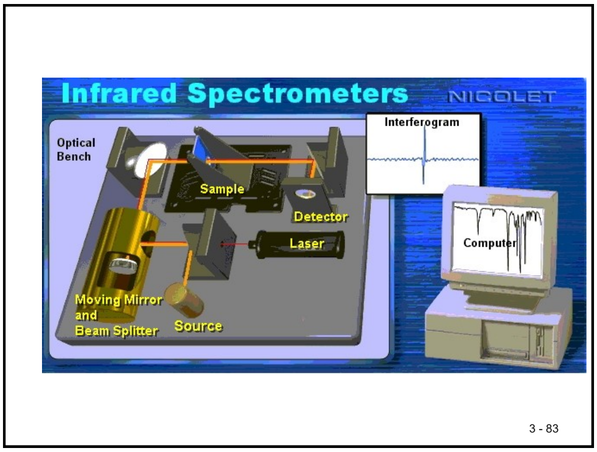
FRM 320

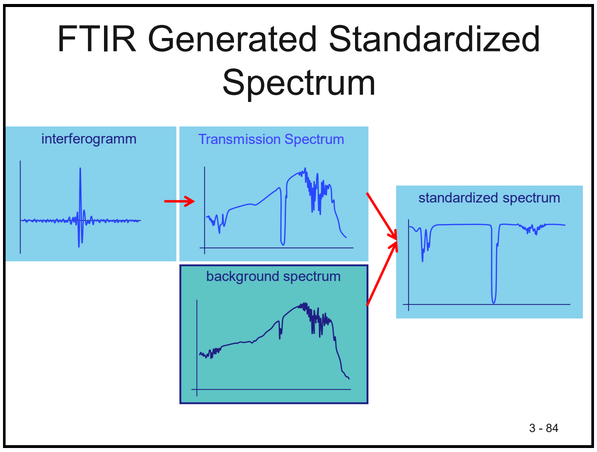
- *"…This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 cm^{-1} (25 to 2.5 um). This method is used to determine compound-specific concentrations in a multi-component vapor phase sample, which is contained in a closed-path cell. Spectra of samples are collected using double beam infrared absorption spectroscopy. A computer program is used to analyze spectra and report compound concentrations."*



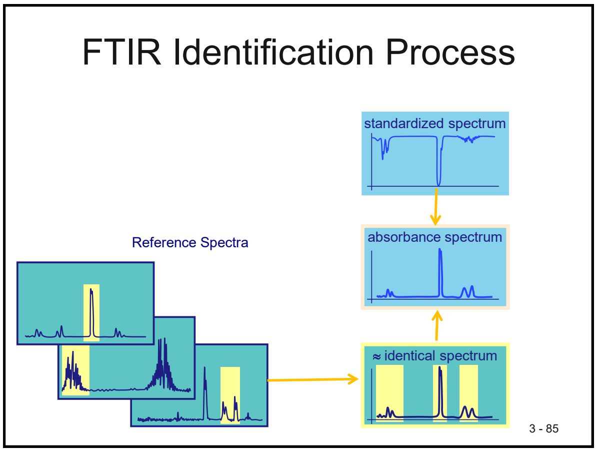


FTIR Layout





FTIR Generated Standardized Spectrum



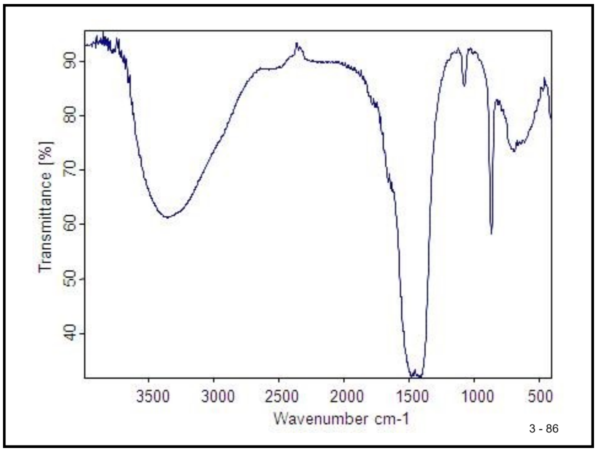
FTIR Identification Process

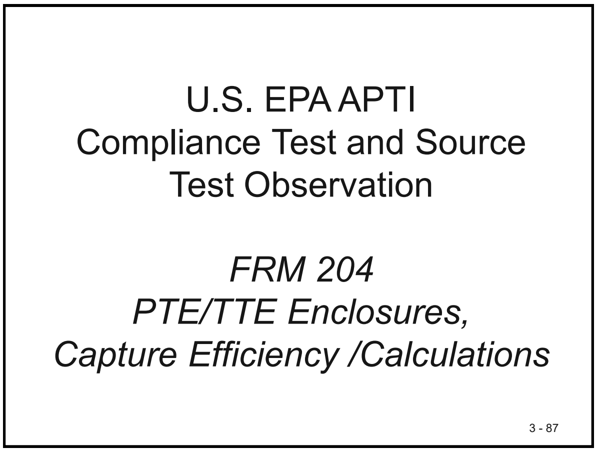
standardized spectrum

absorbance spectrum

Reference Spectra

≈ identical spectrum





U.S. EPA APTI
Compliance Test and Source
Test Observation

FRM 204
PTE/TTE Enclosures,
Capture Efficiency /Calculations

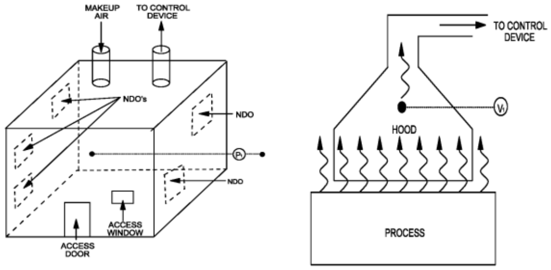
USEPA Method 204

- Procedure used to determine whether a permanent or temporary enclosure meets the criteria for a total enclosure.
- An enclosure is evaluated against a set of criteria. If the criteria are met and if all the exhaust gases from the enclosure are ducted to a control device, then the volatile organic compounds (VOC) capture efficiency (CE) is assumed to be 100 percent, and CE need not be measured

THC/OHAP Control Techniques – Capture Systems

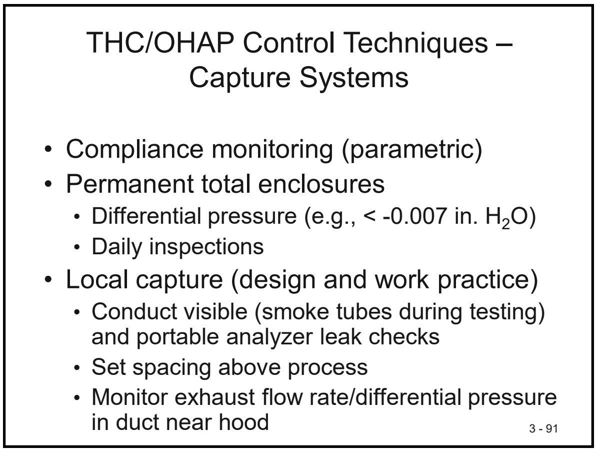
- General description
  - Two types of systems
    - Enclosures and local exhausts (hoods)
  - Two types of enclosures
    - Permanent total (M204 definition) – 100% capture efficiency
    - Non-total or partial – must measure capture efficiency via Method 204
- Total THC control efficiency is product of capture and control device efficiencies

THC/OHAP Control Techniques – Capture System



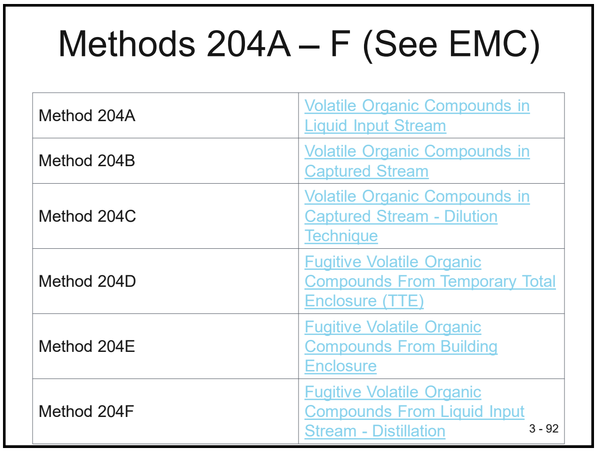
P1 = DIFFERENTIAL PRESSURE SENSOR (BETWEEN ENCLOSURE INTERIOR AND SURROUNDING AREA/ROOM)

V1 = VELOCITY AT HOOD



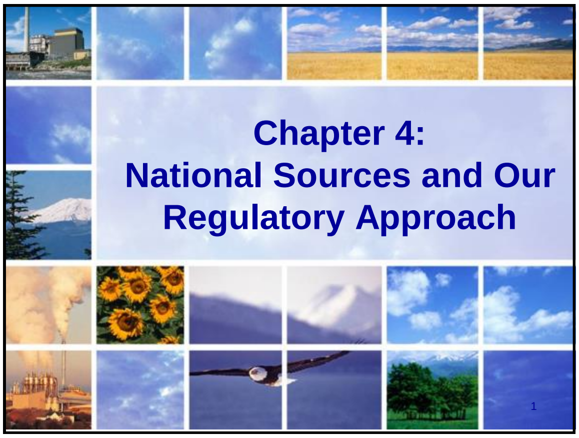
THC/OHAP Control Techniques – Capture Systems

- Compliance monitoring (parametric)
- Permanent total enclosures
  - Differential pressure (e.g., < -0.007 in. H_2O)
  - Daily inspections
- Local capture (design and work practice)
  - Conduct visible (smoke tubes during testing) and portable analyzer leak checks
  - Set spacing above process
  - Monitor exhaust flow rate/differential pressure in duct near hood

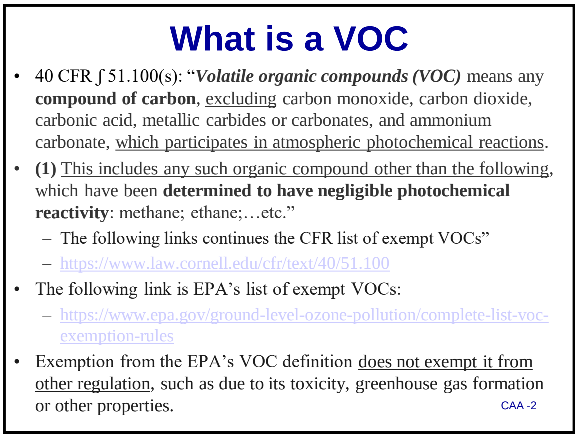


Methods 204A – F (See EMC)

Method 204A	Volatile Organic Compounds in Liquid Input Stream
Method 204B	Volatile Organic Compounds in Captured Stream
Method 204C	Volatile Organic Compounds in Captured Stream - Dilution Technique
Method 204D	Fugitive Volatile Organic Compounds From Temporary Total Enclosure (TTE)
Method 204E	Fugitive Volatile Organic Compounds From Building Enclosure
Method 204F	Fugitive Volatile Organic Compounds From Liquid Input Stream - Distillation

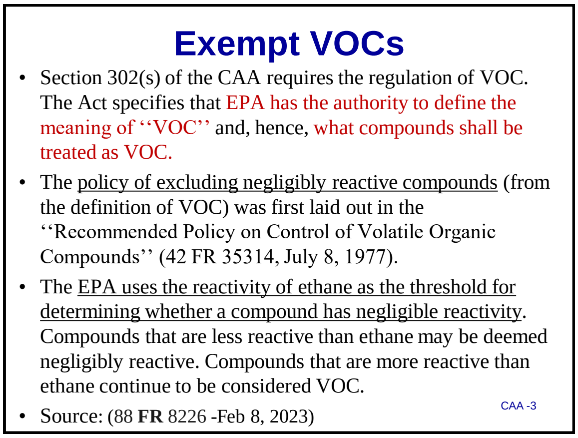


Chapter 4: National Sources and Our Regulatory Approach



What is a VOC

- 40 CFR ʃ 51.100(s): "***Volatile organic compounds (VOC)*** means any **compound of carbon**, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.
- **(1)** This includes any such organic compound other than the following, which have been **determined to have negligible photochemical reactivity**: methane; ethane;…etc."
  - The following links continues the CFR list of exempt VOCs"
  - https://www.law.cornell.edu/cfr/text/40/51.100
- The following link is EPA's list of exempt VOCs:
  - https://www.epa.gov/ground-level-ozone-pollution/complete-list-voc-exemption-rules
- Exemption from the EPA's VOC definition does not exempt it from other regulation, such as due to its toxicity, greenhouse gas formation or other properties.

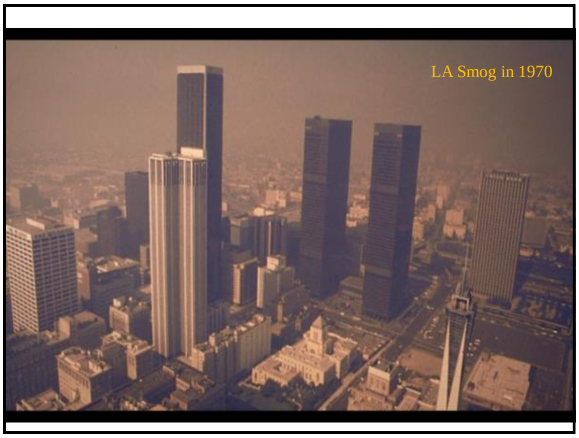


Exempt VOCs

- Section 302(s) of the CAA requires the regulation of VOC. The Act specifies that EPA has the authority to define the meaning of ''VOC'' and, hence, what compounds shall be treated as VOC.
- The policy of excluding negligibly reactive compounds (from the definition of VOC) was first laid out in the ''Recommended Policy on Control of Volatile Organic Compounds'' (42 FR 35314, July 8, 1977).
- The EPA uses the reactivity of ethane as the threshold for determining whether a compound has negligible reactivity. Compounds that are less reactive than ethane may be deemed negligibly reactive. Compounds that are more reactive than ethane continue to be considered VOC.
- Source: (88 **FR** 8226 -Feb 8, 2023)

VOC Sources and Effects of Ozone

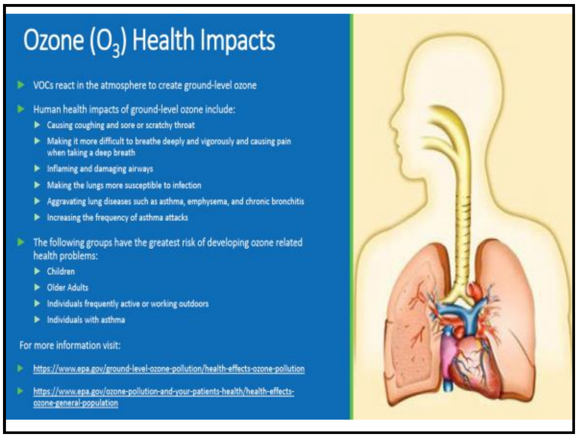
- Effects of Ozone
- Ozone Formation
- VOC Emission Sources and Emission Trends



LA Smog in 1970

LA Smog Problem: a Hot Political Issue

- In 1946, LA addressed smudge pots to heat citrus groves.
  - Thought smog caused by SO_2 – like in other big cities
- In 1947, Cal governor Earl Warren signed first state Air Pollution Control Act, creating an AP Control District in every county.
- 1949 to early 1950's: Professor Haagen-Smit of Caltech studied the causes & effects of smog. That a photochemical reaction was responsible for smog rather than particulates.



Ozone (O_3) Health Impacts

- VOCs react in the atmosphere to create ground-level ozone
- Human health impacts of ground-level ozone include:
  - Causing coughing and sore or scratchy throat
  - Making it more difficult to breathe deeply and vigorously and causing pain when taking a deep breath
  - Inflaming and damaging airways
  - Making the lungs more susceptible to infection
  - Aggravating lung diseases such as asthma, emphysema, and chronic bronchitis
  - Increasing the frequency of asthma attacks
- The following groups have the greatest risk of developing ozone related health problems:
  - Children
  - Older Adults
  - Individuals frequently active or working outdoors
  - Individuals with asthma

For more information visit:

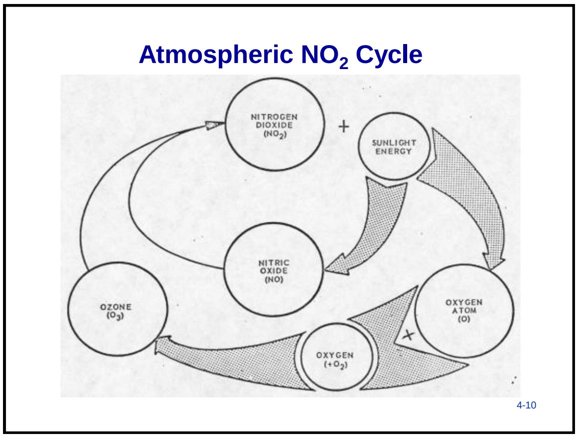
- https://www.epa.gov/ground-level-ozone-pollution/health-effects-ozone-pollution
- https://www.epa.gov/ozone-pollution-and-your-patients-health/health-effects-ozone-general-population

Environmental Effects of Ozone

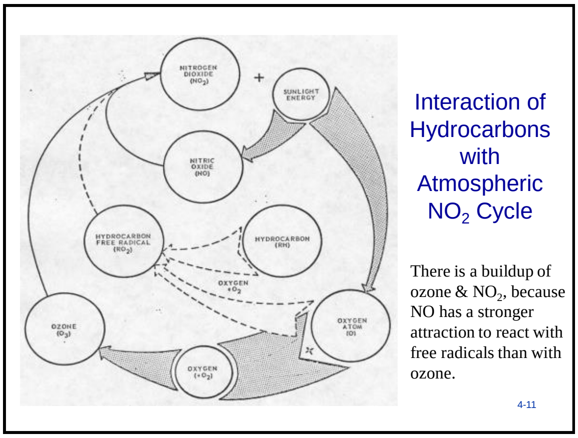
- Scientific evidence shows that repeated exposure to ozone has harmful effects on plants and trees.
- These effects include visible injury to leaves, decreased photosynthesis, reduced vegetation growth, and reduced yield and quality of agricultural crops.

Sources of Ozone

- Ozone is not emitted directly into air, but is formed as a byproduct of the reaction of VOC and NO_X in the presence of sunlight.
- In order to reduce ambient ozone, VOC sources are studied and regulated.

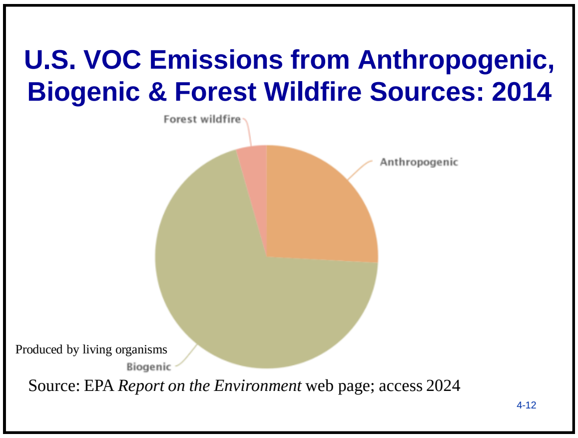


Atmospheric NO_2 Cycle



Interaction of Hydrocarbons with Atmospheric NO_2 Cycle

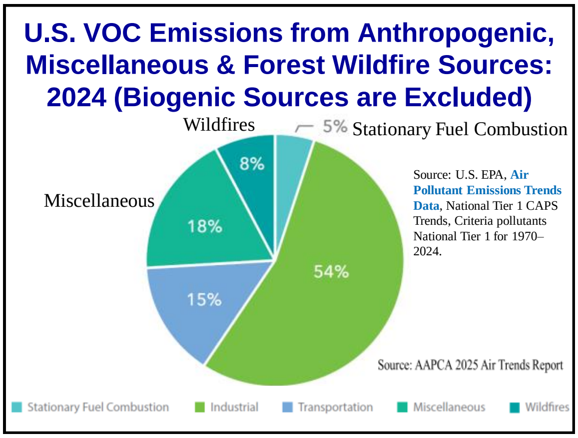
There is a buildup of ozone & NO_2, because NO has a stronger attraction to react with free radicals than with ozone.



U.S. VOC Emissions from Anthropogenic, Biogenic & Forest Wildfire Sources: 2014

Produced by living organisms

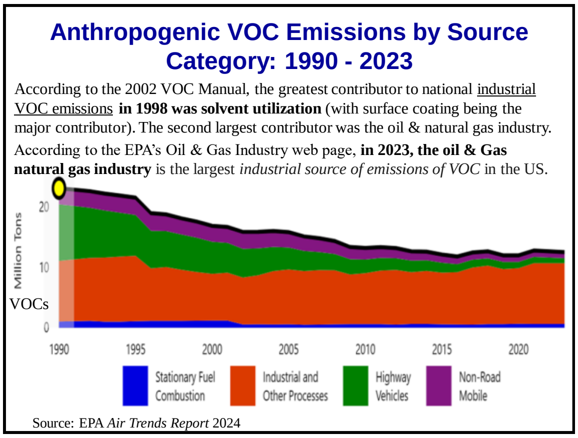
Source: EPA *Report on the Environment* web page; access 2024



U.S. VOC Emissions from Anthropogenic, Miscellaneous & Forest Wildfire Sources: 2024 (Biogenic Sources are Excluded)

Source: U.S. EPA, **Air Pollutant Emissions Trends Data**, National Tier 1 CAPS Trends, Criteria pollutants National Tier 1 for 1970–2024.

Source: AAPCA 2025 Air Trends Report

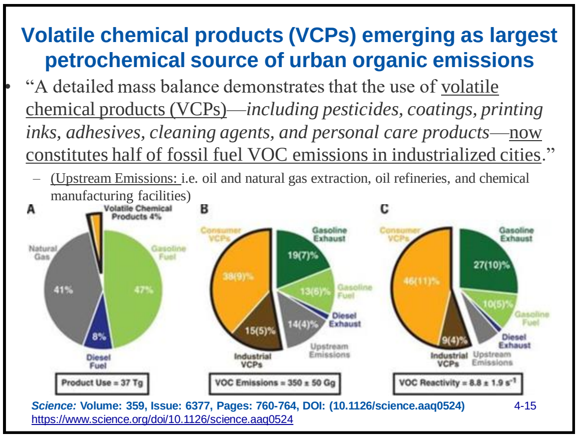


Anthropogenic VOC Emissions by Source Category: 1990 - 2023

According to the 2002 VOC Manual, the greatest contributor to national industrial VOC emissions **in 1998 was solvent utilization** (with surface coating being the major contributor). The second largest contributor was the oil & natural gas industry.

According to the EPA's Oil & Gas Industry web page, **in 2023, the oil & Gas natural gas industry** is the largest *industrial source of emissions of VOC* in the US.

Source: EPA *Air Trends Report* 2024



Volatile chemical products (VCPs) emerging as largest petrochemical source of urban organic emissions

- "A detailed mass balance demonstrates that the use of volatile chemical products (VCPs)—*including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products*—now constitutes half of fossil fuel VOC emissions in industrialized cities."
  - (Upstream Emissions: i.e. oil and natural gas extraction, oil refineries, and chemical manufacturing facilities)

Science: Volume: 359, Issue: 6377, Pages: 760-764, DOI: (10.1126/science.aaq0524) 4-15
https://www.science.org/doi/10.1126/science.aaq0524

Regulatory Approach for Ozone Under the CAA

Donora Episode: Oct. 26, 1948

- Start of a 5-day temperature inversion
- City surrounded by mountains
- 50% of all residents sick (6,000 people)
  - Chest pains & labored breathing, etc.
- 20 people died
- Investigations resulted, but none could produce direct evidence of air pollution's harm. Surgeon General, Scheele, wrote in the foreword of a 1949 report studying the air pollution effects of the Donora episode: "*This study is the opening move …in improving the nations health. We have realized during our growing impatience with the annoyance of smoke, that pollution from gases, fumes & microscopic particles was also a factor to be reckoned with.*"

Federal Legislative Landmarks

- 1955 Air Poll. Control Act: Fed research funding
- *Debates:* Fed or state responsibility
- 1963 CAA: (compromise) Funding for state air programs
- 1965 CAAA: Auto emission stds. (CO & HxCx)
- *Debates*: national stds. vs. regional stds.
  ambient air stds. vs. emission stds.
- 1967 Air Quality Act: States set regional air quality stds. based on federal air quality criteria
  - States failed to set stds., collect ambient air data & conduct emission inventories (21 SIPs submitted; none approved)
  - HEW (understaffed) failed to set air quality control regions
- 1970 CAAA: (sharply increased fed authority)
  - Uniform NAAQS, SIP, NSPS, NESHAP, & mobile sources

Passage of the 1970 CAA

President Richard Nixon signs the CAA on Dec 31, 1970

Senator Edmund Muskie: Chairman of the Subcommittee on Water and Air Pollution

Federal Legislative Landmarks

- **1977 CAA Amendments:**
- Prevention of Significant Depreciation (PSD) program created
- Non-attainment provisions (added Part D to the CAA)
- Visibility impairment addressed for first time

Federal Legislative Landmarks

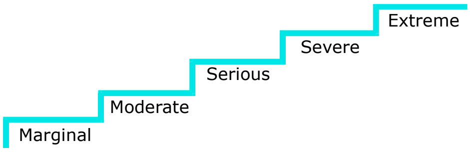
1990 CAA Amendments

- Revised HAP program
- Acid Rain & Ozone depletion
- Title V Operating Permits
- Strengthened enforcement provisions
- New classifications for non-attainment areas

Rep. Henry Waxman (D-Calif.)

Ozone Nonattainment Regions

Sub-classified on severity of non-attainment (under CAA Subpart II)



Extreme

Severe

Serious

Moderate

Marginal

Regulatory Approach for Ozone Under the CAA

- NAAQS
- Ozone Nonattainment Classifications
- History of the Ozone NAAQS
- Nonattainment Area SIP Requirements
- HAP Program for Regulating VOC HAPs
- NSPS & NSR for VOC Sources
- Title V
- Interstate Transport of Ozone

NAAQS

- 6 criteria pollutants:
  - NO_2 , CO, SO_2 , Ozone, Lead. PM10 & PM2.5
  - https://www.epa.gov/criteria-air-pollutants/naaqs-table
- Primary standard: (public health)
  - "*adequate margin of safety*" to protect people regardless of age, health etc.
  - EPA cannot consider "costs" of implementation in setting the standard.
- Secondary standard: (public welfare)
- EPA to review NAAQS every 5 years

National Ambient Air Quality Standards

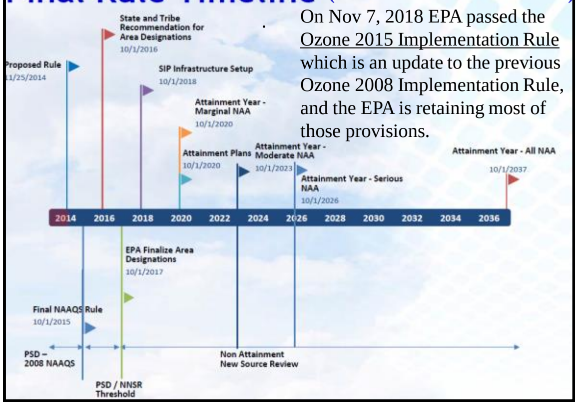
Pollutant	*Averaging Time*	*Primary*	*Secondary*
PM-2.5 *(2024)*	Annual	9 $\mu g/m^3$	None
PM-2.5 *(2006)*	Annual	None	15 $\mu g/m^3$
PM-2.5 *(2006)*	24-hour	35 $\mu g/m^3$	Same
PM-10 *(1987)*	24-hour	150 $\mu g/m^3$	Same
SO_2 *(2010)*	1-hour	75 ppb	None
(2024)	Annual	None	10 ppb
CO *(1971)*	8-hour	9 ppm	None
(1971)	1-hour	35 ppm	None
Ozone *(2015)*	**8-hour/day**	**0.070 ppm**	**Same**
NO_2 *(2010)*	1-hour/day	100 ppb	None
(1971)	Annual	53 ppb	Same
Lead *(2008)*	3mo. average	0.15 $\mu g/m^3$	Same

History of Ozone NAAQS

- 1971: EPA set primary/secondary standards for "total photochemical oxidants" (ozone is one of them) at 0.08ppm (1 hr.)
  - Primary & secondary standards were also set for HxCx at 0.24ppm (3hr.)
  - In 1983 HxCx was delisted because of no direct adverse health effects
- 1979: EPA set primary/secondary standards for "ozone" at 0.12ppm (1 hr.).
- 1997: EPA set primary/secondary standards for "ozone" at 0.08ppm (8 hr.).
  - All nonattainment areas use classification scheme.
- 2008: EPA set primary/secondary standards for "ozone" at 0.075ppm (8 hr.).
- 2015: EPA set primary/secondary standards for ozone at **0.070ppm (8 hr.)**.

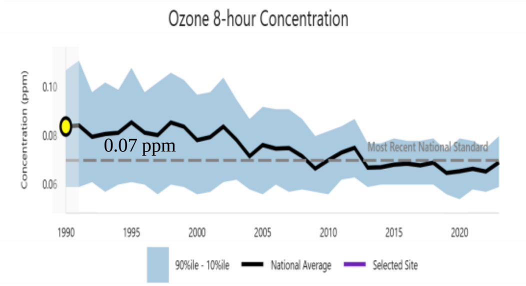
EPA history timeline of ozone standards: https://www.epa.gov/ground-level-ozone-pollution/timeline-ozone-national-ambient-air-quality-standards-naaqs

Final Rule Timeline (for new 2015 ozone standard)



On Nov 7, 2018 EPA passed the Ozone 2015 Implementation Rule which is an update to the previous Ozone 2008 Implementation Rule, and the EPA is retaining most of those provisions.

Ozone Air Quality, 1990 - 2023



Source: EPA *Trends Report 2024*

Air Quality Control Regions

(247 air quality control regions in USA)

- **Attainment:** Any area that meets the NAAQS
- **Nonattainment**
  - Any area that does not meet primary and secondary NAAQS for that pollutant
  - Any area that *contributes* to the ambient air quality in a nearby areas that does not meet primary and secondary NAAQS for that pollutant
- **Unclassifiable:** Any area with insufficient air quality data to determine the compliance status

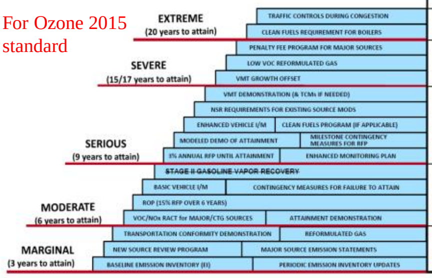
Non-attainment Regions

- Sub-classified on severity of non-attainment (under CAA Subpart II)
- Ozone
  - Extreme
  - Severe (two levels)
  - Serious
  - Moderate
  - Marginal
- CO & and Particulate Matter (PM10 & $PM_{2.5}$)
  - Serious
  - Moderate

Overview of CAA Ozone Nonattainment Area Planning & Control Mandates by Classification

1. Extend the compliance date &
2. Different substantive requirements (cumulative)

For Ozone 2015 standard



NSR offset ratio	Major source threshold
1.5 : 1 Extreme	10
1.3 : 1 Severe	25
1.2 : 1 Serious	50
1.15 : 1 Moderate	100
1.1 : 1 Marginal	100

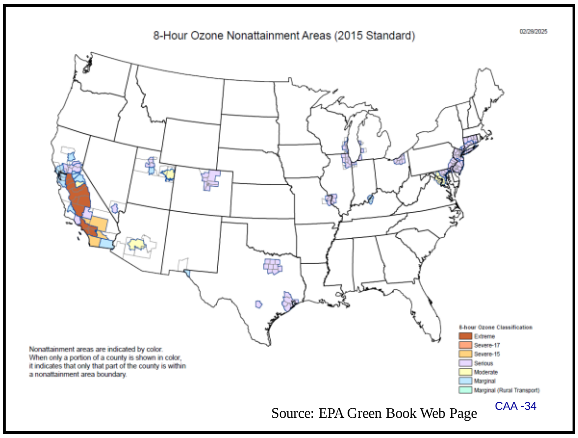
Non-attainment Classification

- <u>Non-attainment classification</u> is based on a criteria pollutant's "<u>design value</u>" falling in between a designated "<u>design value" range</u> established for the classification category.
  - <u>Ozone</u>: *design value ranges* shown in next slide.
  - Ozone *design value* is the 4th highest daily maximum 8-hour concentration averaged across the last 3 consecutive years.

Design Values Ranges: 2015 Ozone Standard

Area Class	*Design Value (PPM)*	*Attainment Date: 6/15*
Marginal	0.071 to 0.081	2021 – 3yrs
Moderate	0.081 to 0.093	2024 - 6yrs
Serious	0.093 to 0.105	2027 - 9yrs
Severe-15	0.105 to 0.111	2033 - 15yrs
Severe-17	0.111 to 0.163	2035 - 17yrs
Extreme	0.163 and above	2038 - 20yrs

If a nonattainment area <u>does not meet the required attainment date</u>, then they will be reclassified "<u>bumped up</u>" to the next higher classification.



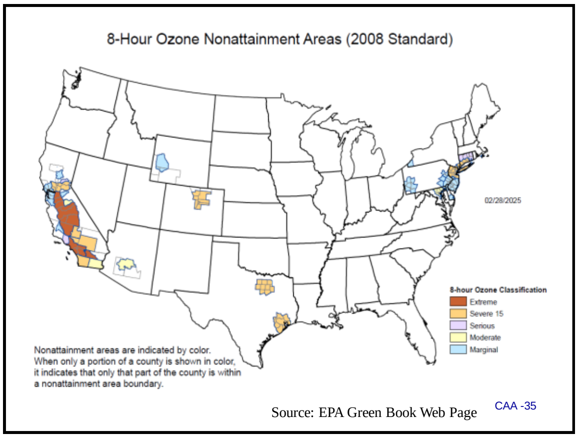
8-Hour Ozone Nonattainment Areas (2015 Standard)

02/28/2025

Nonattainment areas are indicated by color. When only a portion of a county is shown in color, it indicates that only that part of the county is within a nonattainment area boundary.

Source: EPA Green Book Web Page

CAA -34



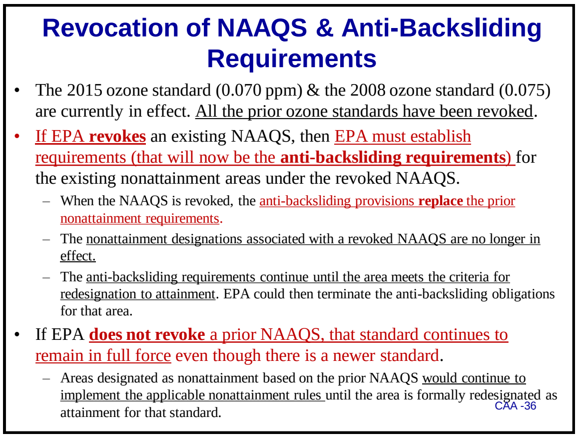
8-Hour Ozone Nonattainment Areas (2008 Standard)

02/28/2025

Nonattainment areas are indicated by color. When only a portion of a county is shown in color, it indicates that only that part of the county is within a nonattainment area boundary.

Source: EPA Green Book Web Page

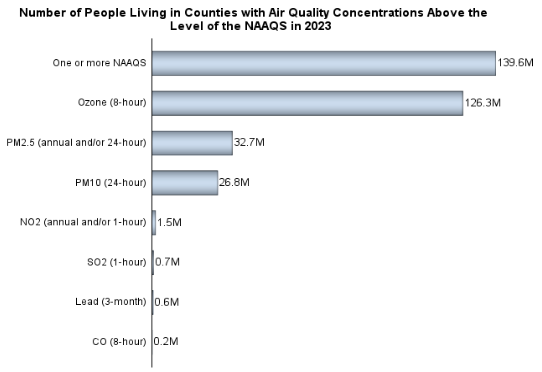
CAA -35



Revocation of NAAQS & Anti-Backsliding Requirements

- The 2015 ozone standard (0.070 ppm) & the 2008 ozone standard (0.075) are currently in effect. All the prior ozone standards have been revoked.
- If EPA **revokes** an existing NAAQS, then EPA must establish requirements (that will now be the **anti-backsliding requirements**) for the existing nonattainment areas under the revoked NAAQS.
  - When the NAAQS is revoked, the anti-backsliding provisions **replace** the prior nonattainment requirements.
  - The nonattainment designations associated with a revoked NAAQS are no longer in effect.
  - The anti-backsliding requirements continue until the area meets the criteria for redesignation to attainment. EPA could then terminate the anti-backsliding obligations for that area.
- If EPA **does not revoke** a prior NAAQS, that standard continues to remain in full force even though there is a newer standard.
  - Areas designated as nonattainment based on the prior NAAQS would continue to implement the applicable nonattainment rules until the area is formally redesignated as attainment for that standard.

CAA -36



Source: EPA's Air Trends Website; access 2024

State Implementation Plan (SIP)

- *A SIP is the air pollution measures & strategies* adopted by a state for attaining and maintaining the NAAQS
  - i.e. new emission standards, emission inventories, monitoring, modeling, & enforcement program etc.
- A state SIP must be approved by the EPA
- If SIP is disapproved, EPA must promulgate a *Federal Implementation Plan (FIP) & other sanctions*:
  - FIP implemented 1.5 years after federal disapproval
  - Under CAA §179: Highway funding reduced &
  - New source offset at a 2 to 1 ratio

Nonattainment Area SIP Requirements

- CAA δ172 requires that nonattainment area SIPs must implement "*Reasonable Available Control Measures*" (**RACM**). These include:
  - Existing major stationary sources must use (**RACT**) "*Reasonably Available Control Technology*" (considers economic and technological feasibility)
  - Transportation control measures
  - Novel alternatives (i.e. market emission trading)
- *Reasonable further progress* (annual increments) towards attaining NAAQS by the attainment date.

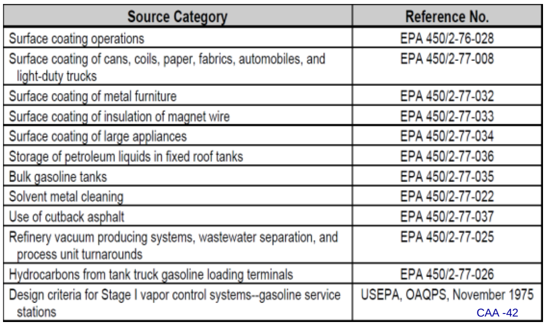
Control Technology Guidelines (CTGs)

- In order to provide the states guidance in setting RACT emission limits, EPA 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.
- Although the CTG process (including public review) has not been active since the mid-1990s, the *Alternative Control Technology* (ACT) documents were developed after 1990. These documents are issued without review; however, they contain only descriptions of alternative controls, with no recommended RACT emission limit.

Control Technology Guidelines (CTGs)

- *Control Techniques Guidelines* are used to define VOC RACT while *Alternative Control Techniques* (ACTs) describe available control technologies and their respective cost effectiveness.
- The following link is to EPA’s CTGs & ACTs:
  - https://www.epa.gov/ground-level-ozone-pollution/control-techniques-guidelines-and-alternative-control-techniques

The following is a limited list of stationary source categories for which a CTGs has been developed



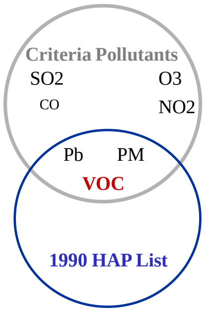
Source Category	Reference No.
Surface coating operations	EPA 450/2-76-028
Surface coating of cans, coils, paper, fabrics, automobiles, and light-duty trucks	EPA 450/2-77-008
Surface coating of metal furniture	EPA 450/2-77-032
Surface coating of insulation of magnet wire	EPA 450/2-77-033
Surface coating 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

Re-designation

- **EPA re-designates an area <u>from nonattainment to attainment</u>**
  - Need <u>3 years of violation free data</u>
  - State submits a <u>request satisfying 5 requirements</u> (CAA δ107(d)(3)(e))(includes a "**maintenance plan**")
- **Maintenance Plan** is a SIP revision to assure continued compliance
  - Specifies what you are <u>going to do if the standard is violated</u> after being re-designated attainment

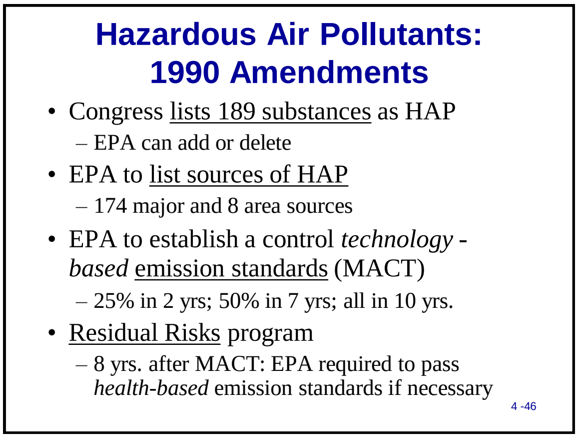
Overlap Between HAPs and Criteria Pollutants

- Many HAPs are VOC:
  - Ozone formation



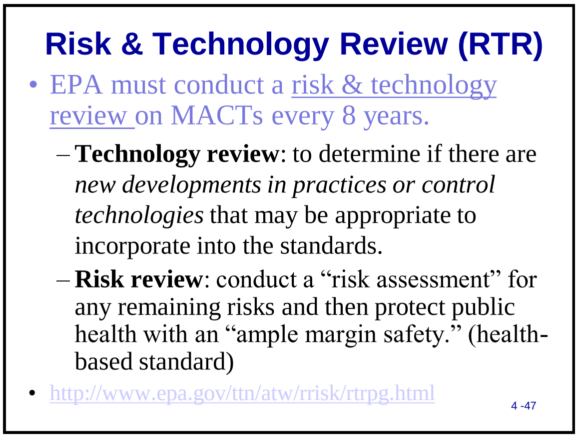
1970 CAAA Air Toxics Program Required EPA to:

- <u>List</u> chemicals they decide are hazardous:
  - Arsenic, asbestos, beryllium, mercury, benzene, vinyl chloride, radionuclides and coke oven emissions
- Set an <u>emission limitation</u> (NESHAP) in 1 year (after listing) with "ample margin of safety" protection.
  - 1976: EPA originally set NESHAP by:
    - 1st *Does it cause cancer?* Yes, then "shut it down."
    - If shutting it down is impractical, then (2nd) take action to *reduce risk by considering cost & technical feasibility.*
- *NRDC v EPA* (1987): vinyl chloride case
  - NRDC contended: use <u>zero emission</u> when no safe level can be determined
  - Held: use 2 step process
  - <u>Health based</u> standard



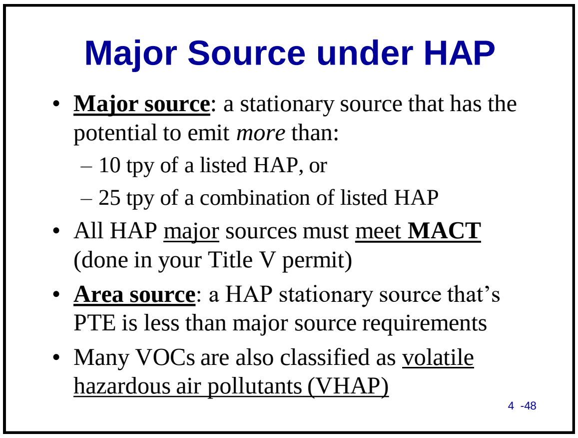
Hazardous Air Pollutants: 1990 Amendments

- Congress lists 189 substances as HAP
  - EPA can add or delete
- EPA to list sources of HAP
  - 174 major and 8 area sources
- EPA to establish a control *technology - based* emission standards (MACT)
  - 25% in 2 yrs; 50% in 7 yrs; all in 10 yrs.
- Residual Risks program
  - 8 yrs. after MACT: EPA required to pass *health-based* emission standards if necessary



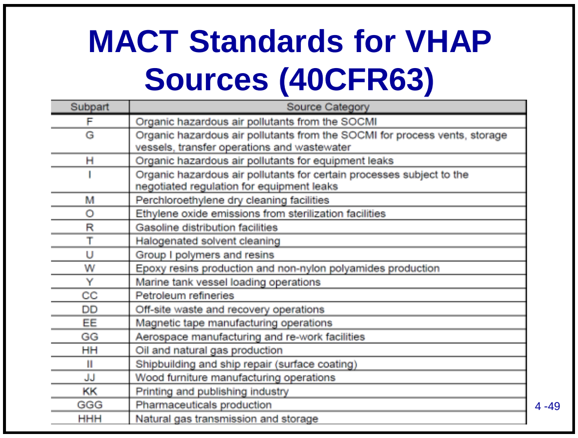
Risk & Technology Review (RTR)

- EPA must conduct a risk & technology review on MACTs every 8 years.
  - **Technology review**: to determine if there are *new developments in practices or control technologies* that may be appropriate to incorporate into the standards.
  - **Risk review**: conduct a “risk assessment” for any remaining risks and then protect public health with an “ample margin safety.” (health-based standard)
- http://www.epa.gov/ttn/atw/rrisk/rtrpg.html



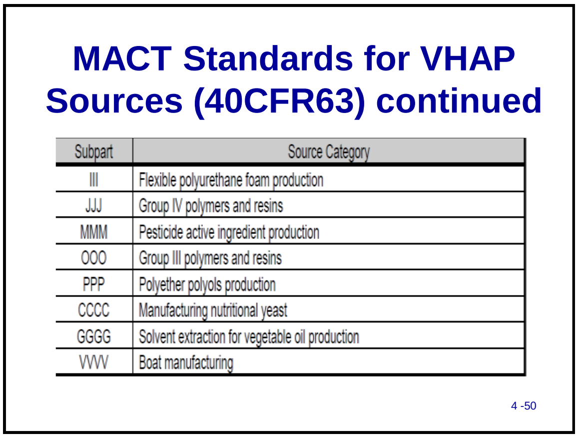
Major Source under HAP

- **Major source**: a stationary source that has the potential to emit *more* than:
  - 10 tpy of a listed HAP, or
  - 25 tpy of a combination of listed HAP
- All HAP major sources must meet **MACT** (done in your Title V permit)
- **Area source**: a HAP stationary source that’s PTE is less than major source requirements
- Many VOCs are also classified as volatile hazardous air pollutants (VHAP)



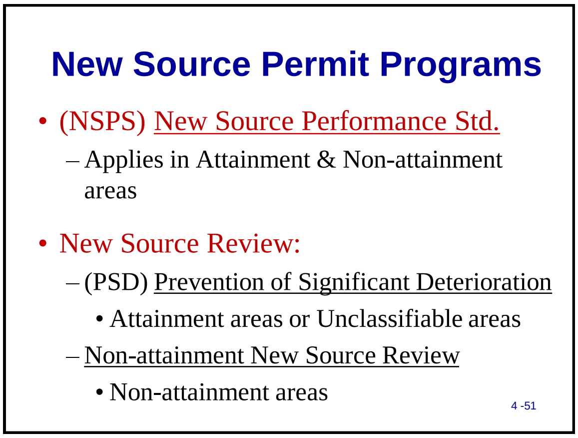
MACT Standards for VHAP Sources (40CFR63)

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



MACT Standards for VHAP Sources (40CFR63) continued

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



New Source Permit Programs

- (NSPS) <u>New Source Performance Std.</u>
  - Applies in Attainment & Non-attainment areas
- New Source Review:
  - (PSD) <u>Prevention of Significant Deterioration</u>
    - Attainment areas or Unclassifiable areas
  - <u>Non-attainment New Source Review</u>
    - Non-attainment areas

New Source Performance Stds (NSPS)

- EPA sets "NSPS" for new sources that "contribute significantly to air pollution."
  - 85 industrial categories identified (40 CFR Part 60)
  - https://www.epa.gov/stationary-sources-air-pollution/new-source-performance-standards
  - Applies in attainment and non-attainment areas
- NSPS are emission or performance standards
  - new sources must meet standard once promulgated
- NSPS sets emission limits by application of **the "best system of emission reduction" (BSER)**.
  - "costs" are considered
- NSPS to be reviewed every 8 years.

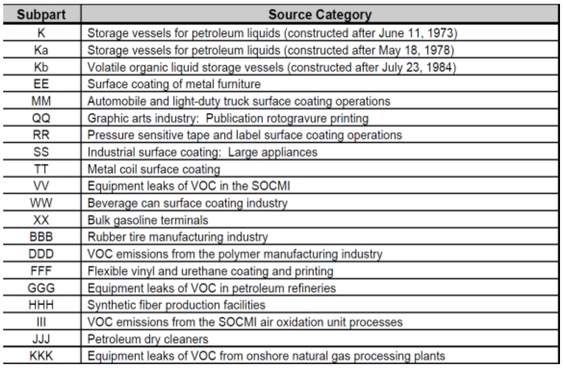
CAA -52

New Source Performance Stds (NSPS)

- Cannot use *bubble* concept to define "source"
  - NSR (entire facility) uses annual emissions (tons/yr.)
  - NSPS (individual emission units) hourly emission rate (#/hr.)
- Includes modifications to existing sources
  - No increase in hourly emission rate (no *significant levels* used)
  - Exemptions: *routine maintenance & repair*, etc.
    - EPA 1992: "what is common in the industry"

CAA -53

NSPS 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

NSPS for VOC Sources (Continued) (40CFR60)

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

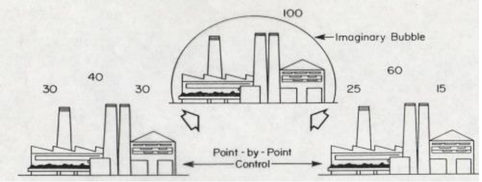
Prevention of Significant Deterioration (PSD)

Rule:

In **attainment areas**, major *new* stationary sources and major modifications to *existing* major sources are subject to PSD program requirements.

PSD: Source

- Use “bubble theory” to define source
  - Total emissions from the entire plant instead of individual components:



- entire plant includes:
  - Same SIC
  - Contiguous & adjacent property
  - Controlled by same person

PSD: Major Source

- A PSD Major Source has the "potential to emit" a ***regulated NSR pollutant*** greater than or equal to*:*
  - – 250 tons/year, or
  - – 100 tons/year (if the source is one of the 28 source categories listed in CAA §169)

- 1. Fossil fuel-fired steam electric plants of more than 250 million Btu/hr heat input
- 2. Coal cleaning plants (with thermal dryers)
- 3. Kraft pulp mills
- 4. Portland cement plants
- 5. Primary zinc smelters
- 6. Iron and steel mill plants
- 7. Primary aluminum ore reduction plants
- 8. Primary copper smelters
- 9. Municipal incinerators capable of charging more than 250 tons of refuse per day
- 10. Hydrofluoric acid plants
- 11. Sulfuric acid plants
- 12. Nitric acid plants
- 13. Petroleum refineries
- 14. Lime plants
- 15. Phosphate rock processing plants
- 16. Coke oven batteries
- 17. Sulfur recovery plants
- 18. Carbon black plants (furnace plants)
- 19. Primary lead smelters
- 20. Fuel conversion plants
- 21. Sintering plants
- 22. Secondary metal production plants
- 23. Chemical process plants
- 24. Fossil fuel boilers (or combinations thereof) totaling more than 250million Btu/hr heat input
- 25. Petroleum storage and transfer units with a total storage capacity exceeding 300,000 barrels
- 26. Taconite ore processing plants
- 27. Glass fiber processing plants
- 28. Charcoal production plants

Potential To Emit (PTE)

- **PTE** means the *maximum* capacity of a stationary source to emit any air pollutant under its physical and operational *design*.
  - – Source operating 24 hours per day, 365 days per year, at maximum design and emission rates
- **Can restrict PTE** "*design limitation*" only if the limitation is "federally enforceable." These include:
  - – the use of air pollution control equipment
  - – restrictions on hours of operation
  - – restrictions on the type or amount of material combusted, stored, or processed

PSD: Major Modification

- **Major modification** … is a change at an existing major source that causes a "*significant" emissions increase*.
  - – "Significant" Emission increase for Ozone is a rate of emissions that would equal or exceed **40 tons/yr. of VOCs or NO_X** .
    - Add up all source emission increases & decreases 5 years before new construction begins (**Netting**).

PSD Permit Requirements

- Air Quality **Modeling**
  - Show that the background plus proposed source concentration does not exceed the Ozone NAAQS
- **BACT:** Best Available Control Technology
  - “Maximum degree of reduction achievable..”
  - “Costs” considered
  - More stringent than NSPS

BACT Determinations Steps

Step 1: Identify available pollution control options.

Step 2: Eliminate technically infeasible options.

Step 3: Rank controls by control effectiveness.

Step 4: Evaluate controls by cost and energy & environmental impacts.

Step 5: Make the BACT selection.

BACT Determination Example

- Control A: 60% efficient @ cost = $50,000/yr.
- Control B: 90% efficient @ cost = $60,000/yr.
- Control C: 94% efficient @ cost = $90,000/yr.

- Control B would be BACT because it is the most *cost effective* for tons of pollutant removed.

Non-attainment Preconstruction Review: *Rule*

In **non-attainment areas**, major *new* stationary sources and major modifications to *existing* major sources are subject to non-attainment new source review program requirements.

Non-attainment Preconstruction:

- Source
  - Defined same as PSD
  - Use “bubble theory”
- Non-attainment area
  - Does not meet the NAAQS
  - Non-attainment “classification” changes:
    - What is a “major source”
    - What is a “major modification”

Non-attainment: Major Source

- Potential to emit more than 100 tpy of any non-attainment (criteria or its precursors) pollutant, or
- Depends on non-attainment classification

Area Classification		*PTE (tpy)*
Ozone *(either VOC or NO_X)*	Marginal & Moderate	100
	Serious	50
	Severe	25
	Extreme	10

VOCs & NOx are primary pollutant, precursors for the criteria pollutant, ozone, and therefore their emissions are regulated.

Non-attainment: Major Modification

Major modifications to existing major sources:
- An increase over "*significant quantity*"
- Depends on non-attainment classification:

Area Designation		*Significant Quantity (tpy)*
Ozone	Marginal & Moderate	40 (VOC or NO_X)
	Serious & Severe	25
	Extreme	0

Non-attainment Permit

- LAER: Lowest achievable emission rate
  - "Most stringent emission limitation .. ..achievable in practice" by similar sources
  - More stringent than "BACT"
- Company's other sources must meet air regs
  - Same ownership and control
  - Same state
- Offset: take out more than you are putting in
  - Higher offsets as non-attainment classification increases.

Federal Offset Ratio

Area Classification		*Offset Ratio*
Ozone	Marginal	1.1 to 1
	Moderate	1.15 to 1
	Serious	1.2 to 1
	Severe	1.3 to 1
	Extreme	1.5 to 1

Title V

- 1990 CAAA created the Title V Operating Permit Program
  - States (& locals) become the Title V permit authority upon approval by the EPA.
- Purpose of Title V Permit is to *specify all the CAA "applicable requirements" under one permit*.
- Major Stationary Sources are Required to Obtain a Title V Permit
  - Major sources are:
    - Any CAA air pollutant ≥ 100 tons/yr. except GHGs
    - HAPs ≥ 10 tons/yr (1 HAP) or 25 tons/yr (total HAPs)
    - NSR Permits: PSD & Nonattainment (including lower thresholds in nonattainment areas)

Title V Required Reporting

- **Deviation Reports**: Prompt reporting of any deviations from permit requirements (including upsets)
  - Must identify the cause of deviation & corrective actions and/ or preventive measures taken.
- **Semi-annual Reports** of any required monitoring
  - All deviations of permit requirements must be clearly identified (& certified by a "responsible official").
- **Annual Compliance Certification**
  - Statement of compliance from a "responsible official"
  - Must specify methods used to determine compliance (i.e. monitoring, recordkeeping, testing, etc.)

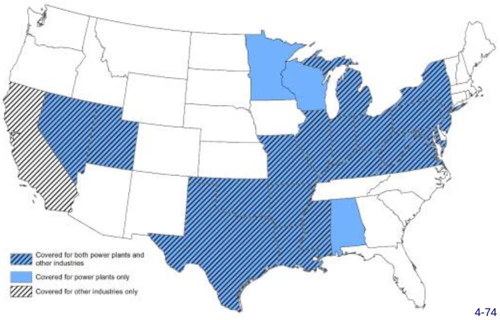
Interstate Transport of Pollution

- *Interstate transport of pollution can cause nonattainment of a NAAQS in a downwind state.*
- **CAA Section 184** established the "*Northeast Ozone Transport Commission*" (OTC) and to require states in the OTC to include in their SIPs *regional planning measures* to control VOC sources.
- **CAA Section 126** gives a state the authority to ask EPA to set emissions limits for specific sources of air pollution in other states that *significantly contribute to nonattainment* of NAAQS in the petitioning state.
  - This is another enforcement mechanism for EPA's "Good Neighbor Provision"

Interstate Transport of Pollution

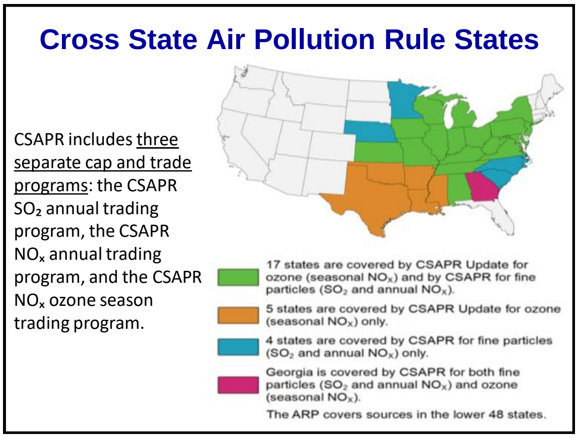
- **CAA Section 110(a)(D)(i)** establishes the "*Good Neighbor Provisions*" which requires a state SIP to include provisions that prevent their emission sources from "contribute significantly" to nonattainment of a NAAQS in a downwind state.
- On March 15, 2023, EPA issued its ***Good Neighbor Plan***, which secures significant reductions in ozone-forming emissions of **NO_X** from power plants and industrial facilities from the 23 significantly contributing upwind states.
- On June 27, 2024, the U.S. Supreme Court granted a stay of the *Good Neighbor Plan* pending judicial review because EPA likely didn't adequately respond to comments about the plan's application.

Map of States Covered by the Final Good Neighbor Plan



Interstate Transport of Pollution

- 2005: EPA passed **Clean Air Interstate Rule (CAIR)** to limit the interstate transport of emissions of NO_X and SO_2 from *power plants* that contribute to fine particle matter ($PM_{2.5}$) and ozone in downwind states.
  - NO_x and SO_2 contributes to fine PM formation & NO_x contributes to O_3 formation.
- 2011 EPA replace CAIR with the **Cross State Air Pollution Rule (CSAPR)** to achieve emission reductions beyond those originally required by CAIR.
- Both rules required certain states to utilize **cap & trade programs** to limit annual NO_x and SO_2 emissions.
- Passed pursuant "*Good Neighbor Provision*" of CAA Section110(a)(D)(i)



Cross State Air Pollution Rule States

CSAPR includes <u>three separate cap and trade programs</u>: the CSAPR SO_2 annual trading program, the CSAPR NO_x annual trading program, and the CSAPR NO_x ozone season trading program.

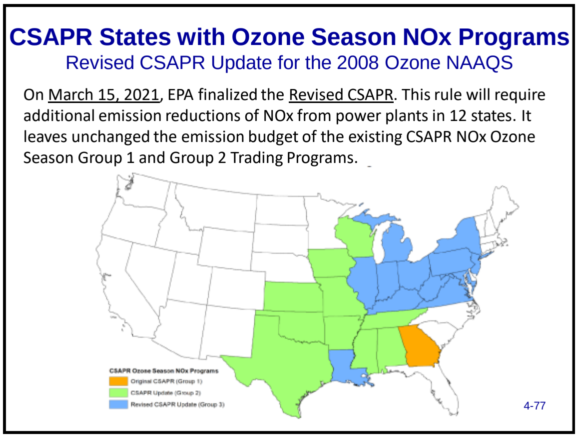
🟩 17 states are covered by CSAPR Update for ozone (seasonal NO_X) and by CSAPR for fine particles (SO_2 and annual NO_X).

🟧 5 states are covered by CSAPR Update for ozone (seasonal NO_X) only.

🟦 4 states are covered by CSAPR for fine particles (SO_2 and annual NO_X) only.

🟥 Georgia is covered by CSAPR for both fine particles (SO_2 and annual NO_X) and ozone (seasonal NO_X).

The ARP covers sources in the lower 48 states.



CSAPR States with Ozone Season NOx Programs

Revised CSAPR Update for the 2008 Ozone NAAQS

On <u>March 15, 2021</u>, EPA finalized the <u>Revised CSAPR</u>. This rule will require additional emission reductions of NOx from power plants in 12 states. It leaves unchanged the emission budget of the existing CSAPR NOx Ozone Season Group 1 and Group 2 Trading Programs.

CSAPR Ozone Season NOx Programs
🟧 Original CSAPR (Group 1)
🟩 CSAPR Update (Group 2)
🟦 Revised CSAPR Update (Group 3)

Chapter 5

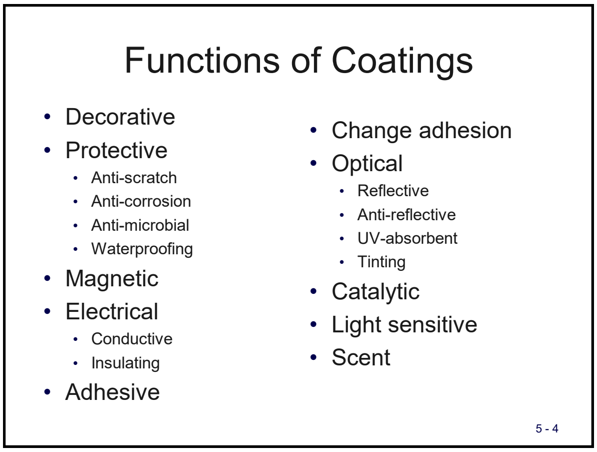
Surface Coating

Surface Coating

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.

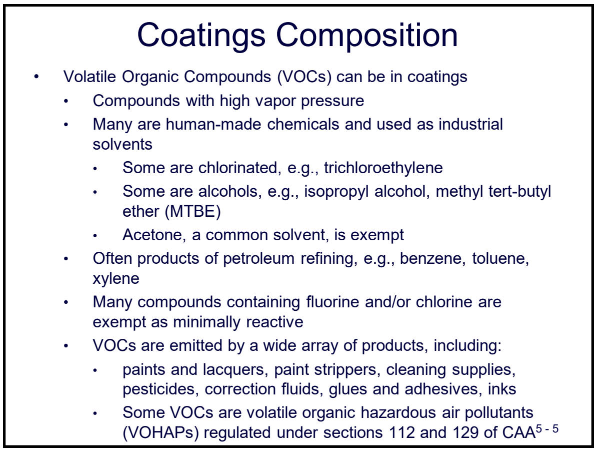
What is a Coating

- In general, coatings consist of:
  - Solids – include resins and pigments (color; metallics; corrosion protection, e.g., zinc chromate)
  - Water
  - VOCs
  - Exempt solvents
  - Other functional additives; e.g., UV inhibitors, drying agents
- Also, can be two-part coatings that form solids when mixed
  - Epoxies
  - Polyurethanes



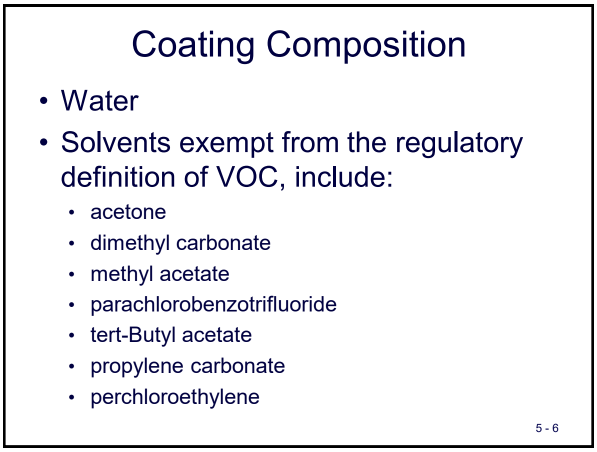
Functions of Coatings

- Decorative
- Protective
  - Anti-scratch
  - Anti-corrosion
  - Anti-microbial
  - Waterproofing
- Magnetic
- Electrical
  - Conductive
  - Insulating
- Adhesive
- Change adhesion
- Optical
  - Reflective
  - Anti-reflective
  - UV-absorbent
  - Tinting
- Catalytic
- Light sensitive
- Scent



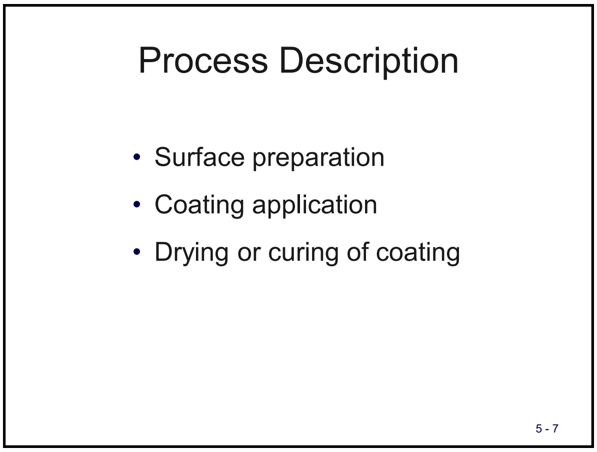
Coatings Composition

- Volatile Organic Compounds (VOCs) can be in coatings
  - Compounds with high vapor pressure
  - Many are human-made chemicals and used as industrial solvents
    - Some are chlorinated, e.g., trichloroethylene
    - Some are alcohols, e.g., isopropyl alcohol, methyl tert-butyl ether (MTBE)
    - Acetone, a common solvent, is exempt
  - Often products of petroleum refining, e.g., benzene, toluene, xylene
  - Many compounds containing fluorine and/or chlorine are exempt as minimally reactive
  - VOCs are emitted by a wide array of products, including:
    - paints and lacquers, paint strippers, cleaning supplies, pesticides, correction fluids, glues and adhesives, inks
    - Some VOCs are volatile organic hazardous air pollutants (VOHAPs) regulated under sections 112 and 129 of CAA



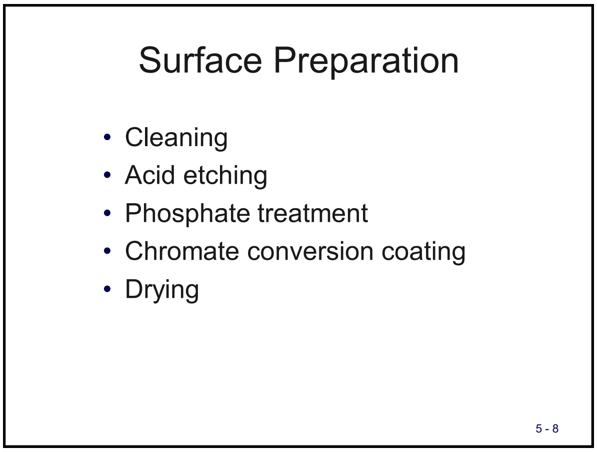
Coating Composition

- Water
- Solvents exempt from the regulatory definition of VOC, include:
  - acetone
  - dimethyl carbonate
  - methyl acetate
  - parachlorobenzotrifluoride
  - tert-Butyl acetate
  - propylene carbonate
  - perchloroethylene



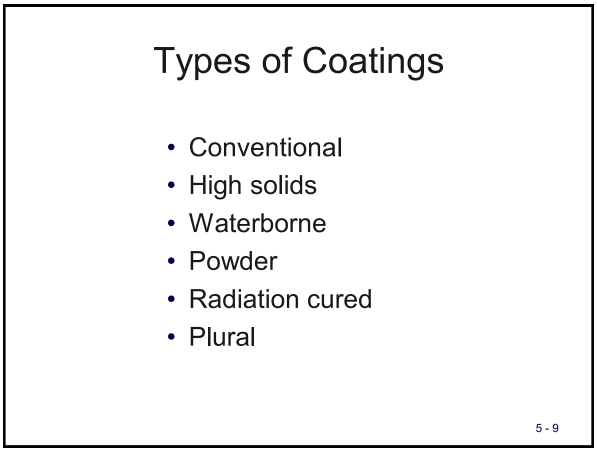
Process Description

- Surface preparation
- Coating application
- Drying or curing of coating



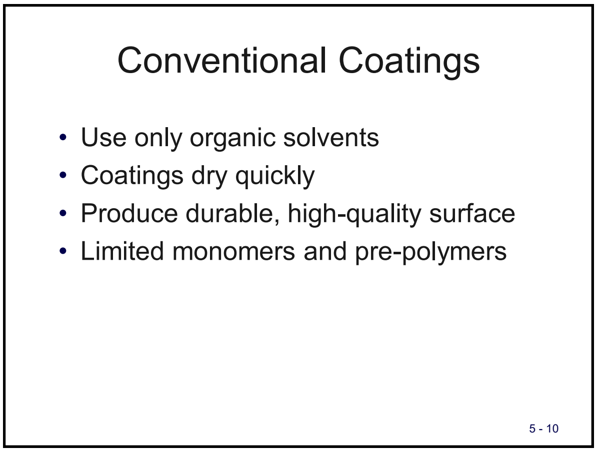
Surface Preparation

- Cleaning
- Acid etching
- Phosphate treatment
- Chromate conversion coating
- Drying



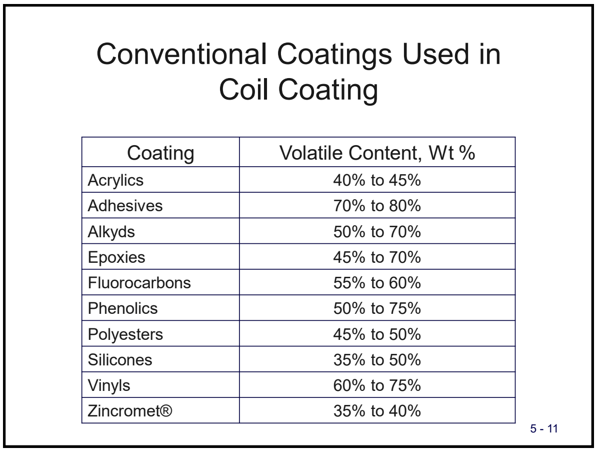
Types of Coatings

- Conventional
- High solids
- Waterborne
- Powder
- Radiation cured
- Plural



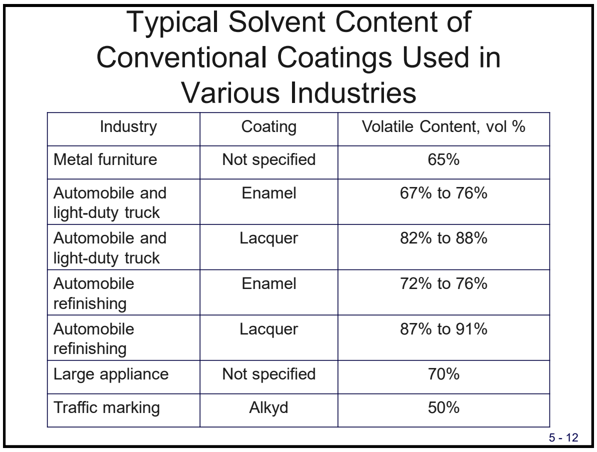
Conventional Coatings

- Use only organic solvents
- Coatings dry quickly
- Produce durable, high-quality surface
- Limited monomers and pre-polymers



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%



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%

High-Solids Coatings

- Typically greater than 60% solids by volume
- Less drum handling
- Reduced freight costs
- Reduced solvent removal energy
- Increased viscosity

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%

Waterborne Coatings

- Contain 2-15% by volume organic solvent
- Types of waterborne coatings:
  - Water-soluble dispersions
  - Water-soluble polymers
  - Emulsions

Waterborne Coatings

- Wide range of formulations
- Can be used with high solids
- Easier clean up
- Increased drying energy
- Need better surface preparation
- Corrosion potential

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%

Powder Coatings

- Contain no solvent carrier
- Thermoplastic coatings melt when heated
- Thermosetting coatings polymerize
- Small quantities of VOC may be emitted during polymerization

Powder Coatings

- Better chemical and abrasion resistance
- Decreased curing energy
- Excess powder easily recovered
- Higher coating cost
- Limited number of formulations
- Higher capital equipment costs
- Higher temperatures required for curing
- Color mixing may occur during changes

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%

Radiation-Cured Coatings

- Contain no solvent carrier
- Cures by polymerization with UV or electron beam radiation
- High line speeds
- Decreased operating cost
- Reduced floor space
- Higher coating cost
- Limited number of formulations
- Higher capital equipment costs
- Operational hazards

Coating Application

- Spray coating
- Dip coating
- Flow coating
- Roller coating
- Electrodeposition coating

Coating Application Methods for Various Industries

Method	Coil Coating	Metal Furniture	Auto & Light Truck	Large Appliances
Air-atomized spray			X	X
Airless spray				X
Electrostatic spray		X	X	X
HVLP			X	
Electrostatic bell & disk				X
Dip		X		X
Flow		X		X
Roller	X			
Electrodeposition	X		X	X

Coating Application Methods for Various Industries (cont'd)

Method	Can	Auto Refinish	Traffic Marking	Wood Bldg Products	Fabric
Air-atomized spray	X	X	X	X	X
Airless spray		X		X	X
Electrostatic spray		X		X	X
HVLP		X		X	X
Electrostatic bell & disk				X	X
Dip				X	X
Flow				X	
Roller	X			X	X
Electrodeposition					

Transfer Efficiency

$$\text{Transfer efficiency} = \frac{\text{Solids applied to surface}}{\text{Total solids used}} \times 100$$

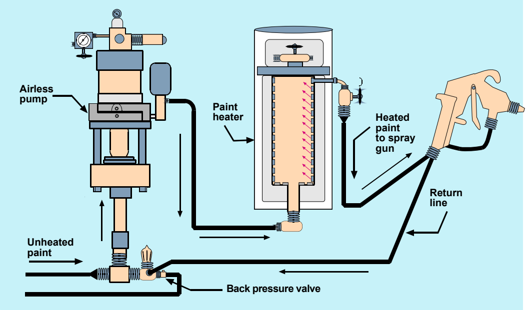
Spray Coating

- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure (HVLP) spray
- Low-volume, low-pressure (LVLP) spray

Spray Coating

- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure (HVLP) spray
- Low-volume, low-pressure (LVLP) spray

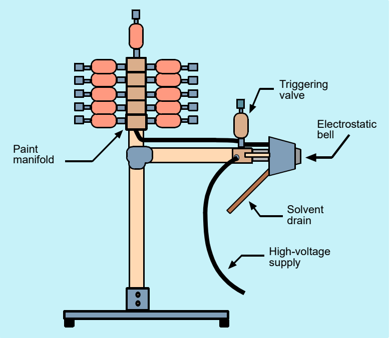
Airless Spray Gun

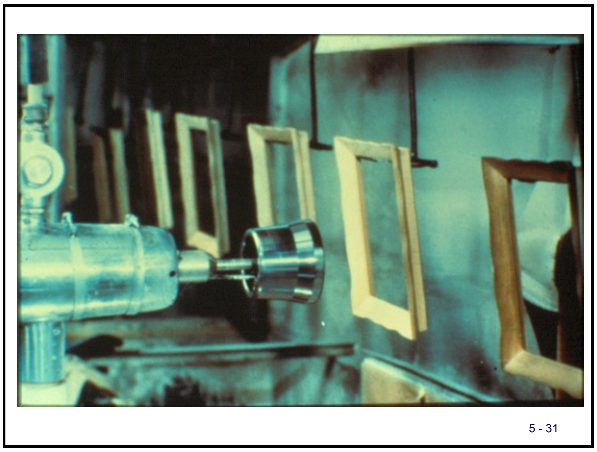


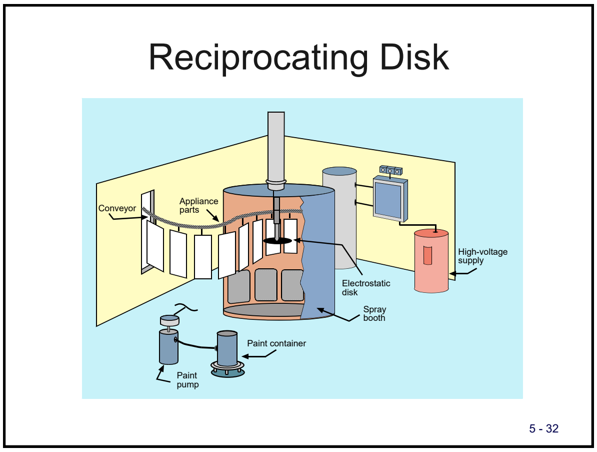
Spray Coating

- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure (HVLP) spray
- Low-volume, low-pressure (LVLP) spray

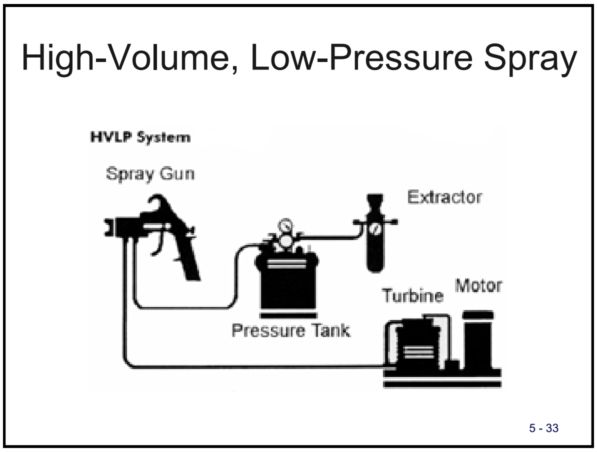
Electrostatic Bell







Reciprocating Disk



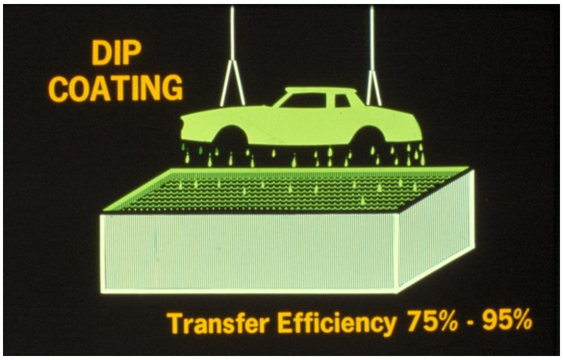
High-Volume, Low-Pressure Spray

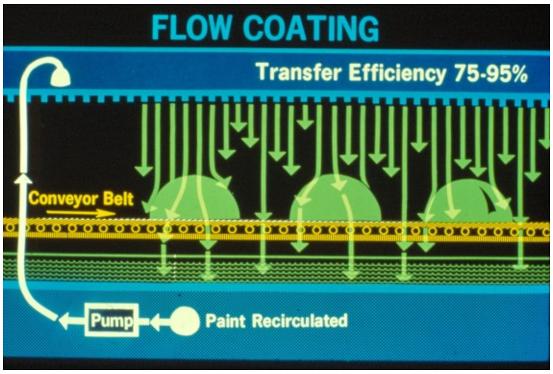
Spray Coating

- Air atomized spray
- Airless spray
- Electrostatic spray
- High-volume, low-pressure (HVLP) spray
- Low-volume, low-pressure (LVLP) spray

Transfer Efficiencies for Spray Application

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





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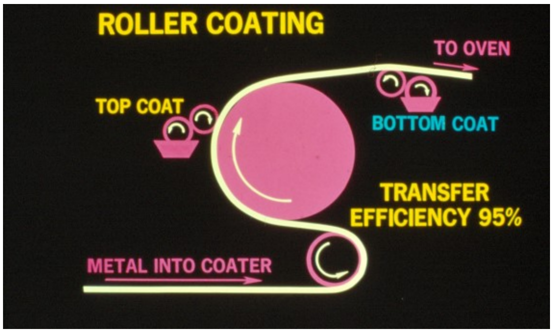

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Electrodeposition Coating

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Curing

- Pre-drying
- Staged temperature ovens
- Explosion potential
- Cooling

Emission Control Techniques

- Reduced-VOC coating
- Higher transfer efficiency application
- Add-on control equipment

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

Add-on Control Equipment

- It’s 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.
- 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.

Emission Regulations

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

Recommended standard:

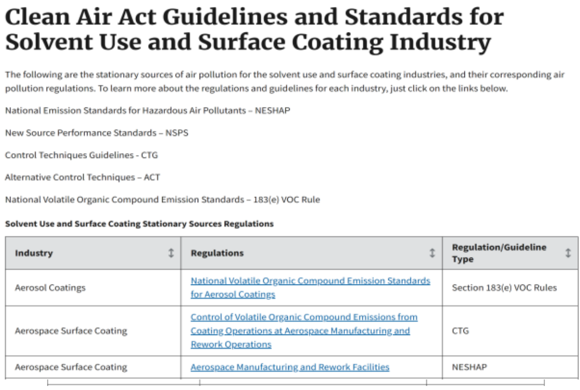
An emission limit of 2.8 lbs of VOC

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



Clean Air Act Guidelines and Standards for Solvent Use and Surface Coating Industry

The following are the stationary sources of air pollution for the solvent use and surface coating industries, and their corresponding air pollution regulations. To learn more about the regulations and guidelines for each industry, just click on the links below.

National Emission Standards for Hazardous Air Pollutants – NESHAP

New Source Performance Standards – NSPS

Control Techniques Guidelines - CTG

Alternative Control Techniques – ACT

National Volatile Organic Compound Emission Standards – 183(e) VOC Rule

Solvent Use and Surface Coating Stationary Sources Regulations

Industry	Regulations	Regulation/Guideline Type
Aerosol Coatings	National Volatile Organic Compound Emission Standards for Aerosol Coatings	Section 183(e) VOC Rules
Aerospace Surface Coating	Control of Volatile Organic Compound Emissions from Coating Operations at Aerospace Manufacturing and Rework Operations	CTG
Aerospace Surface Coating	Aerospace Manufacturing and Rework Facilities	NESHAP

Clean Air Act Guidelines and Standards for Solvent Use and Surface Coating Industry | US EPA

Process Inspection

- Review coating composition and consumption records
- Observe coating preparation
- Observe coating application
- Observe pre-drying area
- Observe curing area

Review Coating Composition and Consumption Records

- Composition data evaluated to determine compliance with permit and regulations
  - Solvent content
  - Solids content
  - Water content
  - Solvent density
  - Coating density
- Consumption data evaluated to determine compliance with permit

Observe Coating Preparation

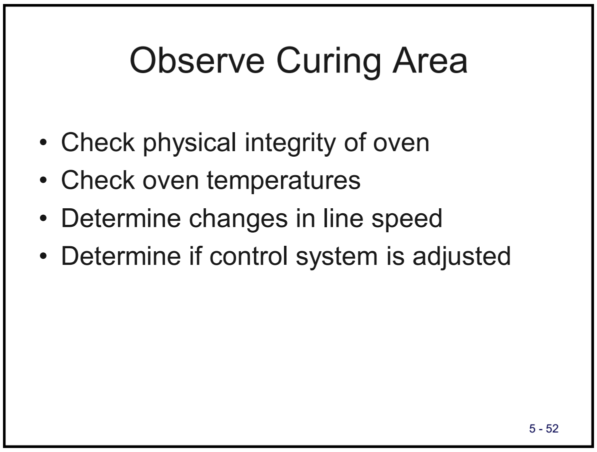
- Determine if area is ventilated
- Note if drums are kept closed
- Determine if solvents have changed
- Observe spill cleanup
- Get sample of “as applied” coating

Observe Coating Application

- Determine if area is ventilated
- Note changes in application method
- Determine changes in application rate
- Determine if control system is adjusted
- Observe spill cleanup

Observe Pre-Drying Area

- Determine if area is ventilated
- Determine if control system is adjusted



Observe Curing Area

- Check physical integrity of oven
- Check oven temperatures
- Determine changes in line speed
- Determine if control system is adjusted

Chapter 6

Graphic Arts

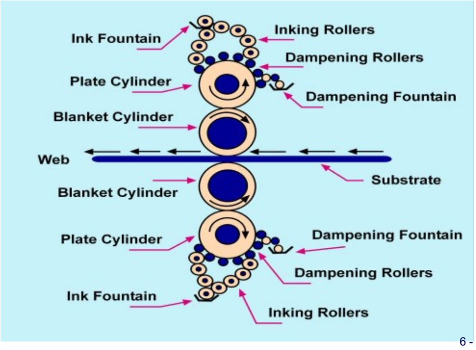
Printing Operations

- Offset lithography
- Flexography
- Rotogravure
- Screen

Offset Lithography

- Uses a planographic printing surface
- Printing unit components:
  - Inking system
  - Dampening system
  - Plate cylinder
  - Blanket cylinder
  - Impression cylinder

Offset Lithography Printing Unit



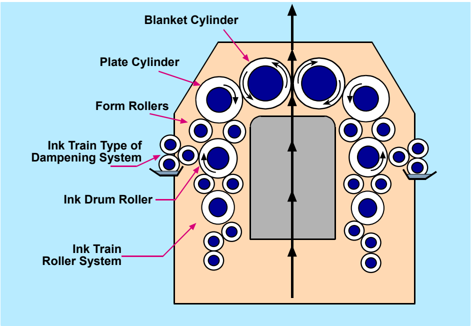
Offset Lithography Processes

- Non-heatset web printing
- Heatset web printing
- Sheetfed printing

Non-heatset Web Printing

- Prints on continuous web of paper
- Line speed 600-2100 fpm
- Uses semifluid inks
- Does not require heat for curing
- Fountain solution is >99.5% water and uses low volatility solvents

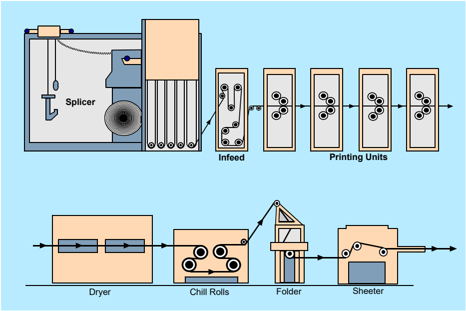
Non-heatset Web Printing Unit



Heatset Web Printing

- Uses fluid inks that dry by evaporation
- Some inks cure by chemical reaction
- Typical dryer temperatures are 225-325°F
- 40-90% of ink solvent evaporates in dryer
- Fountain solution is 5-20% IPA or 2-5% low volatility solvents
- 0-5% of fountain solution solvent remains in web
- Automatic blanket washers evaporate solvent in dryer during wash cycle

Heatset Web Printing Press

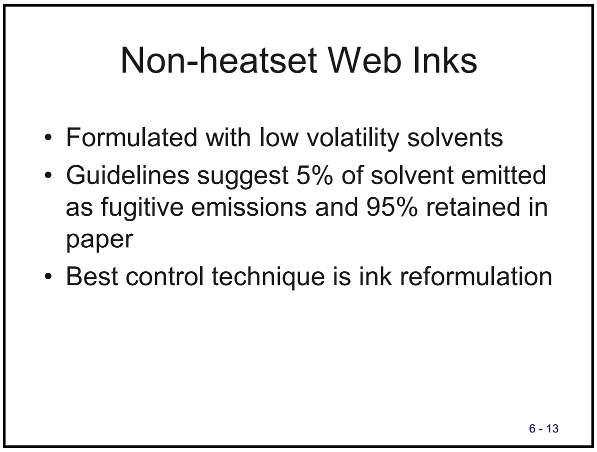


Sheetfed Printing

- Applies images to individual sheets
- Typically uses semifluid inks
- May use radiation curing inks
- Fountain solution is 5-20% IPA or 2-5% low volatility solvents
- Finishes are frequently applied

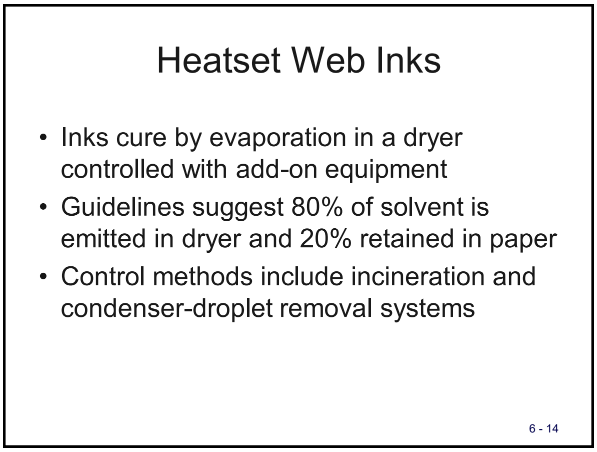
Emission Control Techniques

- Inks
- Fountain solution
- Press cleaning



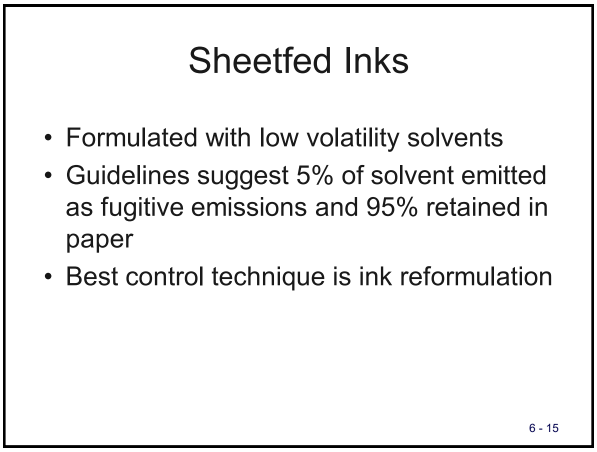
Non-heatset Web Inks

- Formulated with low volatility solvents
- Guidelines suggest 5% of solvent emitted as fugitive emissions and 95% retained in paper
- Best control technique is ink reformulation



Heatset Web Inks

- Inks cure by evaporation in a dryer controlled with add-on equipment
- Guidelines suggest 80% of solvent is emitted in dryer and 20% retained in paper
- Control methods include incineration and condenser-droplet removal systems



Sheetfed Inks

- Formulated with low volatility solvents
- Guidelines suggest 5% of solvent emitted as fugitive emissions and 95% retained in paper
- Best control technique is ink reformulation

Fountain Solution

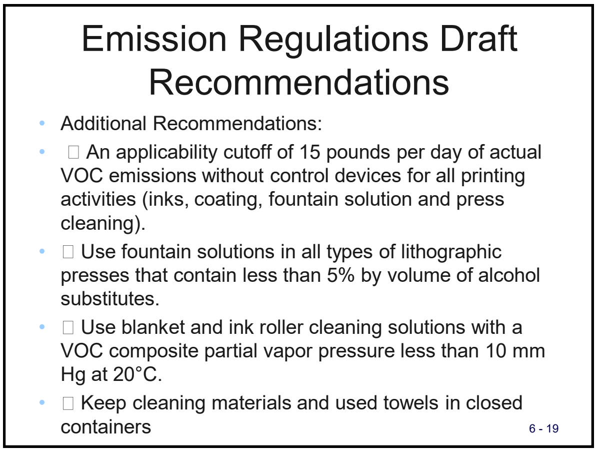
- Most volatile additive is IPA
- Use low volatility dampening agents
- Refrigerate fountain solution to 55-60°F
- For non-heatset and sheetfed printing, guidelines suggest 100% of solvent emitted as fugitive emissions
- For heatset printing, guidelines suggest 30% of solvent emitted as fugitive emissions and 70% emitted in dryer

Press Cleaning

- Reduce VOC content of cleaning solution
- Use less volatile solvents
- Add water and detergent to cleaning solution or use aqueous cleaner
- Put rags and wipes in sealed containers
- For heatset printers with automatic blanket washers, guidelines suggest 60% of solvent emitted as fugitive emissions and 40% emitted in dryer

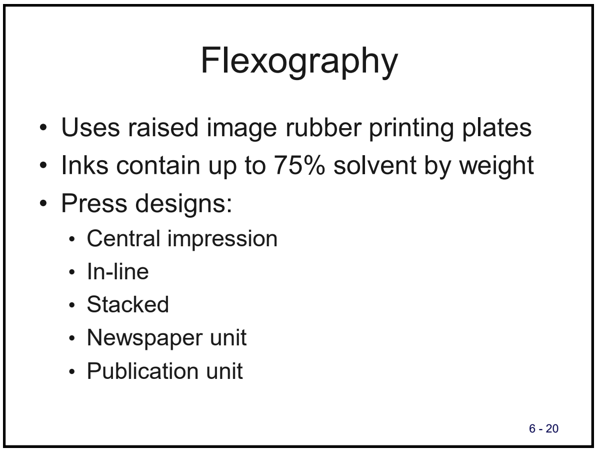
Emission Regulations Draft Recommendations

- 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.



Emission Regulations Draft Recommendations

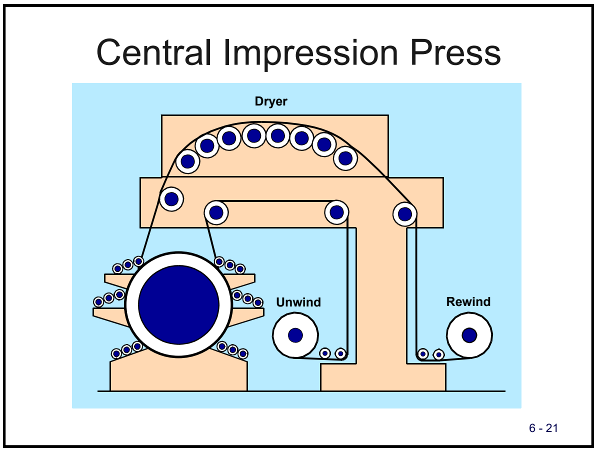
- Additional Recommendations:
- An applicability cutoff of 15 pounds per day of actual VOC emissions without control devices for all printing activities (inks, coating, fountain solution and press cleaning).
- Use fountain solutions in all types of lithographic presses that contain less than 5% by volume 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

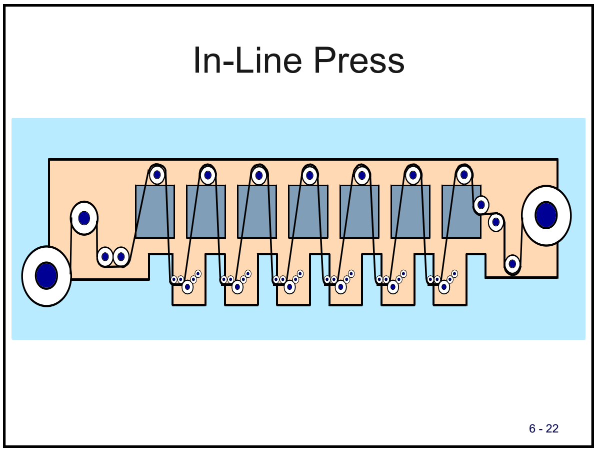


Flexography

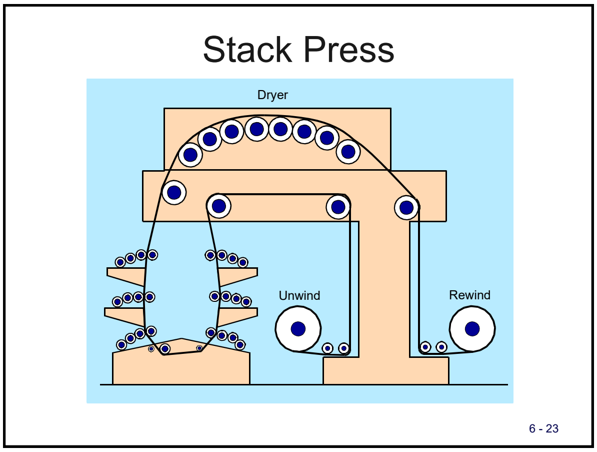
- Uses raised image rubber printing plates
- Inks contain up to 75% solvent by weight
- Press designs:
  - Central impression
  - In-line
  - Stacked
  - Newspaper unit
  - Publication unit

Central Impression Press

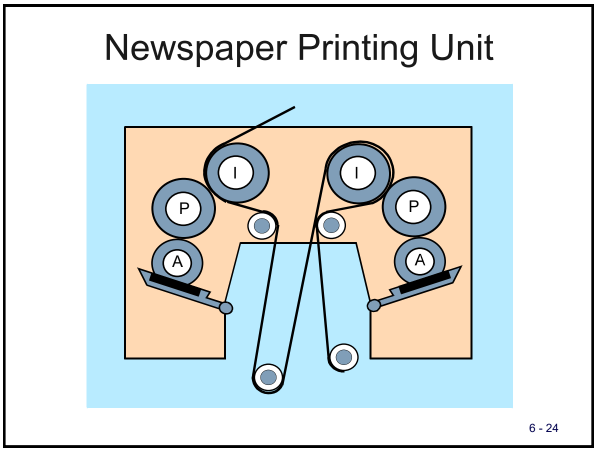




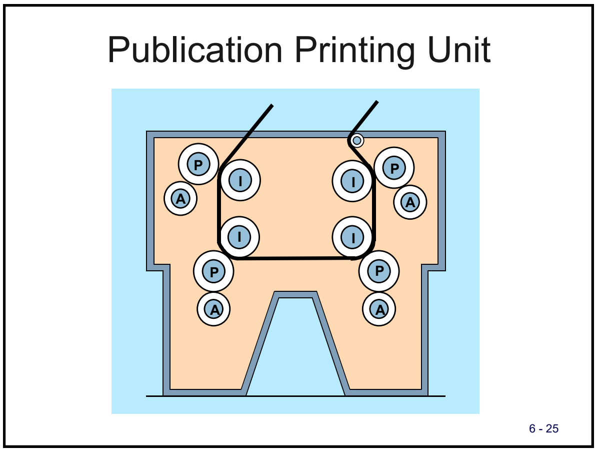
In-Line Press



Stack Press



Newspaper Printing Unit



Publication Printing Unit

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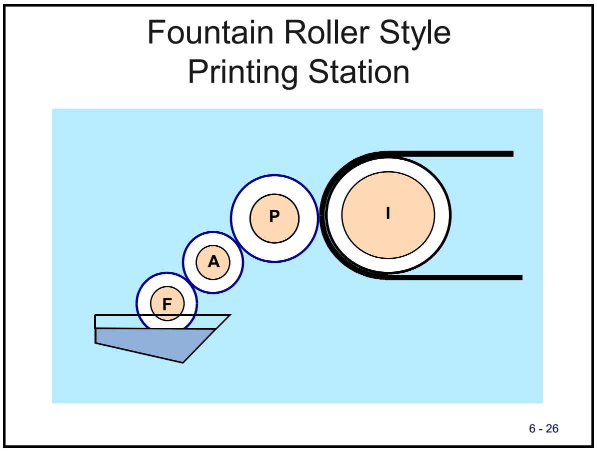

Fountain Roller Style
Printing Station

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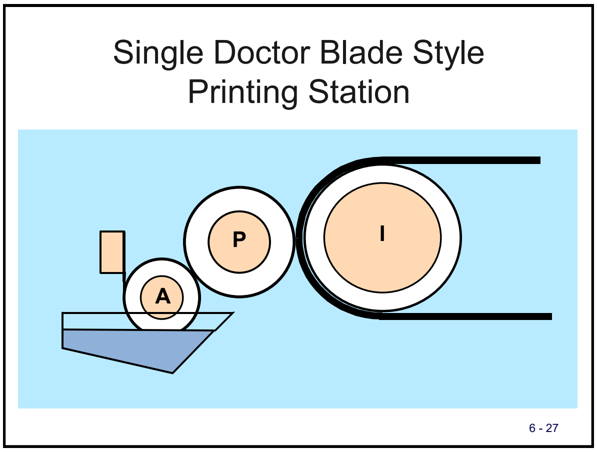

Single Doctor Blade Style
Printing Station

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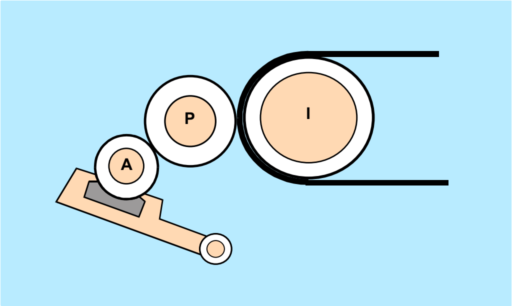
Double Doctor Blade Style Printing Station

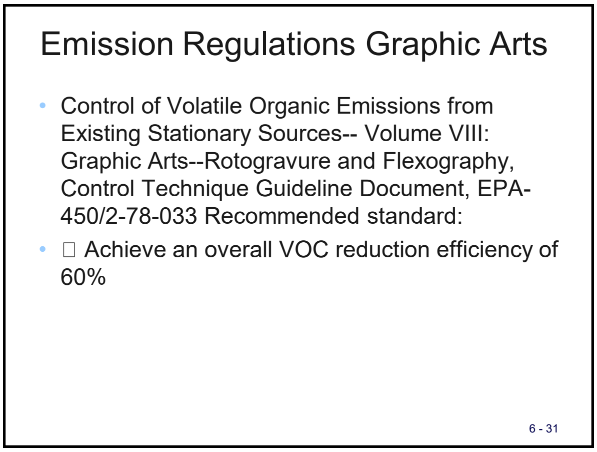


Types of Inks

- Organic solvent based
- Water based
- Radiation curable

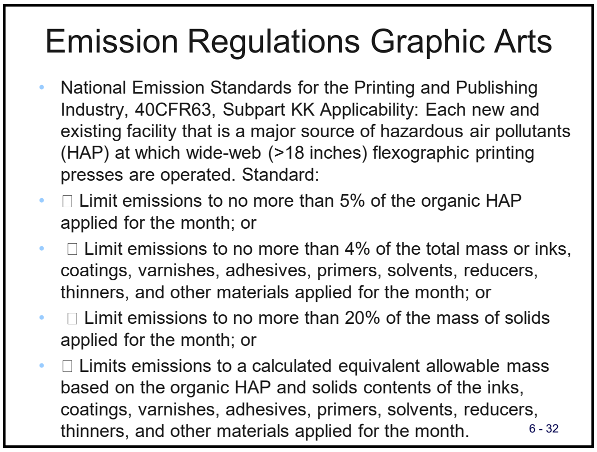
Emission Control Techniques

- Reduced-VOC ink
- Reduced-VOC cleaning
- Add-on control equipment
  - Incineration
  - Adsorption
  - Condensation



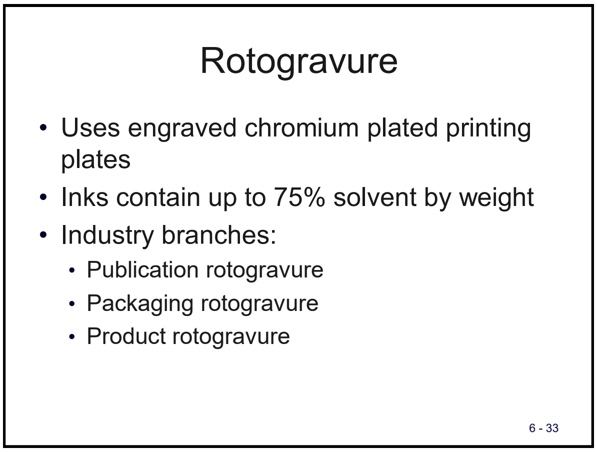
Emission Regulations Graphic Arts

- 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%



Emission Regulations Graphic Arts

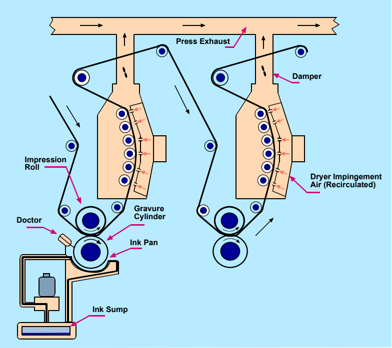
- National Emission Standards for the Printing and Publishing Industry, 40CFR63, Subpart KK Applicability: Each new and existing facility that is a major source of hazardous air pollutants (HAP) at which wide-web (>18 inches) flexographic printing presses are operated. Standard:
- □ Limit emissions to 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.



Rotogravure

- Uses engraved chromium plated printing plates
- Inks contain up to 75% solvent by weight
- Industry branches:
  - Publication rotogravure
  - Packaging rotogravure
  - Product rotogravure

Rotogravure Press



Emission Control Techniques

- Reduced-VOC ink
- Reduced-VOC cleaning
- Add-on control equipment
  - Incineration
  - Adsorption
  - Condensation

Emission Regulations

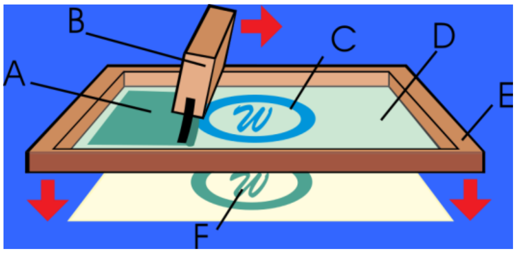
- Control of Volatile Organic Emissions from Existing Stationary Sources-- Volume VIII: Graphic Arts--Rotogravure and Flexography, Control Technique Guideline Document, EPA-450/2-78-033 Recommended standard:
- Achieve an overall VOC reduction efficiency of 75% for publication rotogravure.
- Achieve an 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.

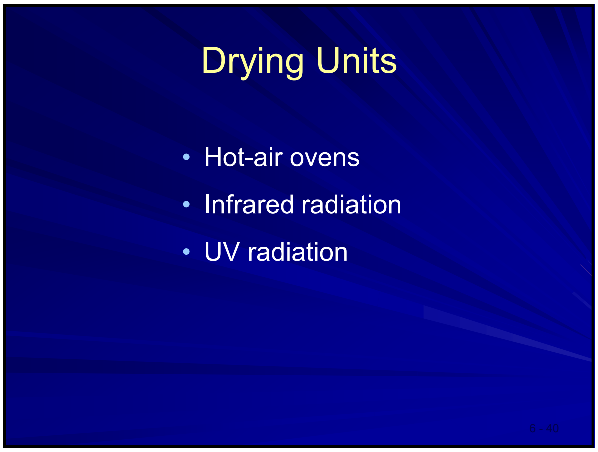
Emission Regulations

- 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

Screen Printing

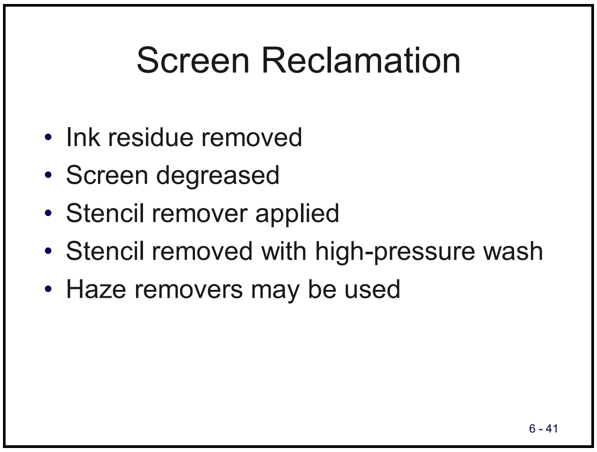
- Ink flows through screen with stencil bonded to it
- Types of inks:
  - Solvent based
  - Water based
  - UV curable
  - Plastisols





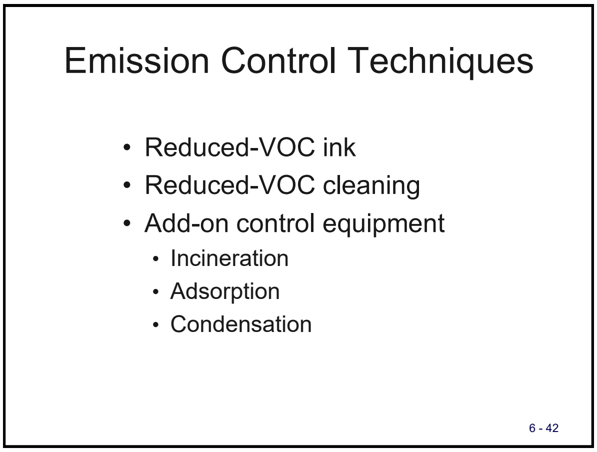
Drying Units

- Hot-air ovens
- Infrared radiation
- UV radiation



Screen Reclamation

- Ink residue removed
- Screen degreased
- Stencil remover applied
- Stencil removed with high-pressure wash
- Haze removers may be used



Emission Control Techniques

- Reduced-VOC ink
- Reduced-VOC cleaning
- Add-on control equipment
  - Incineration
  - Adsorption
  - Condensation

Process Inspection

- Review ink composition and consumption records
- Observe ink preparation
- Observe printing area
- Observe curing area

Review Ink Composition and Consumption Records

- Composition data evaluated to determine compliance with permit and regulations
  - Solvent content
  - Solids content
  - Water content
  - Solvent density
  - Ink density
- Consumption data evaluated to determine compliance with permit

Observe Ink Preparation

- Determine if area is ventilated
- Note if drums are kept closed
- Determine if solvents have changed
- Observe spill cleanup
- Get sample of “as applied” ink

Observe Printing Area

- Determine if area is ventilated
- Note changes in printing method
- Determine changes in application rate
- Determine if control system is adjusted
- Observe spill cleanup

Observe Curing Area

- Check physical integrity of oven
- Check oven temperatures
- Determine changes in line speed
- Determine if control system is adjusted

Chapter 7

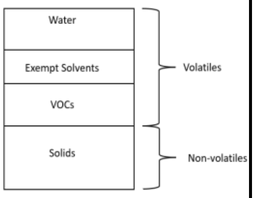
Calculating the VOC Content of Coatings and Inks

VOC Calculations

Using the calculation method for determining VOC content of coatings and inks is more convenient, and often more reliable, than it is to measure VOC emission directly.

EPA Reference Methods 24 and 24A

- Properties and composition of coating or ink are needed to calculate surface coating VOC content for regulatory applicability or compliance determinations
- Data needed include:
  - Coating density
  - Solvent (VOC) density
  - VOC content, by weight or volume
  - Solids content, by weight or volume
  - Water content, by weight or volume



Calculation Information

- Form of emission limitation
- Data on the properties and compositions of coatings and inks
- Transfer efficiency and performance specifications
- Production rates and coating or ink usage

Forms of Emission Limitations for Surface Coating

- 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

Forms of Emission Limitations for Graphic Arts

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

Coating and Ink Data

- Standard methods
- Data sheets
- Material safety data sheets (MSDS)

Standard Methods

- Method 24
  - Weight fraction of volatile matter
  - Weight fraction of water
  - Volume fraction of solids
  - Coating density
- Method 24A
  - Weight fraction of VOC
  - Ink density
  - Solvent density

Method 24

- Method 24 is used to measure the volatile organic compound (VOC) content of coatings and inks and was developed for a variety of coating and printing source categories.
- Method 24 should only be applied to coating and printing type sources.
- Method does not provide step-by-step procedures for collection of the coating and ink samples; however, EPA does have a document entitled "Standard Procedure for Collection of Coating and Ink Samples for Analysis By Reference Method 24 and 24A" dated September 1991.

Method 24

- Method 24 references several American Society of Testing and Materials (ASTM) methods.
- The basic premise of Method 24 is an indirect measurement of the VOC content of Coatings. The non-volatile content of the coating is first determined by drying a known weight of coating and determining the amount of dry film left (this is the non-volatile portion).

Method 24

- The volatile fraction of sample (including water) is determined by subtracting the non-volatile portion from the initial weight of sample.
- Other ASTM methods are used to measure the amount of water and exempt solvents in the coating, and these values are subtracted from the volatile matter, leaving what is considered to be the amount of VOC's.
- Method 24 is conducted in the laboratory.

Method 24A

- This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.
- Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating.

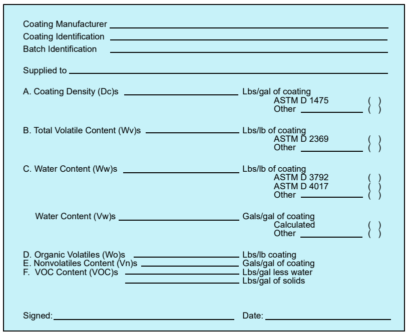
Method 24A

- The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature.
- The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

Material Safety Data Sheets

- The MSDS lists:
  - hazardous ingredients of a product
  - physical and chemical characteristics (e.g., flammability, explosive properties)
  - effect on human health
  - chemicals with which it can adversely react
  - handling precautions
  - types of measures used to control exposure emergency and first aid procedures
  - methods to contain a spill.

Manufacturer Data Sheet



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: ____________

User Data Sheet

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 ________ ( )

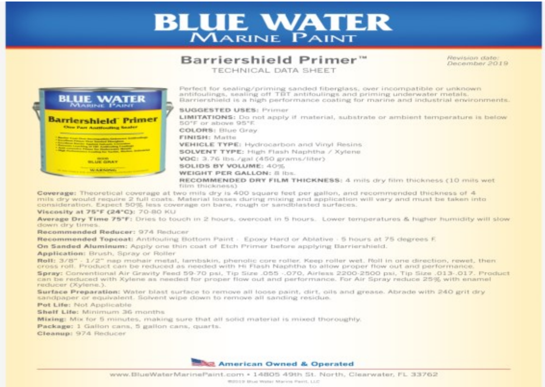
C. Water Content (Ww)a ____________ Lbs/lb of coating
ASTM D 3792 ( )
ASTM D 4017 ( )
Other ________ ( )

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

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



BLUE WATER
MARINE PAINT

Barriershield Primer™
TECHNICAL DATA SHEET

Revision date: December 2019

Perfect for sealing/priming sanded fiberglass, over incompatible or unknown antifoulings, sealing off TBT antifoulings and priming underwater metals. Barriershield is a high performance coating for marine and industrial environments.

SUGGESTED USES: Primer
LIMITATIONS: Do not apply if material, substrate or ambient temperature is below 50°F or above 95°F.
COLORS: Blue Gray
FINISH: Matte
VEHICLE TYPE: Hydrocarbon and Vinyl Resins
SOLVENT TYPE: High Flash Naphtha / Xylene
VOC: 3.76 lbs./gal (450 grams/liter)
SOLIDS BY VOLUME: 40%
WEIGHT PER GALLON: 8 lbs.
RECOMMENDED DRY FILM THICKNESS: 4 mils dry film thickness (10 mils wet film thickness)
Coverage: Theoretical coverage at two mils dry is 400 square feet per gallon, and recommended thickness of 4 mils dry would require 2 full coats. Material losses during mixing and application will vary and must be taken into consideration. Expect 50% less coverage on bare, rough or sandblasted surfaces.
Viscosity at 75°F (24°C): 70-80 KU
Average Dry Time 75°F: Dries to touch in 2 hours, overcoat in 5 hours. Lower temperatures & higher humidity will slow down dry times.
Recommended Reducer: 974 Reducer
Recommended Topcoat: Antifouling Bottom Paint - Epoxy Hard or Ablative - 5 hours at 75 degrees F.
On Sanded Aluminum: Apply one thin coat of Etch Primer before applying Barriershield.
Application: Brush, Spray or Roller
Roll: 3/8" - 1/2" nap mohair metal, lambskin, phenolic core roller. Keep roller wet. Roll in one direction, rewet, then cross roll. Product can be reduced as needed with Hi Flash Naphtha to allow proper flow out and performance.
Spray: Conventional Air Gravity Feed 59-70 psi, Tip Size .055 -.070, Airless 2200-2500 psi, Tip Size .013-.017. Product can be reduced with Xylene as needed for proper flow out and performance. For Air Spray reduce 25% with enamel reducer (Xylene.).
Surface Preparation: Water blast surface to remove all loose paint, dirt, oils and grease. Abrade with 240 grit dry sandpaper or equivalent. Solvent wipe down to remove all sanding residue.
Pot Life: Not Applicable
Shelf Life: Minimum 36 months
Mixing: Mix for 5 minutes, making sure that all solid material is mixed thoroughly.
Package: 1 Gallon cans, 5 gallon cans, quarts.
Cleanup: 974 Reducer

American Owned & Operated

www.BlueWaterMarinePaint.com • 14805 49th St. North, Clearwater, FL 33762

TDS-BW-Barriershield-Primer-11-20-19.pdf

Environmental Data Sheets

ENVIRONMENTAL DATA SHEET
(Certified Product Data Sheet)

07 00 [3514]

Date of Preparation
Dec 16, 2024

PRODUCT NUMBER
CM0110944
PRODUCT NAME
Exempt Solvent Reducer
MANUFACTURER'S NAME
THE SHERWIN-WILLIAMS COMPANY
101 W. Prospect Avenue
Cleveland, OH 44115

This document includes all data required by 40 CFR 63.801(a) for a Certified Product Data Sheet under criteria specified in 40 CFR 63.805(a). All data given below are MAXIMUM THEORETICAL VALUES based on the product AS CURRENTLY FORMULATED and rely on information provided to us by our raw material suppliers. Our suppliers often provide an estimated value or range less than a certain upper limit. We calculate MAXIMUM THEORETICAL VALUES using defined values, if provided, or the upper limit reported by our supplier. Additionally, the suppliers' information may include amounts present in the product as unintentional byproducts or impurities. Variations may occur in individual batches due to adjustments made during production.

Hazard Category (for SARA 311,312)
CM0110944 = | Acute | Chronic | Fire |

Product Weight	**Specific Gravity**	**FLASH POINT**
8.88 lb/gal	1.07	2 °F PMCC

Volatile Ingredients

Chemical / Compound	SARA 302 EHS	CERCLA	SARA 313 TC	HAPS 112	% by Weight	% by Volume
p-Chlorobenzotrifluoride 98-56-6	N	N	N	N	63	50
Acetone 67-64-1	N	Y	N	N	37	50

Volatile Organic Compounds - U.S. EPA / Canada

	CM0110944	
	LB/Gal	g/L
Coating Density	8.88	1064
	By wt	By vol
Total Volatiles	100.0%	100.0%
Federally exempt solvents		
Water	0.0%	0.0%
P-Chlorobenzotrifluoride	63.0%	50.1%
Acetone	37.0%	49.9%
Organic Volatiles	0.0%	0.0%
Percent Non-Volatile	0.0%	0.0%
VOC Content	LB/Gal	g/L
Total	0.00	0
Less exempt solvents	0.00	0
Of solids	0.00	0
Of solids	0.00 lb/lb	0.00 kg/kg
	By wt	
By wt LVP-VOC	0.0%	

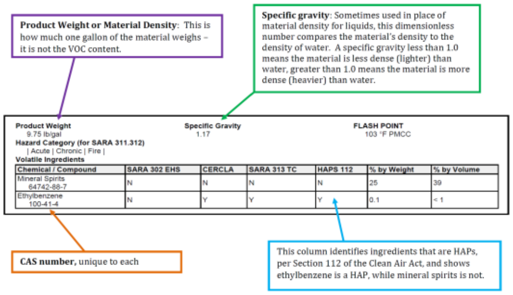
Maximum Incremental Reactivity (MIR) (per US EPA Aerosol Ctg Rule, MIR Values 2009) **0.22**

MyPDF.pdf

Coating and Ink Data

- Standard methods
- Data sheets
- Material safety data sheets (MSDS) (SDS)

What data is needed from the EDS or Technical Data Sheet?



Product Weight or Material Density: This is how much one gallon of the material weighs – it is not the VOC content.

Specific gravity: Sometimes used in place of material density for liquids, this dimensionless number compares the material's density to the density of water. A specific gravity less than 1.0 means the material is less dense (lighter) than water, greater than 1.0 means the material is more dense (heavier) than water.

Product Weight
9.75 lb/gal

Specific Gravity
1.17

FLASH POINT
103 °F PMCC

Hazard Category (for SARA 311.312)
| Acute | Chronic | Fire |

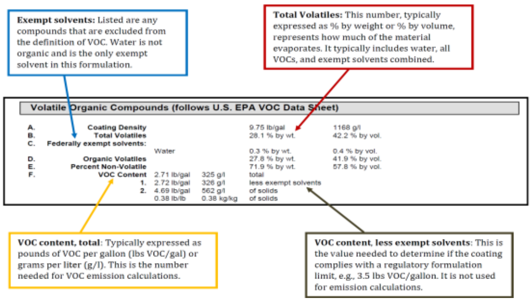
Volatile Ingredients

Chemical / Compound	SARA 302 EHS	CERCLA	SARA 313 TC	HAPS 112	% by Weight	% by Volume
Mineral Spirits 64742-88-7	N	N	N	N	25	39
Ethylbenzene 100-41-4	N	Y	Y	Y	0.1	< 1

CAS number, unique to each

This column identifies ingredients that are HAPs, per Section 112 of the Clean Air Act, and shows ethylbenzene is a HAP, while mineral spirits is not.

Physical/Chemical Properties Section of the EDS contains



Exempt solvents: Listed are any compounds that are excluded from the definition of VOC. Water is not organic and is the only exempt solvent in this formulation.

Total Volatiles: This number, typically expressed as % by weight or % by volume, represents how much of the material evaporates. It typically includes water, all VOCs, and exempt solvents combined.

Volatile Organic Compounds (follows U.S. EPA VOC Data Sheet)

A. **Coating Density** 9.75 lb/gal 1168 g/l
B. **Total Volatiles** 28.1 % by wt. 42.2 % by vol.
C. **Federally exempt solvents:**
Water 0.3 % by wt. 0.4 % by vol.
D. **Organic Volatiles** 27.8 % by wt. 41.9 % by vol.
E. **Percent Non-Volatile** 71.9 % by wt. 57.8 % by vol.
F. **VOC Content** 2.71 lb/gal 325 g/l total
1. 2.72 lb/gal 326 g/l less exempt solvents
2. 4.69 lb/gal 562 g/l of solids
0.38 lb/lb 0.38 kg/kg of solids

VOC content, total: Typically expressed as pounds of VOC per gallon (lbs VOC/gal) or grams per liter (g/l). This is the number needed for VOC emission calculations.

VOC content, less exempt solvents: This is the value needed to determine if the coating complies with a regulatory formulation limit, e.g., 3.5 lbs VOC/gallon. It is not used for emission calculations.

Transfer Efficiency

- Baseline transfer efficiencies are specified in some CTG documents and NSPS
- Enhanced transfer efficiencies are determined under actual operating conditions

Capture and Control Efficiencies

- Claimed efficiencies can be determined from manufacturer's information
- Actual efficiencies are determined by performance testing on the specific source

Process Records

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

Emission Calculations

Consider the following coating:

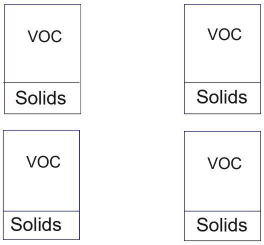
Solids content	35% by weight
Water content	10% by weight
Solids density	29.7 lbs/gal
Solvent content (by volume)	83.3% xylene 16.7% MEK

How much coating is needed to do a particular job?

- The same volume of coating solids must be deposited on an object to coat it to a desired film thickness regardless of the type of coating or volatile organic compound content of the c:oating used. Solids make the film. Volatiles (VOC, water, and non-photochemically reactive solvents) evaporate.

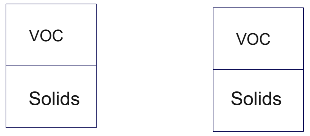
How much coating is needed to do a particular job?

- Four gallons of a 25 percent by volume (v/o) solids coating must be used to get one gallon of coating solids.



How much coating is needed to do a particular job?

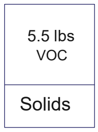
- But, only two gallons of a 50 v/o solids coating must be used to get one gallon of coating solids.



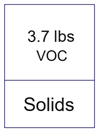
- This means that twice as much work can be done with a gallon of 50 v/o solids coating than with a gallon of 25 v/o solids coating. Twice as many gallons of 25 percent solids coating are needed than gallons of 50 percent solids coating to do the same job.

How Do Emissions From Different Coatings Compare?

- Comparisons of the percent difference in emissions between two, coatings, or between a coating and an emission limit, must be done on a solids basis.
- Each gallon of the 25 v/o solids coating contains 5.5 pounds of VOC.



- So, for each gallon of coating solids, 22.0 pounds of VOC are emitted.
- 5.5 pounds VOC X 4 gallons coating
- gallon coating gallon of solids
- Each gallon of the 50 v/o solids coating contains 3.7 pound of VOC



- So, for each gallon of coating solids, 7.4 pounds of VOC are emitted.

$$\frac{3.7 \text{ pounds VOC}}{\text{gallon coating}} \times \frac{2 \text{ gallons coating}}{\text{gallon of solids}}$$

- Thus, emissions from the 50 v/o solids coatings are 66 percent less than from the 25 v/o solids coating when providing an equal amount of solids to the process.

$$\frac{22.0 - 7.4}{22.0} = 0.66$$

- What emission reduction is needed to meet an emission limit?
- This calculation, which must also be done on a solids basis, is the same as that used above to compare emissions, from two different coatings.
- A coater who uses a 25 v/o solids coating containing 5.5 pounds of VOC per gallon, less water, must reduce emissions by 66 percent to meet an emission limit of 3.7 pounds of VOC per gallon, less water.

How much do improvements in transfer efficiency help a source to comply?

- The coater may want to use a coating that does not comply with a regulation and compensate by improvements in the transfer efficiency with which the coating is applied to meet an equivalent emission level. In order to calculate credit for VOC reductions which result from improvements in transfer efficiency, calculations should be done using units of:
- 1b VOC/gallon solids deposited.

Transfer Efficiency Calculations

- These units are determined by dividing 1b VOC/gallon solids by the transfer efficiency expressed as a decimal fraction. For example, if the starting transfer efficiency is 60 percent, the units would be:

$$\frac{\text{lb VOC}}{\text{gal solids deposited (with the old system)}} = \frac{\text{lbs VOC}}{\text{gallon Solids (in coating used)}} \times \frac{\text{1 gal. solids in coating used}}{\text{0.6 gal solids deposited}}$$

Transfer Efficiency Calculations

- If the same paint were now to be sprayed with 90 percent transfer efficiency, the new value

$$\frac{\text{lb VOC}}{\text{gal solids deposited (with new system)}} = \frac{\text{lbs VOC}}{\text{gallon Solids (in new coating used)}} \times \frac{\text{1 gal. solids in coating used}}{\text{0.9 gal solids deposited}}$$

Transfer Efficiency Calculations

- If both the sol vent content of the coating and the transfer efficiency are changed, the situation becomes:

$$\frac{\text{lb VOC}}{\text{gal solids deposited (with new paint and new transfer efficiency)}} = \frac{\text{1b VOC}}{\text{gal solids in new coating used}} \times \frac{\text{1.0 gal solids in new coating used}}{\text{T x gallon solids}}$$

- where T the new transfer efficiency expressed as a decimal

Calculation of Mixed Solvent Density

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.

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

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

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

$$=7.36\frac{\text{lbs solvent}}{\text{gal solvent}}$$

Calculation of Coating Density

Solvent content = 100 lbs coating - 35 lbs solids - 10 lbs water = 55 lbs

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

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

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

Calculation of Coating Density
(Continued)

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

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

Coating composition by volume:

Solids	**12.0%**
Water	**12.2%**
Solvent	**75.8%**

Calculation of VOC Emissions on the Basis of Coating Volume

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

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

Calculation of VOC Emissions on the Basis of Coating Volume
(Continued)

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

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

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

Calculation of VOC Emissions on the Basis of Coating Volume
(Continued)

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

Calculation of VOC Emissions on the Basis of Solids Volume

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

or

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

Calculation of VOC Emissions on the Basis of Solids Volume

(Continued)

Assume a transfer efficiency of 75%:

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

Graphic Arts Calculations

Consider the following ink:

Solids content	10% by volume
Water content	70% by volume
Solvent content	20% by volume

Volume Percent VOC in the Volatile Fraction

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

Volume Percent Water in the Volatile Fraction

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

Volume Percent Solids in the Ink Less Water

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

Calculating emissions (lbs/hr) of individual HAP's

- Data needed:
- 1) topcoat: product density = 8.5 lbs/gal, 5% wt xylene, 8% wt MIBK from EDS
- 2) reducer: product density = 7.5 lbs/gal, 10% wt xylene, 20% wt toluene from EDS
- 3) mix ratio = 4 gallons topcoat to 1 gallon reducer
- 4) mixed coating application rate = 2.5 gallons/hour
-

Calculating emissions (lbs/hr) of individual HAP's

Xylene content of mixed coating:

$$\frac{(8.5\ \text{lbs/gal} \times 0.05 \times 4\ \text{gal}) + (7.5\ \text{lbs/gal} \times 0.10 \times 1\ \text{gal})}{4\ \text{gal} + 1\ \text{gal}} = 0.49\ \text{lb xylene/gal}$$

Toluene content of mixed coating:

$$\frac{(7.5\ \text{lbs/gal} \times 0.20 \times 1\ \text{gal})}{4\ \text{gal} + 1\ \text{gal}} = 0.30\ \text{lb toluene/gal}$$

MIBK content of mixed coating:

$$\frac{(8.5\ \text{lbs/gal} \times 0.08 \times 4\ \text{gal})}{4\ \text{gal} + 1\ \text{gal}} = 0.54\ \text{lb MIBK/gal}$$

Calculating emissions (lbs/hr) of individual HAP's

Xylene emissions: 0.49 lbs/gal X 2.5 gal/hr = 1.23 lbs/hr xylene

Toluene emissions: 0.30 lbs/gal X 2.5 gal/hr = 0.75 lb/hr toluene

MIBK emissions: 0.54 lbs/gal X 2.5 gal/hr = 1.35 lbs/hr MIBK

Large Appliance Coating Line Using Several Types of Spray Equipment

- A large appliance manufacturer has a coating operation that employs electrostatic and manual spray coating equipment. The following data are available regarding operation. Determine the compliance status and what percent reduction is required to achieve compliance.

Large Appliance Coating Line Using Several Types of Spray Equipment

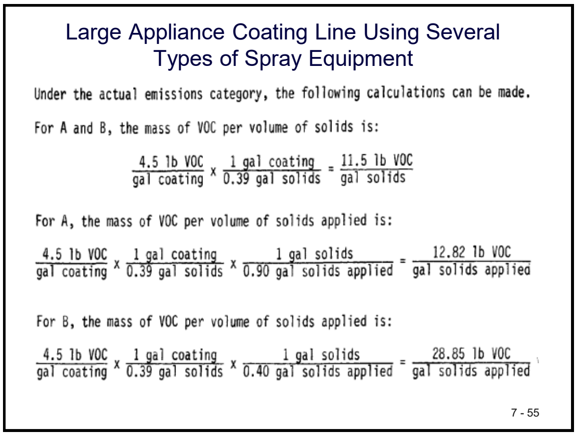
	(A) Electrostatic coating	(B) Manual coating
Transfer efficiency, percent	90	40
Average volume percent of solids in coating	39	39
VOC content, lb VOC/gal coating less water	4.5	4.5
Gallons of coating used per day	30.4	47.1
Emission limit, lb/gallon less water	2.8	2.8
Baseline transfer efficiency for large appliances, percent	60	60

The baseline transfer efficiency is 60 percent for a large appliance coater. Table 3 is a tabulation of the available data and calculation results. The actual calculations follow.

Large Appliance Coating Line Using Several Types of Spray Equipment

TABLE 3. LARGE APPLIANCE MULTITRANSFER EFFICIENCY CALCULATION.

Spray type	Gallons of coating/day	Solids, vol. %	Lb VOC/gallon coating	Lb VOC/gallon solids	% TE	Lb VOC/gallon solids applied	Gallons of solids applied/day	Pounds of VOC/day
				Actual emissions				
A	30.4	39	4.5	11.5	90	12.8	10.7	136.8
B	47.1	39	4.5	11.5	40	28.8	7.3	212.0
Total								348.8
				Allowed emissions				
A	28.8	62	2.8	4.5	60	7.5	10.7	80.6
B	19.6	62	2.8	4.5	60	7.5	7.3	54.9
Total								135.5



Large Appliance Coating Line Using Several Types of Spray Equipment

Under the actual emissions category, the following calculations can be made.

For A and B, the mass of VOC per volume of solids is:

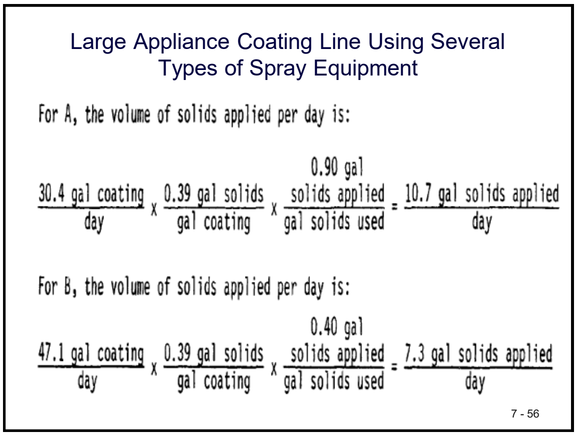
$$\frac{4.5\ \text{lb VOC}}{\text{gal coating}} \times \frac{1\ \text{gal coating}}{0.39\ \text{gal solids}} = \frac{11.5\ \text{lb VOC}}{\text{gal solids}}$$

For A, the mass of VOC per volume of solids applied is:

$$\frac{4.5\ \text{lb VOC}}{\text{gal coating}} \times \frac{1\ \text{gal coating}}{0.39\ \text{gal solids}} \times \frac{1\ \text{gal solids}}{0.90\ \text{gal solids applied}} = \frac{12.82\ \text{lb VOC}}{\text{gal solids applied}}$$

For B, the mass of VOC per volume of solids applied is:

$$\frac{4.5\ \text{lb VOC}}{\text{gal coating}} \times \frac{1\ \text{gal coating}}{0.39\ \text{gal solids}} \times \frac{1\ \text{gal solids}}{0.40\ \text{gal solids applied}} = \frac{28.85\ \text{lb VOC}}{\text{gal solids applied}}$$



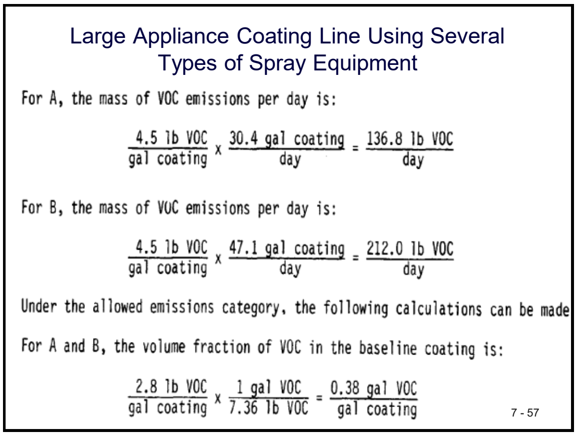
Large Appliance Coating Line Using Several Types of Spray Equipment

For A, the volume of solids applied per day is:

$$\frac{30.4\ \text{gal coating}}{\text{day}} \times \frac{0.39\ \text{gal solids}}{\text{gal coating}} \times \frac{0.90\ \text{gal solids applied}}{\text{gal solids used}} = \frac{10.7\ \text{gal solids applied}}{\text{day}}$$

For B, the volume of solids applied per day is:

$$\frac{47.1\ \text{gal coating}}{\text{day}} \times \frac{0.39\ \text{gal solids}}{\text{gal coating}} \times \frac{0.40\ \text{gal solids applied}}{\text{gal solids used}} = \frac{7.3\ \text{gal solids applied}}{\text{day}}$$



Large Appliance Coating Line Using Several Types of Spray Equipment

For A, the mass of VOC emissions per day is:

$$\frac{4.5\ \text{lb VOC}}{\text{gal coating}} \times \frac{30.4\ \text{gal coating}}{\text{day}} = \frac{136.8\ \text{lb VOC}}{\text{day}}$$

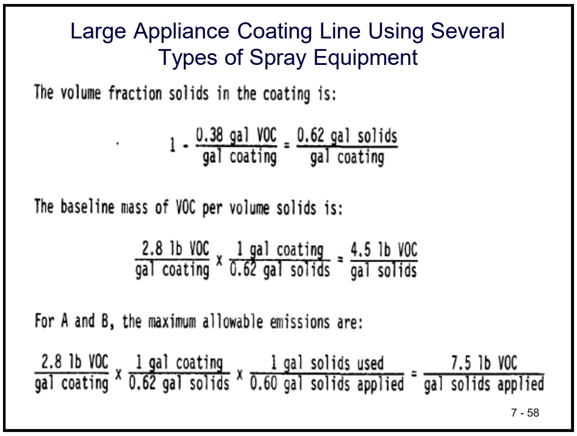
For B, the mass of VOC emissions per day is:

$$\frac{4.5\ \text{lb VOC}}{\text{gal coating}} \times \frac{47.1\ \text{gal coating}}{\text{day}} = \frac{212.0\ \text{lb VOC}}{\text{day}}$$

Under the allowed emissions category, the following calculations can be made

For A and B, the volume fraction of VOC in the baseline coating is:

$$\frac{2.8\ \text{lb VOC}}{\text{gal coating}} \times \frac{1\ \text{gal VOC}}{7.36\ \text{lb VOC}} = \frac{0.38\ \text{gal VOC}}{\text{gal coating}}$$



Large Appliance Coating Line Using Several Types of Spray Equipment

The volume fraction solids in the coating is:

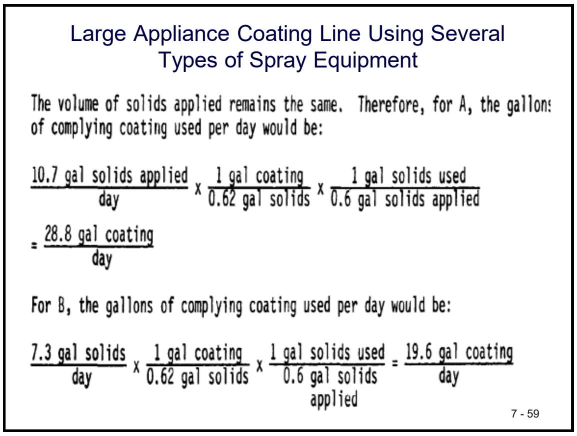
$$1 - \frac{0.38 \text{ gal VOC}}{\text{gal coating}} = \frac{0.62 \text{ gal solids}}{\text{gal coating}}$$

The baseline mass of VOC per volume solids is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} = \frac{4.5 \text{ lb VOC}}{\text{gal solids}}$$

For A and B, the maximum allowable emissions are:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{1 \text{ gal solids used}}{0.60 \text{ gal solids applied}} = \frac{7.5 \text{ lb VOC}}{\text{gal solids applied}}$$



Large Appliance Coating Line Using Several Types of Spray Equipment

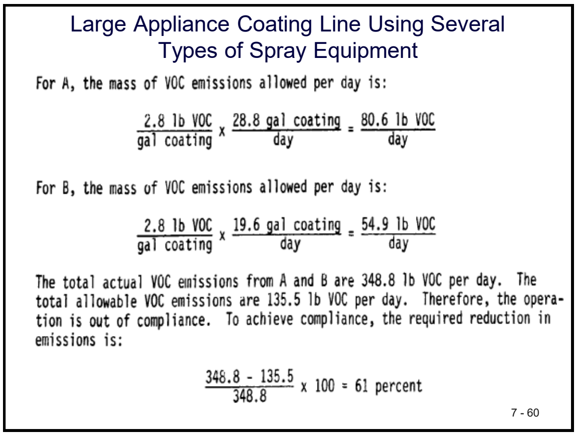
The volume of solids applied remains the same. Therefore, for A, the gallons of complying coating used per day would be:

$$\frac{10.7 \text{ gal solids applied}}{\text{day}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{1 \text{ gal solids used}}{0.6 \text{ gal solids applied}}$$

$$= \frac{28.8 \text{ gal coating}}{\text{day}}$$

For B, the gallons of complying coating used per day would be:

$$\frac{7.3 \text{ gal solids}}{\text{day}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{1 \text{ gal solids used}}{0.6 \text{ gal solids applied}} = \frac{19.6 \text{ gal coating}}{\text{day}}$$



Large Appliance Coating Line Using Several Types of Spray Equipment

For A, the mass of VOC emissions allowed per day is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{28.8 \text{ gal coating}}{\text{day}} = \frac{80.6 \text{ lb VOC}}{\text{day}}$$

For B, the mass of VOC emissions allowed per day is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{19.6 \text{ gal coating}}{\text{day}} = \frac{54.9 \text{ lb VOC}}{\text{day}}$$

The total actual VOC emissions from A and B are 348.8 lb VOC per day. The total allowable VOC emissions are 135.5 lb VOC per day. Therefore, the operation is out of compliance. To achieve compliance, the required reduction in emissions is:

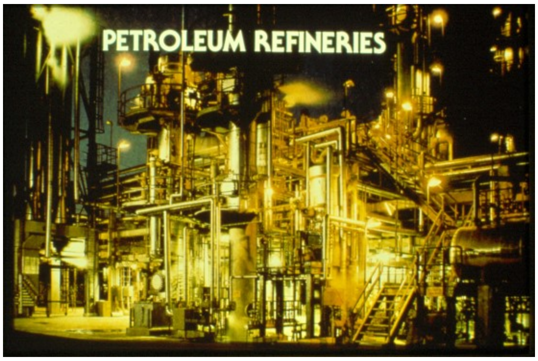
$$\frac{348.8 - 135.5}{348.8} \times 100 = 61 \text{ percent}$$

Chapter 8

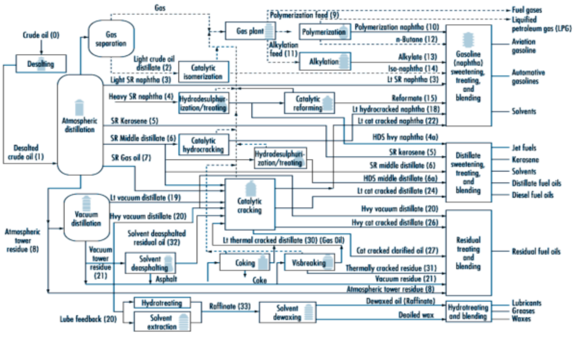
Petroleum Refining

Wellhead Pump

VID00073.AVI



Overview of Petroleum Refining Processes



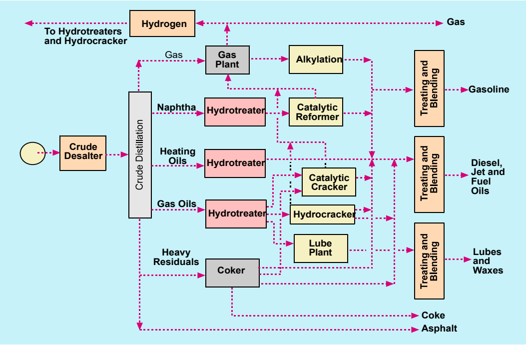
Note: Numbers in parentheses refer to typical product process flow routes.
Source: OSHA 1996.

Refinery Overview

Categories of Refining Operations

- Separation processes
- Conversion processes
- Treatment processes
- Formulating and Blending
- Auxiliary processes

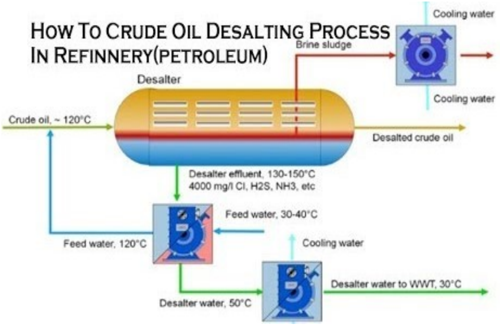
Typical Processing Steps



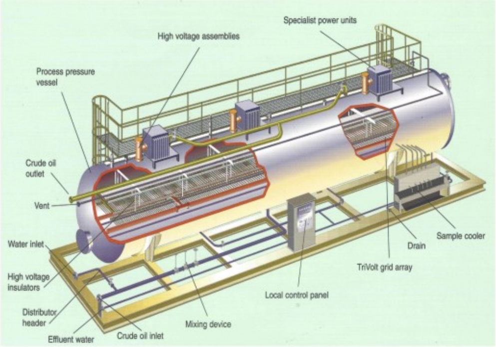
Separation Processes

- Desalting
- Distillation
- Deasphalting

Desalting



Electrostatic Dehydrator and Desalter

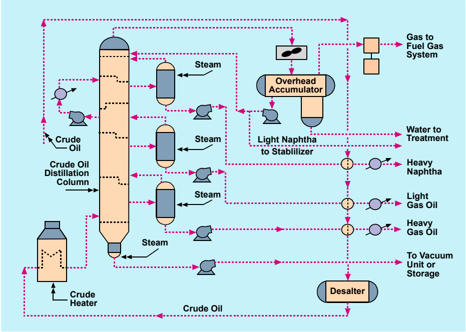


https://howe-baker.com/oil-treatment/

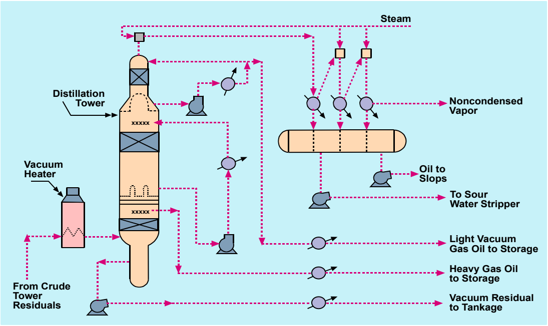
Distillation

- Atmospheric distillation
- Vacuum distillation

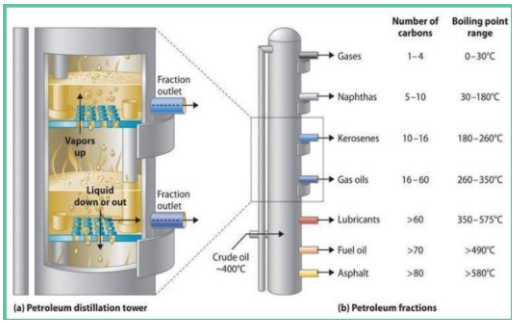
Atmospheric Distillation Unit



Vacuum Distillation



Petroleum Distillation Tower and Fractionation Information

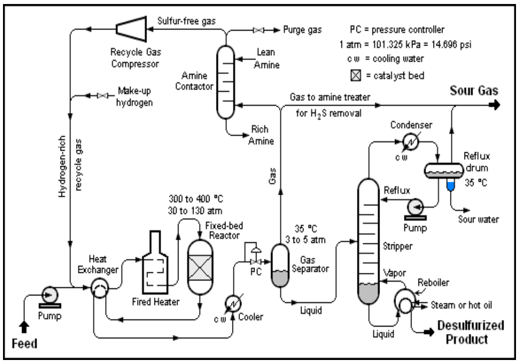


	Number of carbons	Boiling point range
Gases	1–4	0–30°C
Naphthas	5–10	30–180°C
Kerosenes	10–16	180–260°C
Gas oils	16–60	260–350°C
Lubricants	>60	350–575°C
Fuel oil	>70	>490°C
Asphalt	>80	>580°C

(a) Petroleum distillation tower

(b) Petroleum fractions

Hydrotreating



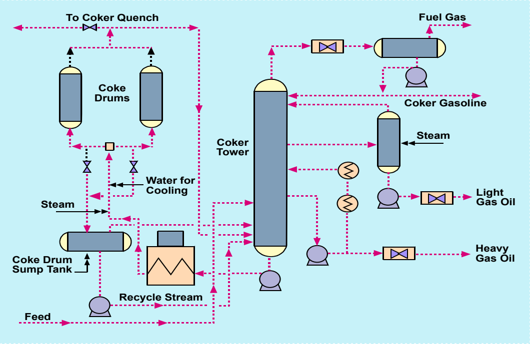
Deasphalting

Separates asphaltic compounds using liquid-liquid extraction with liquid propane

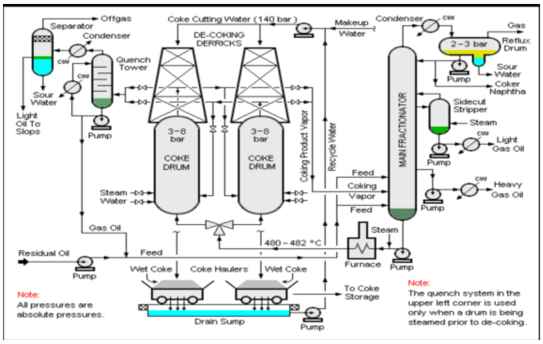
Conversion Processes

- Coking
- Visbreaking
- Catalytic cracking
- Polymerization
- Alkylation
- Isomerization
- Reforming

Delayed Coking Unit



Delayed Coking Unit Schematic Flow Diagram



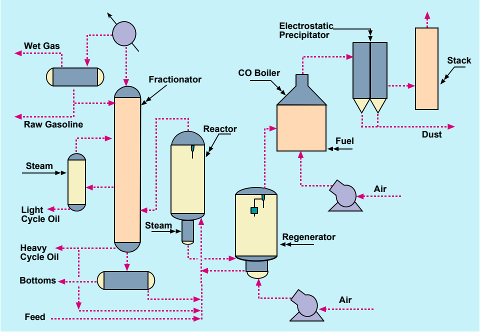
Note:
All pressures are absolute pressures.

Note:
The quench system in the upper left corner is used only when a drum is being steamed prior to de-coking.

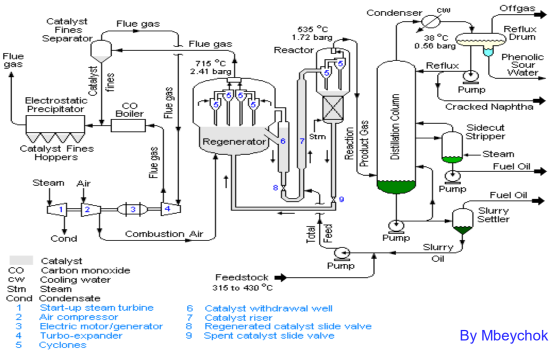
Visbreaking

- Milder form of cracking than coking
- Residues from atmospheric and vacuum distillation fed to process heater
- Thermal cracking produces residual tars, gas oils, gasoline and light gases
- Used to reduce viscosity of residual fractions for blending into fuel oils

Catalytic Cracking Unit



FCC Unit



FCC Internal Cyclones

Polymerization

- Catalytic conversion of olefin gases to liquid condensation products
- Provided a gasoline blending stock when octane level were low
- Rarely used today
- Polymers are valuable as additives for motor oil

Alkylation

- Branched hydrocarbons are synthesized by the catalytic addition of a paraffinic or aromatic hydrocarbon to an olefin
- The product, alkylate, is used as an antiknock additive

Isomerization

- Rearranges feedstock molecular structure to produce branched-chain compounds from straight-chain compounds
- Process is usually applied to butane or mixtures of pentane and hexane

Reforming

- Converts straight-chain naphtha compounds to ring or branched structures
- Predominate use is the dehydrogenation of naphthenes to form aromatics

Treatment Processes

- Hydrotreating
- Amine treating
- Chemical sweetening
- Asphalt blowing

Hydrotreating

- Removes sulfur, nitrogen and metal compounds from intermediate fractions
- In hydrodesulfurization, the petroleum stream is mixed with hydrogen and passed over a fixed-bed catalyst
- Reactor effluent is separated to recover the hydrogen and the hydrogen sulfide and ammonia

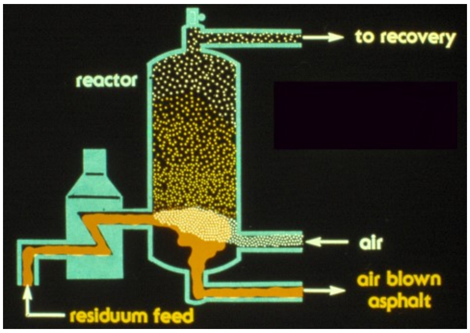
Amine Treating

- Removes acid impurities, mainly hydrogen sulfide and carbon dioxide, from intermediate fractions
- Petroleum stream is contacted with an aqueous amine solution in a tray or packed tower
- Spent amine solution is processed to regenerate the scrubbing solution and producing a concentrated acid-gas stream

Chemical Sweetening

- Sweetens distillates by extraction or conversion of mercaptans
- In conversion process, sour feed is sparged with air and passed over a fixed-bed catalyst wetted by caustic solution
- In extraction process, sour feed is contacted with caustic solution in a packed tower. Spent caustic is regenerated and mecaptans recovered as alkyl disulfides

Asphalt Blowing



Auxiliary Processes

- Sulfur recovery
- Wastewater treatment
- Fuel gas recovery
- Blowdown systems

Sulfur Recovery

- Sulfur compounds in petroleum fractions are converted into hydrogen sulfide by treatment processes
- Hydrogen sulfide is collected and converted to elemental sulfur, usually with a Claus process

Wastewater Treatment

- Specific design of system varies
- Systems generally include:
  - Drain systems
  - Oil-water separators
  - Air flotation units
- Additional treatment may involve secondary and tertiary processes

Fuel Gas Recovery

- Recovers hydrocarbon vapors from various refinery processes
- Collected gases are compressed, condensed and separated into constant vapor pressure mixtures
- Recovered mixtures used as refinery fuel or feedstock or sold

Blowdown Systems

- Provides for safe disposal of liquid and gaseous hydrocarbons from pressure-relief devices
- Blowdown is separated into liquid and vapor fractions and recycled or flared

Emission Control Techniques

- Flares
- Incinerators
- Process heaters
- Covers
- Fugitive emission control

Flares

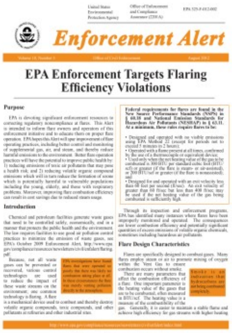
There several different types of flares, but the most common is the elevated steam-assisted flare. They are designed and operated to handle large fluctuations in flow rate and VOC content are

Well Operating Flare – High Combustion Efficiency

Poorly Operating/Over Steamed Flare - Low Combustion Efficiency

Enclosed Refinery Flare

Flare Efficiency Alert



United States Environmental Protection Agency
Office of Enforcement and Compliance Assurance (2201A)

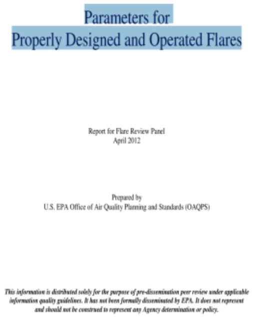
Enforcement Alert

EPA Enforcement Targets Flaring Efficiency Violations

Purpose

Introduction

Flare Design Characteristics



Parameters for
Properly Designed and Operated Flares

Report for Flare Review Panel
April 2012

Prepared by
U.S. EPA Office of Air Quality Planning and Standards (OAQPS)

This information is distributed solely for the purpose of pre-dissemination peer review under applicable information quality guidelines. It has not been formally disseminated by EPA. It does not represent and should not be construed to represent any Agency determination or policy.

Incinerators – Thermal Oxidizers

- Thermal and Catalytic Incinerators – TO's
- Destruction Efficiencies up to 95% - 99%
- Not well suited to streams with highly variable flow
- Supplementary fuel typically required
- Fuel requirements may be reduced by energy recovery

Process Heaters

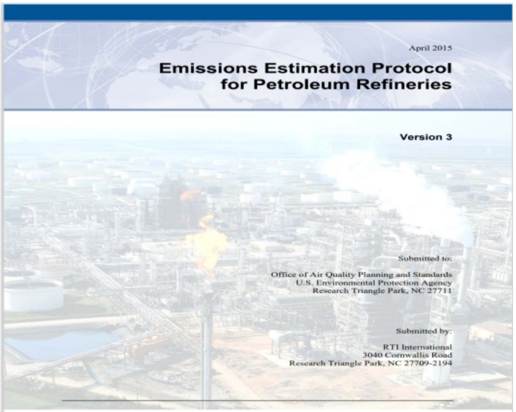
- Can be used to control emission streams if gas stream > 150 Btu/SCF
- Typically can oxidize VOC's > 98%
- Gas stream must not reduce the heaters performance or reliability
- Not suitable for gas streams with varying flows or heating value (high or low)
- Not suitable for corrosive gas streams

Covers

- 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, equipped with a vent pipe.
- Fixed or floating roof covers on oil-water separators can control emissions ranging from 85% to 98% efficiency.
- Covering components in the wastewater system, can be enclosed and vented to a control device.

Fugitive Emission Control

- Control with preventive maintenance and housekeeping.
- Having an effective inspection and training program
- Have an effective (timely repair) Leak Detection and Repair LDAR program (typically mandatory)



April 2015

Emissions Estimation Protocol
for Petroleum Refineries

Version 3

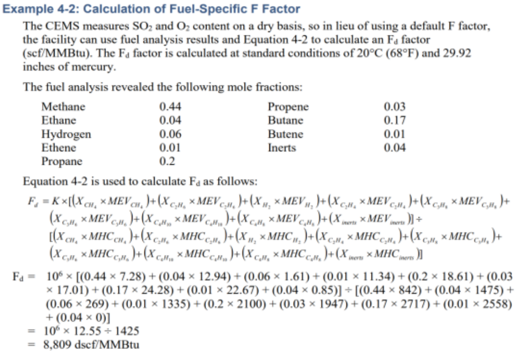
Submitted to:

Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Submitted by:

RTI International
3040 Cornwallis Road
Research Triangle Park, NC 27709-2194

Example from Refinery Emissions Protocol



Example 4-2: Calculation of Fuel-Specific F Factor

The CEMS measures SO_2 and O_2 content on a dry basis, so in lieu of using a default F factor, the facility can use fuel analysis results and Equation 4-2 to calculate an F_d factor (scf/MMBtu). The F_d factor is calculated at standard conditions of 20°C (68°F) and 29.92 inches of mercury.

The fuel analysis revealed the following mole fractions:

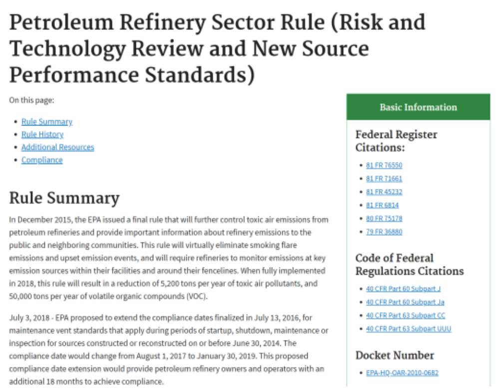
Methane	0.44	Propene	0.03
Ethane	0.04	Butane	0.17
Hydrogen	0.06	Butene	0.01
Ethene	0.01	Inerts	0.04
Propane	0.2		

Equation 4-2 is used to calculate F_d as follows:

$$F_d = K \times [(X_{CH_4} \times MEV_{CH_4}) + (X_{C_2H_6} \times MEV_{C_2H_6}) + (X_{H_2} \times MEV_{H_2}) + (X_{C_2H_4} \times MEV_{C_2H_4}) + (X_{C_3H_8} \times MEV_{C_3H_8}) + (X_{C_3H_6} \times MEV_{C_3H_6}) + (X_{C_4H_{10}} \times MEV_{C_4H_{10}}) + (X_{C_4H_8} \times MEV_{C_4H_8}) + (X_{inerts} \times MEV_{inerts})] \div [(X_{CH_4} \times MHC_{CH_4}) + (X_{C_2H_6} \times MHC_{C_2H_6}) + (X_{H_2} \times MHC_{H_2}) + (X_{C_2H_4} \times MHC_{C_2H_4}) + (X_{C_3H_8} \times MHC_{C_3H_8}) + (X_{C_3H_6} \times MHC_{C_3H_6}) + (X_{C_4H_{10}} \times MHC_{C_4H_{10}}) + (X_{C_4H_8} \times MHC_{C_4H_8}) + (X_{inerts} \times MHC_{inerts})]$$

$$\begin{aligned} F_d &= 10^6 \times [(0.44 \times 7.28) + (0.04 \times 12.94) + (0.06 \times 1.61) + (0.01 \times 11.34) + (0.2 \times 18.61) + (0.03 \times 17.01) + (0.17 \times 24.28) + (0.01 \times 22.67) + (0.04 \times 0.85)] \div [(0.44 \times 842) + (0.04 \times 1475) + (0.06 \times 269) + (0.01 \times 1335) + (0.2 \times 2100) + (0.03 \times 1947) + (0.17 \times 2717) + (0.01 \times 2558) + (0.04 \times 0)] \\ &= 10^6 \times 12.55 \div 1425 \\ &= 8{,}809 \text{ dscf/MMBtu} \end{aligned}$$

Process Inspection



Petroleum Refinery Sector Rule (Risk and Technology Review and New Source Performance Standards)

On this page:

- Rule Summary
- Rule History
- Additional Resources
- Compliance

Rule Summary

In December 2015, the EPA issued a final rule that will further control toxic air emissions from petroleum refineries and provide important information about refinery emissions to the public and neighboring communities. This rule will virtually eliminate smoking flare emissions and upset emission events, and will require refineries to monitor emissions at key emission sources within their facilities and around their fencelines. When fully implemented in 2018, this rule will result in a reduction of 5,200 tons per year of toxic air pollutants, and 50,000 tons per year of volatile organic compounds (VOC).

July 3, 2018 - EPA proposed to extend the compliance dates finalized in July 13, 2016, for maintenance vent standards that apply during periods of startup, shutdown, maintenance or inspection for sources constructed or reconstructed on or before June 30, 2014. The compliance date would change from August 1, 2017 to January 30, 2019. This proposed compliance date extension would provide petroleum refinery owners and operators with an additional 18 months to achieve compliance.

Basic Information

Federal Register Citations:

- 81 FR 76550
- 81 FR 71661
- 81 FR 45232
- 81 FR 6814
- 80 FR 75178
- 79 FR 36880

Code of Federal Regulations Citations

- 40 CFR Part 60 Subpart J
- 40 CFR Part 60 Subpart Ja
- 40 CFR Part 63 Subpart CC
- 40 CFR Part 63 Subpart UUU

Docket Number

- EPA-HQ-OAR-2010-0682

https://www.epa.gov/stationary-sources-air-pollution/petroleum-refinery-sector-rule-risk-and-technology-review-and-new

Petroleum Refinery Fenceline Monitoring Requirement

Schedule

Milestones	Dates
Refineries install fenceline monitoring systems	Present – January 29, 2018
Refineries begin collecting data • Collect 12 months of data to calculate annual average	January 30, 2018
Refineries report data to EPA's emissions data system • Refineries continue to report data on quarterly basis • Refineries compare annual average to 9 micrograms per cubic meter	Spring 2019
EPA public release of benzene data on web page 30 days after quarterly reporting period ends • Data will be refreshed quarterly on EPA's public web page	Summer 2019

Fenceline Monitoring – Monitor Siting

- ► 12-24 monitors (based on size of facility) are required around the perimeter of each refinery
- ► Additional monitors required if sources are near fenceline
- ► Monitors will be placed following requirements in EPA Method 325A
- ► Geographic coordinates for each monitoring location will be reported

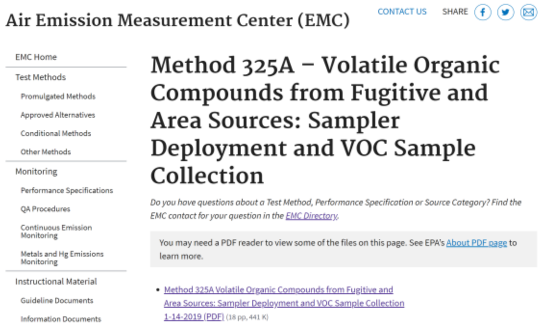
Fenceline Monitoring – Data Collection

- ► At least one sample collected from each individual monitoring location every two weeks
- ► Samples analyzed for benzene following requirements in EPA Method 325B
- ► The highest and lowest benzene concentration is identified for each biweekly sampling period
- ► The "delta C (ΔC)" for that monitoring period is calculated as the difference of these two concentrations
- ► 26 consecutive bi-week ΔC values are averaged to calculate an annual average ΔC value
- ► Collect benzene data for one year to develop first annual average ΔC value

Fenceline Monitoring – Data Reporting

- ► Upon completion of the first year of monitoring, benzene data are reported to EPA through EPA's data management system
- ► Includes actual measurements for each 2 week period for each monitoring station
- ► Refinery owners must maintain the annual average ΔC value at or below 9 micrograms per cubic meter, μg/m3 (2.8 parts per billion by volume, ppbv)

Method 325A



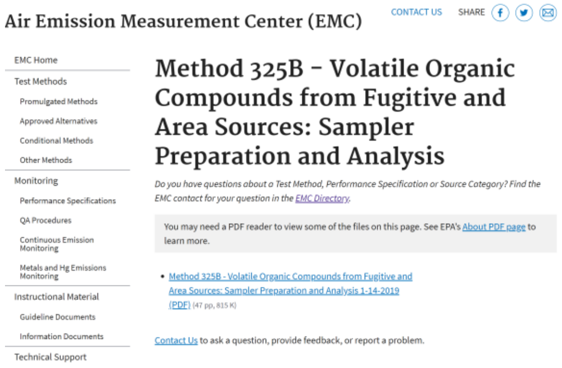
Method 325A – Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection

Do you have questions about a Test Method, Performance Specification or Source Category? Find the EMC contact for your question in the EMC Directory.

You may need a PDF reader to view some of the files on this page. See EPA's About PDF page to learn more.

- Method 325A Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection 1-14-2019 (PDF) (18 pp, 441 K)

Method 325B


Air Emission Measurement Center (EMC)

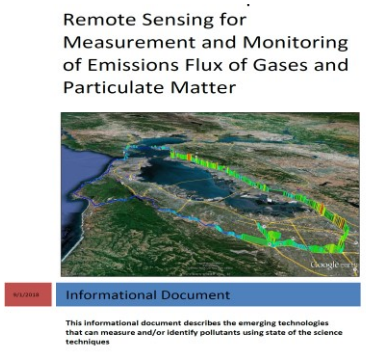
Method 325B – Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis

Do you have questions about a Test Method, Performance Specification or Source Category? Find the EMC contact for your question in the EMC Directory.

You may need a PDF reader to view some of the files on this page. See EPA's About PDF page to learn more.

- Method 325B - Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis 1-14-2019 (PDF) (47 pp, 815 K)

Contact Us to ask a question, provide feedback, or report a problem.

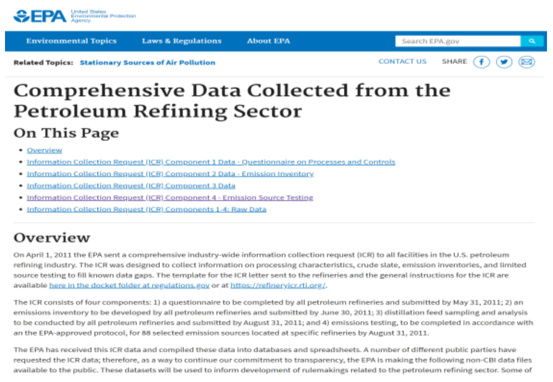

Remote Sensing for
Measurement and Monitoring
of Emissions Flux of Gases and
Particulate Matter

9/1/2018

Informational Document

This informational document describes the emerging technologies that can measure and/or identify pollutants using state of the science techniques

EPA 454/B-18-008 August 2018



Related Topics: Stationary Sources of Air Pollution

Comprehensive Data Collected from the Petroleum Refining Sector

On This Page

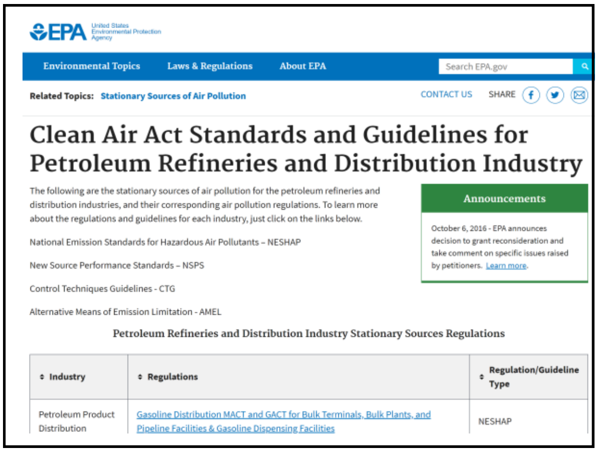
- Overview
- Information Collection Request (ICR) Component 1 Data - Questionnaire on Processes and Controls
- Information Collection Request (ICR) Component 2 Data - Emission Inventory
- Information Collection Request (ICR) Component 3 Data
- Information Collection Request (ICR) Component 4 - Emission Source Testing
- Information Collection Request (ICR) Components 1-4: Raw Data

Overview

On April 1, 2011 the EPA sent a comprehensive industry-wide information collection request (ICR) to all facilities in the U.S. petroleum refining industry. The ICR was designed to collect information on processing characteristics, crude slate, emission inventories, and limited source testing to fill known data gaps. The template for the ICR letter sent to the refineries and the general instructions for the ICR are available here in the docket folder at regulations.gov or at https://refineryicr.rti.org/.

The ICR consists of four components: 1) a questionnaire to be completed by all petroleum refineries and submitted by May 31, 2011; 2) an emissions inventory to be developed by all petroleum refineries and submitted by June 30, 2011; 3) distillation feed sampling and analysis to be conducted by all petroleum refineries and submitted by August 31, 2011; and 4) emissions testing, to be completed in accordance with an the EPA-approved protocol, for 88 selected emission sources located at specific refineries by August 31, 2011.

The EPA has received this ICR data and compiled these data into databases and spreadsheets. A number of different public parties have requested the ICR data; therefore, as a way to continue our commitment to transparency, the EPA is making the following non-CBI data files available to the public. These datasets will be used to inform development of rulemakings related to the petroleum refining sector. Some of



Related Topics: Stationary Sources of Air Pollution

Clean Air Act Standards and Guidelines for Petroleum Refineries and Distribution Industry

The following are the stationary sources of air pollution for the petroleum refineries and distribution industries, and their corresponding air pollution regulations. To learn more about the regulations and guidelines for each industry, just click on the links below.

National Emission Standards for Hazardous Air Pollutants – NESHAP

New Source Performance Standards – NSPS

Control Techniques Guidelines - CTG

Alternative Means of Emission Limitation - AMEL

Announcements

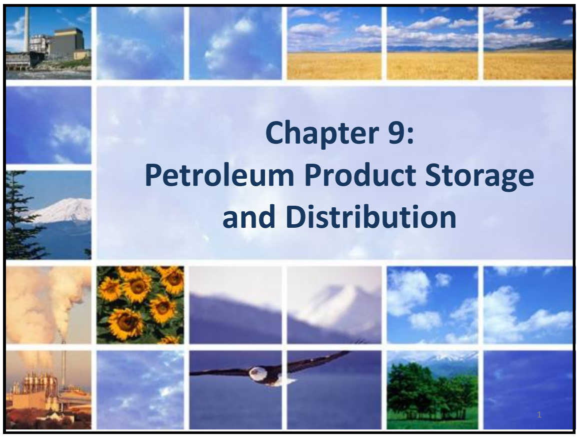
October 6, 2016 - EPA announces decision to grant reconsideration and take comment on specific issues raised by petitioners. Learn more.

Petroleum Refineries and Distribution Industry Stationary Sources Regulations

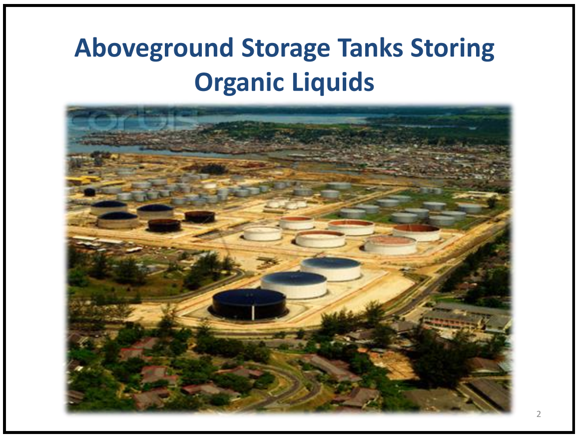
Industry	Regulations	Regulation/Guideline Type
Petroleum Product Distribution	Gasoline Distribution MACT and GACT for Bulk Terminals, Bulk Plants, and Pipeline Facilities & Gasoline Dispensing Facilities	NESHAP

Crude Oil Distillation Video on Youtube

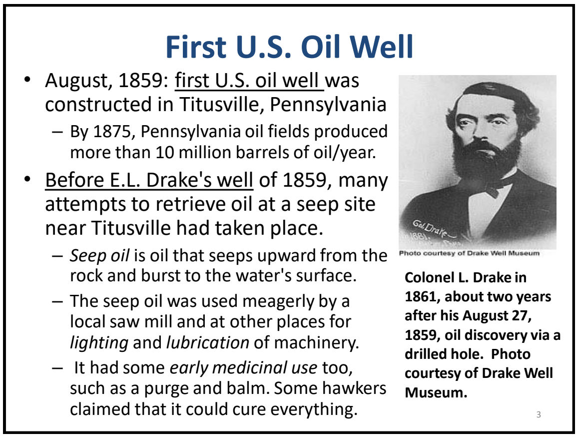
https://www.youtube.com/watch?v=2xzYf8IL_FE



Chapter 9: Petroleum Product Storage and Distribution



Aboveground Storage Tanks Storing Organic Liquids



First U.S. Oil Well

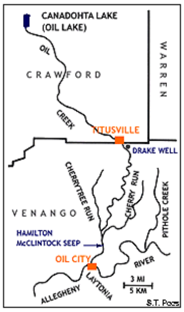
- August, 1859: first U.S. oil well was constructed in Titusville, Pennsylvania
  - By 1875, Pennsylvania oil fields produced more than 10 million barrels of oil/year.
- Before E.L. Drake's well of 1859, many attempts to retrieve oil at a seep site near Titusville had taken place.
  - *Seep oil* is oil that seeps upward from the rock and burst to the water's surface.
  - The seep oil was used meagerly by a local saw mill and at other places for *lighting* and *lubrication* of machinery.
  - It had some *early medicinal use* too, such as a purge and balm. Some hawkers claimed that it could cure everything.

Photo courtesy of Drake Well Museum

Colonel L. Drake in 1861, about two years after his August 27, 1859, oil discovery via a drilled hole. Photo courtesy of Drake Well Museum.

First U.S. Oil Well

- Seep oil on Oil Creek was being exploited by a farm owner, Hamilton McClintock, since the early 1800's.
  - He trapped some of it in a ring of timbers around the main seep.
  - Produced only 20 to 30 barrels/yr.
  - This was the largest oil operation on Oil Creek prior to Drake's well.
- Around 1854, an oil investor, Seneca Oil Company, bought 100 acres near Titusville for $5,000 which later became Drakes Well.

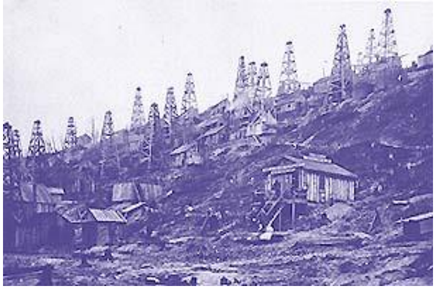


First U.S. Oil Well

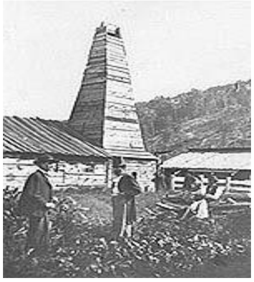
- In 1858, Edwin Drake went to Titusville, as an agent of the Seneca. He found that by collecting seep oil it would only produce about *4 gallons a day*.
- After that Drake dug a shaft, but *water entered* in such quantity that the work couldn't continue.
- Next, he tried drilling a well, but the hole was only 16 feet deep and *kept caving in*.
- Drake then conceived the idea of a drive pipe.
  - The drive pipe consisted of joints ten feet long and was made of cast-iron. The tools could be safely lowered through the pipe which protected the upper hole.

First U.S. Oil Well

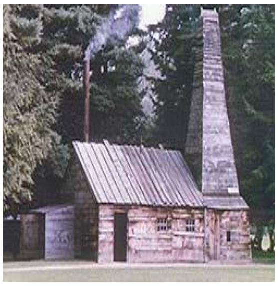
- Drake ran out of company money, and was abandoned by Seneca.
- He used his own money, ran out of that, and then borrowed $ 500 from 2 friends.
- It was called "Drake's Folly" until August 27, 1859; the day he found the reservoir of the seep oil at a dept of 69.5 ft.
- The oil was brought to the surface by a hand pitcher pump, the type used for farm water wells and sinks.
  - The well averaged about *10 barrels daily for a year* or more.
  - The drive pipe was his greatest invention which he unfortunately did not think to patent and died penniless.



Like the 1849 gold rush which saw multitudes of would-be miners arrive in the frontier regions of California, a similar phenomenon took place a decade later in 1859 in America's eastern wilderness, but that time the beacon was crude oil and the place was Oil Creek at Titusville in Northwest Pennsylvania.



Engine house of the Drake Well in Titusville in 1861. Drake with top hat, standing (right). Photo from Drake Well Museum.



Replica of engine house and derrick at the Drake Well Site. It was dedicated in 1946. It now contains a working replica of the original boiler and engine.

U.S. Oil Refinery & John D. Rockefeller

- In 1863, Rockefeller (24 yrs old) started a refinery in Cleveland with 3 other partners. One year later, he bought out 2 partners (kept the refinery expert partner).
- In 1870, Rockefeller bought out all other refiners & formed Standard Oil (at that time Standard controlled 10% of all US refining – by 1877, Standard controlled 90%).
- After 1900, Standard acquired oil fields, tankers, refineries & gas stations to control prices (supply & demand).
- In 1914, Standard was ruled a monopoly & broken up to smaller companies (Exxon & Mobil).

Original Uses for Oil

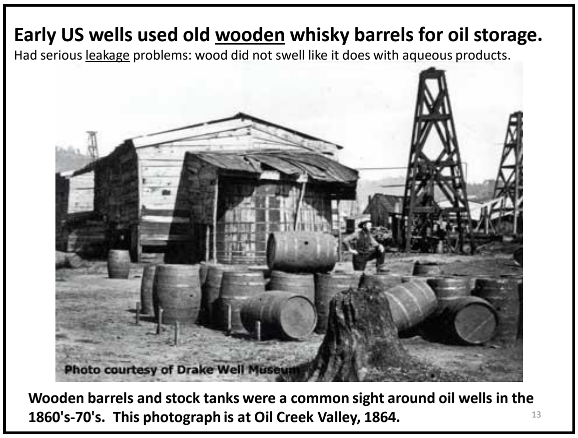
- In the 1700's, whale oil was used as an illuminant in lamps and as candle wax.
  - The whale was sought for its oil when the petroleum industry opened in 1859.
- Lighting, created the original use for oil (kerosene).
  - This led to drilling oil wells along Oil Creek & elsewhere. Other uses soon increased the overall demand.
- In early 1880's Edison discovered electricity, replacing the need for kerosene lamps. Around the same time the development of the 4-stroke engine to power a buggy increased the demand for lubricating oil & gasoline.
  - 1903 first Model A; 1908 first Model T (and was the first mass produced vehicle); By 1913 over one million cars in U.S.

Coal as King of Energy

- Coal became king of energy (over wood) in 1712 when Thomas Newcomen invented a coal-fired device that could pump water from a flooded mineshaft 160 ft below ground in England.
  - Deep mineshafts became flooded. This extremely limited the amount of coal that could be mined.
  - One of these new devices replaced the alternative of using 50 horses for pumping operations.
  - Made coal abundant and cheap.
- This saved the industrial revolution from collapse.
  - Running out of forests; and
  - 1 lb of coal (when burned) releases 5 times more energy than 1 lb of wood.

Oil Replaced Coal as King of Energy

- The coal age ended on January 10, 1901 in Beaumont, TX on a small hill called Spindletop.
  - Al & Curt Hammil drilled 1,100 feet below ground when a plume of oil erupted (it could be seen 4 miles away).
  - For the first time a "rotary drill" was used allowing them to drill deeper (& pierce hard limestone rock) than the old "jackhammer" type drill (rarely went deeper than 300 ft).
- Before Spindletop, world oil production was only a trickle (causing oil to be very expensive).
  - Most early oil wells only delivered 50 to 100 barrels a day.
- After Spindletop, oil became abundant & inexpensive; becoming the king of energy supply.
  - Spindletop delivered 100,000 barrels a day. (They started on 5 new wells each delivering the same amount of oil.)
  - Can now replace coal use in "industry" & "home heating."

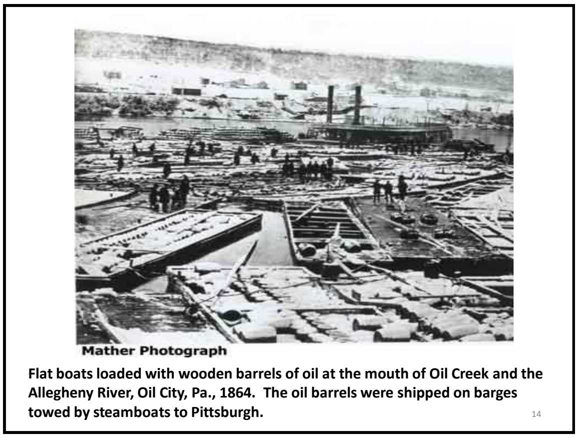


Early US wells used old wooden whisky barrels for oil storage.

Had serious leakage problems: wood did not swell like it does with aqueous products.

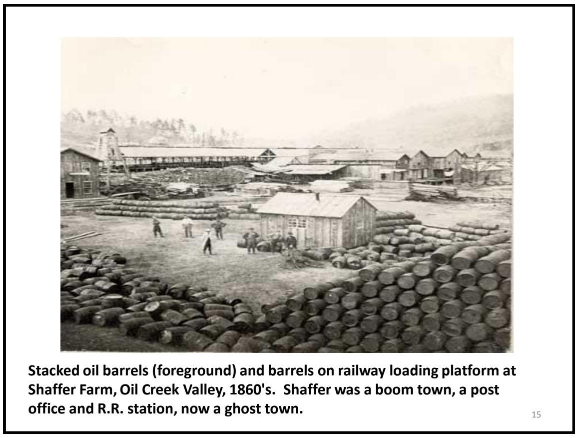
Photo courtesy of Drake Well Museum

Wooden barrels and stock tanks were a common sight around oil wells in the 1860's-70's. This photograph is at Oil Creek Valley, 1864.

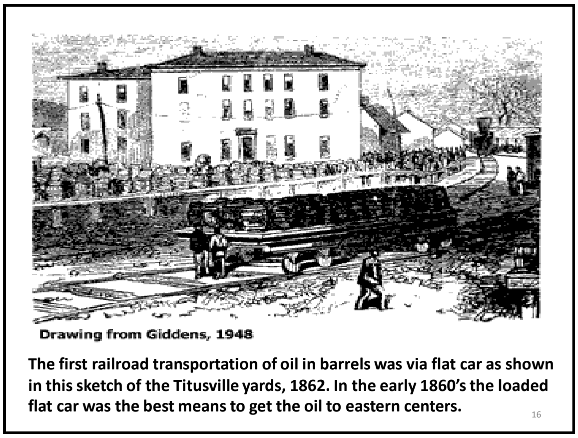


Mather Photograph

Flat boats loaded with wooden barrels of oil at the mouth of Oil Creek and the Allegheny River, Oil City, Pa., 1864. The oil barrels were shipped on barges towed by steamboats to Pittsburgh.

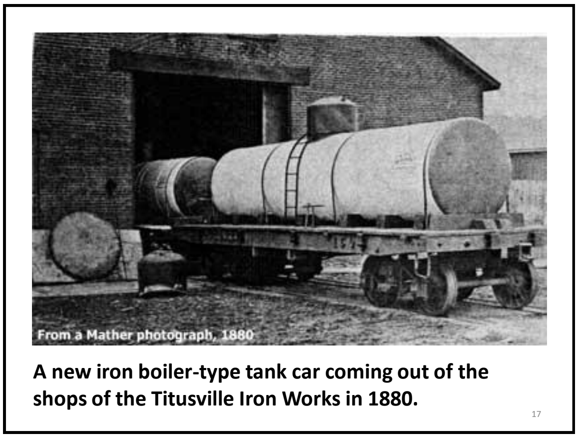


Stacked oil barrels (foreground) and barrels on railway loading platform at Shaffer Farm, Oil Creek Valley, 1860's. Shaffer was a boom town, a post office and R.R. station, now a ghost town.



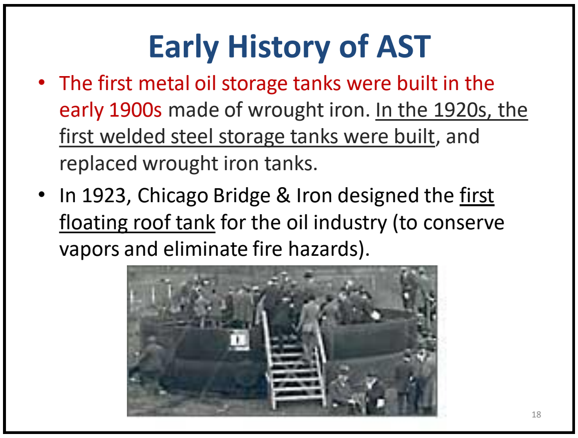
Drawing from Giddens, 1948

The first railroad transportation of oil in barrels was via flat car as shown in this sketch of the Titusville yards, 1862. In the early 1860's the loaded flat car was the best means to get the oil to eastern centers.



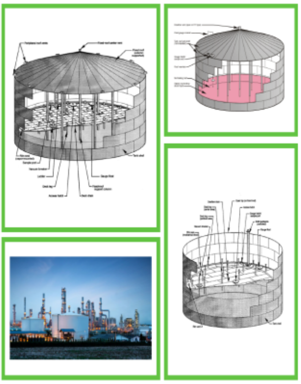
From a Mather photograph, 1880

A new iron boiler-type tank car coming out of the shops of the Titusville Iron Works in 1880.



Early History of AST

- The first metal oil storage tanks were built in the early 1900s made of wrought iron. In the 1920s, the first welded steel storage tanks were built, and replaced wrought iron tanks.
- In 1923, Chicago Bridge & Iron designed the first floating roof tank for the oil industry (to conserve vapors and eliminate fire hazards).



Above Ground Storage Tanks Today

VOL Storage Vessels

- Storage Vessels that emit VOCs include tanks, reservoirs and containers
- Process tanks, subsurface caverns, and porous rock reservoirs are not VOL storage vessels
- There are three main types of tanks discussed in the VOL storage vessel rules
  - Fixed Roof Tank
  - Internal Floating Roof (IFR)
  - External Floating Roof (EFR)

Common Types of Storage Tanks for Organic Liquid Storage

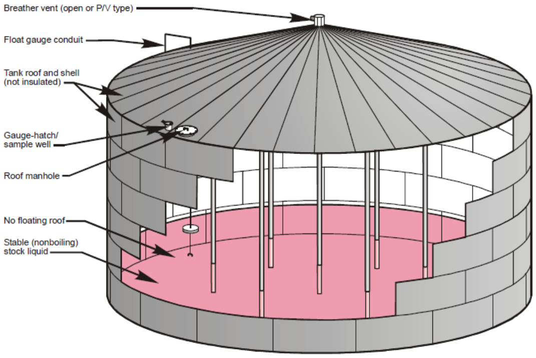
1. *Fixed* roof tanks
   - Fixed roof at top of shell: no floating roof
2. *Internal floating* roof tanks
   - Has both: fixed roof & a <u>light</u> duty floating roof
3. *External floating* roof tanks
   - Open top (no fixed roof), but has a <u>heavyweight</u> floating roof
4. *Domed external (or covered) floating* roof tanks
   - An external type floating roof & a fixed roof
5. *Pressure* tanks: (> 2.5 psig)
   - Used for organic liquids with high vapor pressures.
   - Tanks are horizontal or spherical shape.

Tanks Categorized by Product

Product	Volatility	Vapor Pressure	Tank Type
Crude, Lube Oils	Low	< 1.5 psia	Fixed Roof
Kerosene, Gasoline, & Fuel Oil	Moderate	1.5 – 11.1 psia	Floating Roof
Butane, Propane	High	> 11.1 psia	Pressure

Source: APTI 482 Student Manual "*Sources and Controls of Volatile Organic Compounds*"

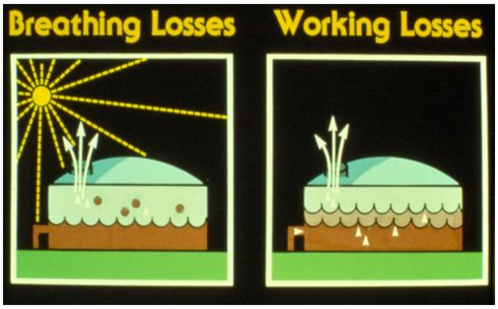
Typical Fixed Roof Tank



Fixed Roof Tank

- No floating roof: VOCs are free to evaporate into the headspace.
- Vented: either *freely* through open vents *or through a pressure/vacuum vent.*
- Least expensive to construct
  - Older tanks: riveted or bolted construction (not vapor tight)
  - Newer tanks: welded construction (vapor tight)
- Generally considered the minimum acceptable equipment for storing VOLs

Fixed Roof Tanks: Two Types of Emission Losses



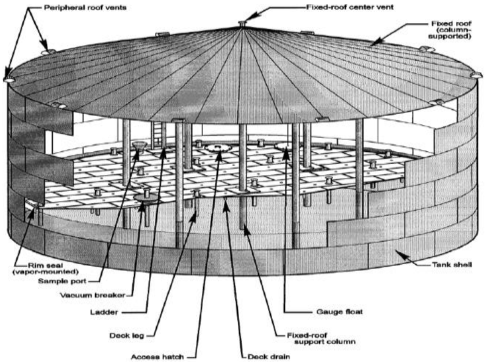
Fixed Roof Tanks: Two Types of Emission Losses

- **Breathing loss** is the expulsion of vapor from a tank through *vapor expansion (evaporation)* as a result of changes in temperature and barometric pressure.
  - This loss occurs without any liquid level change in the tank.
- **Working loss** is the evaporative losses during *filling and emptying* operations.
  - No emissions are attributed to emptying because the flow through the vents would be into the tank

Floating Roof Storage Vessels

- Floating Roof
  - Sits on the liquid surface
  - Reduces vapor space in storage vessel above the liquid
- Floating Roof Components include:
  - Floating Roof Deck
  - Rim Seal Systems
  - Deck Fittings
- Two Types of Floating Roofs
  - External
  - Internal

Internal Floating Roof Tank



Internal Floating Roof Tank

- Has both a permanent fixed roof & a light floating roof inside.
- Internal floating decks are equipped with a rim seal system, which is attached to the deck perimeter and contacts the tank wall.
- The floating deck is also equipped with deck fittings that penetrate the deck and serve operational functions.
- Floating roof covers liquid surface, and the fixed roof is freely vented to atmosphere.
- Floating roof deck is lightweight (aluminum construction)
- Two types of roof decks:
  - Roof that *floats on liquid* surface (contact roof)
  - Roof that is supported by *pontoons* (noncontact roof)
    - Pontoons on & around deck top (above the liquid surface)
    - Pontoons on bottom of deck

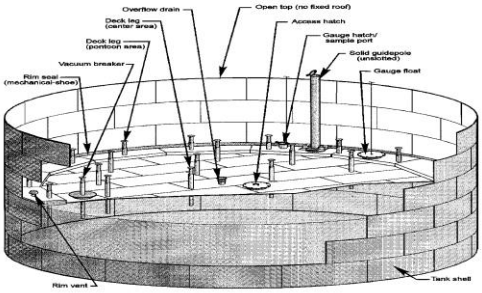
Internal Floating Roof: Aluminum Deck Supported by Pontoons

Contact Aluminum Floating Roof with Bolted Deck Seams

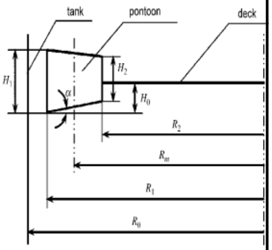
External Floating Roof Tanks

- An external floating roof tank (EFRT) consists of an open-top cylindrical steel shell equipped with a roof that floats on the surface of the stored liquid.
- Floating roof deck is heavyweight & made of welded steel construction (seams are "welded").
- Two types of floating roofs:
  - *Pontoon* (has increased buoyancy & stability):
    - Pontoons occupy 20% to 40% of roof area.
  - *Double deck* is made up of upper & lower decks separated by trusses & bulkheads.
    - Lower deck floats on liquid & the space between decks is separated into liquid- tight compartments.

External Floating Roof (Pontoons)

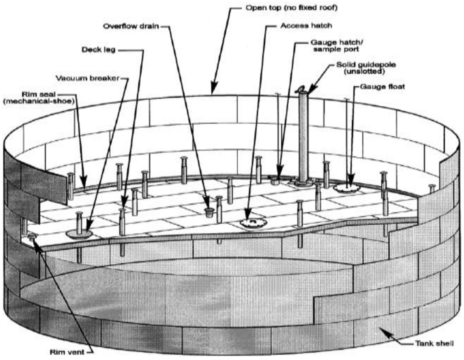


Pontoon Steel Floating Roof

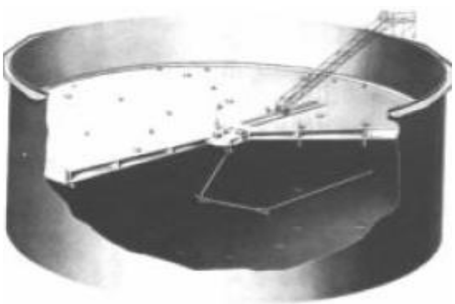


Pontoon Steel Floating Roof

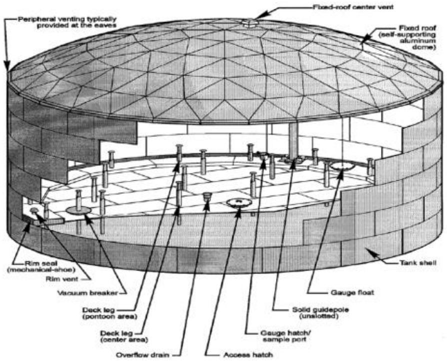
External Floating Roof Tank (Double Deck)



Double Deck Floating Roof



Domed External Floating Roof Tank



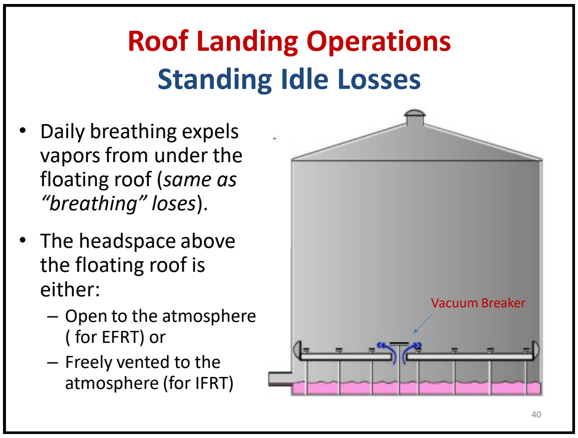
Domed External Floating Roof Tank

- An *external-type* floating roof & a fixed roof
  - Floating roof deck is heavyweight – same as the "external floating roof tank"
  - If floating roof deck is lightweight – tank would then become an "internal floating roof tank."
- Except for weight of floating roof, the "domed external floating roof tank" will have all the same features as an "internal floating roof tank."

Floating Roof Tanks Emissions

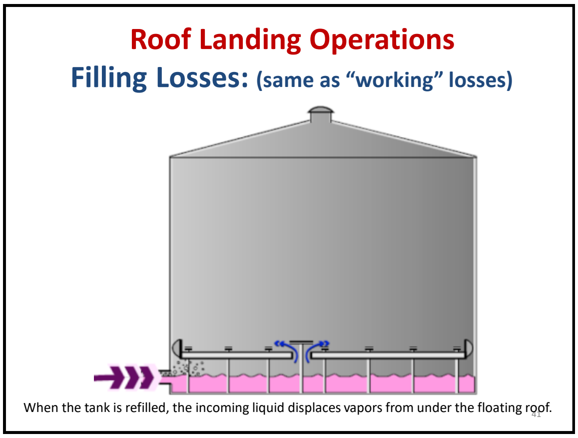
- **There Are *Two Situations* For Estimating Emissions**

1. During **normal operations**
   - Sum of withdrawal losses and standing storage losses
2. During **roof landing operations**: when the tank is emptied to the point that the roof lands on deck legs, *(the roof is not floating)* and other mechanisms must be used to estimate emissions.
   - Sum of "standing idle losses" and "filling losses"



Roof Landing Operations
Standing Idle Losses

- Daily breathing expels vapors from under the floating roof (*same as "breathing" loses*).
- The headspace above the floating roof is either:
  - Open to the atmosphere (for EFRT) or
  - Freely vented to the atmosphere (for IFRT)



Roof Landing Operations
Filling Losses: (same as "working" losses)

When the tank is refilled, the incoming liquid displaces vapors from under the floating roof.

Normal Operations
Floating Roof Tanks Emissions:

- The *emissions* are a *sum* of withdrawal losses and standing storage losses.
- Withdrawal losses result from the evaporation of the *liquid that clings to the tank wall* when the floating roof is lowered.
- Standing storage losses are a result of evaporative losses through *rim seals, deck fittings, and deck seams*.

Floating Roof: Standing Storage Losses

- Deck seams losses from *internal floating roof tanks* with *bolted* decks only. (None from a *welded* deck.)
- Deck fitting losses are the aggregate vapor losses from numerous *fittings that pass through floating roof decks* to accommodate structural support or allow for operational functions.
- The rim seal system slides against the tank wall as the roof is raised and lowered. *It fills the space between the rim and the tank shell* to minimize evaporative losses from this area. Two types of rim seal systems:
  - *Primary seal* or
  - *Secondary seal with a primary seal system*.

External Floating Roof Tanks

- Emission sources:
  - Rim seals,
  - Deck fittings, &
  - Exposed liquid on tank walls (withdrawal losses)
- Floating roof is subject to wind action.
  - Wind action increases rim seal & deck fitting losses.

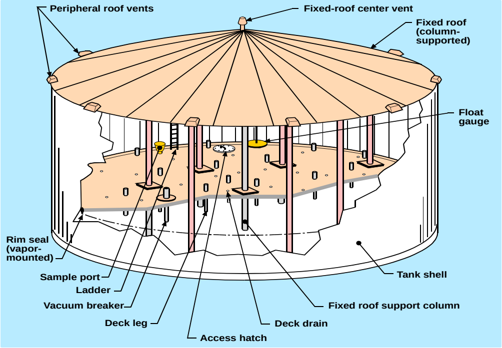
Internal Floating Roof Tanks

- Emission Sources
  - Rim seals,
  - Deck fittings,
  - Deck seams, (because aluminum deck seams cannot be welded, they must be bolted causing emission leaks)
  - Exposed liquid on tank walls (withdrawal losses)
- Wind is not a factor in emissions.
- Converting a *fixed* roof tank to an *internal* floating roof tank reduces emissions by 69% to 98%.

Emission Losses from Floating Roofs

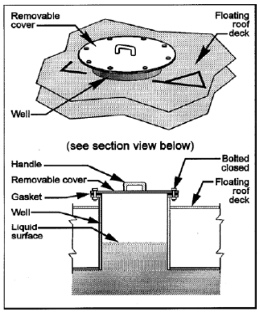
- External Floating Roof VOC emission losses
  - Withdrawal: 4%
  - Rim Seals: 68%
  - Deck Fittings: 28%
- Internal Floating Roof VOC emission losses
  - Withdrawal: 12%
  - Rim Seals: 35%
  - Deck Fittings: 35%
  - Deck Seam losses: 18%
- Note: These % will vary as a function of tank diameter, equipment type (i.e. seals used), & equipment throughput.
- Source: *"Alternative Control Techniques Document: Volatile Organic Liquid Storage in Floating and Fixed Roof Tanks"* EPA-453/R-94-001 (1994)

Internal Floating Roof Tank: Deck Fittings

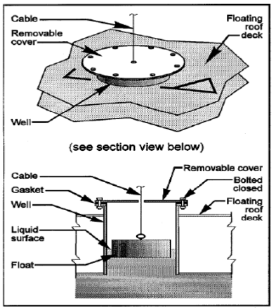


Deck Fittings

Access Hatch: used for construction and servicing

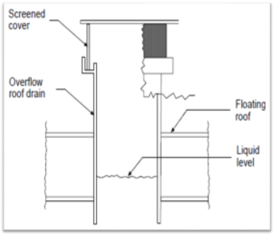


Gauge Float: to indicate the level of liquid within the tank

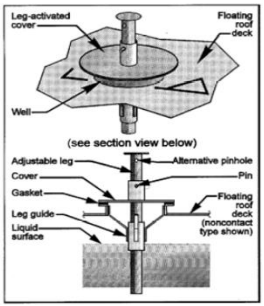


Deck Fittings

<u>Deck Drains</u>: to remove rainwater from an open deck (*external roof only*). 2 types: closed & open: **closed drains** – rainwater never enters product & is drained through a flexible hose. In an **open deck drain** (below) rainwater drains into stored product.



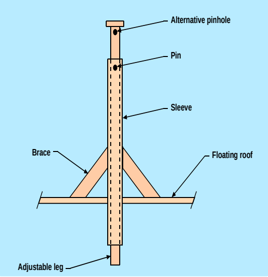
<u>Vacuum Breakers</u>: used to relieve pressure when deck is landed



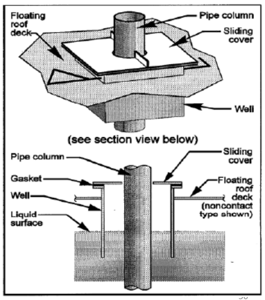
Stub drains. Bolted *internal floating roof decks* are equipped with stub drains to allow any stored product that may be on the deck surface to drain back to the underside of the deck.

Deck Fittings

<u>Deck Leg</u>: to prevent the deck from reaching the tank bottom (when the deck lands). Passes through the deck using a sleeve.



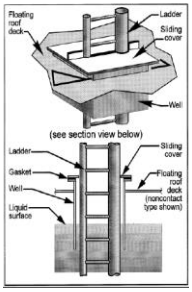
<u>Fixed Roof Support Column</u>: columns used to support fixed roof to tank bottom (passes through floating deck)



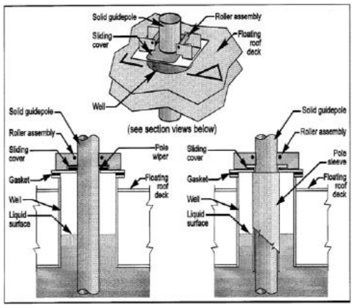
Deck Fittings

<u>Ladder Well</u>

Extends from access hatch on a fixed roof to tank bottom (internal roof only)

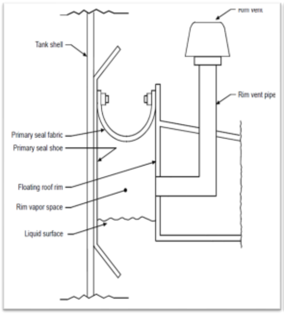


<u>Guide-Poles</u>: attached at top & bottom of tank – used to prevent adverse movement of deck (prevents damaged seals) (slotted & non-slotted)



Rim Seal System & Deck Fittings

Rim Vent: used to release any excess pressure caused by seal



Sample Ports: to allow for sampling of the liquid

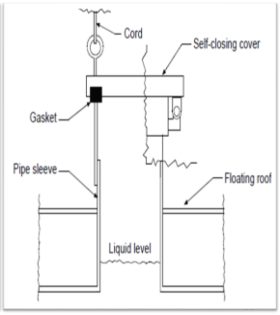


Table 9-3.
Controlled and Uncontrolled Internal Floating Roof Deck Fittings

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

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 System

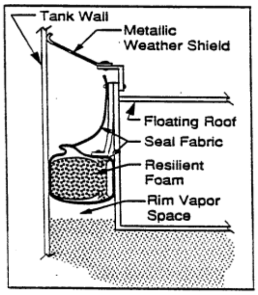
- The rim seal system slides against the tank wall as the roof is raised and lowered. *It fills the space between the rim and the tank shell* to minimize evaporative losses from this area.
- Two types of rim seal systems:
  - *Primary seal* or
  - *Secondary seal with a primary seal system*.

Types of Primary Rim Seals

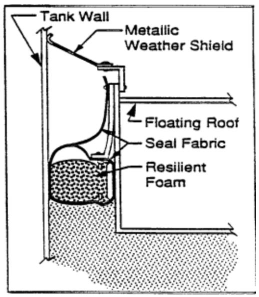
- Vapor-mounted: Highest emissions – fair service history
  - Bottom is not in contact with the liquid surface, therefore there is a vapor space beneath rim seal.
  - Two types: *Flexible-wiper (blade)* type and a *resilient-filled* type (foam within a fabric envelope) (or water-filled)
- Liquid-mounted: lowest emissions – poorest service history
  - Bottom is in contact with liquid surface.
  - *Resilient-filled design* (or water-filled)
- Mechanical-shoe: fairly low emissions – best service history
  - Metallic shoe slides against tank shell;
  - Mechanical device (spring) pushes shoe outward; and
  - Primary seal fabric closes the space between shoe and the rim of the deck

Examples of Primary Seals

Vapor-Mounted Primary Seal



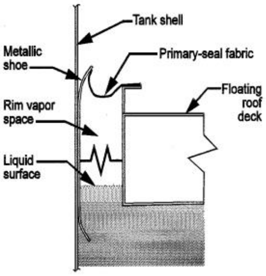
Liquid-Mounted Primary Seal



Examples of Primary Seals

Vapor-Mounted Wiper Primary Seal

Mechanical-Shoe Primary Seal

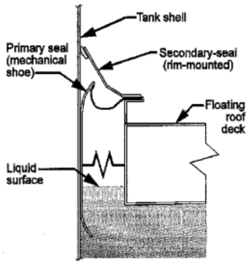


Types of Secondary Rim Seals

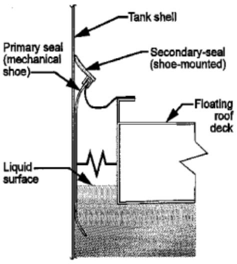
- A secondary seal may be used to provide additional evaporative loss control over that achieved by the primary seal alone.
- Mounted above the primary seal & may be added to any type of primary seal.
- Types of secondary seals are the same as primary seals.

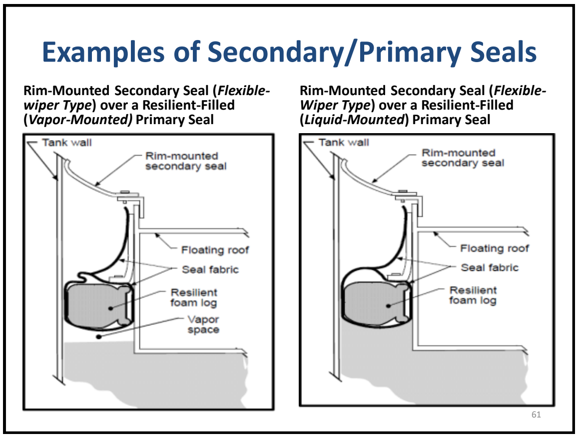
Examples of Secondary/Primary Seals

Rim-Mounted **Secondary Seal (Flexible-wiper Type) over a Mechanical-Shoe Primary Seal**



Shoe-Mounted **Secondary Seal (Flexible-Wiper Type) over a Mechanical-Shoe Primary Seal**

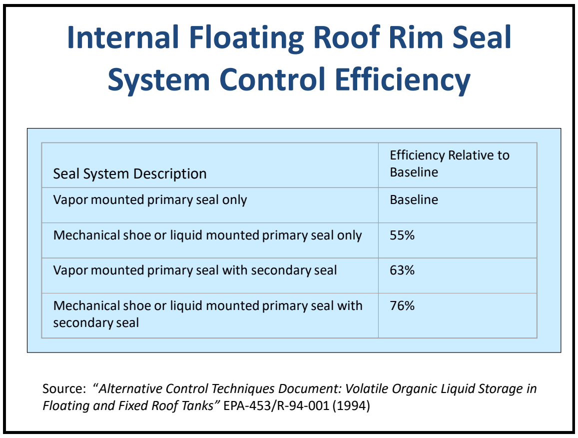




Examples of Secondary/Primary Seals

Rim-Mounted Secondary Seal (*Flexible-wiper Type*) over a Resilient-Filled (*Vapor-Mounted)* Primary Seal

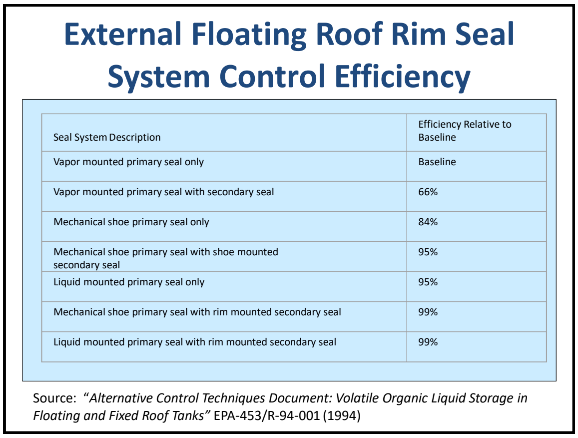
Rim-Mounted Secondary Seal (*Flexible-Wiper Type*) over a Resilient-Filled (*Liquid-Mounted*) Primary Seal



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%

Source: *"Alternative Control Techniques Document: Volatile Organic Liquid Storage in Floating and Fixed Roof Tanks"* EPA-453/R-94-001 (1994)



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%

Source: *"Alternative Control Techniques Document: Volatile Organic Liquid Storage in Floating and Fixed Roof Tanks"* EPA-453/R-94-001 (1994)

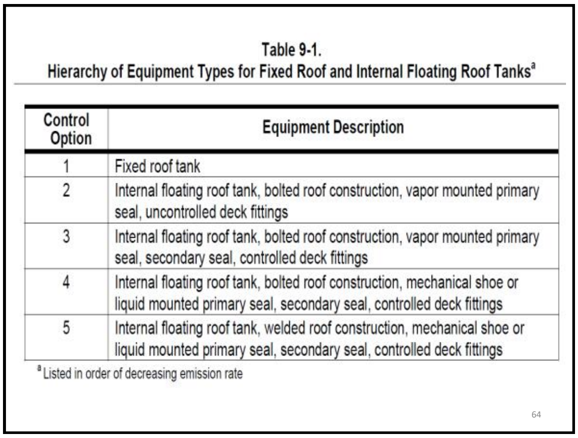


Table 9-1.
Hierarchy of Equipment Types for Fixed Roof and Internal Floating Roof Tanks[a]

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

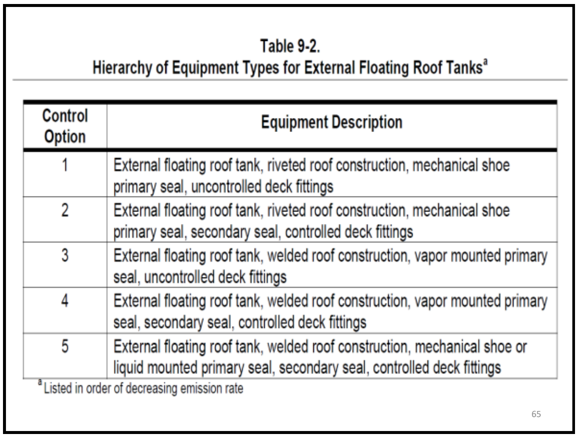
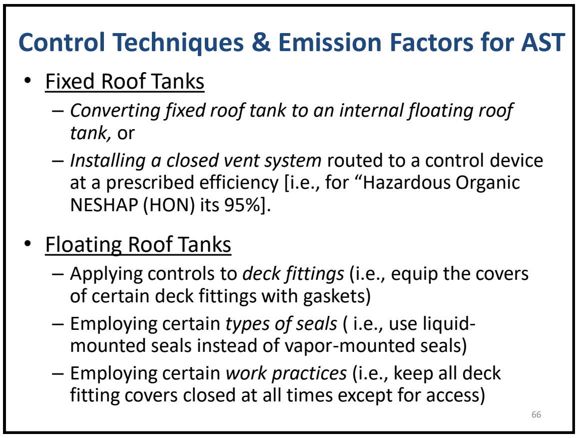


Table 9-2.
Hierarchy of Equipment Types for External Floating Roof Tanks[a]

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



Control Techniques & Emission Factors for AST

- Fixed Roof Tanks
  - *Converting fixed roof tank to an internal floating roof tank,* or
  - *Installing a closed vent system* routed to a control device at a prescribed efficiency [i.e., for "Hazardous Organic NESHAP (HON) its 95%].
- Floating Roof Tanks
  - Applying controls to *deck fittings* (i.e., equip the covers of certain deck fittings with gaskets)
  - Employing certain *types of seals* (i.e., use liquid-mounted seals instead of vapor-mounted seals)
  - Employing certain *work practices* (i.e., keep all deck fitting covers closed at all times except for access)

AP 42 Emission Factors for Storage Tanks

Home / Air Emissions Factors and Quantification

Air Emissions Factors and Quantification

- Basic Information
- AP-42
- Emissions Estimation Tools

Contact Us about Air Emissions Factors

AP 42, Fifth Edition, Volume I Chapter 7: Liquid Storage Tanks

7.0 Introduction to Liquid Storage Tanks (PDF) (1 pg, 10 K, About PDF)

7.1 Organic Liquid Storage Tanks

- Final Section - October 2024 (pdf)
- TANKS Emissions Estimation Software, Version 5

AP 42 Emissions Factors by Chapter

Last updated on December 2, 2024

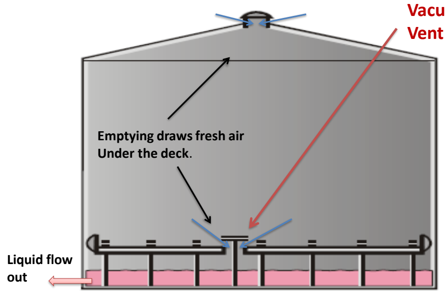
https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-fifth-edition-volume-i-chapter-7-liquid-storage-0

Safety devices for low-pressure storage tanks

- **Vent valves**: These allow for the controlled release of vapors and gases into the atmosphere to maintain internal pressure within safe limits, preventing tank collapse due to vacuum or rupture due to excessive pressure.
- **Emergency relief valve**: Automatically activated to release excess pressure if other control systems fail, they provide safety against excessive pressurization.
- **Flame arrestors**: Installed on vent lines, these prevent an external flame from entering the tank, protecting against explosions.
- **Level indicator**: These devices monitor and control the liquid level inside the tank and prevent overfilling or excessive emptying, both scenarios that could lead to hazardous situations.
- **Automatic leak detection**: Designed to detect the presence of vapors or liquids outside the tanks and alert personnel to take corrective measures.
- **Secondary Containment barriers**: Surrounding structures around the tank to contain the spread of spills or leaks.

Venting for Floating Roof Tanks -When Landed

(To prevent a vacuum that would collapse deck)



Just before the "deck support leg" touches the tank bottom, the "leg-actuated *vacuum breaker*" will contact the bottom first & lift the lid of the vacuum breaker

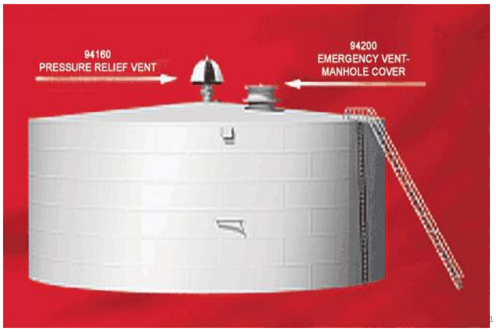
The breather vent remains open until the roof is again floated, so whenever the roof is landed, vapor can be lost through this vent. These losses are called "standing idle losses."

Venting of Fixed-Roof Tanks

- Tank “out-breathing” causes a *positive pressure* within tank. It occurs:
  - From liquid filling operations
  - When heated gases in tank expand, raising the pressure (i.e. caused by the sun).
- Tank “in-breathing” causes a *negative pressure* within tank when liquid is withdrawn from tank.

Venting for Atmospheric Tanks

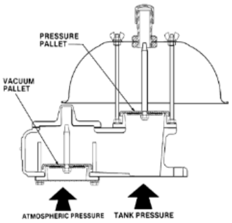
Vents are necessary: 1. To prevent excess pressure & 2. To prevent excess vacuum



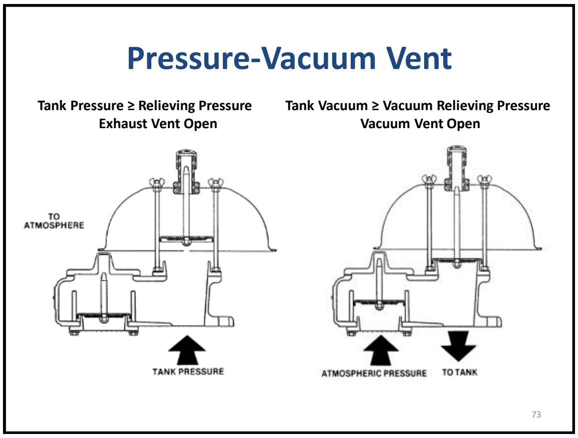
Pressure-Vacuum Vent

L & J Technologies
Open Vent Model: Weight loaded

Vents Closed: Tank at Operating Pressure (Normal Operation)



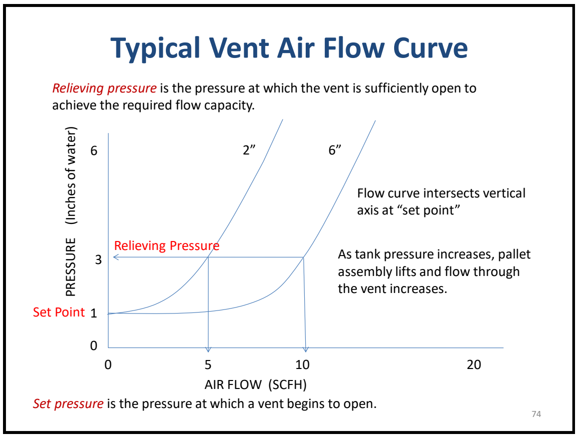
Vents should not leak (< 500ppm from 40 CFR 61 subpart V “Equipment Leaks” sect. 242-11 – standard for closed vent systems).



Pressure-Vacuum Vent

Tank Pressure ≥ Relieving Pressure
Exhaust Vent Open

Tank Vacuum ≥ Vacuum Relieving Pressure
Vacuum Vent Open



Typical Vent Air Flow Curve

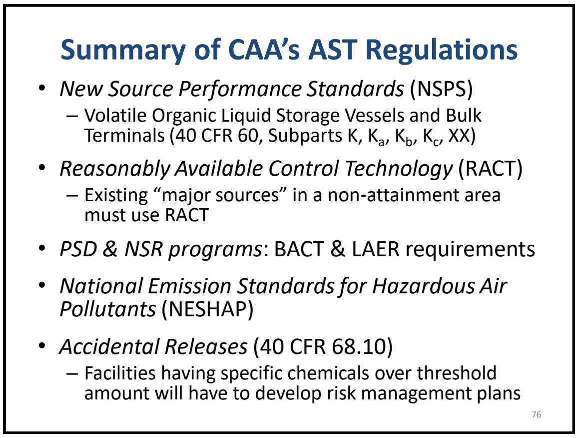
Relieving pressure is the pressure at which the vent is sufficiently open to achieve the required flow capacity.

Flow curve intersects vertical axis at “set point”

As tank pressure increases, pallet assembly lifts and flow through the vent increases.

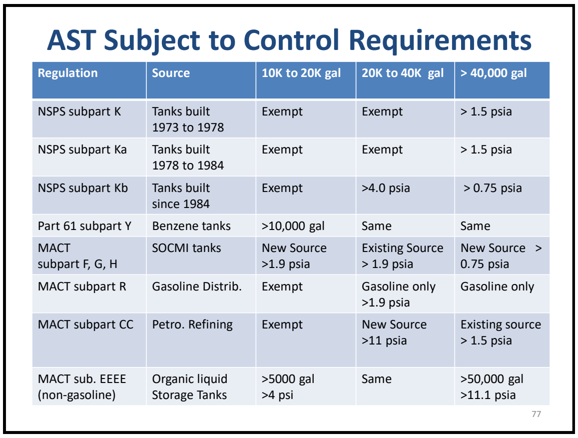
Set pressure is the pressure at which a vent begins to open.

Clean Air Act Regulations for Aboveground Storage Tanks (AST)



Summary of CAA's AST Regulations

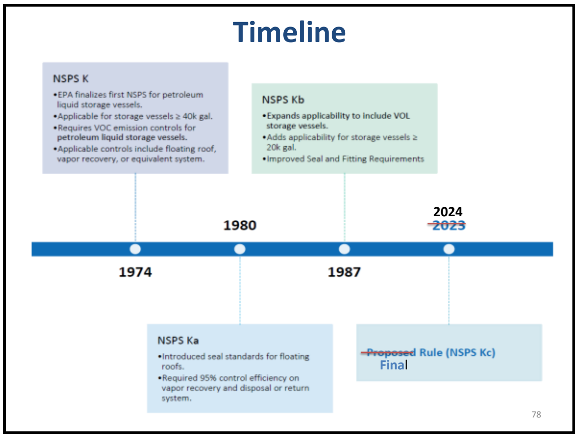
- *New Source Performance Standards* (NSPS)
  - Volatile Organic Liquid Storage Vessels and Bulk Terminals (40 CFR 60, Subparts K, K_a, K_b, K_c, XX)
- *Reasonably Available Control Technology* (RACT)
  - Existing "major sources" in a non-attainment area must use RACT
- *PSD & NSR programs*: BACT & LAER requirements
- *National Emission Standards for Hazardous Air Pollutants* (NESHAP)
- *Accidental Releases* (40 CFR 68.10)
  - Facilities having specific chemicals over threshold amount will have to develop risk management plans



AST Subject to Control Requirements

Regulation	Source	10K to 20K gal	20K to 40K gal	> 40,000 gal
NSPS subpart K	Tanks built 1973 to 1978	Exempt	Exempt	> 1.5 psia
NSPS subpart Ka	Tanks built 1978 to 1984	Exempt	Exempt	> 1.5 psia
NSPS subpart Kb	Tanks built since 1984	Exempt	>4.0 psia	> 0.75 psia
Part 61 subpart Y	Benzene tanks	>10,000 gal	Same	Same
MACT subpart F, G, H	SOCMI tanks	New Source >1.9 psia	Existing Source > 1.9 psia	New Source > 0.75 psia
MACT subpart R	Gasoline Distrib.	Exempt	Gasoline only >1.9 psia	Gasoline only
MACT subpart CC	Petro. Refining	Exempt	New Source >11 psia	Existing source > 1.5 psia
MACT sub. EEEE (non-gasoline)	Organic liquid Storage Tanks	>5000 gal >4 psi	Same	>50,000 gal >11.1 psia

Timeline



NSPS K
- EPA finalizes first NSPS for petroleum liquid storage vessels.
- Applicable for storage vessels ≥ 40k gal.
- Requires VOC emission controls for **petroleum liquid storage vessels.**
- Applicable controls include floating roof, vapor recovery, or equivalent system.

NSPS Kb
- Expands applicability to include VOL storage vessels.
- Adds applicability for storage vessels ≥ 20k gal.
- Improved Seal and Fitting Requirements

NSPS Ka
- Introduced seal standards for floating roofs.
- Required 95% control efficiency on vapor recovery and disposal or return system.

~~Proposed~~ Rule (NSPS Kc) Final

NSPS: 40 CFR 60 Subpart K, Ka, & Kb

- **Subpart K** (§ 60.110 to § 60.113)—Standards of Performance for *Storage Vessels* for *Petroleum Liquids* built after *June 11, 1973*, and Prior to May 19, 1978.
- **Subpart Ka** (§ 60.110a to § 60.115a)—Standards of Performance for *Storage Vessels* for *Petroleum Liquids* built after *May 18, 1978*, and Prior to July 24, 1984.
- **Subpart Kb** (§ 60.110b to § 60.117b) - Standards of Performance for *Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels)* built after *July 23, 1984*.

Organic Liquids Definitions

- Organic liquids in the petroleum industry, usually called *petroleum liquids*, generally are mixtures of hydrocarbons having dissimilar true vapor pressures (i.e., gasoline & crude oil).
- Organic liquids in the chemical industry, usually called *volatile organic liquids*, are composed of chemicals with similar true vapor pressures (for example, benzene or a mixture of isopropyl and butyl alcohols).

Existing Organic Liquid Storage Tanks

- Existing major sources in an ozone nonattainment area may have organic liquid storage tanks.
- RACT will apply to these organic liquid storage tanks.
- States use *Control Technology Guidelines* (CTG) & *Alternative Control Techniques* (ACT) as basis for their RACT determination:
  - 1977 CTG recommended RACT to be like NSPS subpart K
  - 1978 CTG recommended RACT to be like NSPS subpart Ka
  - 1994 ACT recommended RACT to be like NSPS subpart Kb

Subpart K Control Requirements for Storage Vessels > 40,000 Gallons

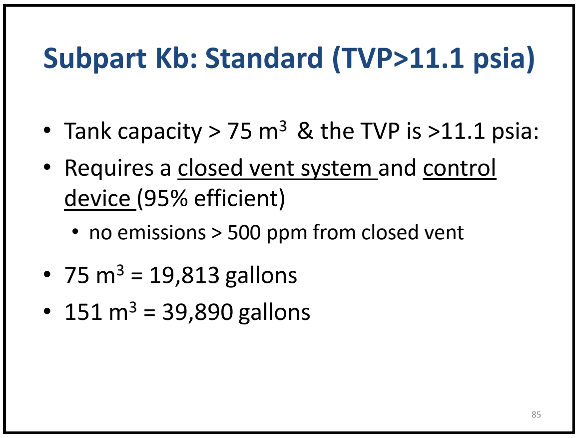
Vapor Pressure (psia)	Fixed Roof Tank	Floating Roof Tank
≥ 1.5 but ≤ 11.1	Install a floating roof	No change required
> 11.1	Vapor recovery or a control system	Vapor recovery or a control system

Subpart Ka Control Requirements for Storage Vessels > 40,000 Gallons

Vapor Pressure (psia)	Internal Floating Roof Tank	External Floating Roof Tank	Fixed Roof Tank
> 1.5 but < 11.1	A Primary seal alone	Primary & secondary seal required; & Pan-type deck is eliminated	Install floating roof with seals <u>or</u> control system that is 95% efficient
> 11.1	Control system that is 95% efficient	Control system that is 95% efficient	Control system that is 95% efficient

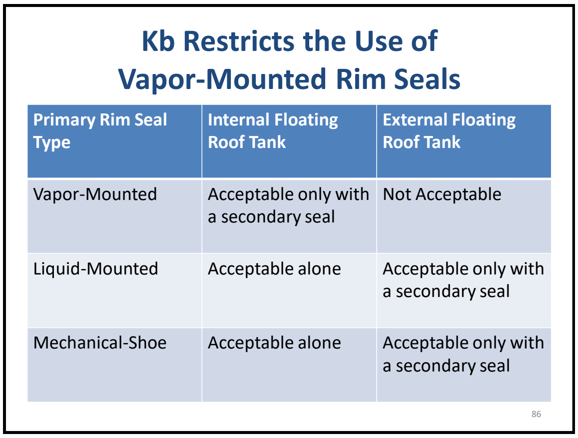
Subpart Kb: Standard (TVP<11.1 psia)

- Tank capacity ≥ 75 m³ but < 151 m³ &
  - TVP ≥4.0 psia but <11.1 psia
- Tank capacity ≥ 151 m³ &
  - TVP ≥ 0.75 psia but <11.1 psia
- For both of these, the vessel shall use one of the following:
  - A pontoon-type or double-deck-type <u>external floating roof</u> that floats on the surface of the liquid and is equipped with a *mechanical shoe or liquid mounted primary seal* <u>and</u> with a *secondary seal* (additional requirements);
  - A fixed roof with an <u>internal floating roof</u> equipped with a *mechanical shoe or liquid mounted primary seal* <u>or</u> with *both primary and secondary seals* (additional requirements); or
  - A <u>closed vent system</u> and <u>control device</u> (95% efficient)
    - no emissions > 500 ppm from closed vent



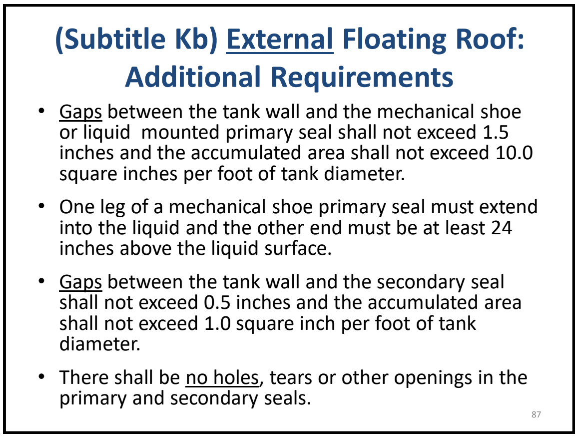
Subpart Kb: Standard (TVP>11.1 psia)

- Tank capacity > 75 m^3 & the TVP is >11.1 psia:
- Requires a closed vent system and control device (95% efficient)
  - no emissions > 500 ppm from closed vent
- 75 m^3 = 19,813 gallons
- 151 m^3 = 39,890 gallons



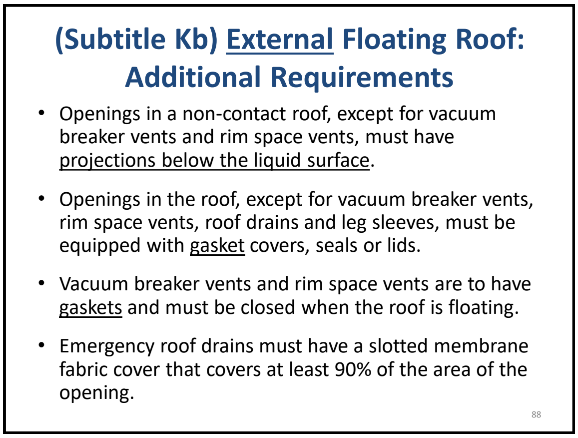
Kb Restricts the Use of Vapor-Mounted Rim Seals

Primary Rim Seal Type	Internal Floating Roof Tank	External Floating Roof Tank
Vapor-Mounted	Acceptable only with a secondary seal	Not Acceptable
Liquid-Mounted	Acceptable alone	Acceptable only with a secondary seal
Mechanical-Shoe	Acceptable alone	Acceptable only with a secondary seal



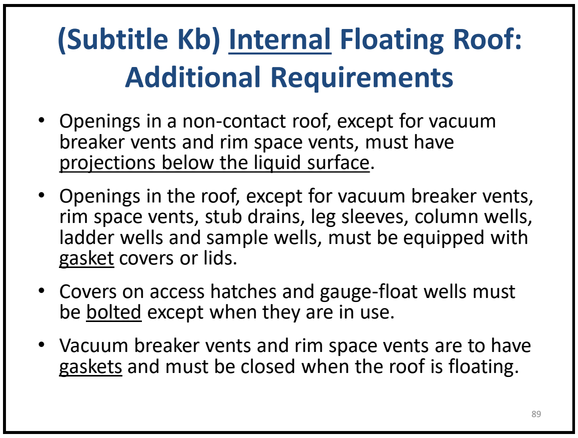
(Subtitle Kb) External Floating Roof: Additional Requirements

- 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.
- 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.
- 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.
- There shall be no holes, tears or other openings in the primary and secondary seals.



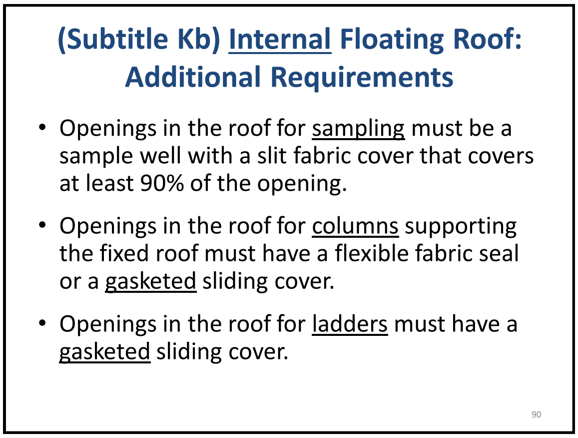
(Subtitle Kb) External Floating Roof: Additional Requirements

- Openings in a non-contact roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface.
- Openings in the roof, except for vacuum breaker vents, rim space vents, roof drains and leg sleeves, must be equipped with gasket covers, seals or lids.
- Vacuum breaker vents and rim space vents are to have gaskets and must be closed when the roof is floating.
- Emergency roof drains must have a slotted membrane fabric cover that covers at least 90% of the area of the opening.



(Subtitle Kb) Internal Floating Roof: Additional Requirements

- Openings in a non-contact roof, except for vacuum breaker vents and rim space vents, must have projections below the liquid surface.
- 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 gasket covers or lids.
- Covers on access hatches and gauge-float wells must be bolted except when they are in use.
- Vacuum breaker vents and rim space vents are to have gaskets and must be closed when the roof is floating.



(Subtitle Kb) Internal Floating Roof: Additional Requirements

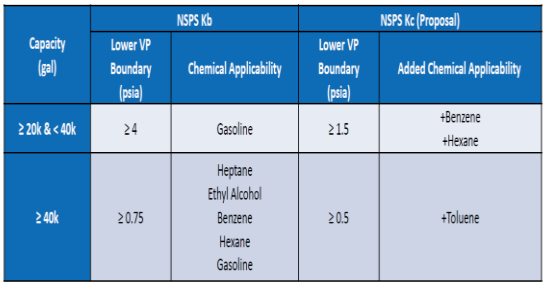
- Openings in the roof for sampling must be a sample well with a slit fabric cover that covers at least 90% of the opening.
- Openings in the roof for columns supporting the fixed roof must have a flexible fabric seal or a gasketed sliding cover.
- Openings in the roof for ladders must have a gasketed sliding cover.

Inspection for Gaps & Holes in Tank Primary and Secondary Seals

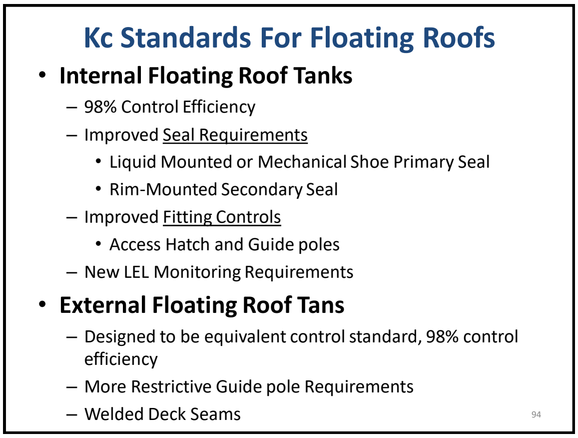
NSPS Subtitle Kc

- **On Oct 15, 2024**, EPA finalized 40 CFR **Subtitle Kc**.
- Subpart Kc applies to facilities that begin construction, or modification after October 4, 2023.
- Subpart Kc, finalized requirements to:
  - reduce the vapor pressure applicability thresholds and
  - revise the (VOC) standards to reflect the best system of emission reduction (BSER) for affected storage vessels.
- In addition, the EPA is finalizing degassing emission controls; clarification of startup, shutdown, and malfunction (SSM) requirements; additional monitoring requirements; and other technical improvements.

Subtitle Kc: Storage Vessels Required to Control

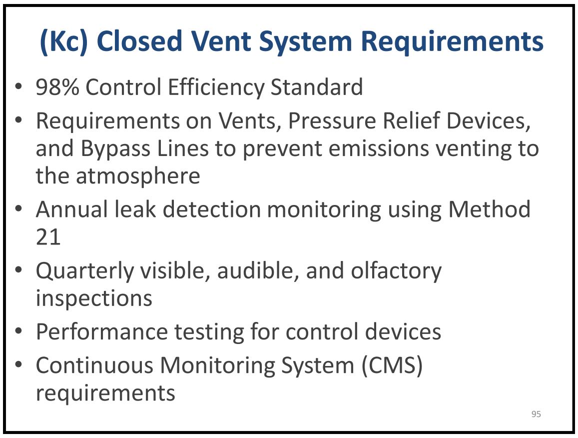


Capacity (gal)	NSPS Kb		NSPS Kc (Proposal)	
	Lower VP Boundary (psia)	Chemical Applicability	Lower VP Boundary (psia)	Added Chemical Applicability
≥ 20k & < 40k	≥ 4	Gasoline	≥ 1.5	+Benzene +Hexane
≥ 40k	≥ 0.75	Heptane Ethyl Alcohol Benzene Hexane Gasoline	≥ 0.5	+Toluene



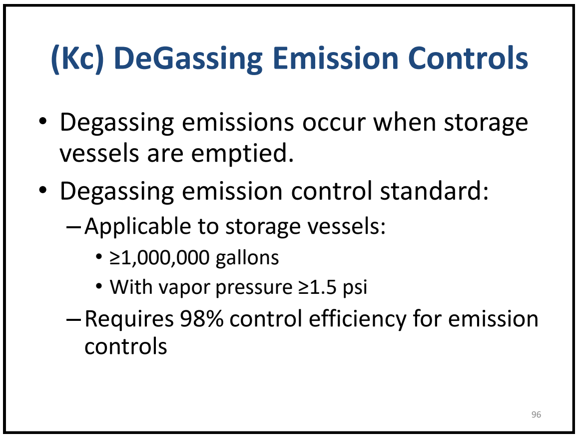
Kc Standards For Floating Roofs

- **Internal Floating Roof Tanks**
  - 98% Control Efficiency
  - Improved Seal Requirements
    - Liquid Mounted or Mechanical Shoe Primary Seal
    - Rim-Mounted Secondary Seal
  - Improved Fitting Controls
    - Access Hatch and Guide poles
  - New LEL Monitoring Requirements
- **External Floating Roof Tans**
  - Designed to be equivalent control standard, 98% control efficiency
  - More Restrictive Guide pole Requirements
  - Welded Deck Seams



(Kc) Closed Vent System Requirements

- 98% Control Efficiency Standard
- Requirements on Vents, Pressure Relief Devices, and Bypass Lines to prevent emissions venting to the atmosphere
- Annual leak detection monitoring using Method 21
- Quarterly visible, audible, and olfactory inspections
- Performance testing for control devices
- Continuous Monitoring System (CMS) requirements



(Kc) DeGassing Emission Controls

- Degassing emissions occur when storage vessels are emptied.
- Degassing emission control standard:
  - Applicable to storage vessels:
    - ≥1,000,000 gallons
    - With vapor pressure ≥1.5 psi
  - Requires 98% control efficiency for emission controls

(Kc) Monitoring, Recordkeeping, & Reporting Requirements

Internal Floating Roofs
- Annual Roof Top Visual Inspections
- Annual Lower Explosive Limit (LEL) Monitoring
- 10-Year Out-of-Service Inspection
- Alarm System for Monitoring Landing Events

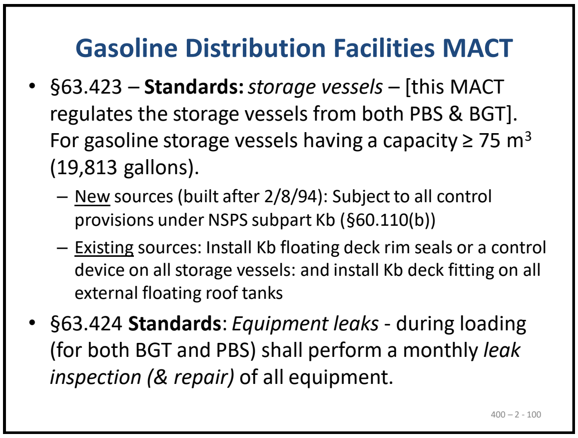
External Floating Roofs
- Gap Measurements
- Annually for Secondary Seal
- Every five years for Primary Seal
- Alarm System for Monitoring Landing Events

Closed Vent Systems
- Requirements on Conservation Vents, Pressure Relief Devices, and Bypass Lines to prevent emissions venting to the atmosphere
- Annual leak detection monitoring using Method 21
- Quarterly visible, audible, and olfactory inspections
- Performance Testing for Control Devices
- Continuous Monitoring System (CMS)

Gasoline Distribution MACT

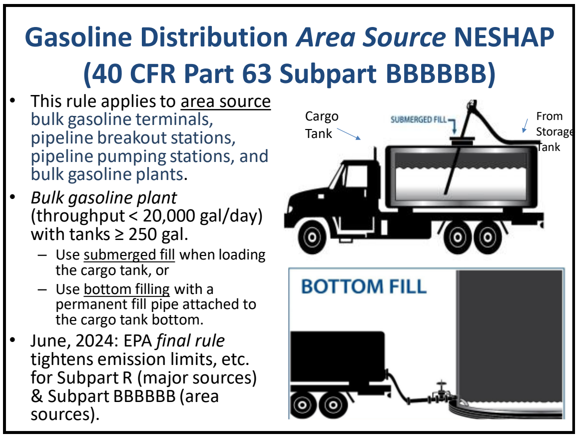
Gasoline Distribution Facilities MACT
40 CFR Part 63 Subpart R

- §63.420 - **Applicability**: Applies to Bulk Gasoline Terminals (BGT) or Pipeline Breakout Stations (PBS) that are a HAP major source.
  - BGT & PBS are then "screen tested" for applicability.
- §63.421 – **Definitions**: PBS means any facility along a pipeline containing *storage vessels* used … to store gasoline from the pipeline… and continue transport…
- §63.422 – **Standards:** *loading racks* **–** [this MACT regulates the *loading racks* from only the BGT]
  - Meet the NSPS for Bulk Gasoline Terminals &
  - Install a vapor collection system with emissions < 10 mg VOC/liter gasoline



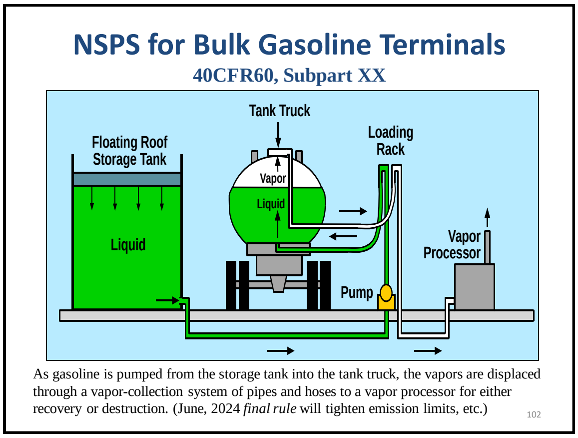
Gasoline Distribution Facilities MACT

- §63.423 – **Standards:** *storage vessels* – [this MACT regulates the storage vessels from both PBS & BGT]. For gasoline storage vessels having a capacity ≥ 75 m^3 (19,813 gallons).
  - New sources (built after 2/8/94): Subject to all control provisions under NSPS subpart Kb (§60.110(b))
  - Existing sources: Install Kb floating deck rim seals or a control device on all storage vessels: and install Kb deck fitting on all external floating roof tanks
- §63.424 **Standards**: *Equipment leaks* - during loading (for both BGT and PBS) shall perform a monthly *leak inspection (& repair)* of all equipment.



Gasoline Distribution *Area Source* NESHAP (40 CFR Part 63 Subpart BBBBBB)

- This rule applies to area source bulk gasoline terminals, pipeline breakout stations, pipeline pumping stations, and bulk gasoline plants.
- *Bulk gasoline plant* (throughput < 20,000 gal/day) with tanks ≥ 250 gal.
  - Use submerged fill when loading the cargo tank, or
  - Use bottom filling with a permanent fill pipe attached to the cargo tank bottom.
- June, 2024: EPA *final rule* tightens emission limits, etc. for Subpart R (major sources) & Subpart BBBBBB (area sources).



NSPS for Bulk Gasoline Terminals

40CFR60, Subpart XX

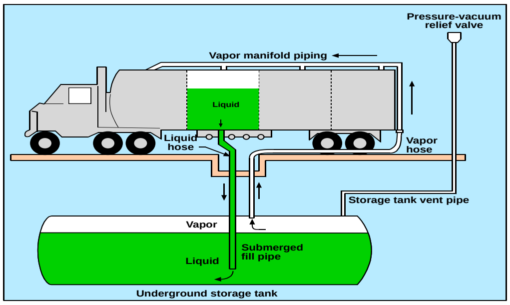
As gasoline is pumped from the storage tank into the tank truck, the vapors are displaced through a vapor-collection system of pipes and hoses to a vapor processor for either recovery or destruction. (June, 2024 *final rule* will tighten emission limits, etc.)

Control Technology Guidelines (CTG) for RACT Determinations for Existing Sources

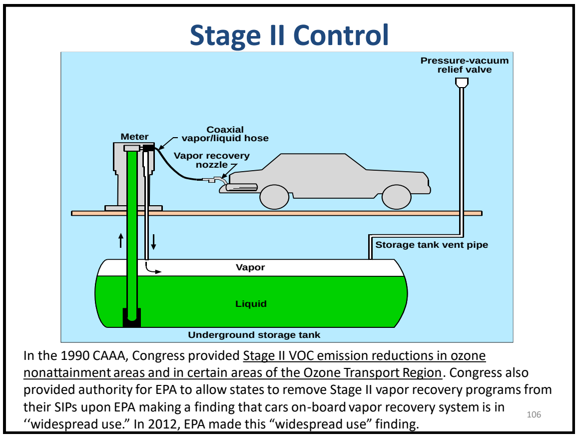
- Control of VOCs from <u>Bulk Gasoline Plants</u>, CTG Document, EPA-450/2-77-035
- Control of VOCs from <u>Tank Truck Gasoline Loading Terminals</u>, CTG Document, EPA-450/2-77-026
- Control of VOC <u>Leaks from Gasoline Tank Trucks and Vapor Collection Systems</u>, CTG Guideline Document, EPA-450/2-78-051

Gasoline Service Station: Stage 1 and Stage 2 Controls

Stage I Control



<u>EPA CTG</u>: ‘‘Design Criteria for Stage I Vapor Control Systems—Gasoline Service Stations’’ (November 1975, EPA 450R75102)



Stage II Control

In the 1990 CAAA, Congress provided Stage II VOC emission reductions in ozone nonattainment areas and in certain areas of the Ozone Transport Region. Congress also provided authority for EPA to allow states to remove Stage II vapor recovery programs from their SIPs upon EPA making a finding that cars on-board vapor recovery system is in ‘‘widespread use.” In 2012, EPA made this “widespread use” finding.

Chapter 10

Degreasing

Federal NESHAPS/MACT For Halogenated Compounds

(40 CFR 63 Subpart T)

- Applicability
- Exemptions
- Standards
- Tests, Recordkeeping & Reporting

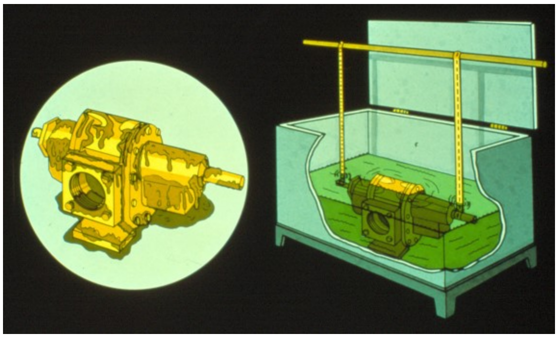
Halogenated Solvents, NESHAP Degreasing

- Sources (regardless of annual emissions) using:
  - Batch Cold Cleaning Machines
  - Batch Vapor Cleaning Machines
  - In-line Vapor Cleaning Machines Using:
    - Methyl Chloride
    - Trichloroethylene
    - Carbon Tetrachloride
    - n-Propyl Bromide
    - Perchloroethylene
    - 1,1,1-trichloroethane
    - Chloroform

Hal. Sol. NESHAP - Degreasing

- Total concentration of one or more of the six solvents must exceed five percent by weight for the rule to apply
- Does not apply to hand wiping
- Contains 2 gallons or Less

Soiling on Surfaces



Soil Categories

- Organics
  - rosins, glycols, oils, greases, waxes
- Water Soluble Inorganic Salts
  - chlorides, sulfates, etc.
- Insoluble Particles
  - dirt, dust, metal fines, etc.

Types of Degreasing Equipment

- Cold cleaners
- Open top vapor cleaners
- In-line cleaners
- Non-air vapor interface

Degreasing Solvents

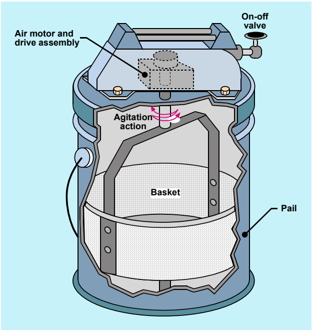
- Mineral spirits
- Stoddard solvents
- Alcohols
- Halogenated solvents
- N-propyl bromide *
- Hydrofluoroether
- Proprietary blends

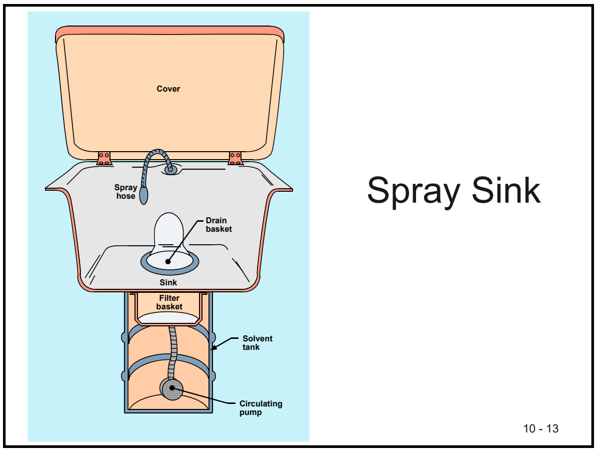
Halogenated Solvents

- Methylene chloride
- Perchloroethylene
- Trichloroethylene
- Hydrochlorofluorocarbons

Cold Cleaners

Carburetor Cleaner

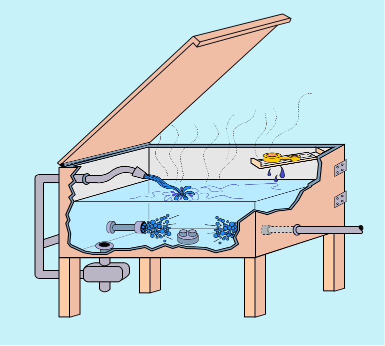


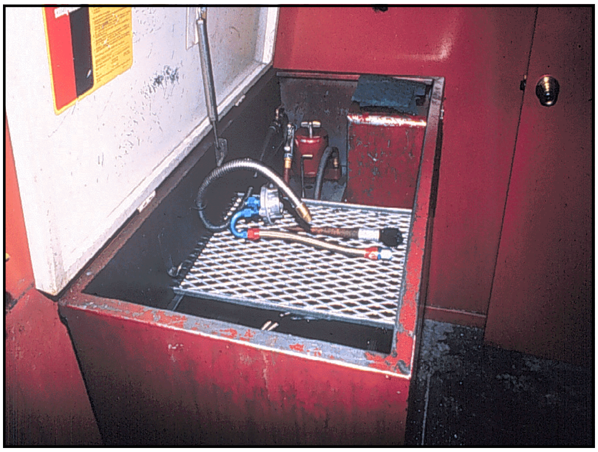


Spray Sink

Wash Basin with Remote Reservoir

Dip Tank Cold Cleaner





Batch Cold Cleaning Machine Standards

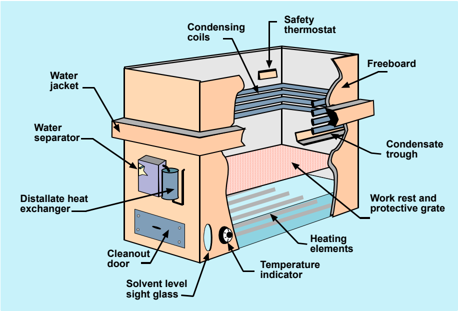
- National Emission Standards for Halogenated Solvent Cleaning, 40 CFR 63, Subpart T Applicability: Batch vapor, in-line vapor, in-line cold and batch cold cleaning machines that contain methylene chloride, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane
- RACT guidelines for degreasers are 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.

Potential Sources of Emissions

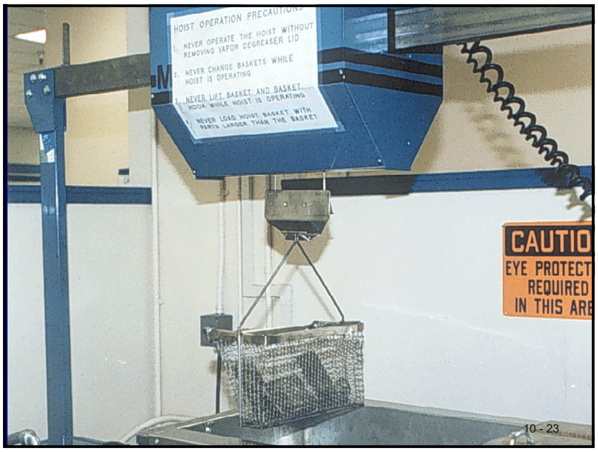
- Waste solvent disposal
- Solvent carryout
- Bath evaporation

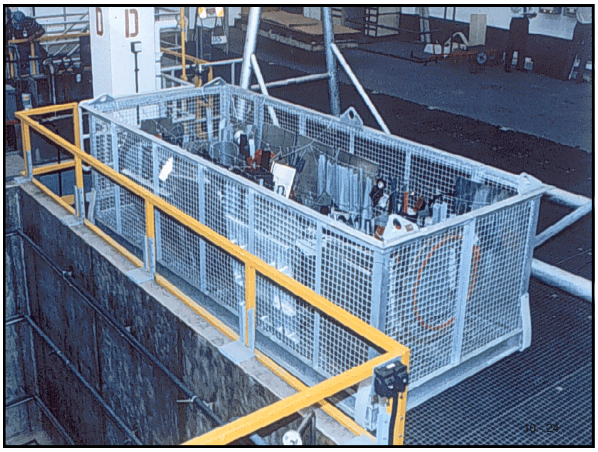
Open Top Vapor Cleaners

Open Top Vapor Cleaner




DEGREASER


HOIST OPERATION PRECAUTIONS
1. NEVER OPERATE THE HOIST WITHOUT REMOVING VAPOR DEGREASER LID
2. NEVER CHANGE BASKETS WHILE HOIST IS OPERATING
3. NEVER LIFT BASKET AND BASKET HOOK WHILE HOIST IS OPERATING
4. NEVER LOAD HOIST BASKET WITH PARTS LARGER THAN THE BASKET
CAUTIO
EYE PROTECT
REQUIRED
IN THIS ARE
10 - 23


10 - 24

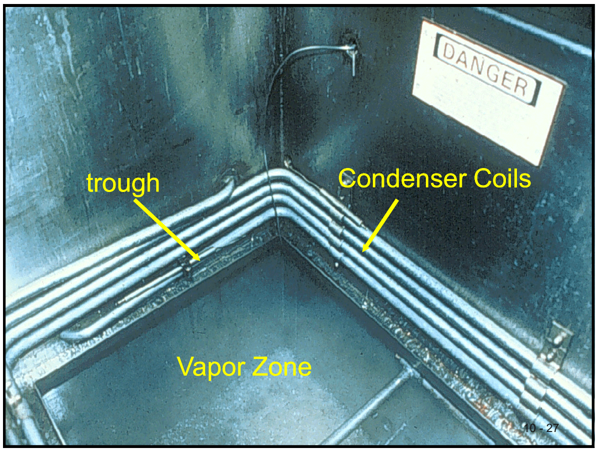
Open Top Vapor Cleaners

Important Elements:

- Condenser Coils
- Freeboard
- Water Separators
- Covers

Cooling Coils

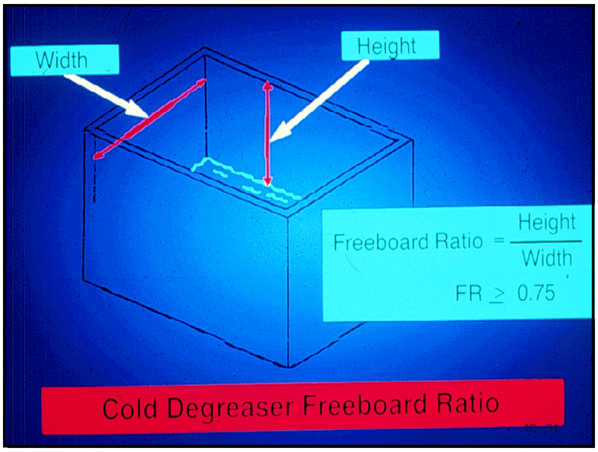
- Located On Inside Walls Of Cleaner
- Contains Vapor Zone With Cool Air Blanket Cover
- Usually Has Water As The Coolant



Freeboard

- Protects The Solvent Vapor Zone From Disturbance Caused By Air Movement Around The Equipment
- Generally Established By The Location Of The Condenser Coils

Measuring Freeboard



Freeboard Ratio = $\frac{\text{Height}}{\text{Width}}$

FR $\geq$ 0.75

Cold Degreaser Freeboard Ratio

High Freeboard

- Distance From The Top Of The Solvent To The Top Of The Tank Reduces Draft Near Air/Solvent interface
- Minimum Recommended Ratio = 0.75
- Ratio Of 1.0 - In the Subpart T Regulation Control Combination Tables
- OSHA Requires at Least 6" For Cold Cleaners

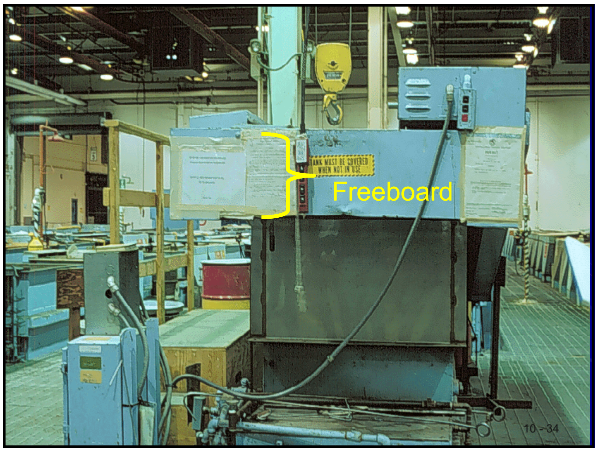
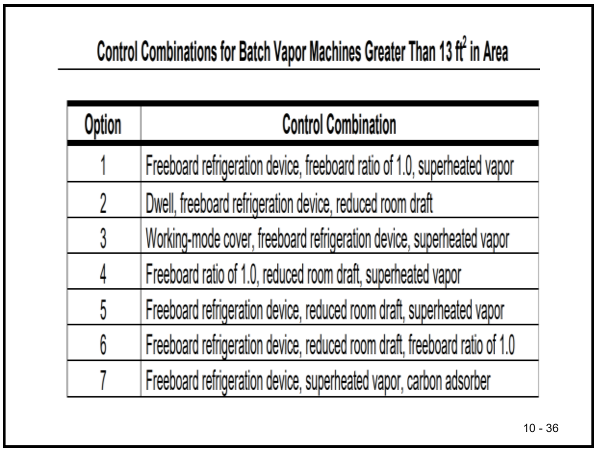


TABLE 1—CONTROL COMBINATIONS FOR BATCH VAPOR SOLVENT CLEANING MACHINES WITH A SOLVENT/AIR INTERFACE AREA OF 1.21 SQUARE METERS (13 SQUARE FEET) OR LESS

- Option Control combinations
- 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.

- (2) Each cleaning machine shall have a freeboard ratio of 0.75 or greater.
- (3) Each cleaning machine shall have an automated parts handling system
- capable of moving parts or parts baskets at a speed of 3.4 meters per minute
- (11 feet per minute) or less from the initial loading of parts through removal of cleaned



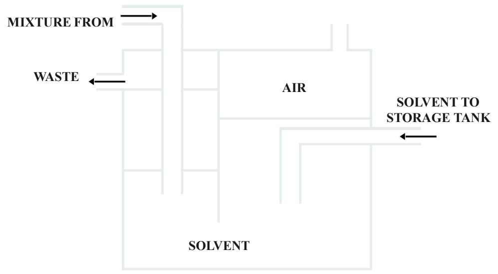
Control Combinations for Batch Vapor Machines Greater Than 13 ft^2 in Area

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

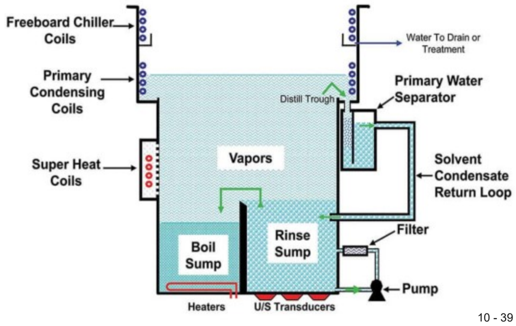
Water Separators

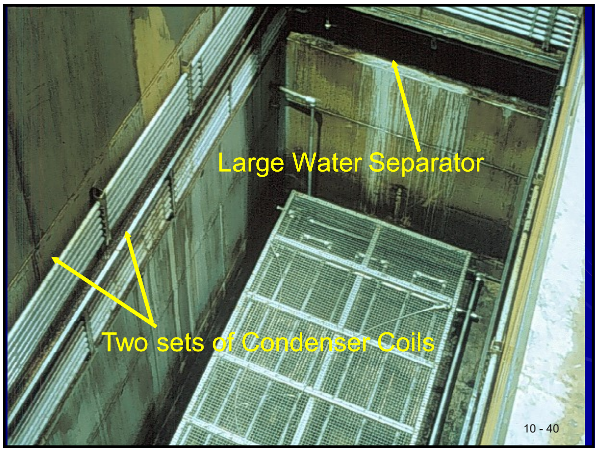
1. Nearly All Vapor Cleaners Have Water Separators
2. These Allow The Water That Condenses On The Coils To Separate From The Solvent Before The Solvent Is Reintroduced In The System

WATER SEPARATOR



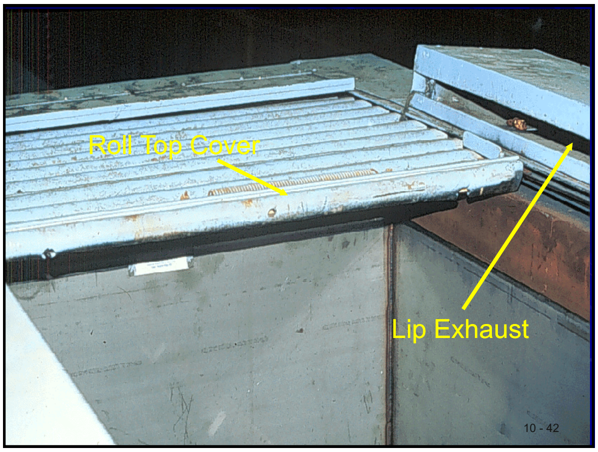
Details of Vapor Degreaser Design





Covers

- Historically Single Piece, Unhinged Metal Cover
- Newer Designs Might Have:
    - Roll-top Plastic Covers
    - Canvas Curtains
    - Hinged Counter Balanced Metal Covers



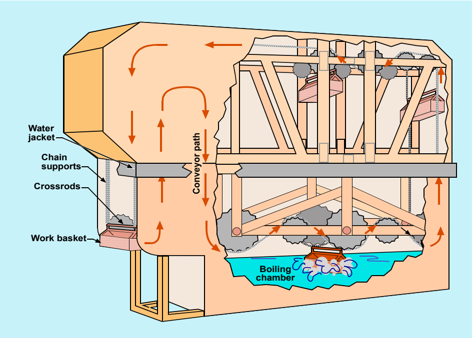
Potential Sources of Emissions

- Waste solvent disposal
- Solvent carryout
- Bath evaporation

In-Line Cleaners

- There Are Seven Different Types:
  - Cross-Rod
  - Monorail
  - Vibra
  - Ferris Wheel
  - Belt
  - Strip
  - Circuit Board

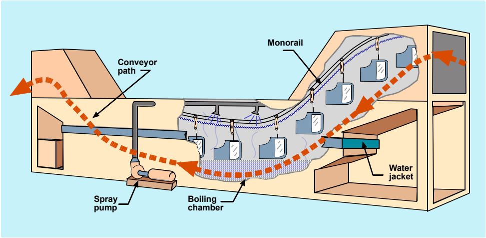
Cross-Rod Cleaner



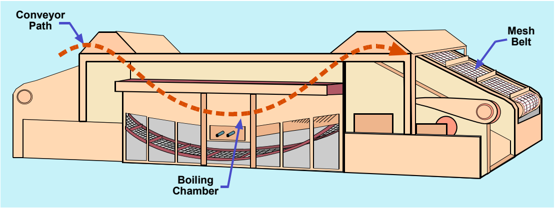
Cross-Rod Degreaser

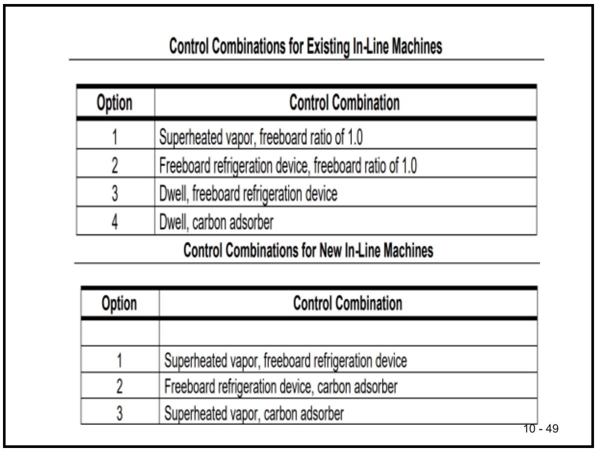
- Parts are supported by Rods Between The two Power Driven Chains.
- Designed To immerse Small Parts.

Monorail Cleaner



Mesh Belt Cleaner



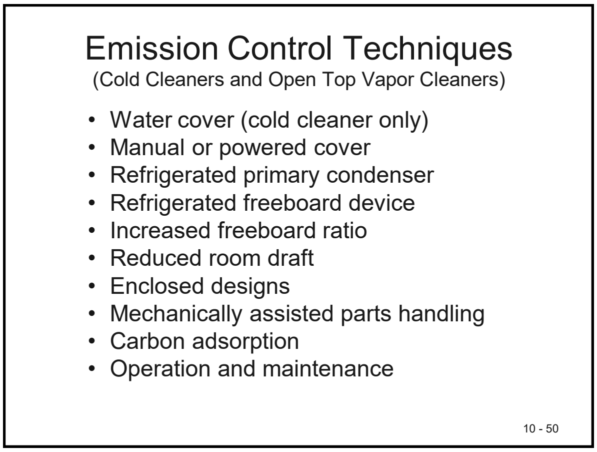


Control Combinations for Existing In-Line Machines

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

Control Combinations for New In-Line Machines

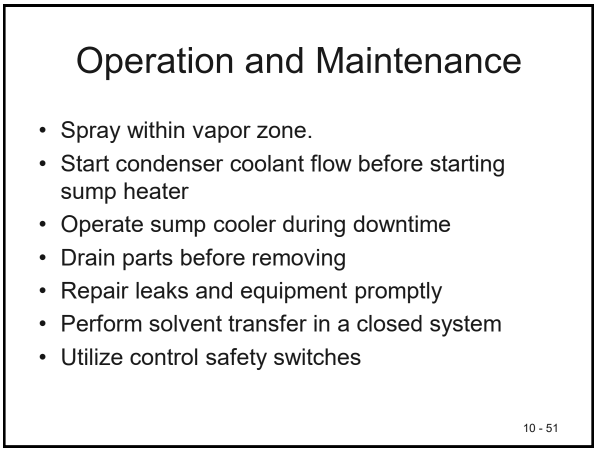
Option	Control Combination
1	Superheated vapor, freeboard refrigeration device
2	Freeboard refrigeration device, carbon adsorber
3	Superheated vapor, carbon adsorber



Emission Control Techniques

(Cold Cleaners and Open Top Vapor Cleaners)

- Water cover (cold cleaner only)
- Manual or powered cover
- Refrigerated primary condenser
- Refrigerated freeboard device
- Increased freeboard ratio
- Reduced room draft
- Enclosed designs
- Mechanically assisted parts handling
- Carbon adsorption
- Operation and maintenance



Operation and Maintenance

- Spray within vapor zone.
- Start condenser coolant flow before starting sump heater
- Operate sump cooler during downtime
- Drain parts before removing
- Repair leaks and equipment promptly
- Perform solvent transfer in a closed system
- Utilize control safety switches

Maintenance Work Inside a Degreaser

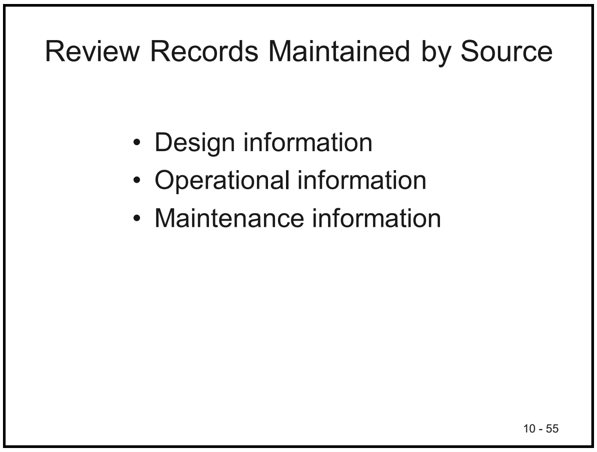
Emission Control Techniques

(In-Line Cleaners)

- Minimized entrance and exit openings
- Refrigerated freeboard device
- Drying tunnels
- Rotating baskets
- Carbon adsorbers
- Hot vapor recycle or superheated vapor
- Operation and maintenance

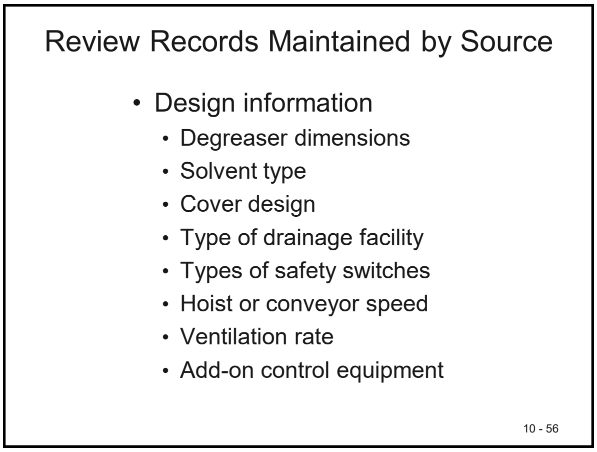
Process Inspection

- Review records maintained by source
- Check equipment operation
- Observe operating procedures
- Observe work area
- Check for liquid leaks
- Review waste solvent disposal procedures



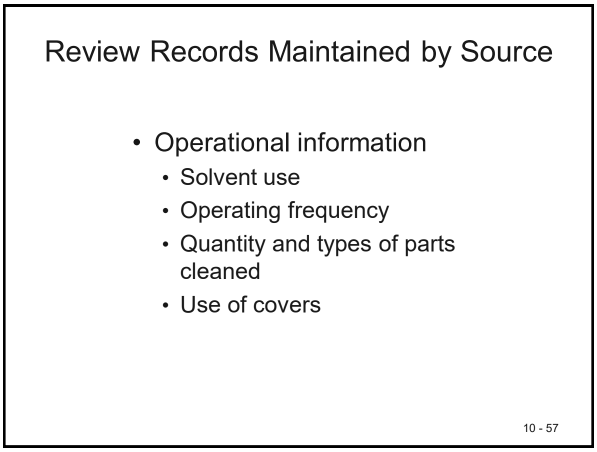
Review Records Maintained by Source

- Design information
- Operational information
- Maintenance information



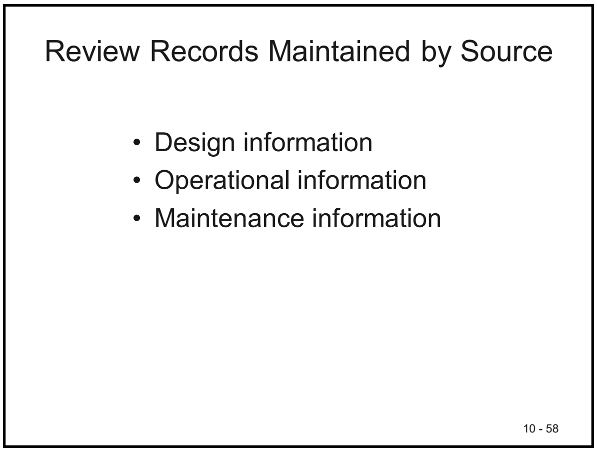
Review Records Maintained by Source

- Design information
  - Degreaser dimensions
  - Solvent type
  - Cover design
  - Type of drainage facility
  - Types of safety switches
  - Hoist or conveyor speed
  - Ventilation rate
  - Add-on control equipment



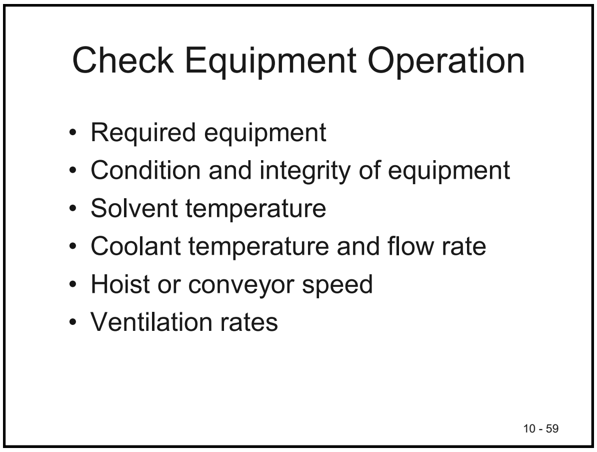
Review Records Maintained by Source

- Operational information
  - Solvent use
  - Operating frequency
  - Quantity and types of parts cleaned
  - Use of covers



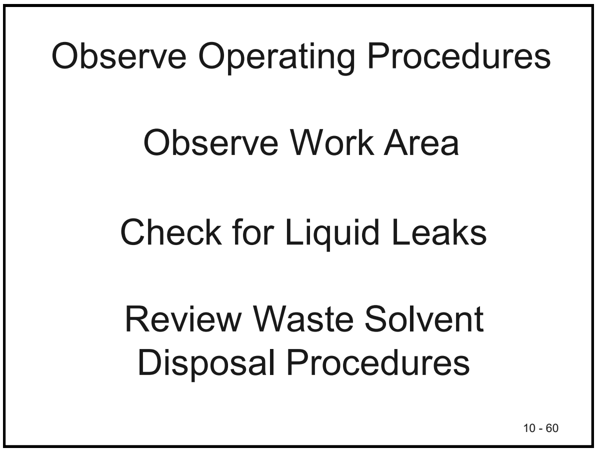
Review Records Maintained by Source

- Design information
- Operational information
- Maintenance information



Check Equipment Operation

- Required equipment
- Condition and integrity of equipment
- Solvent temperature
- Coolant temperature and flow rate
- Hoist or conveyor speed
- Ventilation rates



Observe Operating Procedures

Observe Work Area

Check for Liquid Leaks

Review Waste Solvent Disposal Procedures

Halogenated Solvent Cleaning: National Emission Standards for Hazardous Air Pollutants (NESHAP)

On this page:

- Rule Summary
- Rule History
- Additional Resources
- Compliance

Basic Information

Legal Authority

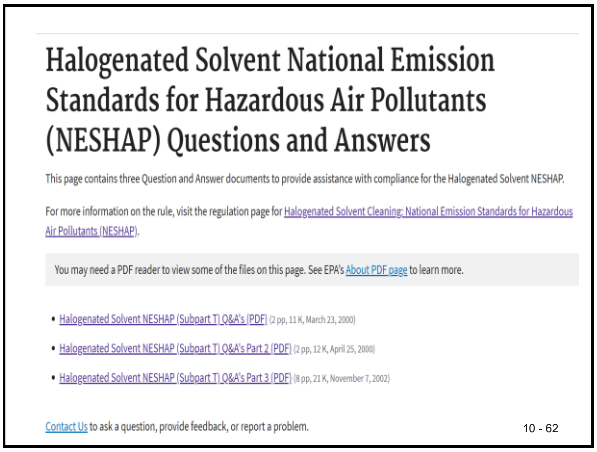
- 42 U.S.C. §7401

Federal Register Citations:

- 73 FR 73631
- 73 FR 62384
- 72 FR 25138
- 71 FR 75182
- 71 FR 47670
- 65 FR 54419
- 64 FR 69637
- 64 FR 67793
- 64 FR 56173

Rule Summary

The halogenated solvent cleaner National Emission Standards for Hazardous Air Pollutants (NESHAP) requires batch vapor solvent cleaning machines and inline solvent cleaning machines to meet emission standards reflecting the application of the maximum achievable control technology (MACT) for major and area sources. Area source batch cold cleaning machines are required to achieve generally available control technology. The rule regulates the emissions of the following halogenated hazardous air pollutants (HAP) solvents: methylene chloride (MC), perchloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), carbon tetrachloride (CT), and chloroform (C).



Halogenated Solvent National Emission Standards for Hazardous Air Pollutants (NESHAP) Questions and Answers

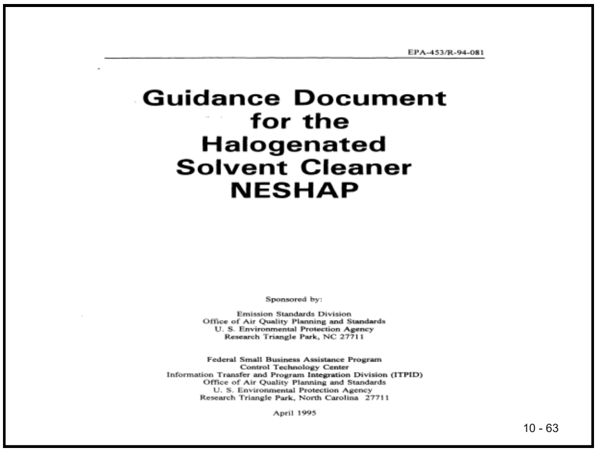
This page contains three Question and Answer documents to provide assistance with compliance for the Halogenated Solvent NESHAP.

For more information on the rule, visit the regulation page for Halogenated Solvent Cleaning: National Emission Standards for Hazardous Air Pollutants (NESHAP).

You may need a PDF reader to view some of the files on this page. See EPA's About PDF page to learn more.

- Halogenated Solvent NESHAP (Subpart T) Q&A's (PDF) (2 pp, 11 K, March 23, 2000)
- Halogenated Solvent NESHAP (Subpart T) Q&A's Part 2 (PDF) (2 pp, 12 K, April 25, 2000)
- Halogenated Solvent NESHAP (Subpart T) Q&A's Part 3 (PDF) (8 pp, 21 K, November 7, 2002)

Contact Us to ask a question, provide feedback, or report a problem.



EPA-453/R-94-081

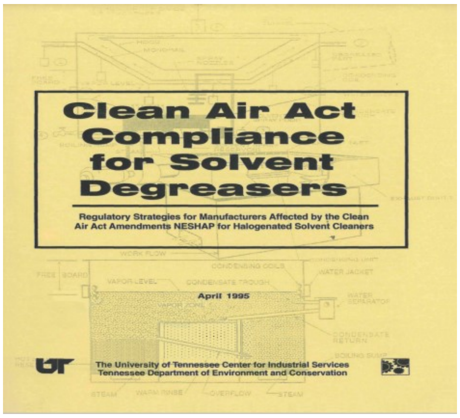
Guidance Document for the Halogenated Solvent Cleaner NESHAP

Sponsored by:

Emission Standards Division
Office of Air Quality Planning and Standards
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

Federal Small Business Assistance Program
Control Technology Center
Information Transfer and Program Integration Division (ITPID)
Office of Air Quality Planning and Standards
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

April 1995

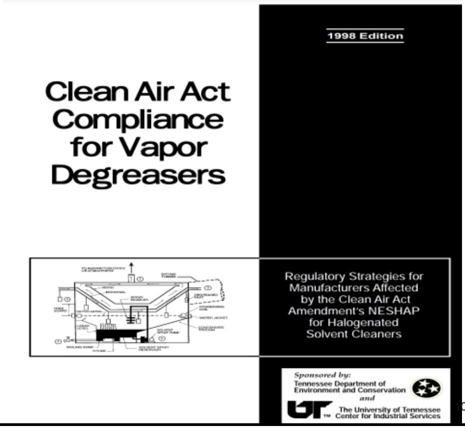


Clean Air Act Compliance for Solvent Degreasers

Regulatory Strategies for Manufacturers Affected by the Clean Air Act Amendments NESHAP for Halogenated Solvent Cleaners

April 1995

The University of Tennessee Center for Industrial Services
Tennessee Department of Environment and Conservation



1998 Edition

Clean Air Act Compliance for Vapor Degreasers

Regulatory Strategies for Manufacturers Affected by the Clean Air Act Amendment's NESHAP for Halogenated Solvent Cleaners

Sponsored by:
Tennessee Department of Environment and Conservation
and
The University of Tennessee Center for Industrial Services

Vapor Degreasing Video Website

- Vapor Degreasing 101 | Reliance Specialty Products (relspec.com)

Chapter 11

Dry Cleaning

What is Dry Cleaning?

A process for cleaning fabrics in which the articles are washed in a non-aqueous solvent and then dried in a heated air stream.

Dry Cleaning Steps

- Washing
- Extraction
- Drying

Dry Cleaning Solvents

- Perchloroethylene (PCE)
- Petroleum solvents
- Cyclic siloxanes (D5) (GreenEarth)
- Glycol ethers (Rynex)
- Liquid carbon dioxide (MiCELL)
- n-propyl bromide
- DF-2000 Hydrocarbon Solvent:
- Wet cleaning

EPA's Proposal and the Toxics Substances Control Act (TSCA)

- In June 2016, Congress amended the Toxic Substances Control Act (TSCA)
  - Amended TSCA requires EPA to assess and address risks from chemicals currently in commerce
  - Amended TSCA imposes statutory timeframes for regulation
  - Provides protection for the public and predictability for the regulated community
- PCE was identified in 2016 as one of the first chemicals for risk evaluation
  - 2020 Risk Evaluation followed a public draft and peer review process
  - EPA determined that PCE presents an unreasonable risk under its conditions of use

Purpose and Overview Of Rulemaking

- The proposal addresses the unreasonable risk identified in the TSCA section 6 risk evaluation of PCE (December 2020) which assessed all uses subject to TSCA
- The proposed rule, when finalized, will prevent consumer and occupational illness while ensuring identified essential uses can continue safely where possible
  - EPA's proposal would allow select uses to continue with strict workplace protections, while prohibiting all remaining uses
- EPA's proposed rule is open for public comment until **August 15, 2023**
- EPA will then consider public comments and finalize new regulations of PCE under TSCA

Proposed Dry Cleaning Phaseout

- EPA is proposing to prohibit PCE use in dry cleaning through a 10-year phaseout to provide dry cleaners time to transition to an alternative process
- For the phaseout timeframe, EPA considered precedents set by state regulations, the dry cleaning NESHAP, and information provided by stakeholders, including:
  - The average lifespan of a PCE dry cleaning machine is 15 to 25 years and few new machines are produced or sold in the U.S.
  - Alternatives are available, such as wet cleaning, hydrocarbons, and multi-solvent dry cleaning machines
  - Use of PCE in dry cleaning is declining as machines are retired and alternatives are adopted

Phaseout Timing (after publication date of the final rule)	
6 months	• Prohibition on use of PCE in any dry cleaning machine acquired 6 months or later
3 years	• Prohibition on use of 3rd generation PCE machines
10 years	• Prohibition on the use of PCE in all dry cleaning and spot cleaning, including in 4th and 5th generation machines • Prohibition on the manufacturing, processing, and distribution in commerce of PCE for use in dry cleaning solvent

Physical Properties of Dry cleaning Solvents

Solvent	Molecular Weight	Boiling Point (F)	Flash Point (F)	Latent Heat of Vaporization	Kauri-butanol Value
PERC	165.8	250	***	90	92
Stoddard	140-150	310	103	118	28-45
CFC-113	187.5	118	***	63	31
1-1-1, Trich.	***	165	***	104	124
DF-2000	140	***	147	***	27

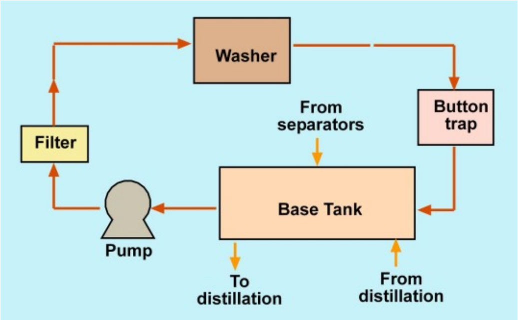
Industry Classes

- Commercial
- Industrial
- Coin operated

Equipment Types

- Transfer
- Dry-to-Dry

Washing Process



Washer

Button trap

From separators

Filter

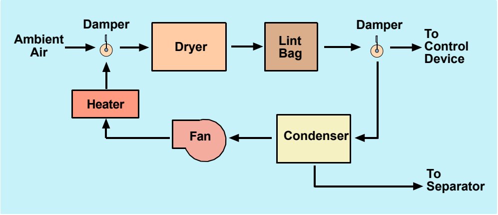
Base Tank

Pump

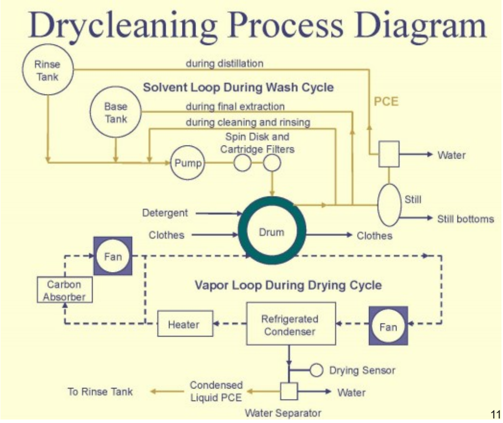
To distillation

From distillation

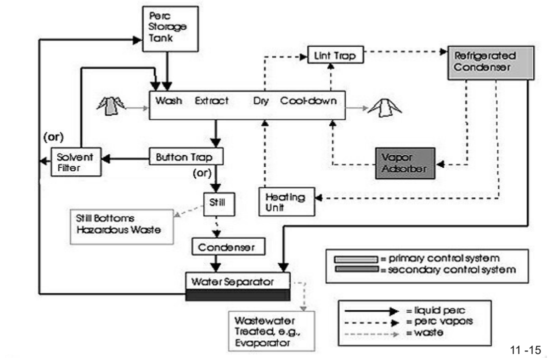
Early Drying Process


Damper
Ambient Air
Dryer
Lint Bag
Damper
To Control Device
Heater
Fan
Condenser
To Separator

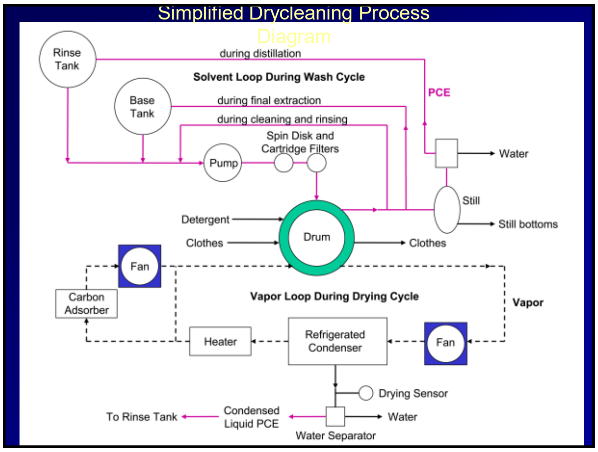
Drycleaning Process Diagram

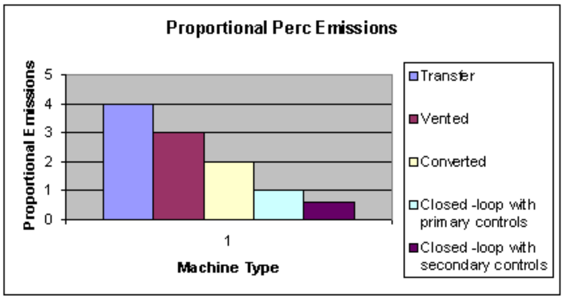


Closed-Loop Process



Simplified Drycleaning Process Diagram





Drycleaning Process
Drycleaning Machine Evolution

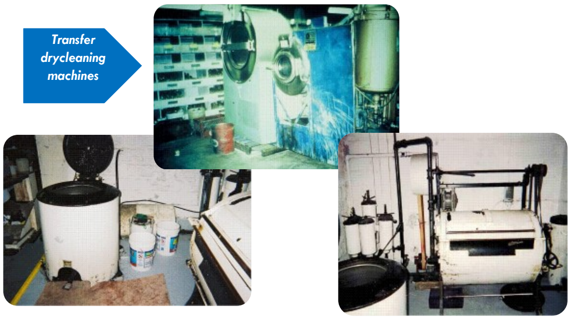
- ✓ **1st Generation: transfer machines –** Requires manual transfer of solvent-laden clothing between a separate washer and dryer. Perc transfer machines are to be phased out as of July 27, 2008 and should no longer be in operation. These machines allow for significant release of solvent into the environment when transferring garments from the washer to the dryer unit.
- ✓ **2nd Generation: dry-to-dry (vented) –** Dry-to-dry machines integrated the washer and dryer into the same unit in the late 1960s. While these machines were more efficient than transfer machines, they were inefficient because they vented solvent vapors directly to the atmosphere and exposed workers to solvent vapor.
- ✓ **3rd Generation: dry-to-dry (nonvented - aka closed-loop) –** Dry-to-dry machines with refrigerated condensers were introduced in the late 1970s and early 1980s. Refrigerated condensers were used to convert solvent vapors for recovery and reuse. These nonvented machines are closed-loop systems, which are only open to the atmosphere when the machine door is opened. These machines reduce vapor emissions and are still commonly used.

Drycleaning Process
Drycleaning Machine Evolution

- ✓ **4th Generation: dry-to-dry (closed-loop with secondary vapor control) –** These machines are essentially "third generation" machines with a carbon absorber to further reduce solvent vapors in the machine. These machines are much more effective at recovering solvent vapors.
- ✓ **5th Generation: dry-to-dry (closed-loop with secondary vapor control and drum monitor) –** These machines have the same features as "fourth generation" machines however, they also have a monitor inside the machine drum and an interlocking system to ensure that the concentration is below approximately 300 ppm before the loading door can be opened.

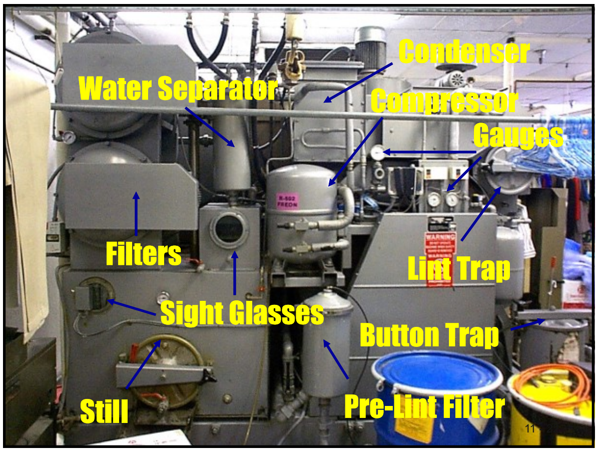
Drycleaning Process
Drycleaning Machine Evolution

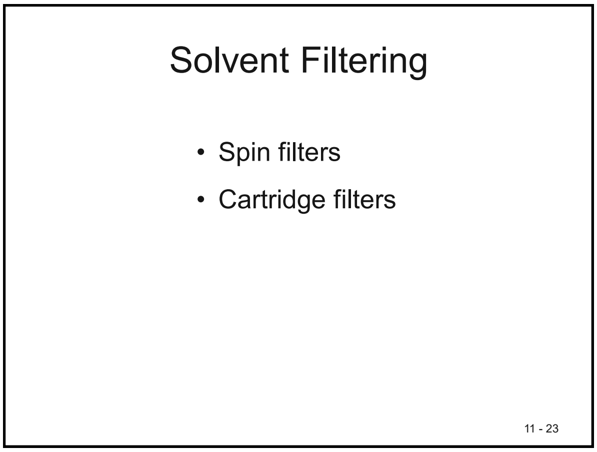
Transfer drycleaning machines



Drycleaning Process
Drycleaning Machine Evolution

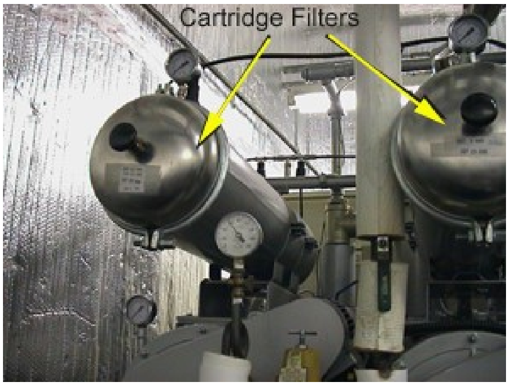
Dry-to-dry drycleaning machines





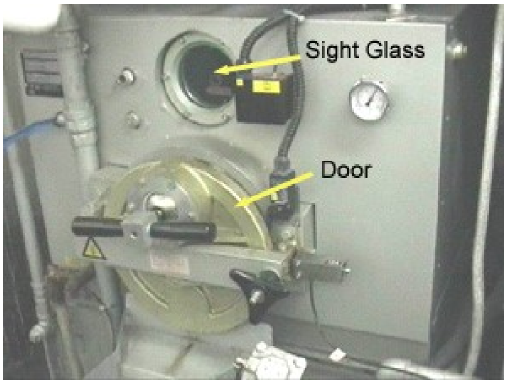
Solvent Filtering

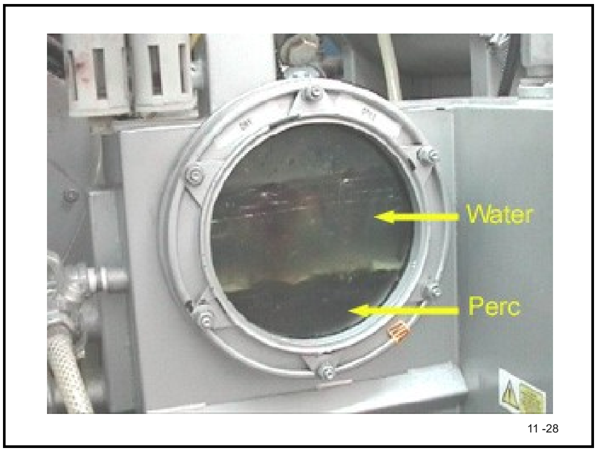
- Spin filters
- Cartridge filters



Solvent Distillation

- Perchloroethylene: 250°F at 1 atm
- Petroleum: 225-235°F at -22 to -27 in. Hg
- Still boil down



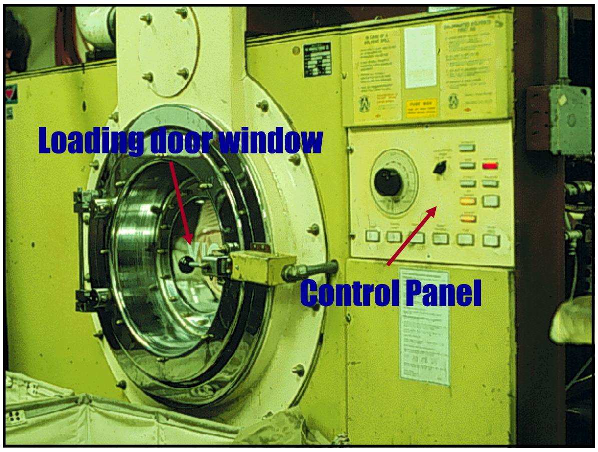


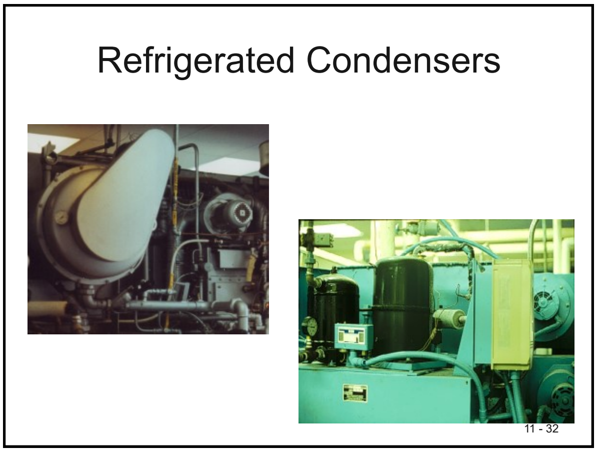
Emission Control Techniques

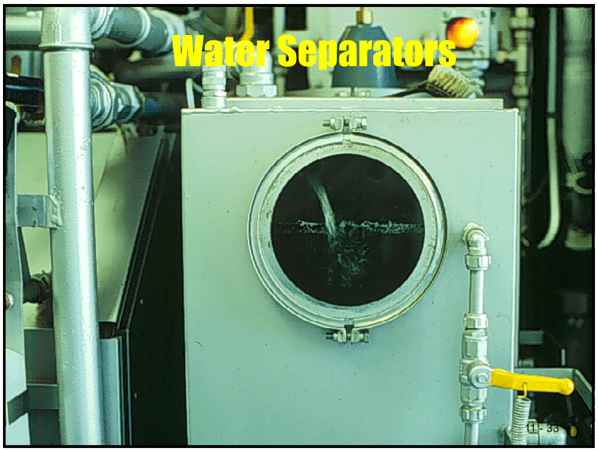
- Refrigeration condensation
- Carbon adsorption
- Fugitive emission control

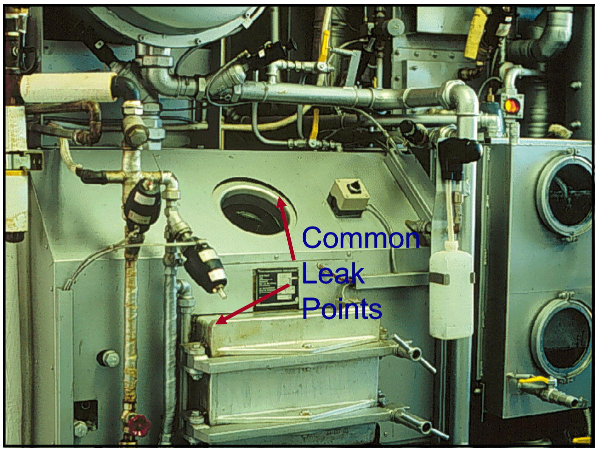
Process Inspection

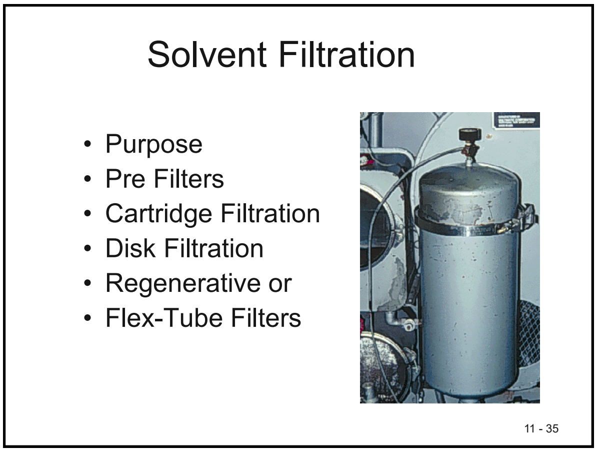
- Review records maintained by source
  - Solvent purchases
  - Internal inspection audits
  - Monitoring checks
  - Maintenance records
- Check for vapor leaks
- Check for liquid leaks




Refrigerated Condensers

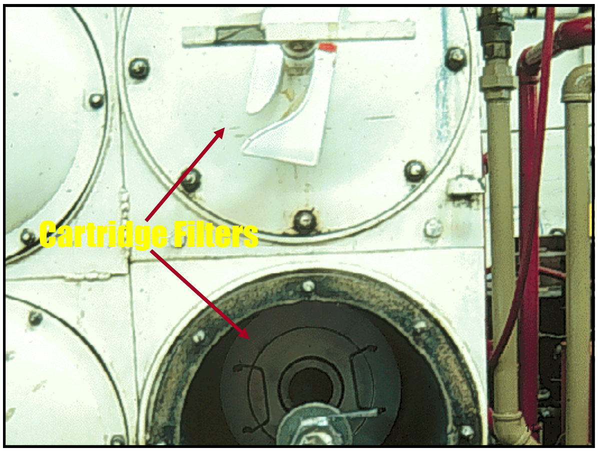

Water Separators





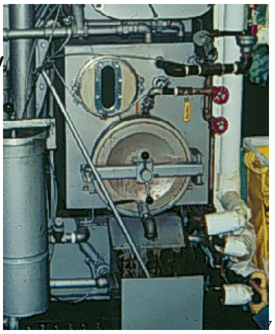
Solvent Filtration

- Purpose
- Pre Filters
- Cartridge Filtration
- Disk Filtration
- Regenerative or
- Flex-Tube Filters



Stills

- Distillation
- PERC Recovery
- 75% Capacity
- Muck Cookers
- Hazardous waste
- Azeotrope

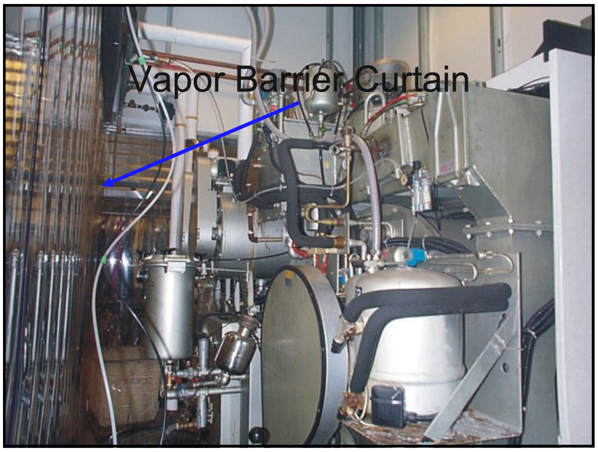


Secondary Control Devices

- Vapor Adsorbers
- During End Of Cool Down Cycle
- Decreases Emissions
- Lowers Operator Exposure

Misc. Equipment & Operations

- Water Separators
- Inductive Door Fans
- Spill Containment Systems
- Ventilation/Exhaust Systems
- Drying Cabinet
- Water Repelling Operations



Required Maintenance

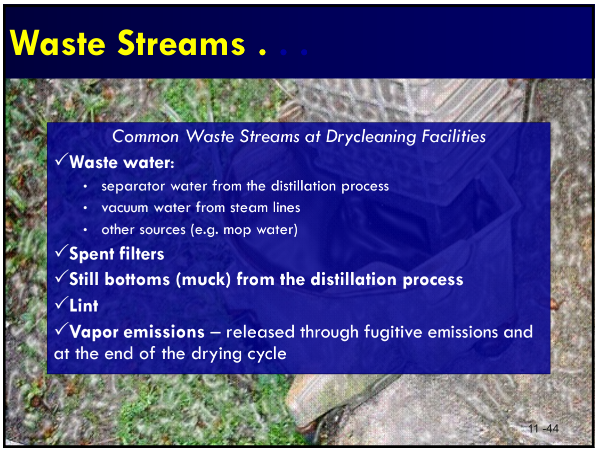
- Refrigerated Condensers
- Carbon Adsorbers
- Cartridge Filtration Systems
- Stills & Muck Cookers
- Button & Lint Traps
- Machine Openings
- Waste Water Treatment Units

Historical Waste Management Practices

The chart below identifies historical waste disposal practices that have contributed to environmental contamination at drycleaning facilities:

Method of Disposal	**Waste Water**	**Spent Filters**	**Still Bottoms**	**Lint**
Outside back door of facility				
Sanitary Sewer, Septic Tank or Storm Sewer				
Dumpster or Municipal Waste				

Waste Streams . . .



Waste Streams . . .

Common Waste Streams at Drycleaning Facilities

✓**Waste water:**
- separator water from the distillation process
- vacuum water from steam lines
- other sources (e.g. mop water)

✓**Spent filters**

✓**Still bottoms (muck) from the distillation process**

✓**Lint**

✓**Vapor emissions** – released through fugitive emissions and at the end of the drying cycle

Waste Streams . . .

Other Water

A commonly overlooked waste stream is "mop water". Through normal housekeeping, mops can collect solvent from vapors, lint and still bottoms at a drycleaning facility.

Improper disposal of contaminated water can pose a threat to the environment. Mop water containing solvent and soap/detergent should be managed as hazardous waste.

The Inspection

- Verify Equipment and Current Owners
- Conduct Leak Inspections
- Check For Closed Containers
- Verify Refrigerated Condenser Temp
- Check All Records
- Review The Inspection Results

Vapor Leak Inspections

- Definitions
- Halogenated Hydrocarbon Detector
- Areas To Check
- When To Check
- How Do You Do It?
- If a Leak is Found?

Vapor Leak Inspections

https://www.youtube.com/watch?v=NybbKb8nnhQ

https://www.youtube.com/watch?v=b5zM_tFpYmM&t=43s

Leak Inspection Areas

Button Trap	**Stills**
Pump area	**Lint Trap**
Filters	**Water Separator**
Misc. Gaskets	**Storage Areas**
Openings	

ATTENTION

Are you located in a building with residents?

All co-residential perc dry cleaners must switch to an alternative solvent or move the machine to a nonresidential building by December 21, 2020!

Are you prepared?

For more information about the National Emissions Standards for Hazardous Air Pollutants (NESHAP) for Perc Dry Cleaners (40 CFR PART 63, SUBPART M) visit: ***www.ildceo.net/enviro*** or call ***800-252-3998*** or email ***dceo.sbeap@illinois.gov***.

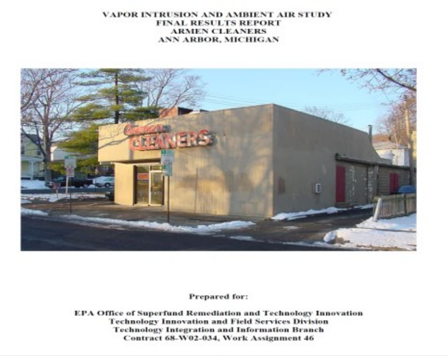
NOTE: Perc dry cleaners changing to petroleum-base solvents must register under the Registration of Smaller Sources Program (ROSS) or apply for an air permit depending on solvent usage.

Best Management Practices

Best Practice Areas

- ✓ Secondary containment
- ✓ Hazardous waste management
- ✓ Direct coupling/closed-loop solvent delivery systems
- ✓ Equipment inspections and maintenance

Vapor Intrusion



VAPOR INTRUSION AND AMBIENT AIR STUDY
FINAL RESULTS REPORT
ARMEN CLEANERS
ANN ARBOR, MICHIGAN

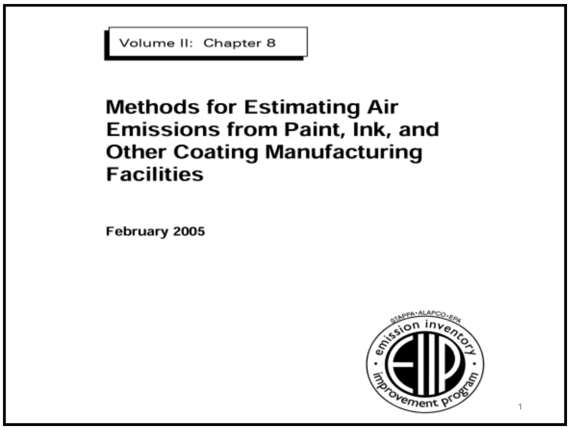
Prepared for:

EPA Office of Superfund Remediation and Technology Innovation
Technology Innovation and Field Services Division
Technology Integration and Information Branch
Contract 68-W02-034, Work Assignment 46

New Focus Area: Chlorinated Solvents

Chlorinated solvents have been used for a variety of commercial and industrial purposes, such as degreasers, drycleaning solutions, paint thinners, herbicides, pesticides, resins, glues, and a host of other mixing and thinning solutions.

Contaminated Site Clean-Up Information (CLU-IN)



Volume II: Chapter 8

Methods for Estimating Air Emissions from Paint, Ink, and Other Coating Manufacturing Facilities

February 2005

- Specialty ink products include textile and silk screen ink, invisible inks, powder inks, carbon paper, typewriter, and duplicating inks. Paint, ink, and other coating manufacturing can be classified as a batch process and generally involves the blending/mixing of resins, pigments, solvents, and additives. Traditional paint, ink, and other coating manufacturing consists of four major steps:
- Preassembly and premix;
- Pigment grinding/milling/dispersing;
- Product finishing/blending; and
- Product filling/packaging.

Preassembly and Premix

- In the preassembly and premix step, liquid raw materials are assembled and then mixed in containers to form a viscous material to which pigments are added.
- For solvent-based paints, the raw ingredients include resins, organic solvents, plasticizers, dry pigment, and pigment extenders.
- Raw materials used in the preassembly and premix step for water-based paints include water, ammonia, dispersant, pigment, and pigment extenders.
- Raw materials for ink manufacturing include pigments, oils, resins, solvents, and driers.
- The premix stage results in the formation of an intermediate product that is referred to as the base or mill base.
- The type of equipment used in the premix step depends on the batch size and the type of coating being produced.
- Drums equipped with a portable mixer may be used for drum-sized batches. These mixers normally have an impeller with three or four blades

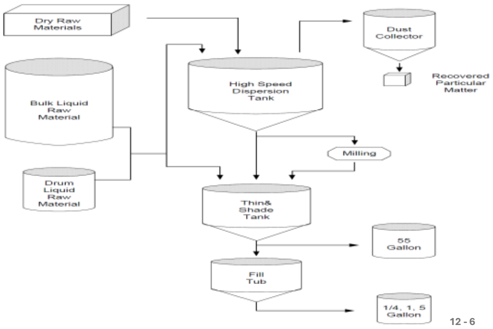
Pigment Grinding or Milling

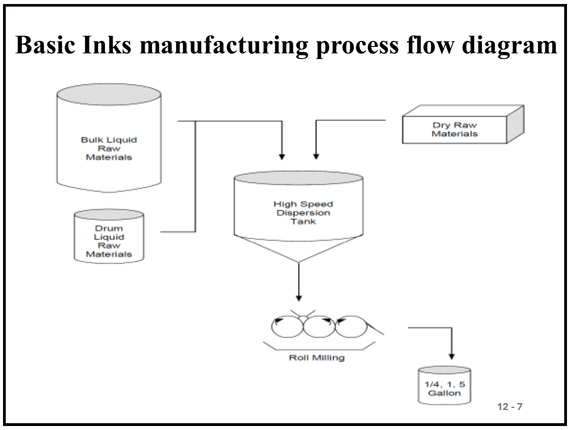
- Pigment grinding or milling entails the incorporation of the pigment into the liquid base of the coating to yield a fine particle dispersion. The three stages of this process include wetting, grinding, and dispersion, which may overlap in any grinding operation.
- The wetting agent, normally a surfactant, wets the pigment particles by displacing air, moisture, and gases that are adsorbed on the surface of the pigment particles.
- Grinding is the mechanical breakup and separation of pigment clusters into isolated particles and may be facilitated by the use of grinding media such as pebbles, balls, or beads.
- Common used equipment include the following: roller mills, ball and pebble mills, attritors, sand mills, bead and shot mills, high-speed stone and colloid mills, high-speed dispersers, high-speed impingement mills, and horizontal media mills.

Product Finishing

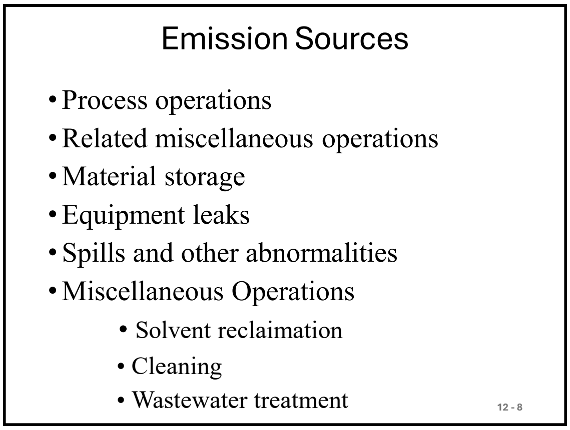
- The final step in the paint, ink, and other coating manufacturing process is the product filling operation. During the filling step, filtration is performed to remove impurities and to catch small particles of grinding media.
- Once the material has been filtered, it can be transferred into pails, drums, totes, tank wagons, or other containers for shipment. Filling may be accomplished either manually or mechanically depending on the number and size of the containers to be filled.

Basic Flow Sheets for Coating Manufacturing Processes



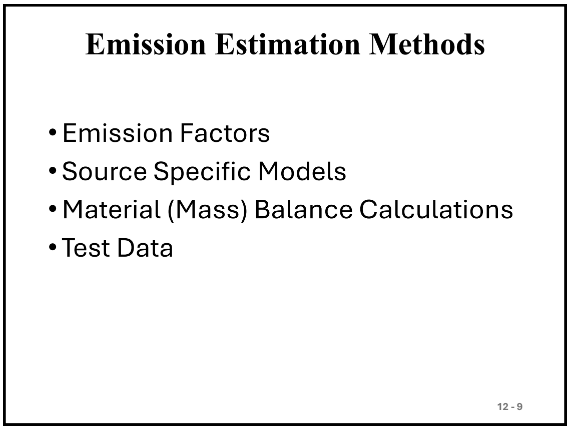


Basic Inks manufacturing process flow diagram



Emission Sources

- Process operations
- Related miscellaneous operations
- Material storage
- Equipment leaks
- Spills and other abnormalities
- Miscellaneous Operations
  - Solvent reclaimation
  - Cleaning
  - Wastewater treatment



Emission Estimation Methods

- Emission Factors
- Source Specific Models
- Material (Mass) Balance Calculations
- Test Data

Emission Factors

- Emission factors may be used to calculate total VOC and PM emissions from a paint and ink manufacturing facility, as well as emissions from specific types of equipment typically found at such a facility.

These types of equipment include the following:

- Process equipment;
- Solvent reclamation systems;
- Parts washing equipment; and
- Process piping.

Source Specific Models

- Emission estimating models/equations are available for the following types of emissions found at paint, ink, or other coating manufacturing facilities:
- Material loading
- Heat-up losses from dispersion/grinding activities
- Surface evaporation during mixing/blending operations
- Filling
- Gas sweep or purge
- Cleaning solvent loading
- Solvent reclamation
- Material storage
- Wastewater treatment and Spills

Material (Mass) Balance Calculations

- The material balance approach to emissions estimation considers the given facility as a sort of “black box,” where one compares the total quantity of raw materials consumed versus amounts of materials leaving the facility as product or waste. Waste can consist of used filter bags or cartridges, spent solvent or still bottoms, dust collector material, pigment bags and/or drum residue, and wastewater.

Types of Items for Material Balance Information

- Delivery of Raw material
- Exact quantities and specifications of finished products
- Amount of raw material contained in waste
- Batch production raw material additions

Test Data

- Testing can be performed to quantify point source or fugitive emissions. In point source testing, effluent gas samples are usually collected from a stack using probes inserted through a port in the stack wall.
- Pollutants in the gas sample are collected in or on various media that are subsequently sent to a laboratory for analysis.
- Industrial hygiene data (concentrations) can be used in conjunction with exhaust system flow rates to calculate fugitive emissions from a room, floor, or building. Direct-reading instruments may be utilized
- that may be used to obtain an instantaneous reading of vapor concentrations include
- photoionization detectors, portable infrared spectrophotometers, and portable gas chromatographs (NPCA, 1995).

Test Data

- Use of stack and/or industrial hygiene test data is likely to be the most accurate method of quantifying air emissions from paint, ink, and other coating manufacturing operations.
- Collection and analysis of air samples from manufacturing facilities can be very expensive and especially complicated for coating manufacturing facilities where a variety of VOCs are emitted and where most of the emissions may be fugitive in nature.
- Test data from one specific process may not be representative of the entire manufacturing operation and may provide only one example (a snapshot) of the facility’s emissions.

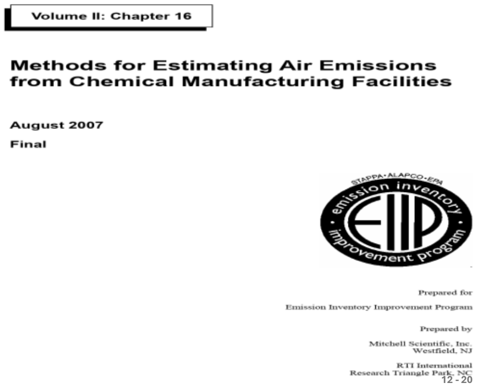
Test Data

- Test data needs to be representative and needs to be collected over a period of time that covers production of multiple coating formulations. It may be necessary to sample multiple production areas.
- In addition, these methods do not address fugitive emissions that occur outside of a building. If testing is performed, care should be taken to ensure that a representative operational cycle has been selected.
- Full cycles should be monitored as opposed to portions of cycles, when possible
- VOC losses from certain operations (e.g., filling of containers) may also be measured by performing a study using a gravimetric analysis such as American Society for Testing and Materials (ASTM) Standard D2369: *Test Method for Volatile Content of Coatings*.

- **Case Study 8.3-1: The Bright Blue Paint Company (in handout)**
- Description
- The Bright Blue Paint Company produces a variety of related paint products that can be considered to have similar formulations. The total production rate is about 2,500,000 gal/yr.
- The four main manufacturing operations at the Bright Blue Paint Company are:
- Preassembly and premix;
- Pigment grinding/milling;
- Product finishing/blending; and
- Product filling/packaging.
- .

- The batch begins with mixing of raw materials in a high speed disperser. The material from the disperser is then transformed to a thindown tank where additional solvent is added. The final product is then transferred to shipping containers. Total batch size is about 1,700 gallons.
- Liquid storage of paint ingredients and cleaning compounds is in bulk tanks ranging from 2,500 to 10,000 gallons and in 55-gallon drums. Powder ingredients are stored in paper sacks or fiber drums ranging from 10 to 200 pounds.
- Equipment is cleaned after each batch. Approximately 75,000 gallons of cleaning solvents are used for equipment cleaning each year. Small parts are also cleaned as necessary using an open-top vapor degreaser.

Example Problem in Handout



Volume II: Chapter 16

Methods for Estimating Air Emissions from Chemical Manufacturing Facilities

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Final

Prepared for
Emission Inventory Improvement Program

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- The majority of emissions that occur from batch chemical manufacturing operations are from volatile organic solvents that evaporate during manufacturing.
- Particulate matter emissions may also occur from the handling of solid powders that are used in manufacturing.
- Several air emission sources have been identified for chemical manufacturing operations; they are as follows: Process operations

- Process operations
- Storage tanks
- Equipment leaks
- Wastewater collection and treatment
- Cleaning Solvent recovery
- Spills

- When a solvent or volatile process mixture is charged into a process vessel then material losses will occur though the process vent in the form of solvent vapors. The amount of solvent that is emitted during this displacement operation is a function of the
- (1) volume of liquid entering the tank,
- (2) the equilibrium vapor pressure of each component that is contained in the inlet stream and/or present in the vessel before the filling operation begins, and
- (3) degree of saturation of the associated vapors. The resulting emission rate is simply a function of how quickly the filling operation takes place. 5

Specific Process Operations Emissions Points

- Material Charging
- Process heating
- Process Depressurization
- Gas Evolution
- Gas sweep and purge operations
- Surface evaporation
- Solvent reclaimation
- Cleaning
- Wastewater treatment
- Storage tanks
- Equipment leaks and spills

Vessel Filling

- When a solvent or volatile process mixture is charged into a process vessel then material losses will occur though the process vent in the form of solvent vapors.
- The amount of solvent that is emitted during this displacement operation is a function of the
- (1) volume of liquid entering the tank,
- (2) the equilibrium vapor pressure of each component that is contained in the inlet stream and/or present in the vessel before the filling operation begins, and
- (3) degree of saturation of the associated vapors. The resulting emission rate is simply a function of how quickly the filling operation takes place.

Vessel Filling

- The equilibrium vapor pressure for each volatile component in the system is calculated by applying Raoult's Law to the pure vapor pressure and the mole fraction of each compound in the inlet stream and/or initial vessel contents.
- If non-idealities exist between molecules in the system then activity coefficient may be used to adjust the vapor pressures accordingly.
- The calculated equilibrium vapor pressure represents the gas space composition assuming that the degree of vapor saturation is 100%.
- It is highly possible that the actual saturation level of the solvent vapors may be less than the assumed 100% level.

Vessel Filling

- Displacement emissions that are caused by charging operations may be calculated using the ideal gas law on the volume of gas that is emitted. This equation assumes that the partial pressure of component i in the vent gas is at saturated levels.
- Ideal Gas Law:
- $E_{n\text{-}I} = p_i V/ RT$ Equation 3.1

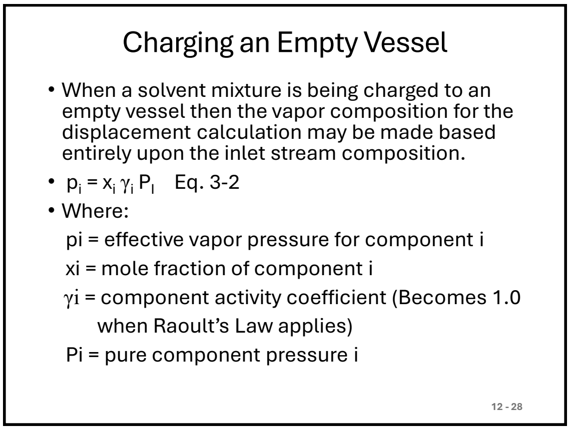
Where: En-i are the moles of component i that are emitted due to vapor displacement

pi is the saturated vapor pressure of component i.

V is the displacement volume that was caused by the filling operation.

R is the ideal gas constant in consistent units,

T is the temperature of the liquid being charged



Charging an Empty Vessel

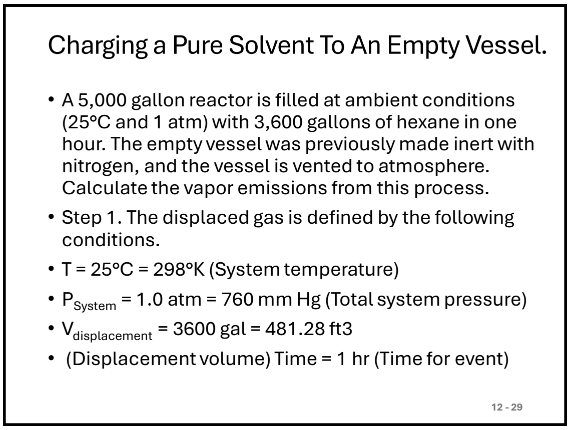
- When a solvent mixture is being charged to an empty vessel then the vapor composition for the displacement calculation may be made based entirely upon the inlet stream composition.
- $p_i = x_i \gamma_i P_I$ Eq. 3-2
- Where:

pi = effective vapor pressure for component i

xi = mole fraction of component i

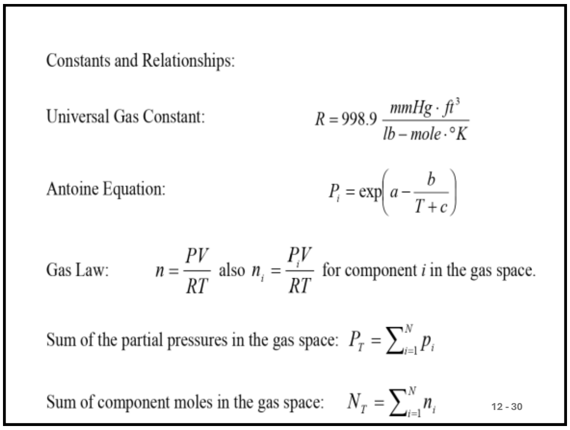
γi = component activity coefficient (Becomes 1.0 when Raoult's Law applies)

Pi = pure component pressure i



Charging a Pure Solvent To An Empty Vessel.

- A 5,000 gallon reactor is filled at ambient conditions (25°C and 1 atm) with 3,600 gallons of hexane in one hour. The empty vessel was previously made inert with nitrogen, and the vessel is vented to atmosphere. Calculate the vapor emissions from this process.
- Step 1. The displaced gas is defined by the following conditions.
- T = 25°C = 298°K (System temperature)
- P_{System} = 1.0 atm = 760 mm Hg (Total system pressure)
- $V_{displacement}$ = 3600 gal = 481.28 ft3
- (Displacement volume) Time = 1 hr (Time for event)



Constants and Relationships:

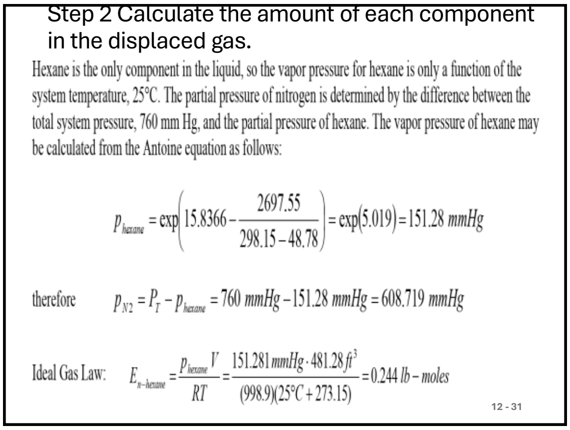
Universal Gas Constant: $R = 998.9 \dfrac{mmHg \cdot ft^3}{lb-mole \cdot {}^\circ K}$

Antoine Equation: $P_i = \exp\left(a - \dfrac{b}{T+c}\right)$

Gas Law: $n = \dfrac{PV}{RT}$ also $n_i = \dfrac{P_i V}{RT}$ for component i in the gas space.

Sum of the partial pressures in the gas space: $P_T = \sum_{i=1}^{N} p_i$

Sum of component moles in the gas space: $N_T = \sum_{i=1}^{N} n_i$



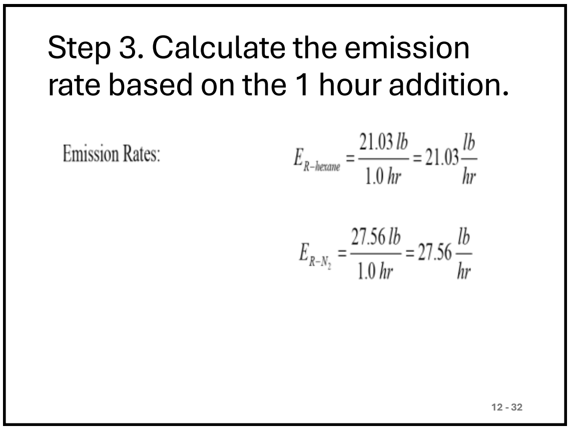
Step 2 Calculate the amount of each component in the displaced gas.

Hexane is the only component in the liquid, so the vapor pressure for hexane is only a function of the system temperature, 25°C. The partial pressure of nitrogen is determined by the difference between the total system pressure, 760 mm Hg, and the partial pressure of hexane. The vapor pressure of hexane may be calculated from the Antoine equation as follows:

$$p_{hexane} = \exp\left(15.8366 - \frac{2697.55}{298.15 - 48.78}\right) = \exp(5.019) = 151.28\ mmHg$$

therefore $p_{N2} = P_T - p_{hexane} = 760\ mmHg - 151.28\ mmHg = 608.719\ mmHg$

Ideal Gas Law: $E_{n-hexane} = \frac{p_{hexane} V}{RT} = \frac{151.281\ mmHg \cdot 481.28\ ft^3}{(998.9)(25°C + 273.15)} = 0.244\ lb - moles$

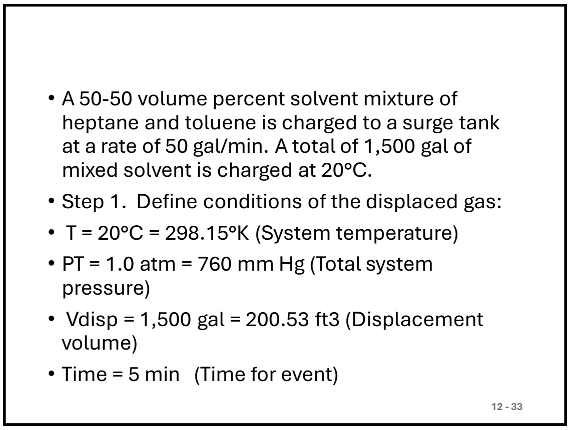


Step 3. Calculate the emission rate based on the 1 hour addition.

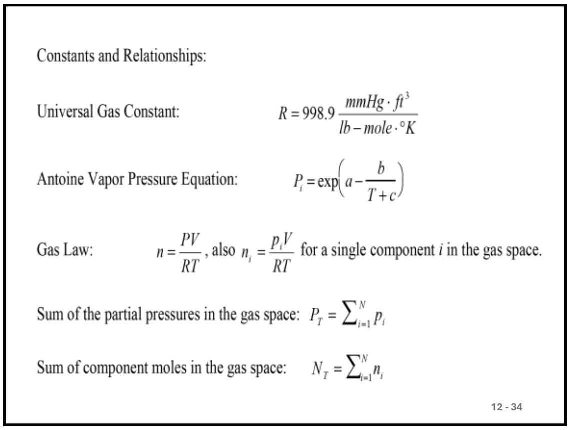
Emission Rates:

$$E_{R-hexane} = \frac{21.03\ lb}{1.0\ hr} = 21.03 \frac{lb}{hr}$$

$$E_{R-N_2} = \frac{27.56\ lb}{1.0\ hr} = 27.56 \frac{lb}{hr}$$



- A 50-50 volume percent solvent mixture of heptane and toluene is charged to a surge tank at a rate of 50 gal/min. A total of 1,500 gal of mixed solvent is charged at 20°C.
- Step 1. Define conditions of the displaced gas:
- T = 20°C = 298.15°K (System temperature)
- PT = 1.0 atm = 760 mm Hg (Total system pressure)
- Vdisp = 1,500 gal = 200.53 ft3 (Displacement volume)
- Time = 5 min (Time for event)



Constants and Relationships:

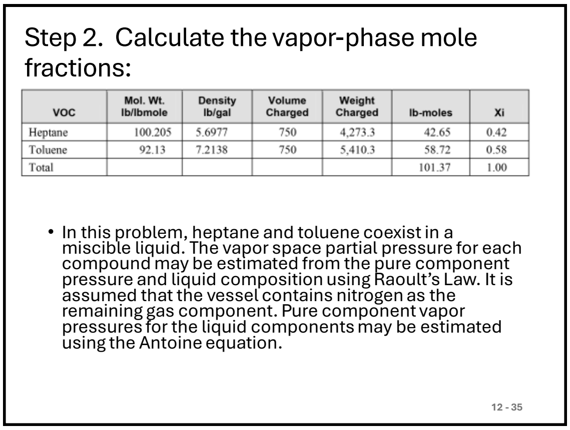
Universal Gas Constant: $R = 998.9\ \frac{mmHg \cdot ft^3}{lb-mole \cdot °K}$

Antoine Vapor Pressure Equation: $P_i = \exp\left(a - \frac{b}{T+c}\right)$

Gas Law: $n = \frac{PV}{RT}$, also $n_i = \frac{p_i V}{RT}$ for a single component i in the gas space.

Sum of the partial pressures in the gas space: $P_T = \sum_{i=1}^{N} p_i$

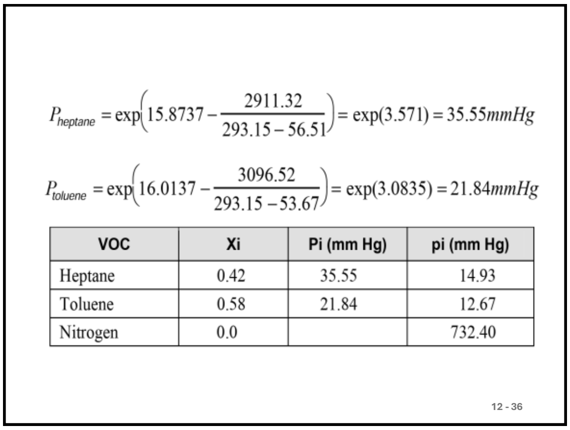
Sum of component moles in the gas space: $N_T = \sum_{i=1}^{N} n_i$



Step 2. Calculate the vapor-phase mole fractions:

VOC	Mol. Wt. lb/lbmole	Density lb/gal	Volume Charged	Weight Charged	lb-moles	Xi
Heptane	100.205	5.6977	750	4,273.3	42.65	0.42
Toluene	92.13	7.2138	750	5,410.3	58.72	0.58
Total					101.37	1.00

- In this problem, heptane and toluene coexist in a miscible liquid. The vapor space partial pressure for each compound may be estimated from the pure component pressure and liquid composition using Raoult's Law. It is assumed that the vessel contains nitrogen as the remaining gas component. Pure component vapor pressures for the liquid components may be estimated using the Antoine equation.



$$P_{heptane} = \exp\left(15.8737 - \frac{2911.32}{293.15 - 56.51}\right) = \exp(3.571) = 35.55 mmHg$$

$$P_{toluene} = \exp\left(16.0137 - \frac{3096.52}{293.15 - 53.67}\right) = \exp(3.0835) = 21.84 mmHg$$

VOC	Xi	Pi (mm Hg)	pi (mm Hg)
Heptane	0.42	35.55	14.93
Toluene	0.58	21.84	12.67
Nitrogen	0.0		732.40

Ideal Gas Law:

$$E_{n\text{-}heptane} = \frac{p_{heptane}V}{RT_{sys}} = \frac{14.93mmHg \cdot 200.53\,ft^3}{(998.9)(293.15)} = 0.0102lb-moles$$

$$n_{n\text{-}toluene} = \frac{p_{toluene}V}{RT_{sys}} = \frac{12.67mmHg \cdot 200.53\,ft^3}{(998.9)(293.15)} = 0.0087lb-moles$$

$$n_{nitrogen} = \frac{p_{air}V}{RT_{sys}} = \frac{732.40\,mmHg \cdot 200.53\,ft^3}{(998.9)(293.15)} = 0.5015\,lb-moles$$

Step 3. Calculate the emission rate in lb/hr units.

- Since 1,500 of solvent mixture is charged at 50 gpm the complete charge is completed in 30 minutes.

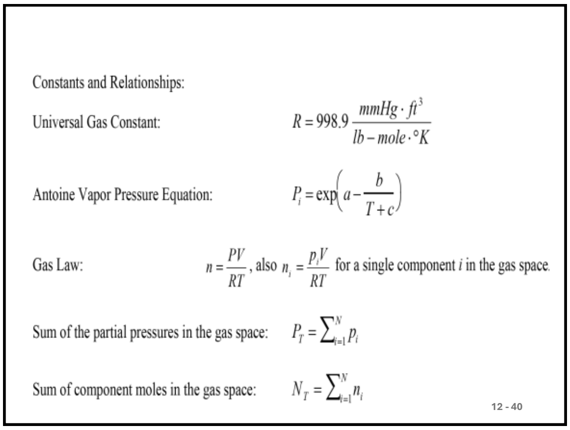
$$E_{R-heptane} = 1.02lbs\left(\frac{60min/hr}{30min}\right) = 2.04\ lbs\,/\,hr$$

$$E_{R-toluene} = 0.80lbs\left(\frac{60min/hr}{30min}\right) = 1.6\ lbs\,/\,hr$$

$$E_{R-nitrogen} = 14.05lbs\left(\frac{60min/hr}{30min}\right) = 28.1\ lbs\,/\,hr$$

Charging a mixture to a partially filled vessel (subsurface addition)

- Three hundred gallons of acetone at 20°C are to be added to the vessel featured in Illustration 2 by way of subsurface addition. For this problem, the initial contents of the vessel are 1,500 gallons of a mixture of heptane (42% mole fraction) and toluene (58% mole fraction) at 20°C. The system pressure is 760 mm Hg and the addition process is complete in 0.5 hour.
- Step 1. Define conditions of the displaced gas.
- T = 20°C = 298.15°K (System temperature)
- PT = 1.0 atm = 760 mm Hg (Total system pressure)
- V_{disp} = 300 gal = 40.1 ft3 (Displacement volume)
- Time = 30 min (Time for event) Acetone = 6.5632 lb/gal @ 20°C



Constants and Relationships:

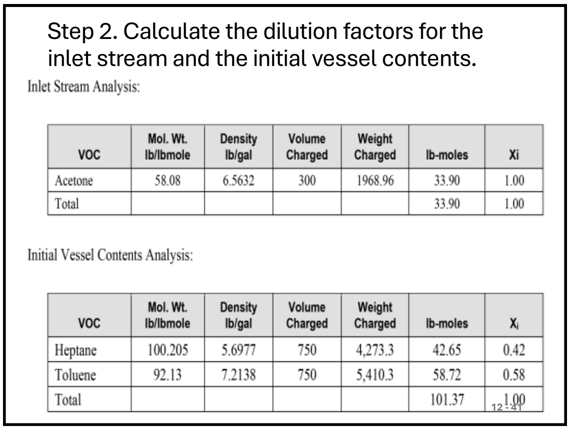
Universal Gas Constant: $R = 998.9 \dfrac{mmHg \cdot ft^3}{lb-mole \cdot °K}$

Antoine Vapor Pressure Equation: $P_i = \exp\left(a - \dfrac{b}{T+c}\right)$

Gas Law: $n = \dfrac{PV}{RT}$, also $n_i = \dfrac{p_i V}{RT}$ for a single component i in the gas space.

Sum of the partial pressures in the gas space: $P_T = \sum_{i=1}^{N} p_i$

Sum of component moles in the gas space: $N_T = \sum_{i=1}^{N} n_i$



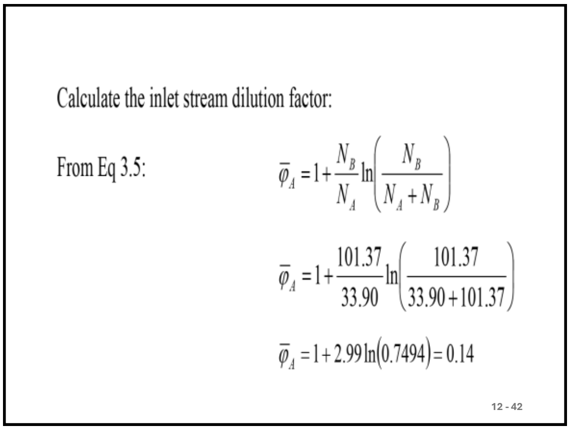
Step 2. Calculate the dilution factors for the inlet stream and the initial vessel contents.

Inlet Stream Analysis:

VOC	Mol. Wt. lb/lbmole	Density lb/gal	Volume Charged	Weight Charged	lb-moles	Xi
Acetone	58.08	6.5632	300	1968.96	33.90	1.00
Total					33.90	1.00

Initial Vessel Contents Analysis:

VOC	Mol. Wt. lb/lbmole	Density lb/gal	Volume Charged	Weight Charged	lb-moles	X_i
Heptane	100.205	5.6977	750	4,273.3	42.65	0.42
Toluene	92.13	7.2138	750	5,410.3	58.72	0.58
Total					101.37	1.00



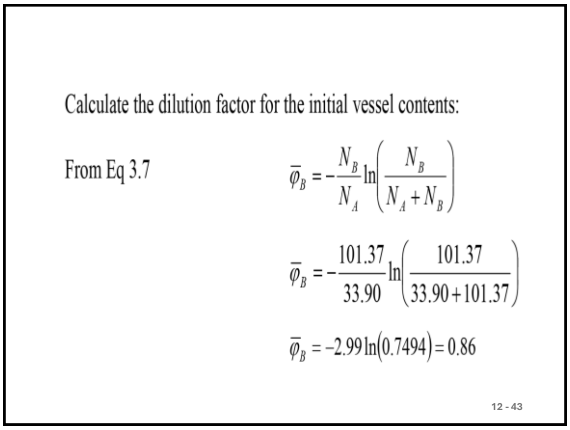
Calculate the inlet stream dilution factor:

From Eq 3.5:

$$\bar{\varphi}_A = 1 + \frac{N_B}{N_A}\ln\left(\frac{N_B}{N_A + N_B}\right)$$

$$\bar{\varphi}_A = 1 + \frac{101.37}{33.90}\ln\left(\frac{101.37}{33.90 + 101.37}\right)$$

$$\bar{\varphi}_A = 1 + 2.99\ln(0.7494) = 0.14$$



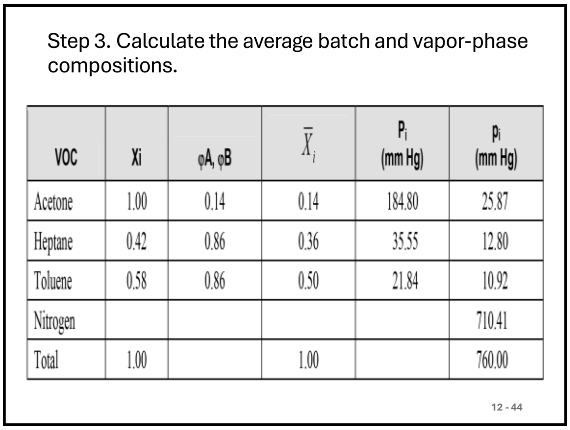
Calculate the dilution factor for the initial vessel contents:

From Eq 3.7

$$\bar{\varphi}_B = -\frac{N_B}{N_A}\ln\left(\frac{N_B}{N_A+N_B}\right)$$

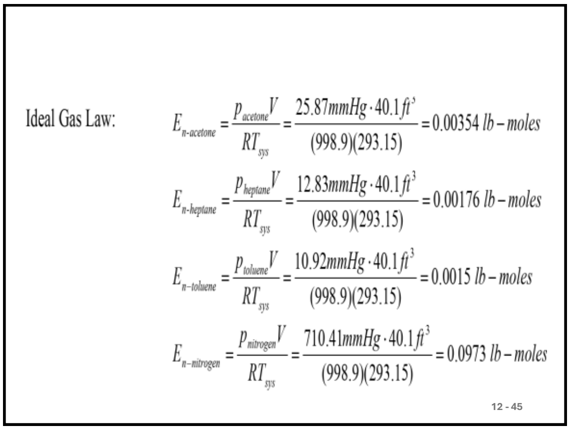
$$\bar{\varphi}_B = -\frac{101.37}{33.90}\ln\left(\frac{101.37}{33.90+101.37}\right)$$

$$\bar{\varphi}_B = -2.99\ln(0.7494) = 0.86$$



Step 3. Calculate the average batch and vapor-phase compositions.

VOC	Xi	φA, φB	$\bar{X}_i$	P_i (mm Hg)	p_i (mm Hg)
Acetone	1.00	0.14	0.14	184.80	25.87
Heptane	0.42	0.86	0.36	35.55	12.80
Toluene	0.58	0.86	0.50	21.84	10.92
Nitrogen					710.41
Total	1.00		1.00		760.00



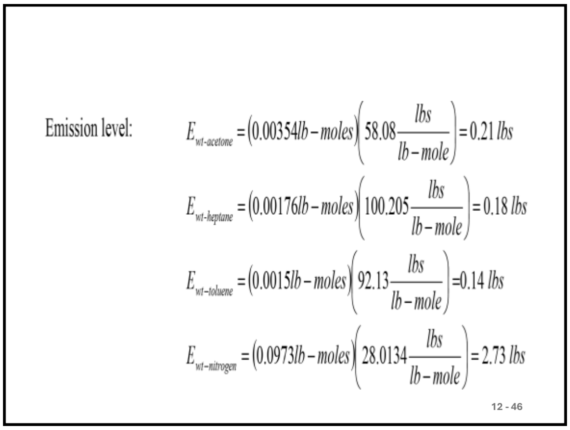
Ideal Gas Law:

$$E_{n\text{-}acetone} = \frac{p_{acetone}V}{RT_{sys}} = \frac{25.87mmHg \cdot 40.1ft^3}{(998.9)(293.15)} = 0.00354\ lb-moles$$

$$E_{n\text{-}heptane} = \frac{p_{heptane}V}{RT_{sys}} = \frac{12.83mmHg \cdot 40.1ft^3}{(998.9)(293.15)} = 0.00176\ lb-moles$$

$$E_{n-toluene} = \frac{p_{toluene}V}{RT_{sys}} = \frac{10.92mmHg \cdot 40.1ft^3}{(998.9)(293.15)} = 0.0015\ lb-moles$$

$$E_{n-nitrogen} = \frac{p_{nitrogen}V}{RT_{sys}} = \frac{710.41mmHg \cdot 40.1ft^3}{(998.9)(293.15)} = 0.0973\ lb-moles$$



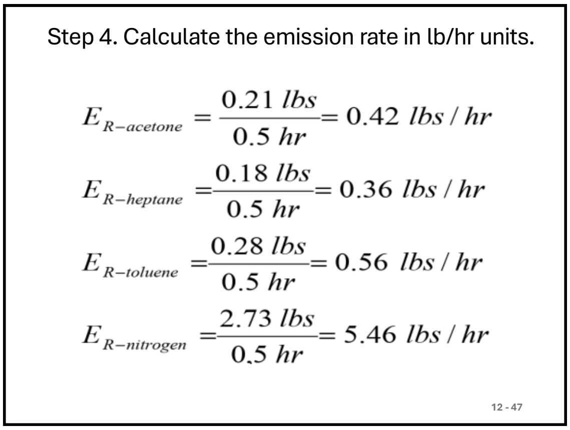
Emission level:

$$E_{wt\text{-}acetone} = (0.00354 lb-moles)\left(58.08 \frac{lbs}{lb-mole}\right) = 0.21\ lbs$$

$$E_{wt\text{-}heptane} = (0.00176 lb-moles)\left(100.205 \frac{lbs}{lb-mole}\right) = 0.18\ lbs$$

$$E_{wt-toluene} = (0.0015 lb-moles)\left(92.13 \frac{lbs}{lb-mole}\right) = 0.14\ lbs$$

$$E_{wt-nitrogen} = (0.0973 lb-moles)\left(28.0134 \frac{lbs}{lb-mole}\right) = 2.73\ lbs$$



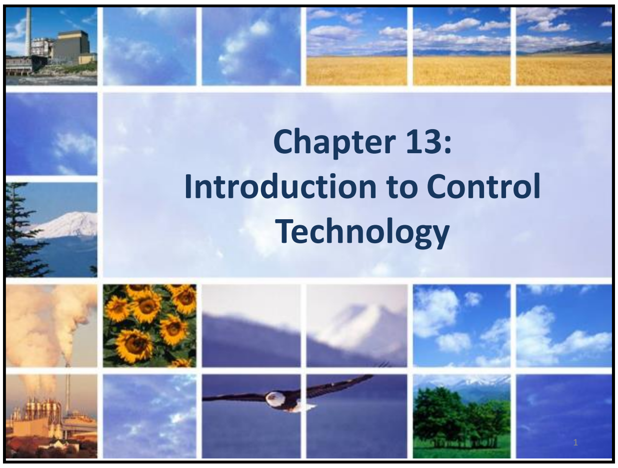
Step 4. Calculate the emission rate in lb/hr units.

$$E_{R-acetone} = \frac{0.21\ lbs}{0.5\ hr} = 0.42\ lbs/hr$$

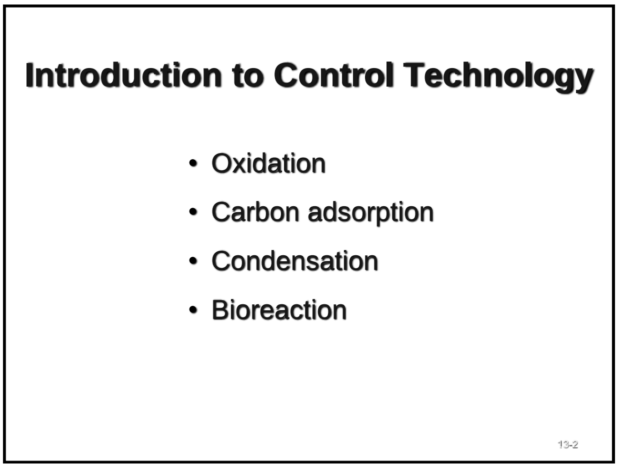
$$E_{R-heptane} = \frac{0.18\ lbs}{0.5\ hr} = 0.36\ lbs/hr$$

$$E_{R-toluene} = \frac{0.28\ lbs}{0.5\ hr} = 0.56\ lbs/hr$$

$$E_{R-nitrogen} = \frac{2.73\ lbs}{0.5\ hr} = 5.46\ lbs/hr$$



Chapter 13: Introduction to Control Technology



Introduction to Control Technology

- Oxidation
- Carbon adsorption
- Condensation
- Bioreaction

Oxidation Systems

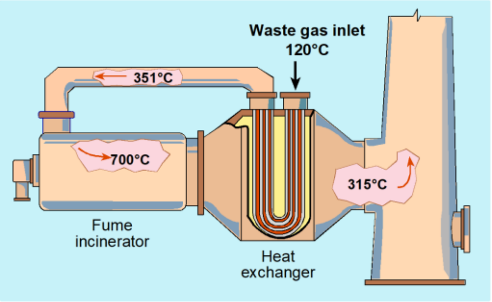
Types of Oxidizers

- **Thermal Oxidation**
  - Direct Flame
  - Flares
  - Process Boilers used for thermal oxidation
- **Catalytic Oxidation**

Types of Heat Exchangers for Oxidation System

- **Recuperative**: Heat is transferred through a metal surface in a tubular or plate heat exchanger.
- **Regenerative**: Heat is transferred using two or more ceramic packed beds that alternately store and release heat.
  - *Particulate matter* can plug the packed bed.
  - Can resist corrosion from *acid gases*.

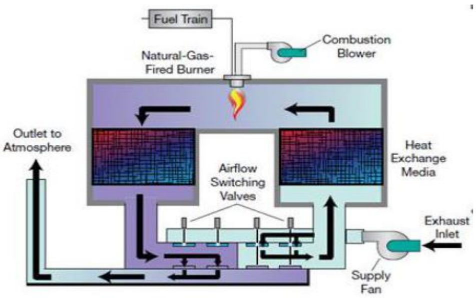
Recuperative Heat Exchanger



Heat recovery in range of 40% to 65% of the total heat released in the combustion chamber.

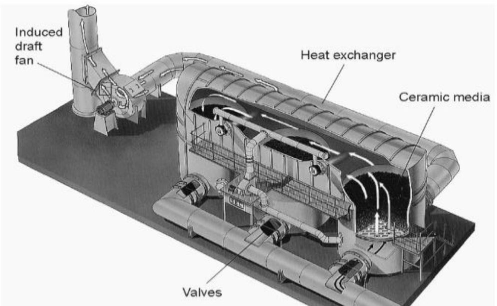
Regenerative Thermal Oxidizers

Heat recovery efficiencies as high as 95%.



- Inlet gas stream is passed through a large packed bed containing <u>preheated ceramic packing.</u>
- Product gas <u>preheats a second bed</u> containing ceramic packing.
- Flow directions are switched periodically.

Regenerative Thermal Oxidizer



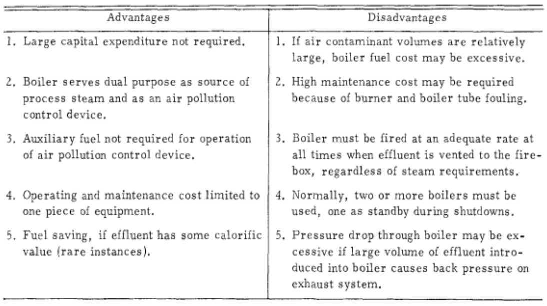
At least <u>two beds are required</u>, three beds are common

Exhaust from afterburner

Process Boilers Used for Thermal Oxidation

- Most plants equipped with one or more process boilers
- Combustion chamber <u>temperatures</u> in excess of 1800°F
- Flue gas <u>residence times</u> in excess of 1 to 2 seconds
- The <u>flow rate</u> of the organic-contaminated stream must not overwhelm the gas-handling capability of the boiler
- <u>Operating schedules</u> of boiler and oxidizer feed gas must match
- In <u>long ductwork</u> (sometimes needed), VOC can condense

Advantages and Disadvantages of Using a Boiler as an Afterburner



Advantages	Disadvantages
1. Large capital expenditure not required.	1. If air contaminant volumes are relatively large, boiler fuel cost may be excessive.
2. Boiler serves dual purpose as source of process steam and as an air pollution control device.	2. High maintenance cost may be required because of burner and boiler tube fouling.
3. Auxiliary fuel not required for operation of air pollution control device.	3. Boiler must be fired at an adequate rate at all times when effluent is vented to the firebox, regardless of steam requirements.
4. Operating and maintenance cost limited to one piece of equipment.	4. Normally, two or more boilers must be used, one as standby during shutdowns.
5. Fuel saving, if effluent has some calorific value (rare instances).	5. Pressure drop through boiler may be excessive if large volume of effluent introduced into boiler causes back pressure on exhaust system.

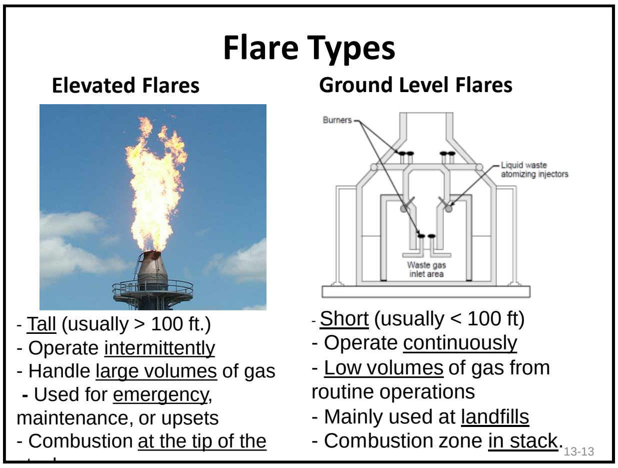
Source: *Air Pollution Engineering Manual* EPA 1973

Flares

Flares are often used at chemical plants and petroleum refineries to control VOC vents and get rid of excess gas.

Flares

- Have destruction efficiencies exceeding 98%.
- Flares can be used to control almost any VOC stream, and can handle fluctuations in
  - VOC concentration,
  - flow rate, &
  - heating value.
- Feed composition may exceed UEL
- Can be elevated or at ground level



Flare Types

Elevated Flares

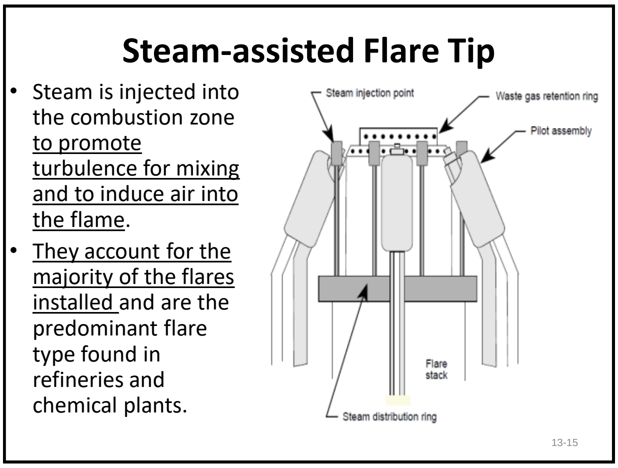
- Tall (usually > 100 ft.)
- Operate intermittently
- Handle large volumes of gas
- Used for emergency, maintenance, or upsets
- Combustion at the tip of the

Ground Level Flares

- Short (usually < 100 ft)
- Operate continuously
- Low volumes of gas from routine operations
- Mainly used at landfills
- Combustion zone in stack.

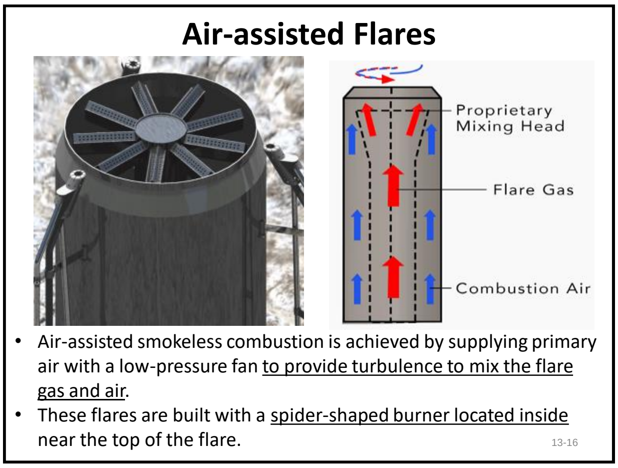
Smokeless Flares

- If a waste gas pressure (momentum) is inadequate & causes smoke, then steam or air are used to make it smokeless.
- **Steam assist:** uses high-pressure steam to provide more momentum (than just "forced air") which will enhances air-fuel mixing (turbulence).
- **Air-assisted flare** is good when steam is not available or freezing is an issue.



Steam-assisted Flare Tip

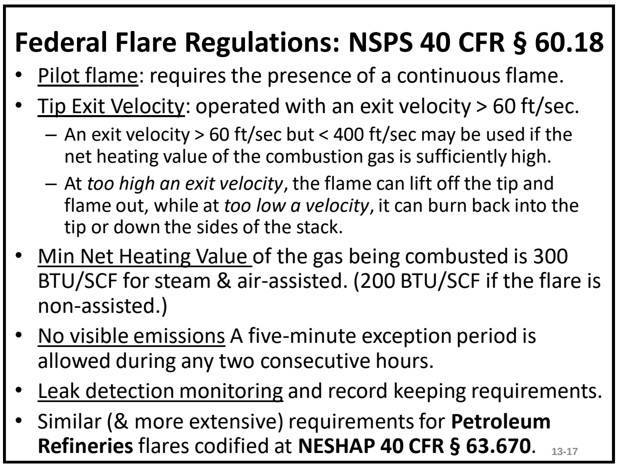
- Steam is injected into the combustion zone to promote turbulence for mixing and to induce air into the flame.
- They account for the majority of the flares installed and are the predominant flare type found in refineries and chemical plants.



Air-assisted Flares

- Air-assisted smokeless combustion is achieved by supplying primary air with a low-pressure fan to provide turbulence to mix the flare gas and air.
- These flares are built with a spider-shaped burner located inside near the top of the flare.

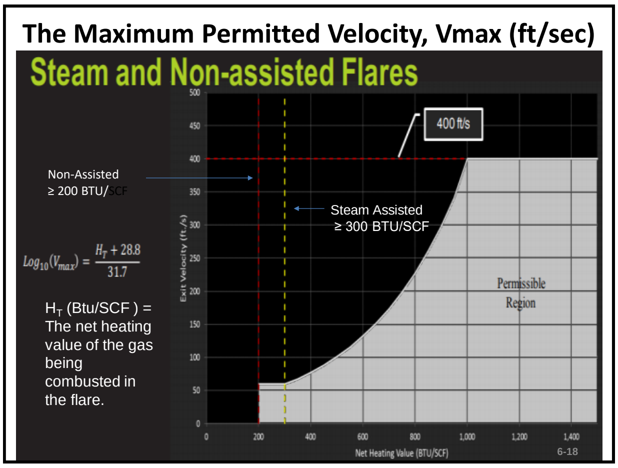
13-16



Federal Flare Regulations: NSPS 40 CFR § 60.18

- Pilot flame: requires the presence of a continuous flame.
- Tip Exit Velocity: operated with an exit velocity > 60 ft/sec.
  - An exit velocity > 60 ft/sec but < 400 ft/sec may be used if the net heating value of the combustion gas is sufficiently high.
  - At *too high an exit velocity*, the flame can lift off the tip and flame out, while at *too low a velocity*, it can burn back into the tip or down the sides of the stack.
- Min Net Heating Value of the gas being combusted is 300 BTU/SCF for steam & air-assisted. (200 BTU/SCF if the flare is non-assisted.)
- No visible emissions A five-minute exception period is allowed during any two consecutive hours.
- Leak detection monitoring and record keeping requirements.
- Similar (& more extensive) requirements for **Petroleum Refineries** flares codified at **NESHAP 40 CFR § 63.670**.

13-17



The Maximum Permitted Velocity, Vmax (ft/sec)

Steam and Non-assisted Flares

Non-Assisted
≥ 200 BTU/SCF

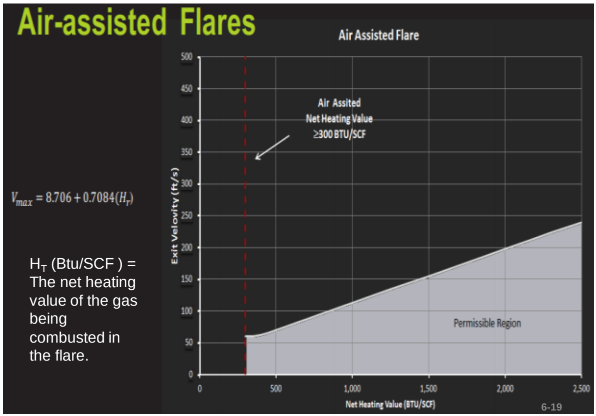
Steam Assisted
≥ 300 BTU/SCF

$$Log_{10}(V_{max}) = \frac{H_T + 28.8}{31.7}$$

H_T (Btu/SCF) = The net heating value of the gas being combusted in the flare.

6-18

The Maximum Permitted Velocity, Vmax (ft/sec)



Air-assisted Flares

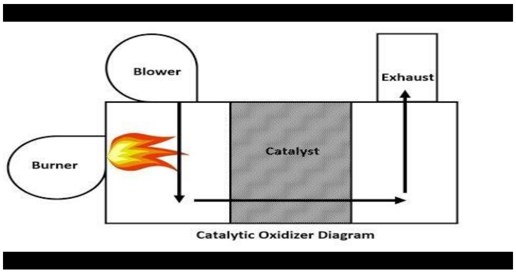
$V_{max} = 8.706 + 0.7084(H_T)$

H_T (Btu/SCF) = The net heating value of the gas being combusted in the flare.

Safety and Operational Problems of Flares

- Thermal radiation: heat given off to the surrounding area may be unacceptable
- Light: may be a nuisance
- Noise: jet-venturi used for mixing at the flare tip can cause excessive noise
- Smoke
- Energy consumption: waste energy because of the need to maintain a constant pilot flame

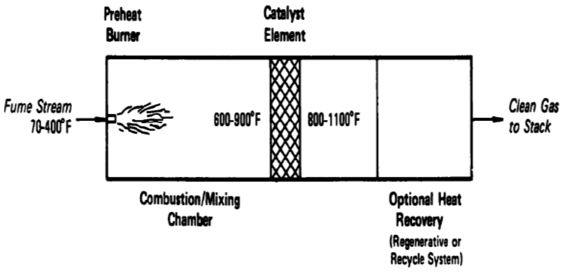
Catalytic Oxidation



Catalytic Oxidizer Diagram

- A waste gas is passed through a catalyst bed, which causes the oxidation reactions to proceed at a *much lower temperature* than in a thermal oxidation.
- A catalytic oxidizer operating at 600°F to 850°F can achieve the same efficiency as a thermal oxidizer operating between 1,000°F and 2,000°F.

Catalytic Oxidation Systems



- The exothermic oxidation reaction in *the catalyst bed* results in an increased gas temperature by 50°F to 300°F.
- Good for treatment of very low VOCs concentration (odors).
- Destruction efficiency is over 90%

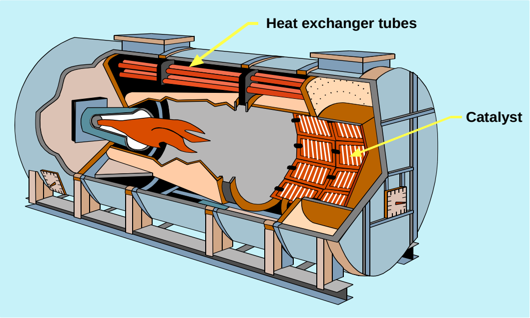
Advantages and Disadvantages

- Advantages
  - Lower temperatures
  - Reduced supplemental fuel requirements
  (in some cases may only be required during start-up)
- Disadvantages
  - Cost of the catalyst
  - Performance problems related to physical and chemical deterioration of catalyst activity
  - Catalyst beds generally last 2 to 5 years

Stationary Sources that Use Catalytic Incineration

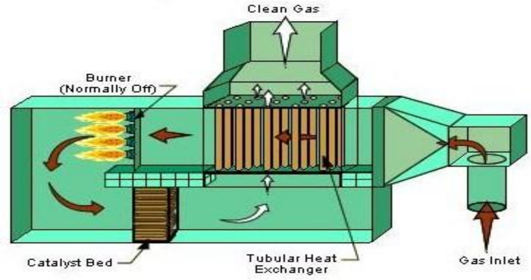
- Surface coating and printing operations widely use catalytic incineration, the others are:
- Varnish cookers;
- Foundry core ovens;
- Filter paper processing ovens;
- Plywood veneer dryers;
- Gasoline bulk loading stations;
- Process vents in the synthetic organic chemical manufacturing industry (SOCMI);
- Rubber products and polymer manufacturing; and
- Polyethylene, polystyrene, and polyester resin manufacturing.

Cutaway of a Catalytic Oxidizer



There is <u>no need for refractory lined combustion chambers</u> due to the low combustion temperatures (this reduces the weight).

Catalytic Incinerator



-<u>Auxiliary fuel</u>, in combination with the preheat from the primary heat exchanger, is used to preheat the waste gas to the reactor inlet temperature.
-The <u>inlet temperature</u> to the catalyst bed itself <u>must be above the *catalytic ignition temperature*</u> required to give the desired destruction efficiency in the incinerator.

The Inlet Temperature to the Catalyst Bed

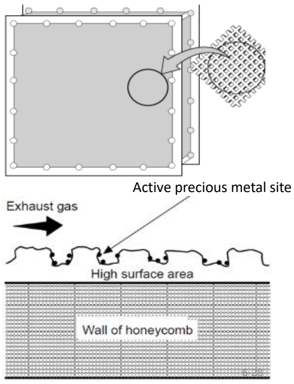
Catalyst <u>Ignition Temperatures</u> Required for Oxidizing 80% of Inlet VOC to CO2, for 2 Catalysts

Compound	Temperature, °F	
	CO_3O_4	Pt - Honeycomb
acrolein	382	294
n-butanol	413	440
n-propylamine	460	489
toluene	476	373
n-butyric acid	517	451
1, 1, 1-trichloroethane	661	>661
dimethyl sulfide	-	512

- **The inlet temperature to the catalyst bed must be above the catalytic ignition temperature** required to give the desired destruction efficiency in the incinerator.
- The catalyst's inlet <u>temperature must be chosen to be sufficiently high to</u> <u>**avoid adsorptive effects**</u> by the pollutants on the catalyst.
- <u>It is impossible to predict the temperature needed for a **mixture of VOCs**</u>. This is because the temperature required for different VOCs on a given catalyst can vary significantly.

Catalyst Bed Honeycombs

- The catalyst bed (or matrix) is generally a metal-mesh mat, ceramic honeycomb, or other ceramic matrix structure <u>designed to maximize catalyst surface area.</u>



Common Types of Catalyst Materials

- **Noble Metals:** *Platinum, Palladium, & Rhodium*
  - Widely used for VOC incineration
  - This preference is due to their high activity, wide operating temperature range, thermal durability, and resistance to deactivation.
  - *Platinum catalysts* are used for oxidation of *sulfur containing VOCs*, although they are rapidly deactivated by the presence of *chlorine*.
- **Metal Oxides:** *chromium oxide, magnesium oxide, & cobalt oxide* (also used for VOC oxidation)
  - <u>Metal oxides used when *halogens* are present</u>, because the *chlorine and fluorine* will deactivate the noble metal catalysts.
- The <u>particular catalyst chosen</u>:
  - Depends on the VOCs that are to be treated.
  - Must be selective to the resistant to deactivation by the VOCs and by other materials present in the gas stream.

Fouling & Masking: *Reduction of Catalyst Activity*

- ***<u>Fouling</u>***: deposits on the surface of the catalyst and blocks the access of the organic compounds, <u>may be reversible.</u>
  - **Particulate matter**
  - **Oil droplets** (unless they are vaporized in the preheat section
- ***<u>Masking</u>*****:** occurs when materials are adsorbed to some catalytic surfaces, reducing the active sites available to the organic compounds (<u>reversible</u>).
  - **Sulfur & halogens compounds**

Catalyst Poisons

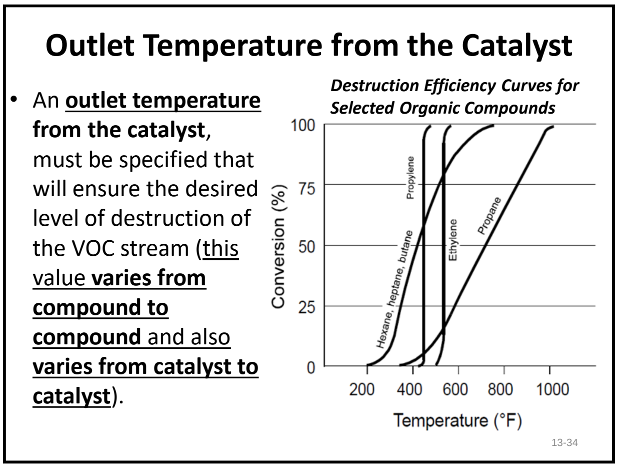
- Certain metals react irreversibly with catalyst, thereby making it inactive (called *catalyst poisoning*). Catalyst poisons can be divided into two categories:
  - (1**) fast acting poisons**: phosphorus, bismuth, arsenic, antimony and mercury, &
  - (2) **slow acting poisons**: iron, lead, tin, & silicon.

High Temperature and Catalyst Life

- All catalysts deteriorate with normal use.
- High temperatures can accelerate catalyst deactivation
  - The desired catalyst bed outlet temperature is typically 700 to 900°F
  - The maximum temperature to which the catalyst bed can be exposed continuously is limited to about 1200°F. (*EPA Cost Manual*)
- Lower operating temperatures generally result in a longer service life.

Typical Ranges for Catalyst Service Life

Industry	Typical Compounds Treated	Number of Years Before Catalyst Replacement
Can Coating	MIBK, Mineral Spirits, Isophorone, DIBK, Butyl Cellosolve	7 to 14
Metal Coatings	MEK, MIBK, Toluene, i-Butanol	7 to 10
Automotive Paint Bake	MEK, Toluene, Xylene, Isopropyl alcohol	5 to 14
Glove Manufacturing	Formaldehyde, Phenolics	5
Phthalic Anhydride	PA, MA, S	16
Synthetic Fabrics	Scotchguard, Thermosol Dye	5



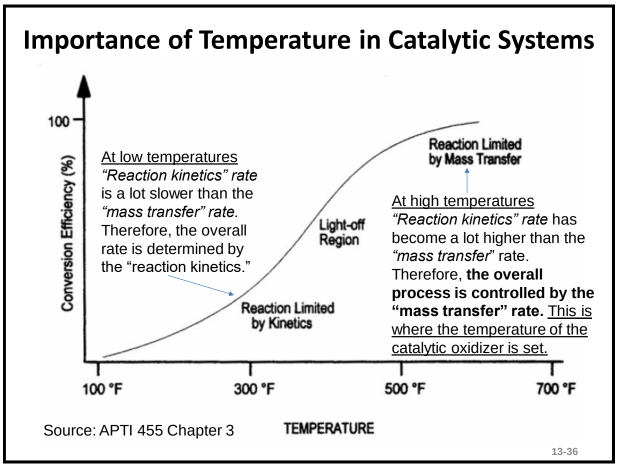
Outlet Temperature from the Catalyst

- An **<u>outlet temperature</u> from the catalyst**, must be specified that will ensure the desired level of destruction of the VOC stream (<u>this value **varies from compound to compound**</u> and also **<u>varies from catalyst to catalyst</u>**).

Destruction Efficiency Curves for Selected Organic Compounds

Catalytic Oxidation Systems

- The <u>overall rate of catalytic oxidation</u> depends on:
  - <u>Rate of mass transfer</u> (diffusion of the VOC to the surface of the catalyst) &
  - The rate of the chemical oxidation reactions on the catalyst (<u>reaction kinetics</u>)
- The temperature of the catalytic oxidizer is set at a level at which the <u>controlling factor</u> is the <u>rate of mass transfer</u>.
- <u>Destruction Efficiency</u> is a function of *length of the catalyst bed* & *mass transfer rates* (see "*Air Pollution Control*" by Cooper & Alley 3rd Ed. page 344).



Importance of Temperature in Catalytic Systems

<u>At low temperatures</u> *"Reaction kinetics" rate* is a lot slower than the *"mass transfer" rate.* Therefore, the overall rate is determined by the "reaction kinetics."

<u>At high temperatures</u> *"Reaction kinetics" rate* has become a lot higher than the *"mass transfer*" rate. Therefore, **the overall process is controlled by the "mass transfer" rate.** <u>This is where the temperature of the catalytic oxidizer is set.</u>

Source: APTI 455 Chapter 3

Space Velocity

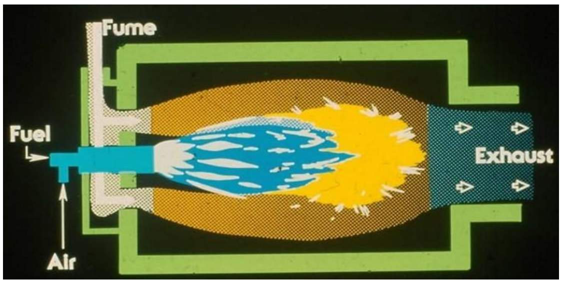
- The amount of catalyst required in a catalytic oxidizer depends on the *space velocity*.
- ***Space velocity*** is defined as the volumetric flow rate (at standard conditions) of gas entering the catalyst bed chamber divided by the volume of the catalyst bed:
  - **Space velocity (hr^{-1}) = Flow rate/Bed Volume**
- The greater the reactivity of the catalyst, the higher the space velocity and the lower the volume of catalyst required for VOC destruction.

Space Velocity & Destruction Efficiency for Catalytic Incinerator System

			Space Velocity- SV (hr^{-1}) SV = Flow rate/Bed Volume	
Required Destruction Efficiency (%)	**Temperature at the Catalyst Bed Inlet °F**	**Temperature at the Catalyst Bed Outlet °F**	**Base Metal**	**Precious Metal**
95	**600**	**1000 - 1200**	**10,000 – 15,000**	**30,000 – 40,000**

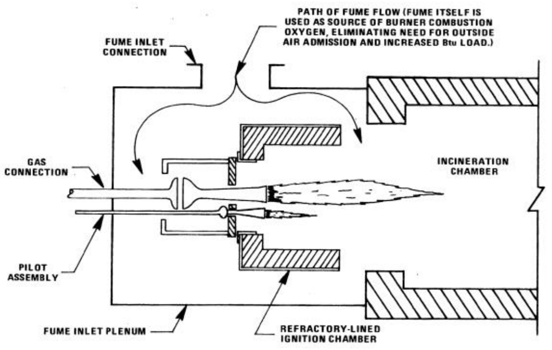
- Space velocities (SV) range from 10,000 hr^{-1} to 100,000 hr^{-1}.

Thermal Oxidizer (with outside air)



- Due to these very high temperatures, thermal oxidizers are refractory-lined combustion chambers.
- Thermal oxidizers usually provide VOC destruction efficiencies that exceed 95% and often exceed 99%.

Thermal Oxidizer (without outside air)

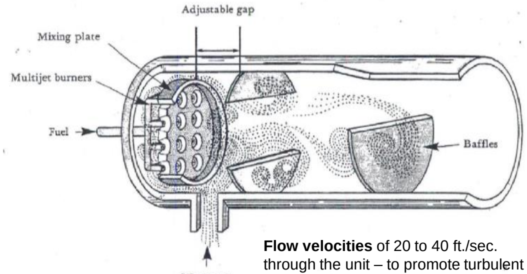


Principles of Operation

Complete combustion is achieved by considering the **three —T's of combustion**

- **Time** (at the desired temperature)
  - 0.5 to 2.0 seconds
  - Time must be allowed for the chemical kinetic reaction to occur.
- **Temperature**
  - 1200 to 1800 °F
- **Turbulence:** The organic-containing waste gases must be thoroughly mixed with the burner combustion gases to ensure complete combustion.

Turbulent Flow Created by Baffles in a Thermal Oxidizer



Flow velocities of 20 to 40 ft./sec. through the unit – to promote turbulent mixing.

Turbulent flow is needed to ensure that the oxidizer feed is well-mixed with the products from the supplemental fuel burners and that none of the pollutants are allowed to bypass the zone of maximum temperature.

Residence Time

- Usually between 0.3 and 2 seconds

$$t = \frac{V}{Q}$$

Where:

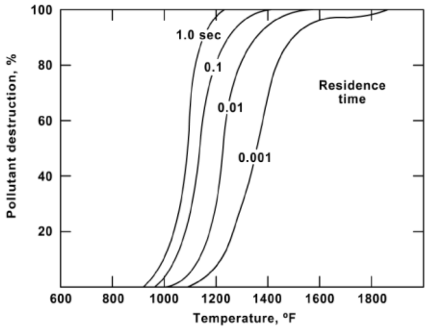
t=Residence time, sec

V=Chamber volume, ft^3

Q=Actual gas volumetric flow rate at combustion conditions, ft^3/sec

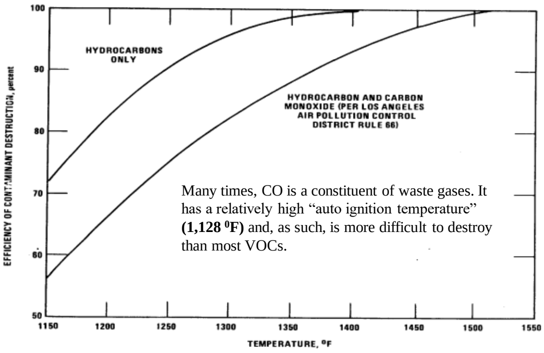
(Note: Adjustments to the flow rate must include any outside air added for combustion.)

The Effects of Time and Temperature



As residence time increase, you can operate at lower temperatures to get the same destruction efficiency.

The Effects of Operating Temperature



Many times, CO is a constituent of waste gases. It has a relatively high "auto ignition temperature" **(1,128 ^{0}F)** and, as such, is more difficult to destroy than most VOCs.

Figure 3-12. Typical effect of operating temperature on effectiveness of thermal afterburner for destruction of hydrocarbons and carbon monoxide.[1]

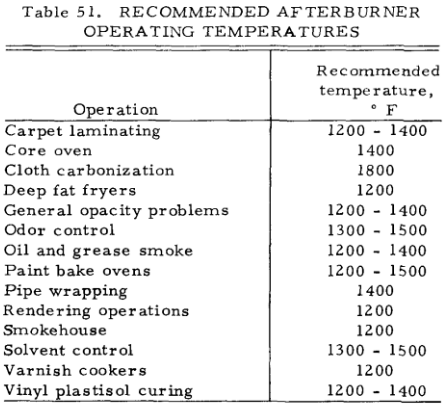


Table 51. RECOMMENDED AFTERBURNER OPERATING TEMPERATURES

Operation	Recommended temperature, ° F
Carpet laminating	1200 - 1400
Core oven	1400
Cloth carbonization	1800
Deep fat fryers	1200
General opacity problems	1200 - 1400
Odor control	1300 - 1500
Oil and grease smoke	1200 - 1400
Paint bake ovens	1200 - 1500
Pipe wrapping	1400
Rendering operations	1200
Smokehouse	1200
Solvent control	1300 - 1500
Varnish cookers	1200
Vinyl plastisol curing	1200 - 1400

Source: *Air Pollution Engineering Manual* 1973

Examples

- Hazardous waste incinerator
  - **99.99%** destruction removal efficiency (DRE) for hazardous VOCs & **99.9999** DRE for waste that contain dioxin & furans (required by NESHAP 40 CFR Part 63 Subpart EEE)
  - Would need about 2000 °F (depends on compounds burned) & minimum of 2 seconds residence time (studies).
- Medical waste incinerator
  - Regulated by NSPS 40 CFR Part 60 Subpart Ce &Ec
    - Subpart Ce: state guidelines for existing sources &
    - Subpart Ec for new sources
    - Bothe give numerical emissions limits for certain pollutants, etc.
  - Would need about 1600°F & 1.0 second residence time (studies).

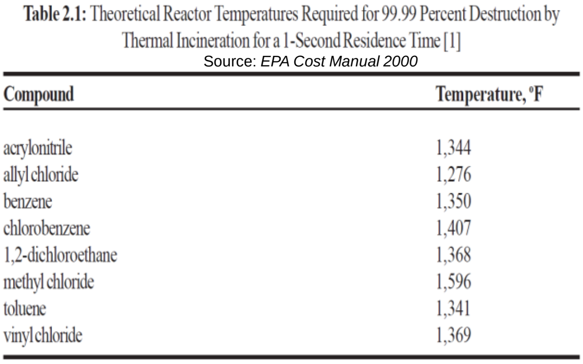
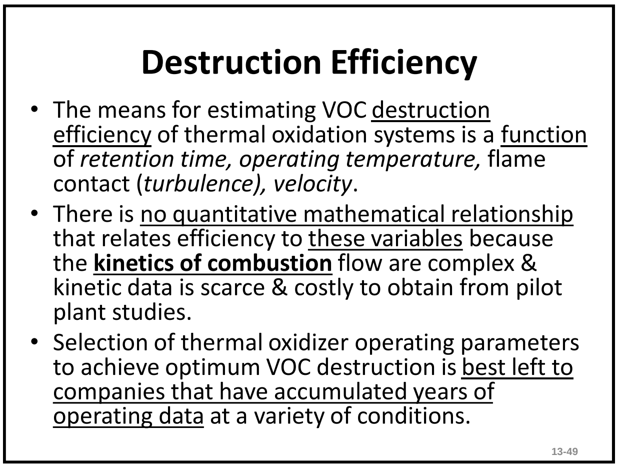


Table 2.1: Theoretical Reactor Temperatures Required for 99.99 Percent Destruction by Thermal Incineration for a 1-Second Residence Time [1]

Source: *EPA Cost Manual 2000*

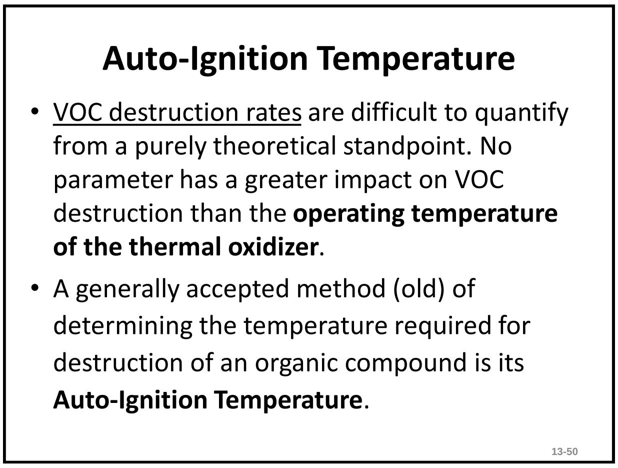
Compound	Temperature, °F
acrylonitrile	1,344
allyl chloride	1,276
benzene	1,350
chlorobenzene	1,407
1,2-dichloroethane	1,368
methyl chloride	1,596
toluene	1,341
vinyl chloride	1,369

The majority of hazardous waste incinerators are operated from 1,200 °F to 3,000 °F. Residence time usually ranges from 0.5 to 2.0. Turbulent mixing is important. (EPA *On Site Incineration – Superfund* 1998)



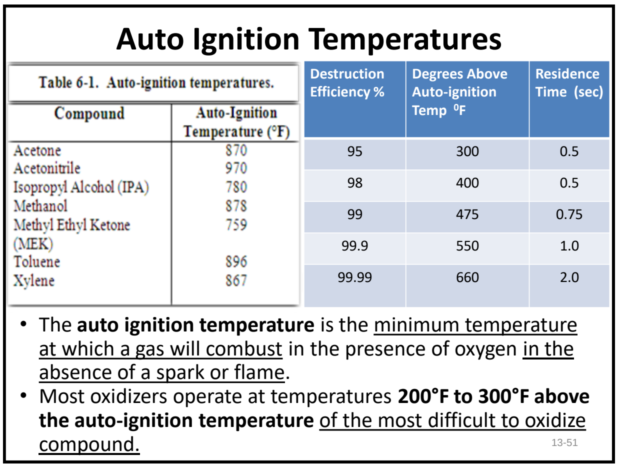
Destruction Efficiency

- The means for estimating VOC destruction efficiency of thermal oxidation systems is a function of *retention time, operating temperature,* flame contact (*turbulence), velocity*.
- There is no quantitative mathematical relationship that relates efficiency to these variables because the **kinetics of combustion** flow are complex & kinetic data is scarce & costly to obtain from pilot plant studies.
- Selection of thermal oxidizer operating parameters to achieve optimum VOC destruction is best left to companies that have accumulated years of operating data at a variety of conditions.



Auto-Ignition Temperature

- VOC destruction rates are difficult to quantify from a purely theoretical standpoint. No parameter has a greater impact on VOC destruction than the **operating temperature of the thermal oxidizer**.
- A generally accepted method (old) of determining the temperature required for destruction of an organic compound is its **Auto-Ignition Temperature**.



Auto Ignition Temperatures

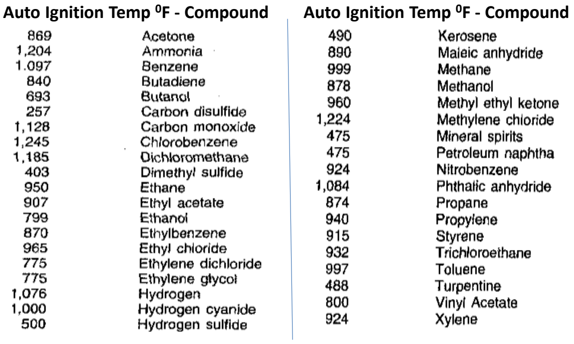
Table 6-1. Auto-ignition temperatures.

Compound	Auto-Ignition Temperature (°F)
Acetone	870
Acetonitrile	970
Isopropyl Alcohol (IPA)	780
Methanol	878
Methyl Ethyl Ketone (MEK)	759
Toluene	896
Xylene	867

Destruction Efficiency %	Degrees Above Auto-ignition Temp °F	Residence Time (sec)
95	300	0.5
98	400	0.5
99	475	0.75
99.9	550	1.0
99.99	660	2.0

- The **auto ignition temperature** is the minimum temperature at which a gas will combust in the presence of oxygen in the absence of a spark or flame.
- Most oxidizers operate at temperatures **200°F to 300°F above the auto-ignition temperature** of the most difficult to oxidize compound.

Auto-Ignition Temperatures



Auto Ignition Temp ⁰F	Compound	Auto Ignition Temp ⁰F	Compound
869	Acetone	490	Kerosene
1,204	Ammonia	890	Maleic anhydride
1.097	Benzene	999	Methane
840	Butadiene	878	Methanol
693	Butanol	960	Methyl ethyl ketone
257	Carbon disulfide	1,224	Methylene chloride
1,128	Carbon monoxide	475	Mineral spirits
1,245	Chlorobenzene	475	Petroleum naphtha
1,185	Dichloromethane	924	Nitrobenzene
403	Dimethyl sulfide	1,084	Phthalic anhydride
950	Ethane	874	Propane
907	Ethyl acetate	940	Propylene
799	Ethanol	915	Styrene
870	Ethylbenzene	932	Trichloroethane
965	Ethyl chloride	997	Toluene
775	Ethylene dichloride	488	Turpentine
775	Ethylene glycol	800	Vinyl Acetate
1,076	Hydrogen	924	Xylene
1,000	Hydrogen cyanide		
500	Hydrogen sulfide		

Source : *METAL FINISHING* NOVEMBER 1996

Design Considerations

- Residence time
- Amount of fuel required to reach the *required temperature* for complete combustion
- Proper flow velocity through the unit
  - Flow velocities of 20 to 40 ft./sec. (to promote turbulent mixing)
- VOCs should be less than 25% LEL

Combustion Products and Gas Volumes

- In all high temperature combustion processes, a complex set chemical reactions occur simultaneously
- Objective is to oxidize all carbon to CO_2, hydrogen to H_2O, and sulfur to SO_2
- Represent the set of simultaneous reactions by the single generalized reaction

$$C_xH_yS_zO_w + \left(x + \frac{y}{4} + z - \frac{w}{2}\right)O_2 \longrightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O + zSO_2$$

Minor Components in Waste Gas

- Sulfur
  - ≥ 98% converted to SO_2
  - Small amount of SO_3 may be formed
- Chlorine –converted to HCl
- Fluorine –converted to HF
- Nitrogen (in waste gas) –may be converted to N_2, NO, or NO_2
- Cl, F, N (in waste gas) <u>normally neglected</u> in material balance calculations

Composition of Air

- Oxygen is almost always supplied by air
- Air composition: 21% O_2
  79% N_2
- Neglect minor components in material balance calculations
- For Air: $x = \frac{0.79\ moles\ of\ N_2}{0.21\ moles\ of\ O_2}$

  X = mole fraction of air = volume fraction of air

  $N_1/N_2 = V_1/V_2$ (at constant T & P – from PV=NRT)

Combustion Air Requirements

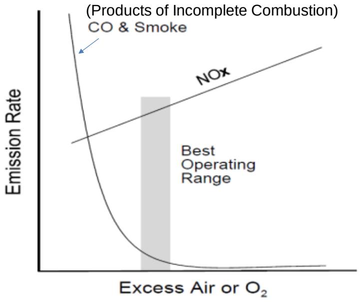
- To achieve complete combustion of the fuel (e.g., natural gas, propane, No. 2 oil), <u>a sufficient supply of oxygen must be present</u> in the burner flame to convert all of the carbon to CO_2. This quantity of oxygen is referred to as the ***stoichiometric* (or theoretical) *amount***.
- For example, 1 mole of methane (the major component of natural gas) requires 2 moles of oxygen for complete combustion

$$\mathbf{CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O}$$

Lean and Rich

- *Rich* - there is insufficient O_2 available for complete oxidation.
  - This reduces the peak flame temperature and results in the formation of CO and other partially-oxidized compounds
- *Lean* - the amount of O_2 exceeds the amount required for complete oxidation.
  - The excess air (un-reacted oxygen and nitrogen) will carry away a portion of the heat released by the combustion reactions, and therefore reduce the peak flame temperature.
- Normal operation –10% to 30% excess air

NOx and CO Emissions vs. Excess Air

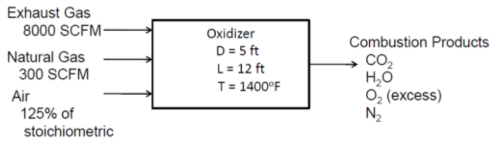


The **reason that NOx increases with excess air** is that as we increase excess air, large amount of nitrogen enters with the combustion air and more of the combustion is occurring in a region with extra oxygen.

Example Problem 6-1

- Emissions from a paint baking oven are controlled by a thermal oxidizer. The cylindrical unit has a diameter of 5 feet and a length of 12 feet, with all combustion air supplied by an auxiliary source.
- The exhaust from the oven is 8,000 SCFM. The oxidizer uses 300 SCFM of natural gas and operates at a temperature of 1,400°F.
- What is the residence time in the combustion chamber? Assume that the fuel is 100% methane, and that the burner is operated at 125% of the stoichiometric requirement.

Solution



t (retention time) sec = V (volume of chamber) ft³ / Q (total flue gas rate) Actual ft³/sec

Q (total flue gas rate) = Q (in) + Q (products of combustion) + Q (excess O_2) + Q (N_2)
Q (products of combustion) = volume of CO_2 & H_2O produced by combustion
Q (in) = exhaust gas from source (unreacted) = 8,000 SCFM
Q (excess O_2) = excess O_2 not combusted
Q (N_2)= unreacted in air

From excess air

Note: we assume that any VOCs in exhaust gas is not oxidized (because VOC concentration is very low).

Solution (continued)

- **Step 1. Write the combustion reaction**

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

  - Stoichiometric oxygen requirement is 2 moles of oxygen for every mole of methane

- **Step 2. Calculate the amount of O_2 required for stoichiometric conditions (no excess air)**

$$300\ \text{SCFM}\left(\frac{\text{lb mole CH}_4}{385.4\ \text{ft}^3}\right) = 0.778\frac{\text{lb mole CH}_4}{\text{min}}$$

$$\text{Stoichiometric O}_2 = 2 \times (\text{lb mole CH}_4)$$

$$\frac{2\ \text{lb mole O}_2}{\text{lb mole CH}_4}\left(0.778\frac{\text{lb mole CH}_4}{\text{min}}\right) = \boxed{1.56\frac{\text{lb mole O}_2}{\text{min}}}$$

Solution (continued)

Step 3. Calculate the air sent to the burner (125% of stoichiometric requirement).

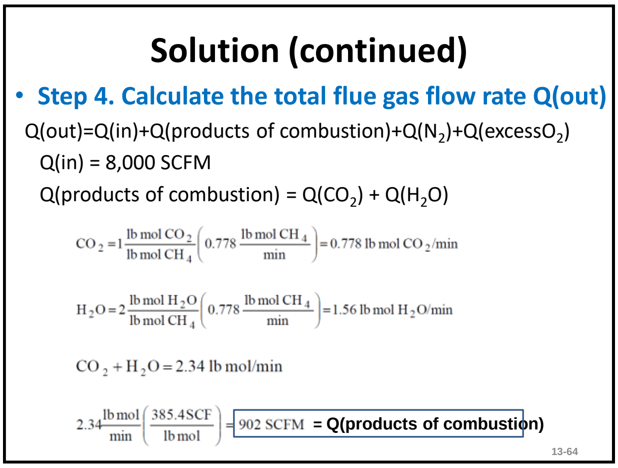
$$\text{Total O}_2\ \text{requirement} = 1.25 \times (\text{stoichiometric requirement})$$

$$= 1.25\left(1.56\frac{\text{lb mole O}_2}{\text{min}}\right) = \boxed{1.95\frac{\text{lb mole O}_2}{\text{min}}}$$

$$\text{Total N}_2 = \frac{0.79\ \text{lb mole N}_2}{0.21\ \text{lb mole O}_2}\left(1.95\frac{\text{lb mole O}_2}{\text{min}}\right)$$

$$= \boxed{7.34\ \text{lb mole N}_2/\text{min}}$$

Continued...



Solution (continued)

- **Step 4. Calculate the total flue gas flow rate Q(out)**

Q(out)=Q(in)+Q(products of combustion)+Q(N_2)+Q(excessO_2)

Q(in) = 8,000 SCFM

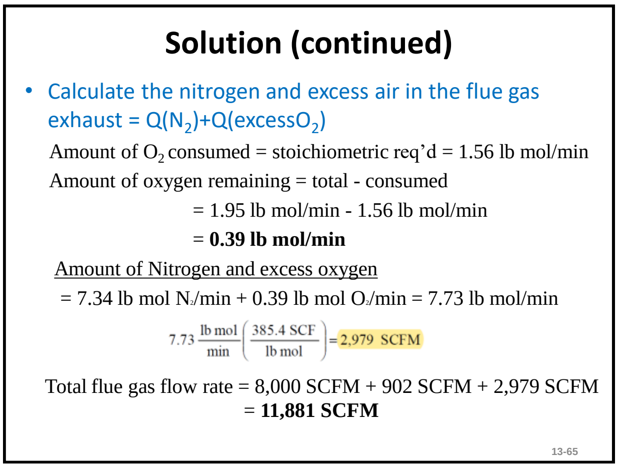
Q(products of combustion) = Q(CO_2) + Q(H_2O)

$$CO_2 = 1\frac{\text{lb mol } CO_2}{\text{lb mol } CH_4}\left(0.778\frac{\text{lb mol } CH_4}{\text{min}}\right) = 0.778 \text{ lb mol } CO_2/\text{min}$$

$$H_2O = 2\frac{\text{lb mol } H_2O}{\text{lb mol } CH_4}\left(0.778\frac{\text{lb mol } CH_4}{\text{min}}\right) = 1.56 \text{ lb mol } H_2O/\text{min}$$

$$CO_2 + H_2O = 2.34 \text{ lb mol/min}$$

$$2.34\frac{\text{lb mol}}{\text{min}}\left(\frac{385.4\text{SCF}}{\text{lb mol}}\right) = \boxed{902 \text{ SCFM}}$$ **= Q(products of combustion)**



Solution (continued)

- Calculate the nitrogen and excess air in the flue gas exhaust = Q(N_2)+Q(excessO_2)

Amount of O_2 consumed = stoichiometric req'd = 1.56 lb mol/min

Amount of oxygen remaining = total - consumed

= 1.95 lb mol/min - 1.56 lb mol/min

= **0.39 lb mol/min**

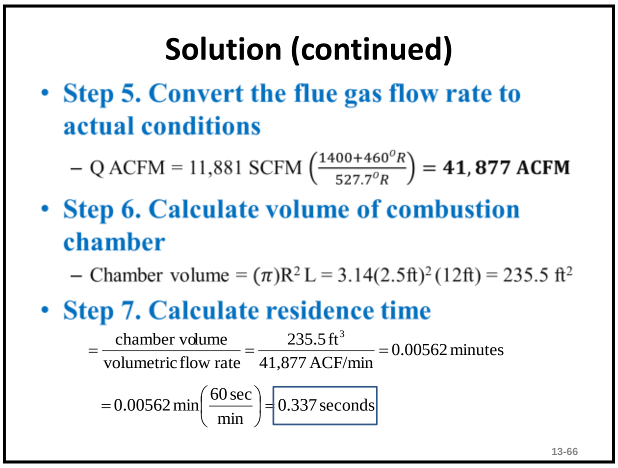
Amount of Nitrogen and excess oxygen

= 7.34 lb mol N_2/min + 0.39 lb mol O_2/min = 7.73 lb mol/min

$$7.73\frac{\text{lb mol}}{\text{min}}\left(\frac{385.4 \text{ SCF}}{\text{lb mol}}\right) = 2{,}979 \text{ SCFM}$$

Total flue gas flow rate = 8,000 SCFM + 902 SCFM + 2,979 SCFM

= **11,881 SCFM**



Solution (continued)

- **Step 5. Convert the flue gas flow rate to actual conditions**
  - $\text{Q ACFM} = 11{,}881 \text{ SCFM}\left(\frac{1400+460^oR}{527.7^oR}\right) = \mathbf{41,877\ ACFM}$
- **Step 6. Calculate volume of combustion chamber**
  - Chamber volume = $(\pi)R^2 L = 3.14(2.5\text{ft})^2(12\text{ft}) = 235.5 \text{ ft}^2$
- **Step 7. Calculate residence time**

$$= \frac{\text{chamber volume}}{\text{volumetric flow rate}} = \frac{235.5\text{ ft}^3}{41{,}877 \text{ ACF/min}} = 0.00562 \text{ minutes}$$

$$= 0.00562 \text{ min}\left(\frac{60 \text{ sec}}{\text{min}}\right) = \boxed{0.337 \text{ seconds}}$$

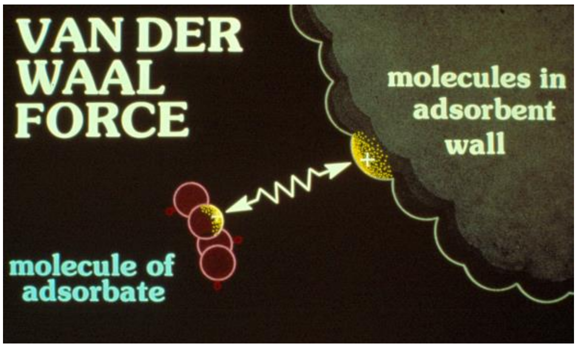
Carbon Adsorption

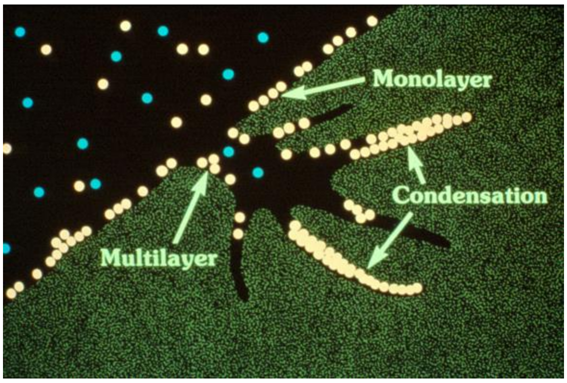
Activated Carbon

- A class of materials
- Produced from coal, wood, nut shells and petroleum-based products
- Activation process
  - Heat material to ~1,100°F without oxygen
  - Use stream, air or CO_2 to increase pore structure

Types of Adsorption Processes

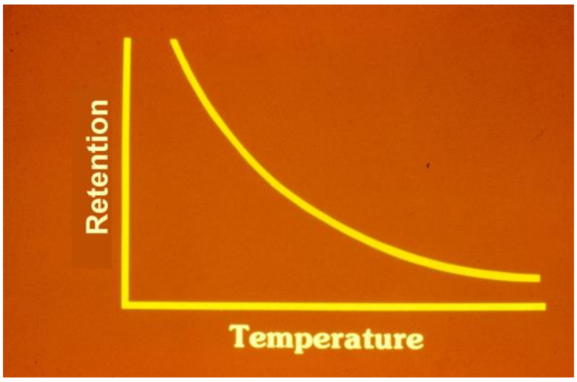
- Chemical adsorption
- Physical adsorption

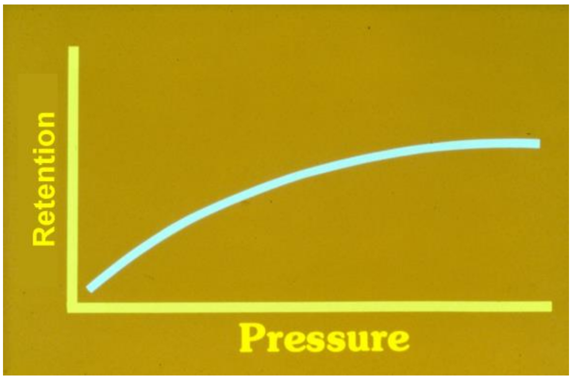


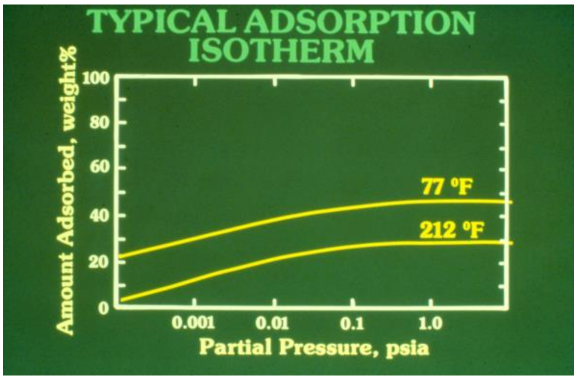


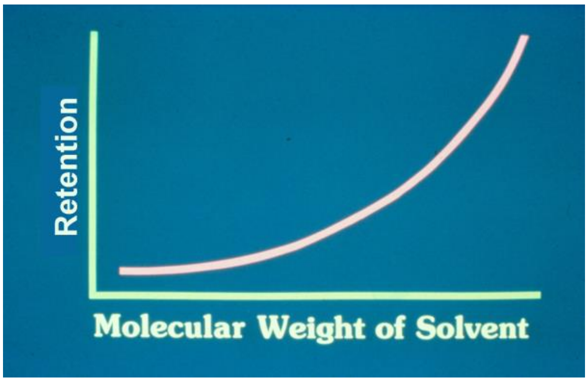
Adsorption Capacity

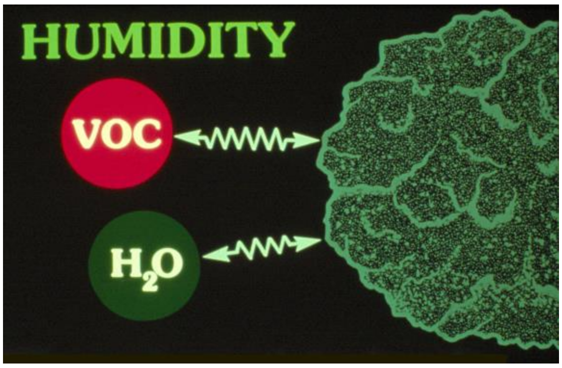
- Retention
- Lbs of VOC adsorbed per 100 lbs of carbon
- Weight percent

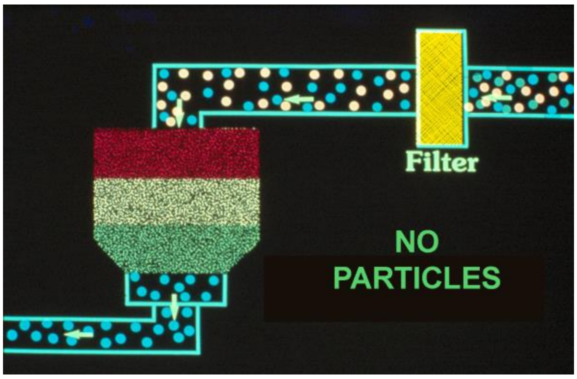

Retention
Temperature


Retention
Pressure


TYPICAL ADSORPTION ISOTHERM
Amount Adsorbed, weight%
100
80
60
40
20
0
77 °F
212 °F
0.001
0.01
0.1
1.0
Partial Pressure, psia


Retention
Molecular Weight of Solvent

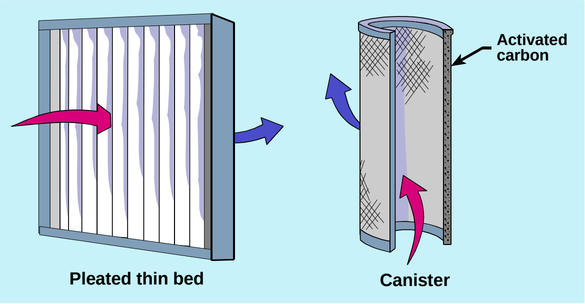

HUMIDITY
VOC
H2O


Filter
NO PARTICLES

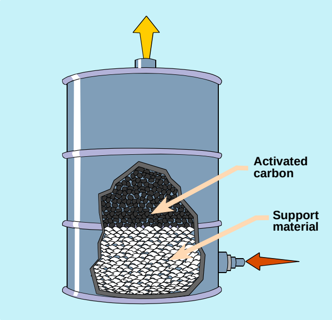
Types of Adsorption Systems

- On-site regeneration
- Off-site regeneration

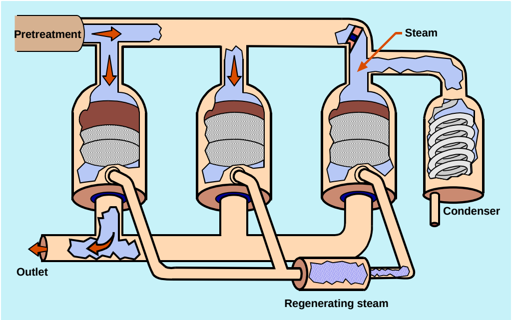
Off-Site Regeneration Adsorbers

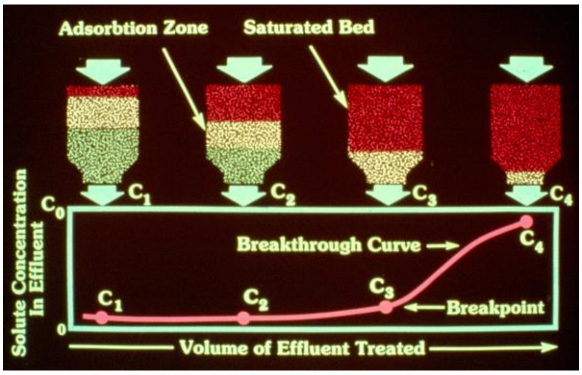


Canister Adsorber



On-Site Regeneration Fixed-Bed System

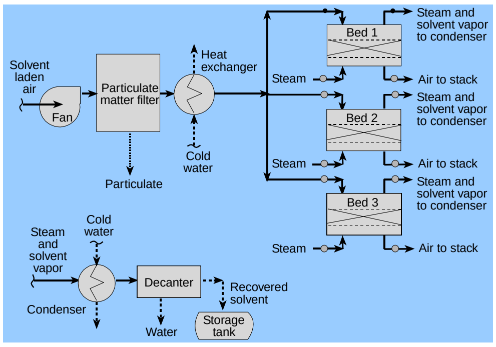




Regeneration Methods

- Thermal swing
  - Steam
  - Hot gas
- Pressure swing

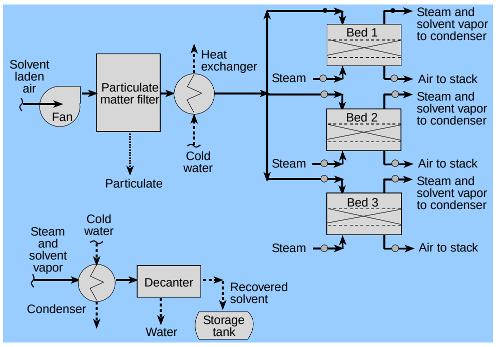
Steam Regeneration



Regeneration Methods

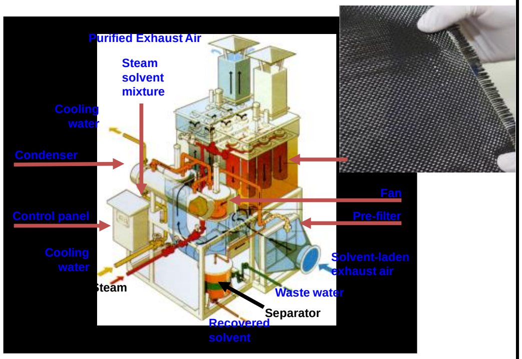
- Thermal swing
  - Steam
  - Hot gas
- Pressure swing

Hot Gas Regeneration

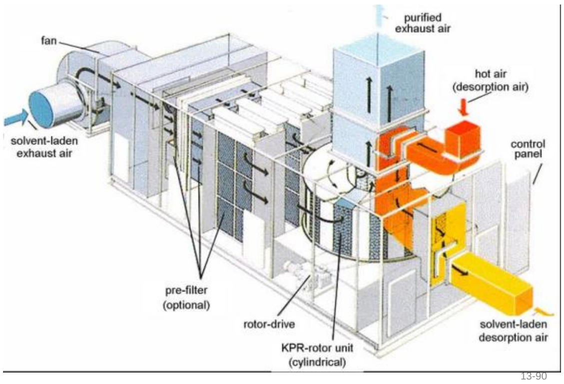


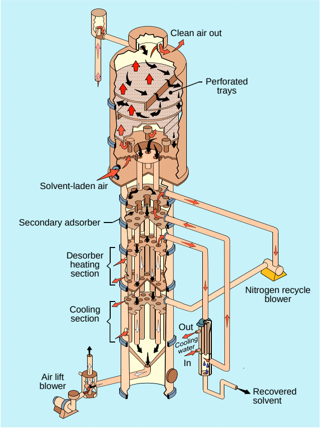
Other Adsorber Designs

Carbon Fiber Adsorber



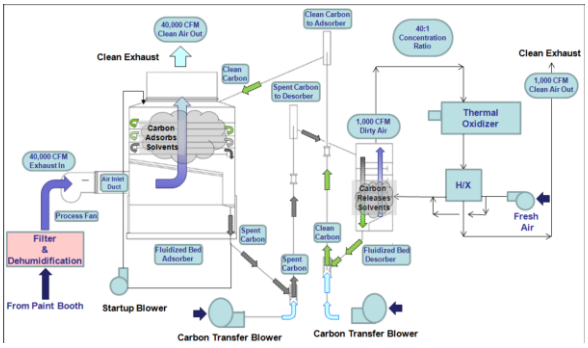
Rotary Bed Adsorber





Fluidized Bed Adsorber

Fluidized Bed Adsorber



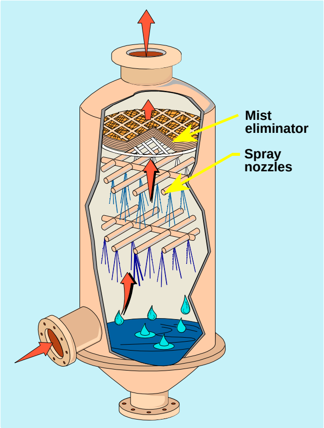
Fluidized Bed Adsorber

Condensation

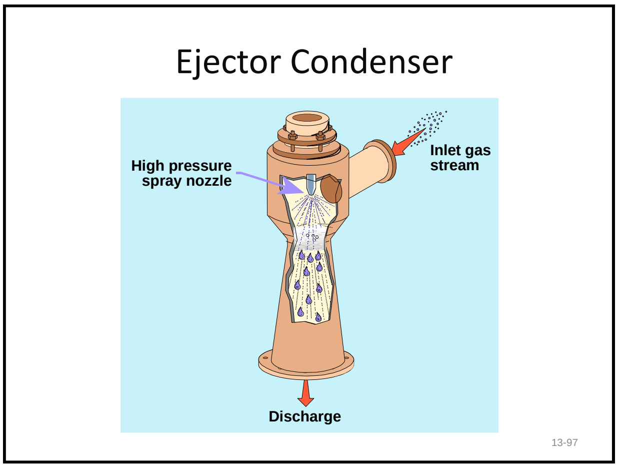
- Conventional systems
- Refrigeration systems
- Cryogenic systems

Types of Condensers

- Direct contact condensers
- Surface condensers

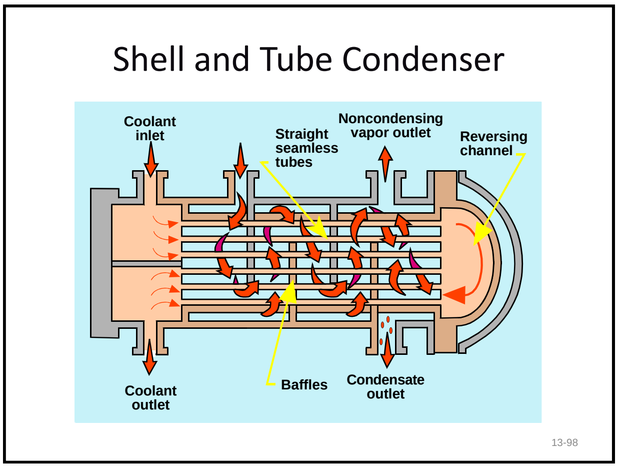


Direct Contact Condenser



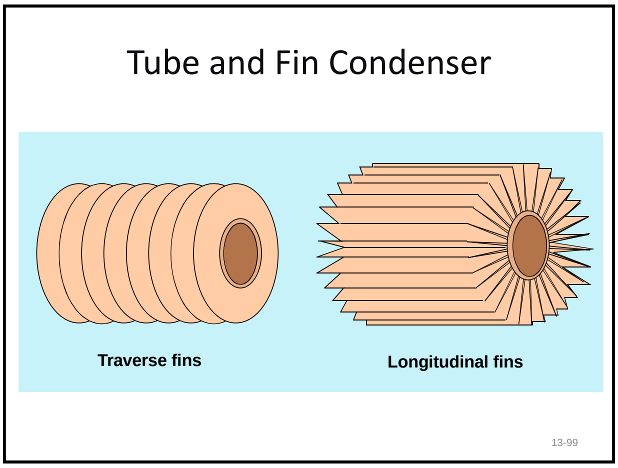
Ejector Condenser

13-97



Shell and Tube Condenser

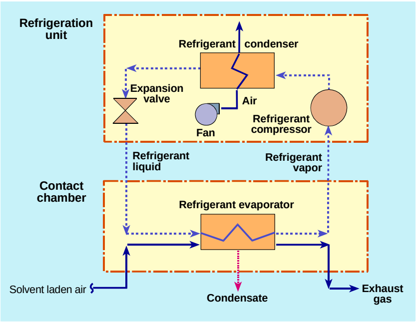
13-98



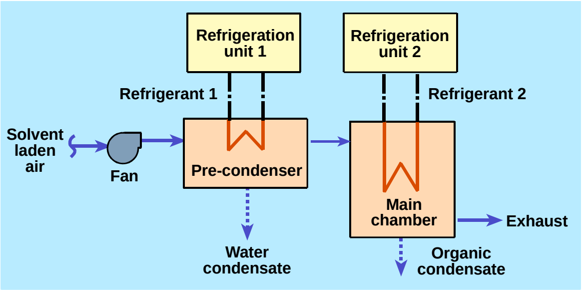
Tube and Fin Condenser

13-99

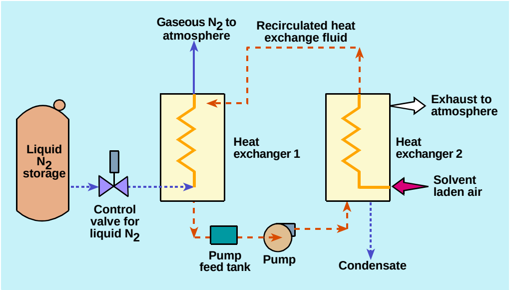
Refrigeration Cycle



Refrigeration System



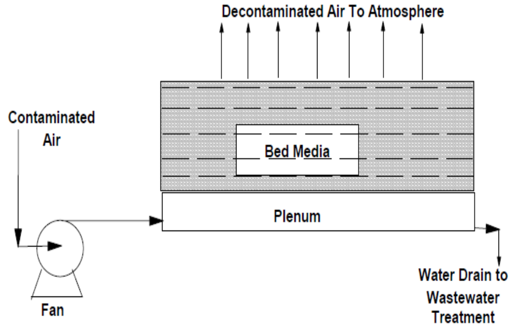
Dual Heat Exchanger Cryogenic System



Bioreaction Controls

- Biofilters
- Biotrickling filters
- Bioscrubbers

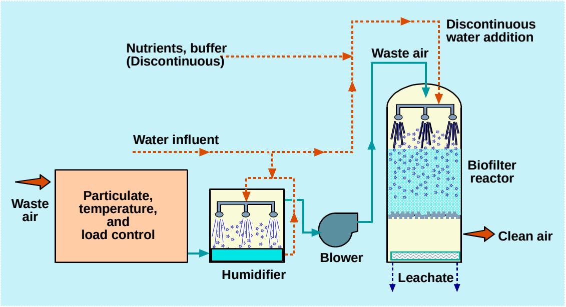
Basic Biofilter



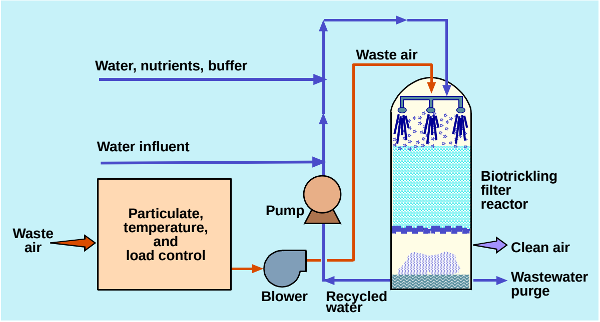
Microbial Population Requirements

- Sufficient moisture
- Sufficient nutrients
- Temperature of 60°F to 85°F
- pH of 6 to 8

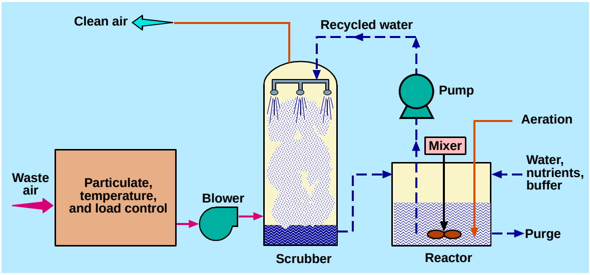
Biofilter System



Biotrickling Filter System



Bioscrubber System



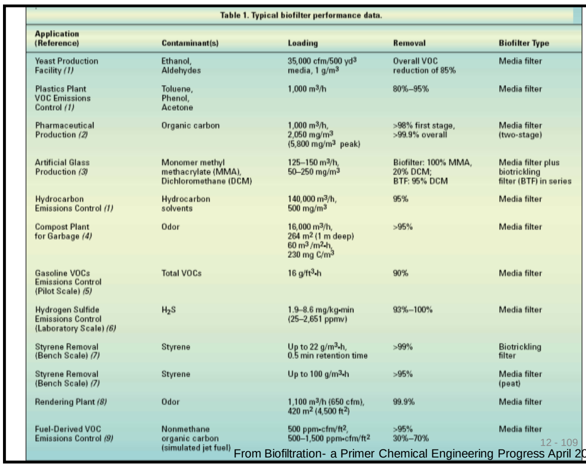


Table 1. Typical biofilter performance data.

Application (Reference)	Contaminant(s)	Loading	Removal	Biofilter Type
Yeast Production Facility *(1)*	Ethanol, Aldehydes	35,000 cfm/500 yd^3 media, 1 g/m^3	Overall VOC reduction of 85%	Media filter
Plastics Plant VOC Emissions Control *(1)*	Toluene, Phenol, Acetone	1,000 m^3/h	80%–95%	Media filter
Pharmaceutical Production *(2)*	Organic carbon	1,000 m^3/h, 2,050 mg/m^3 (5,800 mg/m^3 peak)	>98% first stage, >99.9% overall	Media filter (two-stage)
Artificial Glass Production *(3)*	Monomer methyl methacrylate (MMA), Dichloromethane (DCM)	125–150 m^3/h, 50–250 mg/m^3	Biofilter: 100% MMA, 20% DCM; BTF: 95% DCM	Media filter plus biotrickling filter (BTF) in series
Hydrocarbon Emissions Control *(1)*	Hydrocarbon solvents	140,000 m^3/h, 500 mg/m^3	95%	Media filter
Compost Plant for Garbage *(4)*	Odor	16,000 m^3/h, 264 m^2 (1 m deep) 60 m^3 /m^2•h, 230 mg C/m^3	>95%	Media filter
Gasoline VOCs Emissions Control (Pilot Scale) *(5)*	Total VOCs	16 g/ft^3•h	90%	Media filter
Hydrogen Sulfide Emissions Control (Laboratory Scale) *(6)*	H_2S	1.9–8.6 mg/kg•min (25–2,651 ppmv)	93%–100%	Media filter
Styrene Removal (Bench Scale) *(7)*	Styrene	Up to 22 g/m^3•h, 0.5 min retention time	>99%	Biotrickling filter
Styrene Removal (Bench Scale) *(7)*	Styrene	Up to 100 g/m^3•h	>95%	Media filter (peat)
Rendering Plant *(8)*	Odor	1,100 m^3/h (650 cfm), 420 m^2 (4,500 ft^2)	99.9%	Media filter
Fuel-Derived VOC Emissions Control *(9)*	Nonmethane organic carbon (simulated jet fuel)	500 ppm•cfm/ft^2, 500–1,500 ppm•cfm/ft^2	>95% 30%–70%	Media filter

From Biofiltration- a Primer Chemical Engineering Progress April 2001

US EPA Bioreactor Publication

"USING BIOREACTORS TO CONTROL AIR POLLUTION" EPA-456/R-03-003

http://www.epa.gov/ttn/catc/dir1/fbiorect.pdf

VOC Control

REDUCE VOC AND HAP EMISSIONS

Follow this roadmap to understand the abatement technologies available for controlling emissions of volatile organic compounds and hazardous air pollutants and the criteria for choosing among them.

EDWARD C. MORETTI,
BAKER ENVIRONMENTAL, INC.

Over the past decade, tremendous scientific, political, social and economic changes have impacted air quality and environmental regulations, prompting a new look at the subject of controlling volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions. Some of the significant changes that influence the selection of solutions for reducing emissions of VOCs and HAPs are:

- The implementation of the Maximum Achievable Control Technology (MACT) provisions of the Clean Air Act. Many of the facilities affected by MACT standards consider the reporting and control of HAP emissions to be the single largest driver toward VOC abatement.
- Increased public interest in the environment through web-based access to right-to-know reports. This continues to prompt many companies to find innovative ways to reduce pollution.
- The emergence of regional air-quality initiatives related to ozone transport and market-based incentive programs such as emission-reduction credit trading programs.
- Highly political or newsworthy issues in air quality management, such as the recent legal battle over EPA's ambient air-quality standard for ozone, the public dialogue over smog and urban sprawl, and the efforts to balance the regulation of stationary and mobile sources.
- The refocusing of environmental policy from a command-and-control format to a more collaborative, incentive-based approach that promotes pollution prevention over end-of-pipe control.
- The emergence of international agreements to enhance regional environmental cooperation, avoid potential environmental and trade disputes, promote effective enforcement of environmental laws, and explore transboundary air issues.

This article will help chemical engineers evaluate and select VOC and HAP control technologies. It is excerpted from the book "Practical Solutions for Reducing and Controlling Volatile Organic Compounds and Hazardous Air Pollutants" *(1)*, published by AIChE's Center for Waste Reduction Technologies (CWRT). The book includes information that the Du Pont Co. developed based on technical and economic evaluations of VOC and HAP abatement technologies. The book also includes information from EPA's control-technology guidance documents. EPA's National Risk Management Laboratory, Sustainable Technology Division, provided funding for the book.

Thermal oxidation

Thermal oxidation, or thermal incineration, is the process of oxidizing combustible materials by raising their temperature above the autoignition point in the presence of oxygen and maintaining it at a high temperature for sufficient time to complete combustion to carbon dioxide and water. Time, temperature, turbulence (for mixing) and the amount of oxygen affect the rate and efficiency of the combustion process. These

30 www.cepmagazine.org June 2002 CEP

Chemical Engineering Progress Magazine June 2002
https://www.aiche.org/resources/publications/cep/2002/june/reduce-voc-and-hap-emissions