AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9 – 12, 2026

WESTAR
Western States Air Resources Council

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COURSE GOALS

Those completing this course will gain a basic understanding of the different types of volatile organic emission sources which are present at industrial facilities and the types of control devices that are available for certain emission sources.

2

VOLATILE ORGANIC COMPOUND (VOC)

- VOC means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.
- This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity: Methane; ethane; methylene chloride (dichloromethane)…

40CFR§51.100(s)

3

COURSE TOPICS

Attendees will be able to perform regulatory reviews involving the following elements of gaseous emissions and control:

- Basics of organic chemistry and photochemistry
- VOC properties
- National emissions and regulatory approach
- Source measurement of VOCs
- Surface coating processes
- Graphic arts processes
- Petroleum refining and product storage and distribution
- Liquid asphalt
- Degreasing processes
- Dry cleaning processes
- VOC control methods

4

OBJECTIVES

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

5

AGENDA - DAY 1

Time	Topic	Presentation	Handbook Chapter
08:30 AM – 9:30 AM	Introductions and Pre-test	1	1
09:30 AM – 10:50 AM	National emissions	2	4
10:50 AM – 11:00 AM	Break		
11:00 AM – 12:30 PM	Regulatory approach	3	4
12:30 PM – 1:30 PM	Lunch Break (on your own)		
1:30 PM – 2:50 PM	Review of Organic Chemistry	4	2
2:50 PM – 3:00 PM	Break		
3:00 PM – 4:30 PM	Review of Organic Chemistry (cont'd)	4	2

6

AGENDA - DAY 2

Time	Topic	Presentation	Handbook Chapter
08:30 AM – 9:30 AM	Formation of Ozone and Photochemical Smog	5	2
09:30 AM – 10:50 AM	Properties of Organic Vapor	6	2
10:50 AM – 11:00 AM	Break		
11:00 AM – 12:30 PM	Source Measurement	7	4
12:30 PM – 1:30 PM	Lunch Break (on your own)		
1:30 PM – 2:50 PM	Conversions & Problem Solving	-	2&3
2:50 PM – 3:00 PM	Break		
3:00 PM – 4:30 PM	Surface Coating Processes	8	5

7

AGENDA - DAY 3

Time	Topic	Presentation	Handbook Chapter
08:30 AM – 10:00 AM	Graphic arts processes	9	6
10:00 AM – 10:10 AM	Break		
10:10 AM – 11:00 AM	Problem Solving Coating	10	12
11:00 AM – 11:10 AM	Break		
11:10 AM – 12:30 PM	Petroleum Industry	11	-
12:30 PM – 1:30 PM	Lunch Break (on your own)		
1:30 PM – 2:50 PM	Petroleum Refining	12	8
2:50 PM – 3:00 PM	Break		
3:00 PM – 4:30 PM	Petroleum Product Storage & Distribution	13	9

8

AGENDA - DAY 4

Time	Topic	Presentation	Handbook Chapter
08:30 AM – 10:00 AM	Degreasing	14	10
10:00 AM – 10:10 AM	Break		
10:10 AM – 11:00 AM	Dry Cleaning	15	11
11:00 AM – 11:10 AM	Break		
11:10 AM – 12:00 PM	Liquid Asphalt	16	12
12:00 PM – 1:00 PM	Lunch Break (on your own)		
1:00 PM – 2:20 PM	VOC Control (Part 1)	17	13
2:20 PM – 2:30 PM	Break		
2:30 PM – 3:30 PM	VOC Control (Part 2)	17	13
3:30 PM – 4:30 PM	Post-Test and Course Evaluation		

9

COURSE TOPICS

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

10

COURSE TOPICS

Topic	Chapter
Oil & Gas	-
Petroleum Refining	8
Petroleum Product Storage & Distribution	9
Degreasing	10
Dry Cleaning	11
Introduction to Control Technology	13

11

COURSE MATERIALS

- Student Workbook
  - Contains the course agenda and copies of selected slides presented in each of the topic areas
- Student Manual
  - #482 Continuous Emission Monitoring Systems Student Manual

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PRE-TEST

https://forms.gle/rqeyKMEsABjgfp9g9

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NATIONAL SOURCES

Presentation 2

Chapter 4 – National Sources and the Regulatory Approach

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NATIONAL SOURCES

Presentation 2

Chapter 4 – National Sources and the Regulatory Approach

2

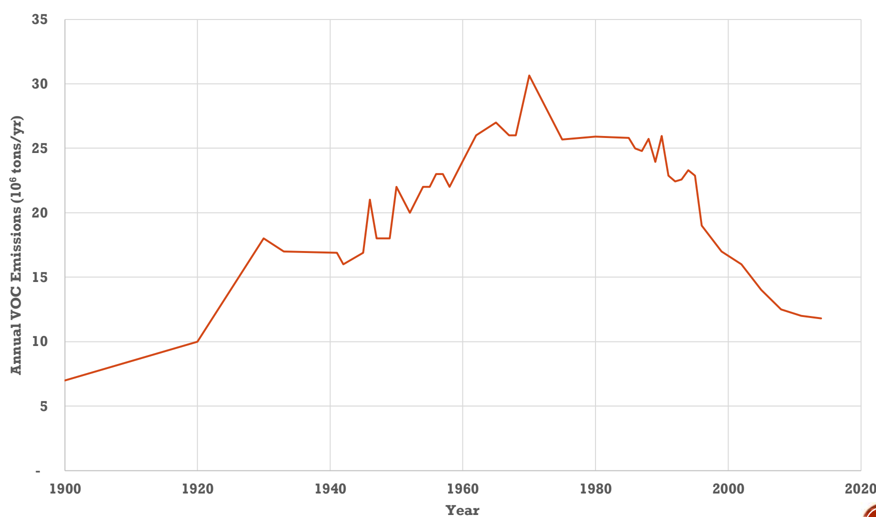
NATIONAL SOURCES AND THE REGULATORY APPROACH

Emission trends

Emission inventory

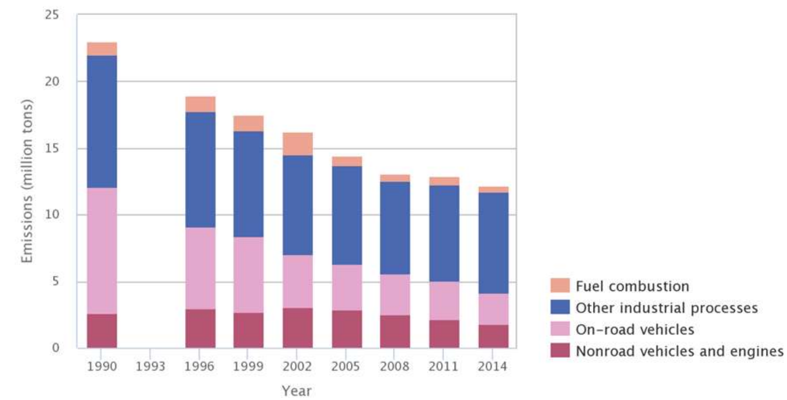
3

TRENDS IN NATIONAL VOC EMISSIONS



4

Exhibit 1. Anthropogenic VOC emissions in the U.S. by source category, 1990–2014



During some parts of the period of record, inventories were only developed every three years, hence the three-year intervals shown here. Data are available for inventory year 1993, but these data have not been updated to allow comparison with data from the other years shown.

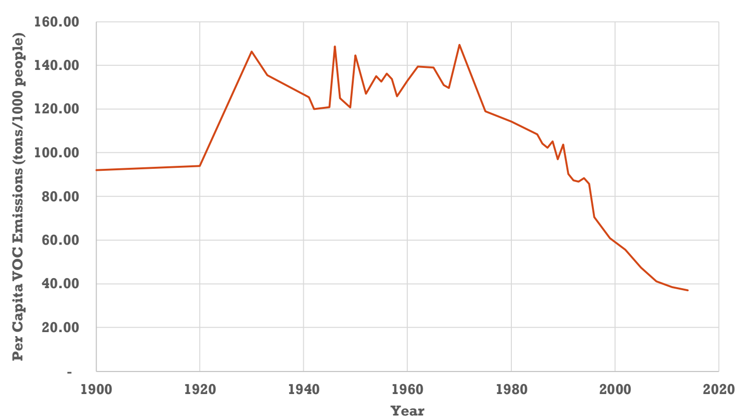
Changes shown from 1990–2014 include both emissions changes and methods changes. While trends shown are generally representative, actual changes from year to year could have been larger or smaller than those shown.

Information on the statistical significance of the trends in this exhibit is not currently available. For more information about uncertainty, variability, and statistical analysis, view the technical documentation for this indicator.

Data source: U.S. EPA, 2018b

5

TRENDS IN NATIONAL VOC EMISSIONS PER CAPITA

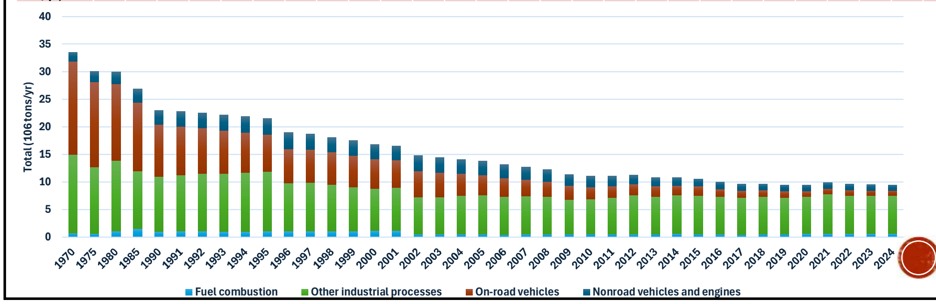


6

Source: National_Tier1_CAPS.XSLX

NATIONAL ANTHROPOGENIC VOC EMISSIONS

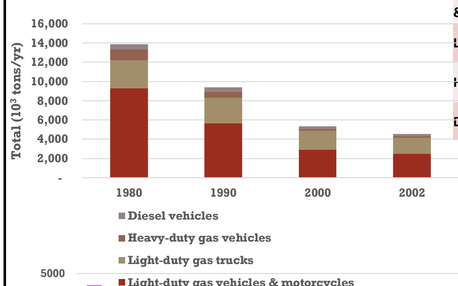
Year	1970	1975	1980	1985	1990	1995	2000	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
Fuel combustion	1	1	1	2	1	1	1	1	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Other industrial processes	14	12	13	10	10	11	8	7	7	7	7	6	6	7	7	7	7	7	7	7	7	7	7	7	7	7	7
On-road vehicles	17	15	14	12	9	7	5	4	3	3	3	3	2	2	2	2	2	2	1	1	1	1	1	1	1	1	1
Nonroad vehicles and engines	2	2	2	2	3	3	3	3	2	2	2	2	2	2	2	2	1	1	1	1	1	1	1	1	1	1	1
Total (106 tons/yr)	34	30	30	27	23	21	17	14	13	13	12	11	11	11	11	11	11	11	10	10	10	9	9	10	10	10	9

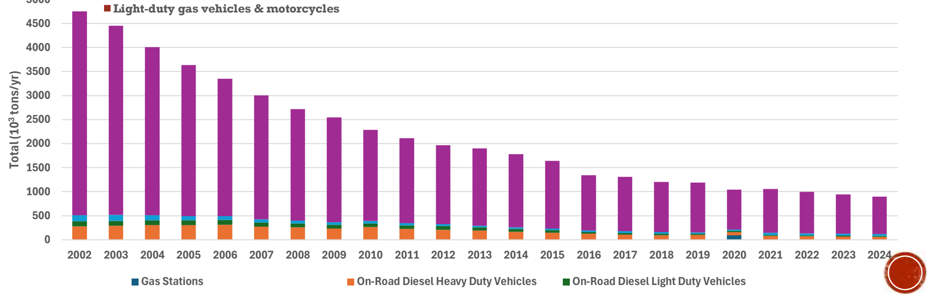


7

EMISSIONS FROM ON-ROAD VEHICLES

	1980	1990	2000	2002
On-road vehicles	13,869	9,388	5,325	4,543
Light-duty gas vehicles & motorcycles	9,304	5,690	2,903	2,496
Light-duty gas trucks	2,864	2,617	1,929	1,638
Heavy-duty gas vehicles	1,198	633	256	201
Diesel vehicles	503	448	238	208





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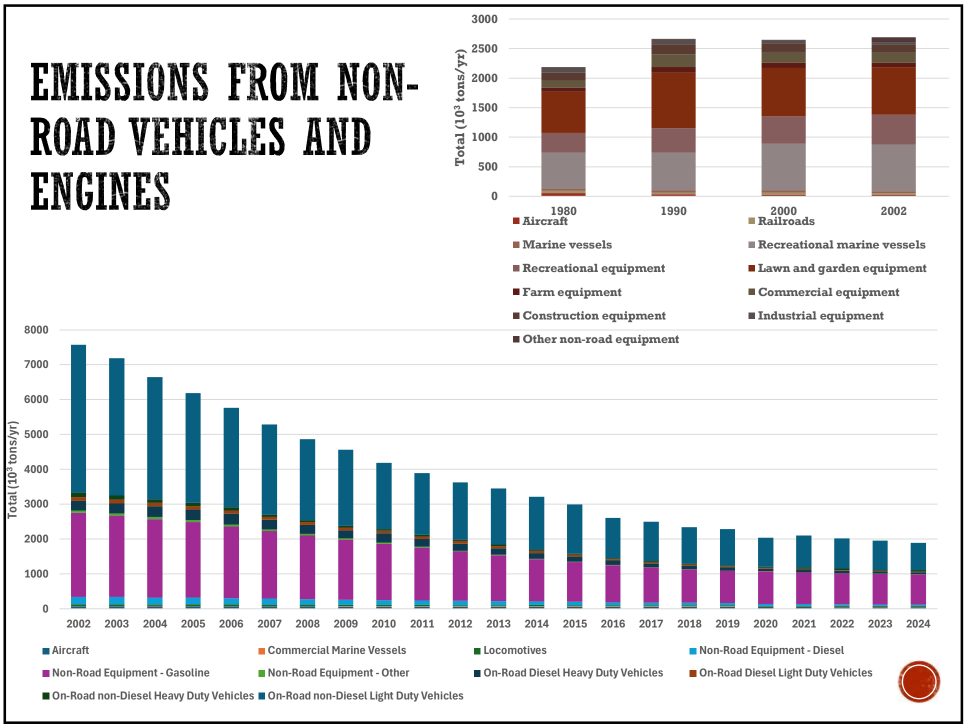
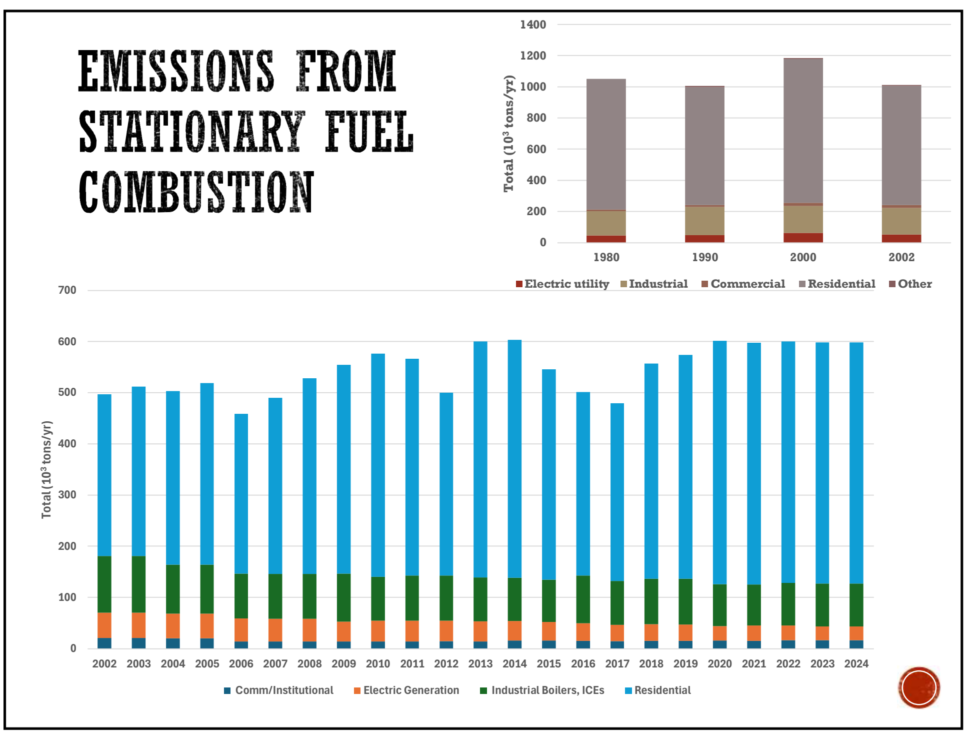

EMISSIONS FROM NON-ROAD VEHICLES AND ENGINES
Total (10³ tons/yr)
1980
1990
2000
2002
Aircraft
Railroads
Marine vessels
Recreational marine vessels
Recreational equipment
Lawn and garden equipment
Farm equipment
Commercial equipment
Construction equipment
Industrial equipment
Other non-road equipment
Total (10³ tons/yr)
2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024
Aircraft
Commercial Marine Vessels
Locomotives
Non-Road Equipment - Diesel
Non-Road Equipment - Gasoline
Non-Road Equipment - Other
On-Road Diesel Heavy Duty Vehicles
On-Road Diesel Light Duty Vehicles
On-Road non-Diesel Heavy Duty Vehicles
On-Road non-Diesel Light Duty Vehicles

9


EMISSIONS FROM STATIONARY FUEL COMBUSTION
Total (10³ tons/yr)
1980
1990
2000
2002
Electric utility
Industrial
Commercial
Residential
Other
Total (10³ tons/yr)
2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024
Comm/Institutional
Electric Generation
Industrial Boilers, ICEs
Residential

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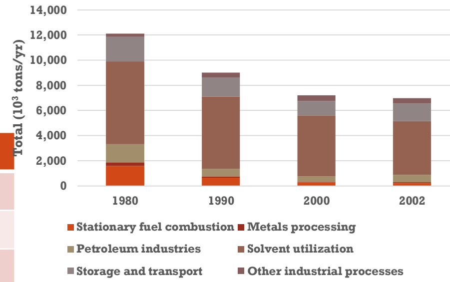
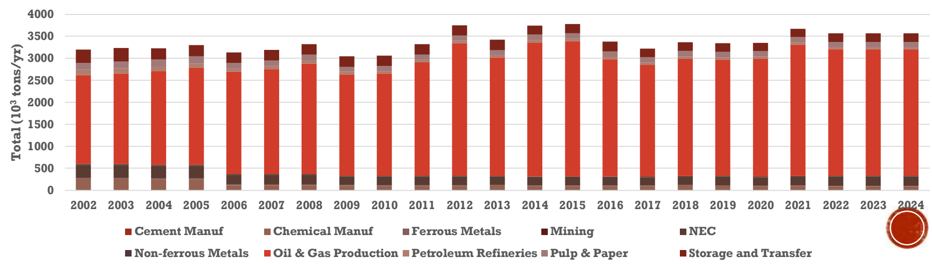
NATIONAL INDUSTRIAL VOC EMISSIONS

	1980	1990	2000	2002
Chemical manufacturing	1,595	634	254	244
Metals processing	273	122	67	46
Petroleum industries	1440	611	428	590
Solvent utilization	6584	5750	4831	4263
Storage and transport	1975	1490	1176	1411
Other industrial processes	237	401	454	428
Total	12104	9008	7210	6982





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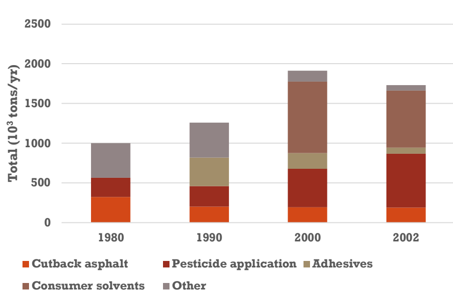
EMISSIONS FROM SOLVENT UTILIZATION

	1980	1990	2000	2002
Solvent utilization	5,578	3,850	2,918	2,961
Degreasing	513	744	393	488
Graphic arts	373	274	261	251
Dry cleaning	320	215	149	65
Surface coating	3,685	2,523	1,953	2,049



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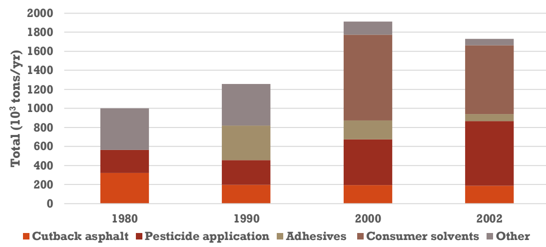
Presentation 2

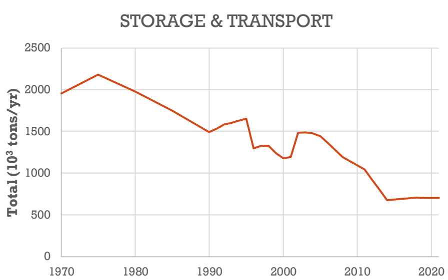
EMISSIONS FROM NON-INDUSTRIAL SOLVENT USE

	1980	1990	2000	2002
Non-industrial solvent use	1,002	1,900	1,913	1,731
Cutback asphalt	323	199	193	189
Pesticide application	241	258	483	676
Adhesives		361	197	76
Consumer solvents			900	721
Other	437	438	140	68

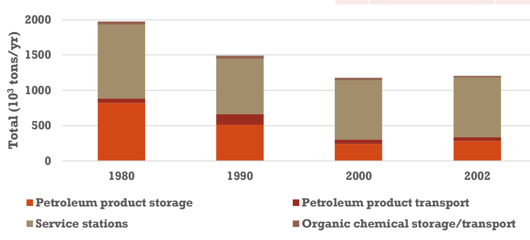


13

EMISSIONS FROM STORAGE AND TRANSPORT



	1980	1990	2000	2002
Storage and transport	1,975	1,490	1,176	1,205
Petroleum product storage	823	511	239	279
Petroleum product transport	61	151	63	56
Service stations	1044	785	843	843
Organic chemical storage/transport	46	40	28	25
Other		2	2	3



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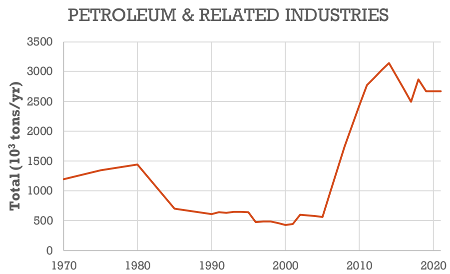
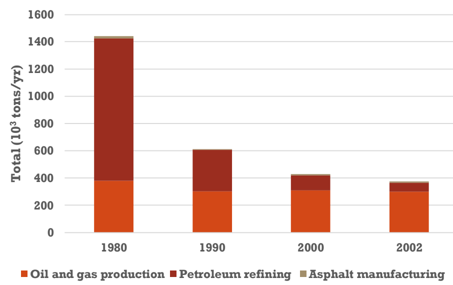
EMISSIONS FROM PETROLEUM INDUSTRY



	1980	1990	2000	2002
Petroleum industries	1,440	611	428	375
Oil and gas production	379	301	309	300
Petroleum refining	1,045	307	110	65
Asphalt manufacturing	16	3	10	10



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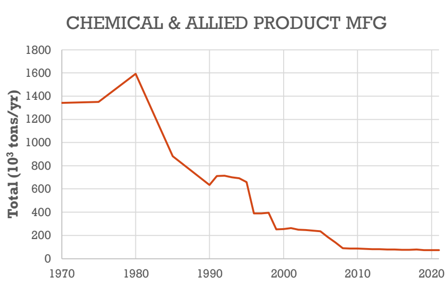
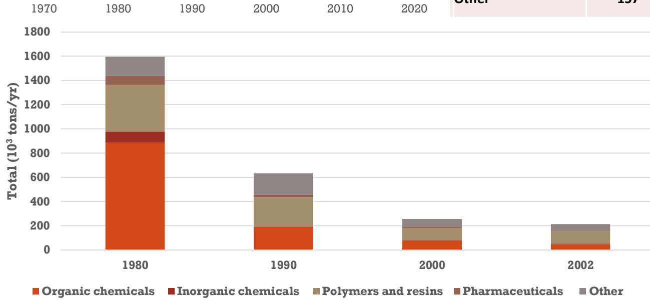
EMISSIONS FROM CHEMICAL MANUFACTURING



	1980	1990	2000	2002
Chemical manufacturing	1,595	634	254	214
Organic chemicals	884	192	76	48
Inorganic chemicals	93	2	4	5
Polymers and resins	384	242	101	99
Pharmaceuticals	77	20	8	4
Other	157	178	66	58



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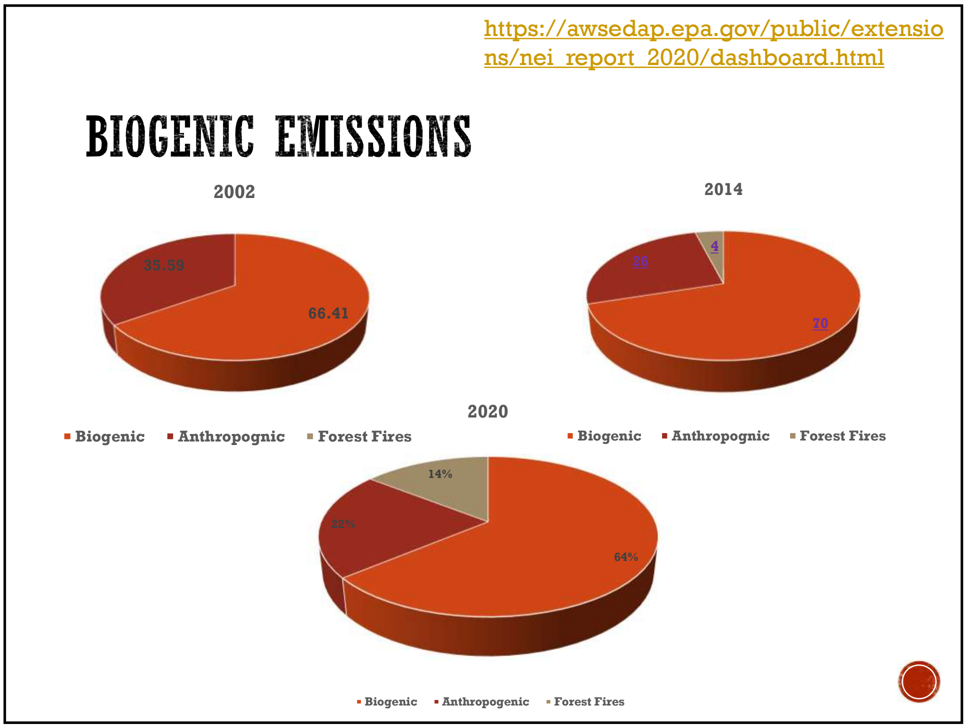
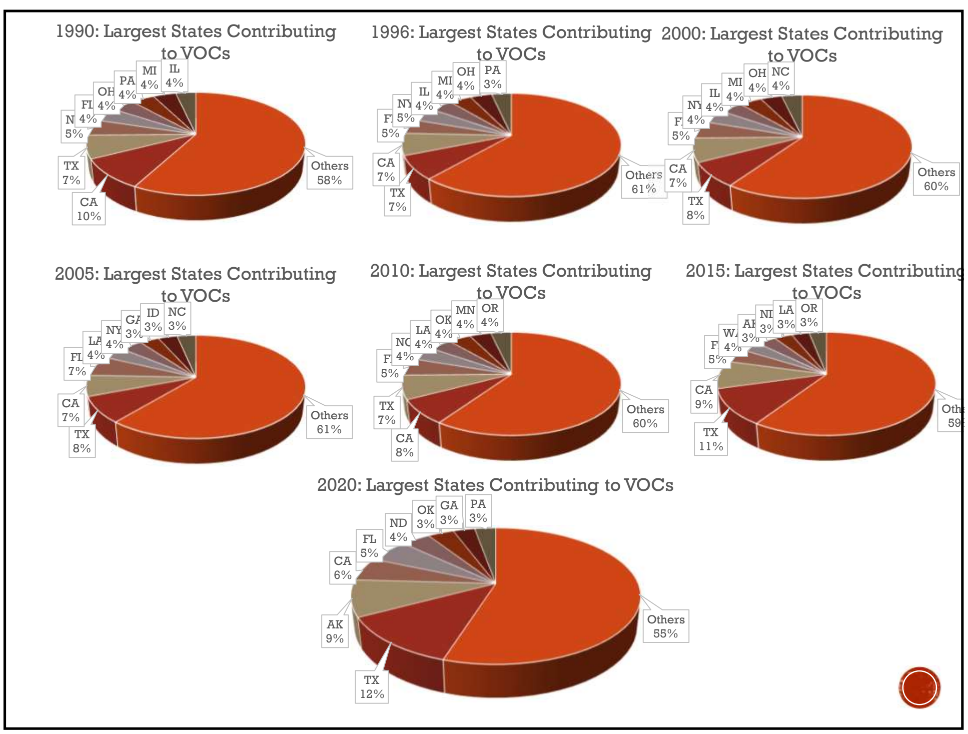

https://awsedap.epa.gov/public/extensions/nei_report_2020/dashboard.html
BIOGENIC EMISSIONS
2002
35.59
66.41
Biogenic
Anthropognic
Forest Fires
2014
4
26
70
Biogenic
Anthropognic
Forest Fires
2020
14%
22%
64%
Biogenic
Anthropognic
Forest Fires

17


1990: Largest States Contributing to VOCs
Others 58%
CA 10%
TX 7%
1996: Largest States Contributing to VOCs
Others 61%
CA 7%
TX 7%
2000: Largest States Contributing to VOCs
Others 60%
CA 7%
TX 8%
2005: Largest States Contributing to VOCs
Others 61%
CA 7%
TX 8%
2010: Largest States Contributing to VOCs
Others 60%
TX 7%
CA 8%
2015: Largest States Contributing to VOCs
CA 9%
TX 11%
2020: Largest States Contributing to VOCs
PA 3%
GA 3%
OK 3%
ND 4%
FL 5%
CA 6%
AK 9%
TX 12%
Others 55%

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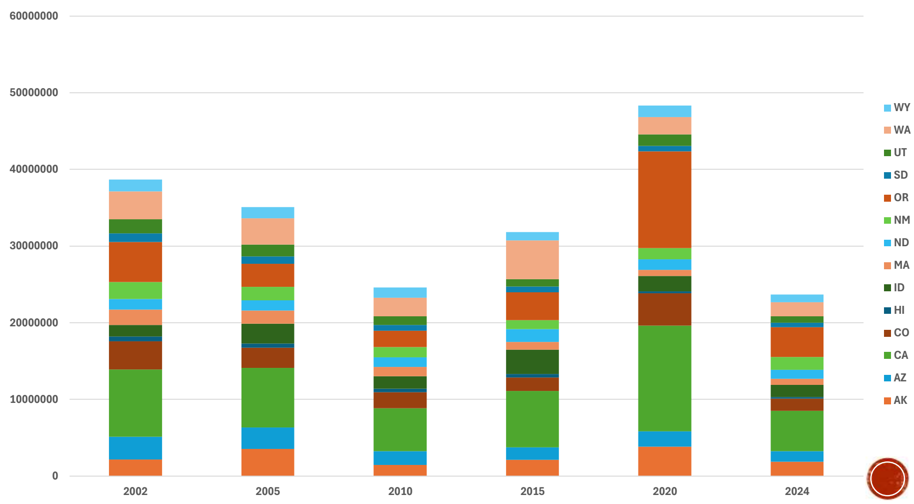
VOCS IN WESTERN STATES



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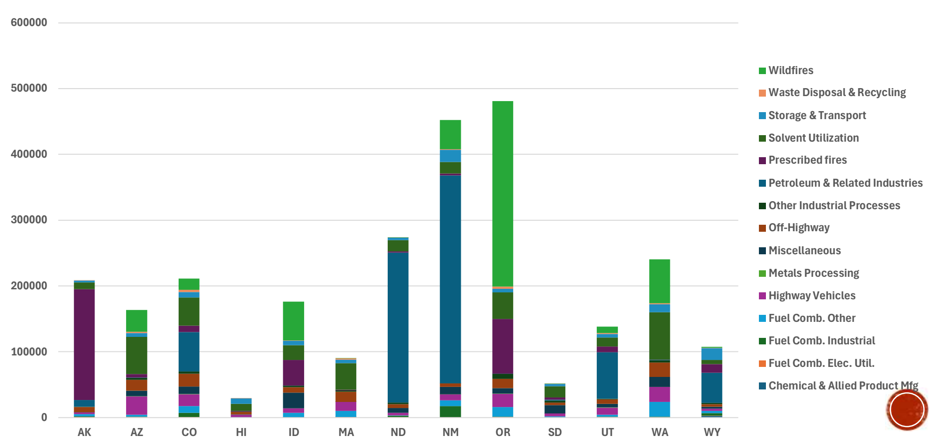
Source: State_Tier1_CAPS.XSLX

VOCS IN WESTERN STATES

AK	AZ	CA	CO	HI	ID	MA	ND	NM	OR	SD	UT	WA	WY
1857	1361	5292	1566	224	1578	793	1186	1661	3885	607	825	1843	977



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REGULATORY APPROACH

Presentation: 3

Chapter 4 – National Sources and the Regulatory Approach

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REGULATORY APPROACH

Presentation: 3

Chapter 4 – National Sources and the Regulatory Approach

2

OZONE NAAQS

- 0.08 ppm 1-hour standard set in 1971
  - (photochemical oxidants)
- 0.12 ppm 1-hour standard set in 1979
- 0.08 ppm 8-hour standard set in 1997
- 0.075 ppm 8-hour standard set in 2008
- 0.07 ppm 8-hour standard set in 2015
- 0.07 ppm 8-hour standard maintained in 2020
- 0.07 ppm 8-hour standard under reconsideration, 2025

The 8-hour Ozone (1997) standard was revoked on April 6, 2015 and the 1-hour Ozone (1979) standard was revoked on June 15, 2005. **The 2008 0.075 ppm standard was effectively superseded** when the 2015 standard was promulgated

More information: https://www.epa.gov/ground-level-ozone-pollution/ozone-national-ambient-air-quality-standards-naaqs

3

2020 8-HOUR OZONE NAAQS

- **0.07 ppm**
- Compliance based on 3-year average of the fourth-highest daily maximum 8-hour average concentration
- Due to the 2023–2025 review activity, 0.07 ppm remains the current standard as of the course date but is under review.

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

4

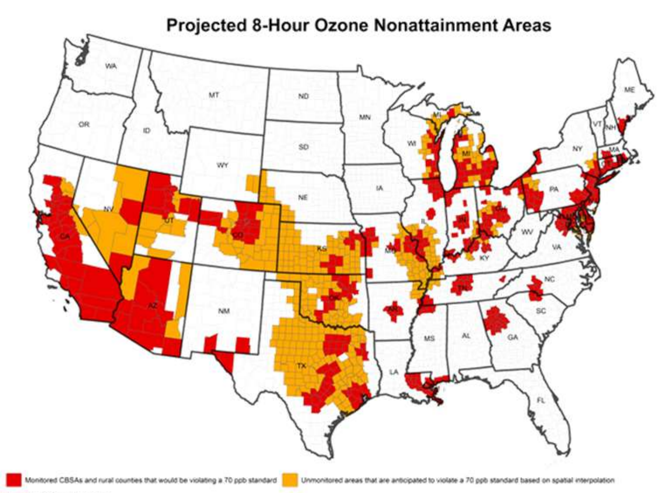
OZONE DESIGNATION AND CLASSIFICATION INFORMATION

- **Nonattainment**: Any area that does not meet (or that contributes to ambient air quality in a nearby area that does not meet) the national primary or secondary ambient air quality standard for a NAAQS.

- **Attainment**: Any area (other than an area identified in clause (i)) that meets the national primary or secondary ambient air quality standard for a NAAQS.

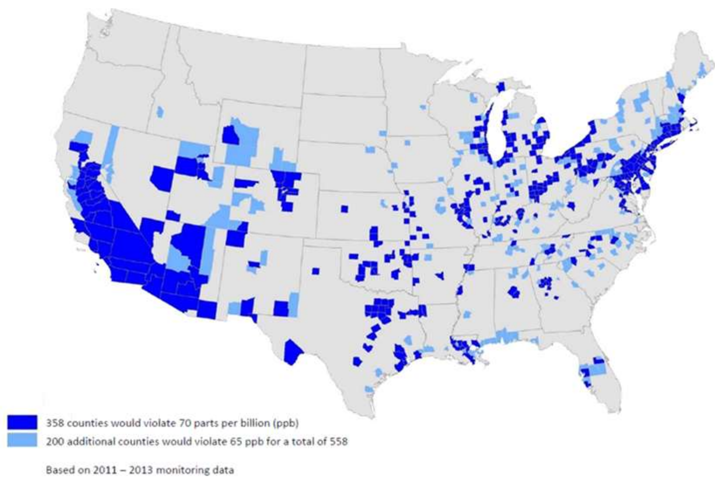
5

COUNTIES WITH MONITORS VIOLATING THE 2015 8-HR OZONE STANDARD OF 0.07 PPM



6

Counties Where Measured Ozone is Above Proposed Range of Standards (65 – 70 parts per billion)



7

IMPLEMENTING THE STANDARD

Promulgation or revision of the NAAQS starts a clock for the EPA to designate areas as either attainment or nonattainment.

2008 Standard

- March 2009 States recommend area designations
- March 2010 EPA issues area designations
- March 2013 States submit SIPs

2015 Standard

- October 2016 States recommend area designations
- July 2018 EPA issues area designations
- August 2021 States submit SIPs

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IMPLEMENTING THE STANDARD

- State recommendations for area designations are due to the EPA within 12 months of promulgating or revising the NAAQS.
- 2018: States recommend area designations
- The EPA generally completes area designations two years after promulgation of a NAAQS
- Revision of SIPs to be submitted within three years of promulgation of a revised NAAQS

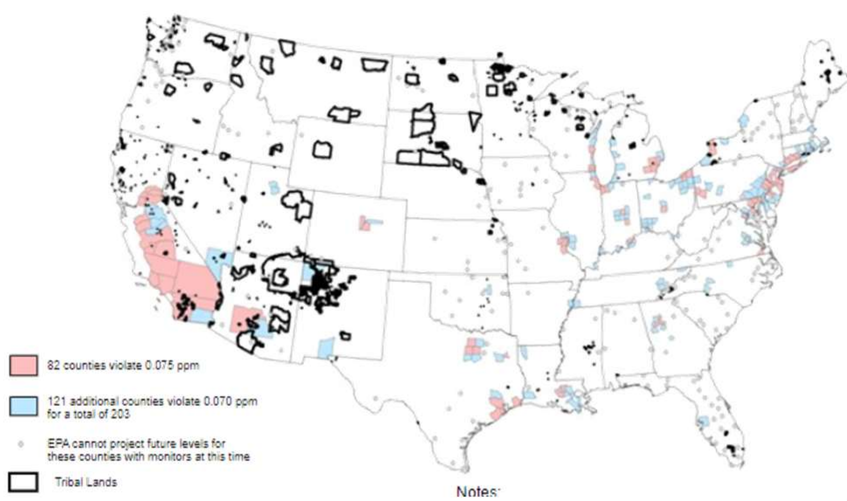
https://www.epa.gov/ozone-designations/ozone-designations-regulatory-actions

Federal Register / Vol. 80, No. 206 / Monday, October 26, 2015 / Rules and Regulations

9

EPA United States Environmental Protection Agency

Counties With Monitors Projected to Violate Alternate 8-hour Ozone Standards of 0.070 and 0.075 parts per million in 2020



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8-HOUR OZONE CLASSIFICATIONS

https://www.epa.gov/ground-level-ozone-pollution/required-sip-elements-nonattainment-classification

	8-hr Design Value (ppm)	
	2008 Standard	*2015 Standard*
Marginal	> 0.076	> 0.071
Moderate	> 0.086	> 0.081
Serious	> 0.100	> 0.093
Severe-15	> 0.113	> 0.105
Severe-17	> 0.119	> 0.111
Extreme	> 0.175	> 0.163

https://www3.epa.gov/airquality/greenbook/ancl.html

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NON-ATTAINMENT 1-HOUR OZONE (1979) REVOKED

COLORADO	CO	Adams County
COLORADO	CO	Arapahoe County
COLORADO	CO	Boulder County
COLORADO	CO	Broomfield County
COLORADO	CO	Denver County
COLORADO	CO	Douglas County
COLORADO	CO	Jefferson County
NEVADA	NV	Washoe County
NEW MEXICO	NM	Dona Ana County
OREGON	OR	Clackamas County
OREGON	OR	Marion County
OREGON	OR	Multnomah County
OREGON	OR	Polk County
OREGON	OR	Washington County
UTAH	UT	Davis County
UTAH	UT	Salt Lake County
WASHINGTON	WA	Clark County
WASHINGTON	WA	King County
WASHINGTON	WA	Pierce County
WASHINGTON	WA	Snohomish County

ARIZONA	AZ	Maricopa County
CALIFORNIA	CA	Alameda County
CALIFORNIA	CA	Butte County
CALIFORNIA	CA	Contra Costa County
CALIFORNIA	CA	El Dorado County
CALIFORNIA	CA	Fresno County
CALIFORNIA	CA	Imperial County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kings County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Madera County
CALIFORNIA	CA	Marin County
CALIFORNIA	CA	Merced County
CALIFORNIA	CA	Monterey County
CALIFORNIA	CA	Napa County
CALIFORNIA	CA	Orange County
CALIFORNIA	CA	Placer County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Sacramento County
CALIFORNIA	CA	San Benito County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Diego County
CALIFORNIA	CA	San Francisco County
CALIFORNIA	CA	San Joaquin County
CALIFORNIA	CA	San Mateo County
CALIFORNIA	CA	Santa Barbara County
CALIFORNIA	CA	Santa Clara County
CALIFORNIA	CA	Santa Cruz County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Sonoma County
CALIFORNIA	CA	Stanislaus County
CALIFORNIA	CA	Sutter County
CALIFORNIA	CA	Sutter County
CALIFORNIA	CA	Tulare County
CALIFORNIA	CA	Ventura County
CALIFORNIA	CA	Yolo County
CALIFORNIA	CA	Yuba County

12

NON-ATTAINMENT 8-HOUR OZONE (1997) REVOKED

ARIZONA	AZ	Maricopa County
ARIZONA	AZ	Pinal County
CALIFORNIA	CA	Alameda County
CALIFORNIA	CA	Amador County
CALIFORNIA	CA	Butte County
CALIFORNIA	CA	Calaveras County
CALIFORNIA	CA	Contra Costa County
CALIFORNIA	CA	El Dorado County
CALIFORNIA	CA	Fresno County
CALIFORNIA	CA	Imperial County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kings County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Madera County
CALIFORNIA	CA	Marin County
CALIFORNIA	CA	Mariposa County
CALIFORNIA	CA	Merced County
CALIFORNIA	CA	Napa County
CALIFORNIA	CA	Nevada County
CALIFORNIA	CA	Orange County
CALIFORNIA	CA	Placer County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Sacramento County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Diego County
CALIFORNIA	CA	San Diego County
CALIFORNIA	CA	San Francisco County
CALIFORNIA	CA	San Joaquin County
CALIFORNIA	CA	San Mateo County
CALIFORNIA	CA	Santa Clara County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Sonoma County
CALIFORNIA	CA	Stanislaus County
CALIFORNIA	CA	Sutter County
CALIFORNIA	CA	Sutter County
CALIFORNIA	CA	Tulare County
CALIFORNIA	CA	Tuolumne County
CALIFORNIA	CA	Ventura County
CALIFORNIA	CA	Yolo County

COLORADO	CO	Adams County
COLORADO	CO	Arapahoe County
COLORADO	CO	Boulder County
COLORADO	CO	Broomfield County
COLORADO	CO	Denver County
COLORADO	CO	Douglas County
COLORADO	CO	Jefferson County
COLORADO	CO	Larimer County
COLORADO	CO	Weld County
NEVADA	NV	Clark County

13

NON-ATTAINMENT 8-HOUR OZONE (2008)

ARIZONA	AZ	Maricopa County
ARIZONA	AZ	Pinal County
CALIFORNIA	CA	Alameda County
CALIFORNIA	CA	Butte County
CALIFORNIA	CA	Calaveras County
CALIFORNIA	CA	Contra Costa County
CALIFORNIA	CA	El Dorado County
CALIFORNIA	CA	Fresno County
CALIFORNIA	CA	Imperial County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kings County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Madera County
CALIFORNIA	CA	Marin County
CALIFORNIA	CA	Mariposa County
CALIFORNIA	CA	Merced County
CALIFORNIA	CA	Napa County
CALIFORNIA	CA	Nevada County
CALIFORNIA	CA	Orange County
CALIFORNIA	CA	Placer County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Sacramento County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Diego County
CALIFORNIA	CA	San Diego County
CALIFORNIA	CA	San Francisco County
CALIFORNIA	CA	San Joaquin County
CALIFORNIA	CA	San Luis Obispo County
CALIFORNIA	CA	San Mateo County
CALIFORNIA	CA	Santa Clara County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Sonoma County
CALIFORNIA	CA	Stanislaus County
CALIFORNIA	CA	Sutter County
CALIFORNIA	CA	Tehama County
CALIFORNIA	CA	Tulare County
CALIFORNIA	CA	Ventura County
CALIFORNIA	CA	Yolo County

COLORADO	CO	Adams County
COLORADO	CO	Arapahoe County
COLORADO	CO	Boulder County
COLORADO	CO	Broomfield County
COLORADO	CO	Denver County
COLORADO	CO	Douglas County
COLORADO	CO	Jefferson County
COLORADO	CO	Larimer County
COLORADO	CO	Weld County

14

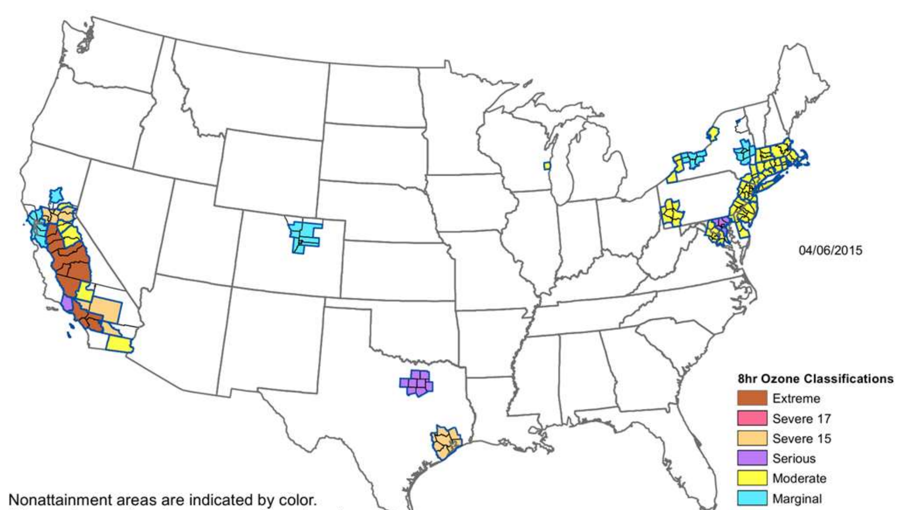
NON-ATTAINMENT 8-HOUR OZONE (2015)

COLORADO	CO	Adams County
COLORADO	CO	Arapahoe County
COLORADO	CO	Boulder County
COLORADO	CO	Broomfield County
COLORADO	CO	Denver County
COLORADO	CO	Douglas County
COLORADO	CO	Jefferson County
COLORADO	CO	Larimer County
COLORADO	CO	Weld County
NEVADA	NV	Clark County
NEW MEXICO	NM	Dona Ana County
UTAH	UT	Davis County
UTAH	UT	Duchesne County
UTAH	UT	Salt Lake County
UTAH	UT	Tooele County
UTAH	UT	Uintah County
UTAH	UT	Utah County
UTAH	UT	Weber County

ARIZONA	AZ	Gila County
ARIZONA	AZ	Maricopa County
ARIZONA	AZ	Pinal County
ARIZONA	AZ	Yuma County
CALIFORNIA	CA	Alameda County
CALIFORNIA	CA	Amador County
CALIFORNIA	CA	Butte County
CALIFORNIA	CA	Calaveras County
CALIFORNIA	CA	Contra Costa County
CALIFORNIA	CA	El Dorado County
CALIFORNIA	CA	Fresno County
CALIFORNIA	CA	Imperial County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kern County
CALIFORNIA	CA	Kings County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Los Angeles County
CALIFORNIA	CA	Madera County
CALIFORNIA	CA	Marin County
CALIFORNIA	CA	Mariposa County
CALIFORNIA	CA	Merced County
CALIFORNIA	CA	Napa County
CALIFORNIA	CA	Nevada County
CALIFORNIA	CA	Orange County
CALIFORNIA	CA	Placer County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Riverside County
CALIFORNIA	CA	Sacramento County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Bernardino County
CALIFORNIA	CA	San Diego County
CALIFORNIA	CA	San Diego County
CALIFORNIA	CA	San Francisco County
CALIFORNIA	CA	San Joaquin County
CALIFORNIA	CA	San Luis Obispo County
CALIFORNIA	CA	San Mateo County
CALIFORNIA	CA	Santa Clara County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Solano County
CALIFORNIA	CA	Sonoma County
CALIFORNIA	CA	Stanislaus County
CALIFORNIA	CA	Sutter County
CALIFORNIA	CA	Sutter County
CALIFORNIA	CA	Tehama County
CALIFORNIA	CA	Tulare County
CALIFORNIA	CA	Tuolumne County
CALIFORNIA	CA	Ventura County
CALIFORNIA	CA	Yolo County

15

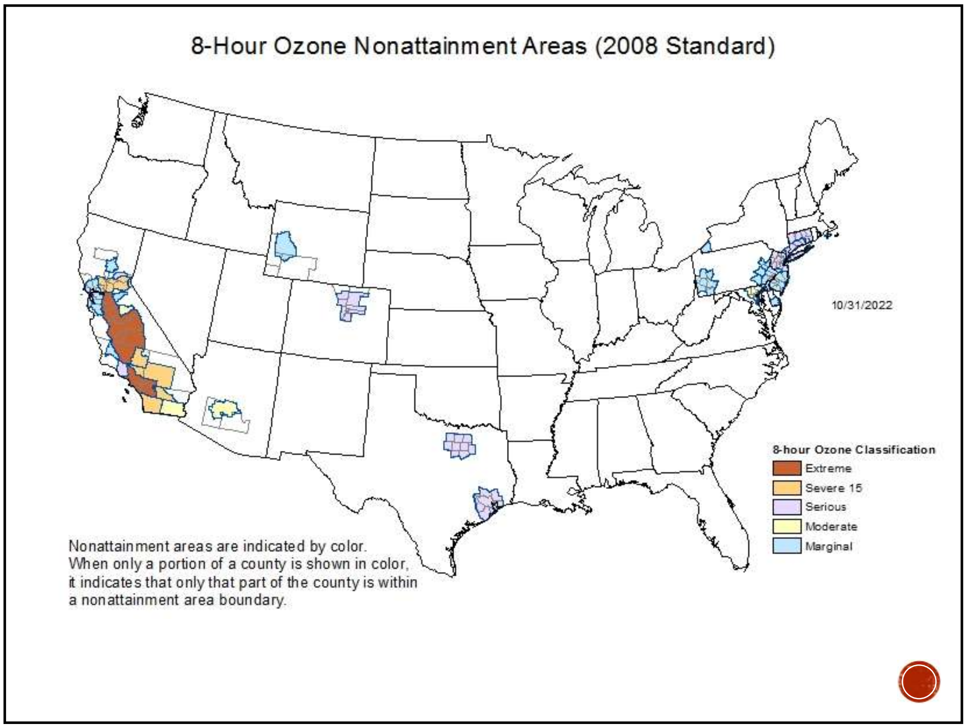
8-Hour Ozone Nonattainment Areas (1997 Standard - Revoked)



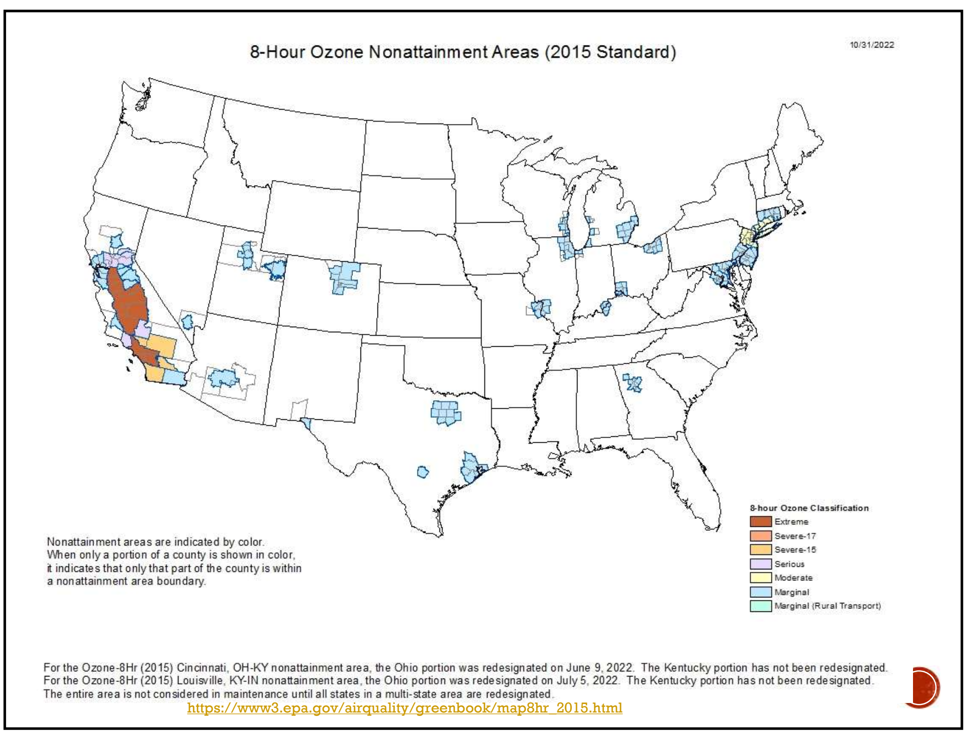
Nonattainment areas are indicated by color. When only a portion of a county is shown in color, it indicates that only that part of the county is within a nonattainment area boundary.

The 1997 Ozone NAAQS was revoked effective April 6, 2015 (80 FR 12264).

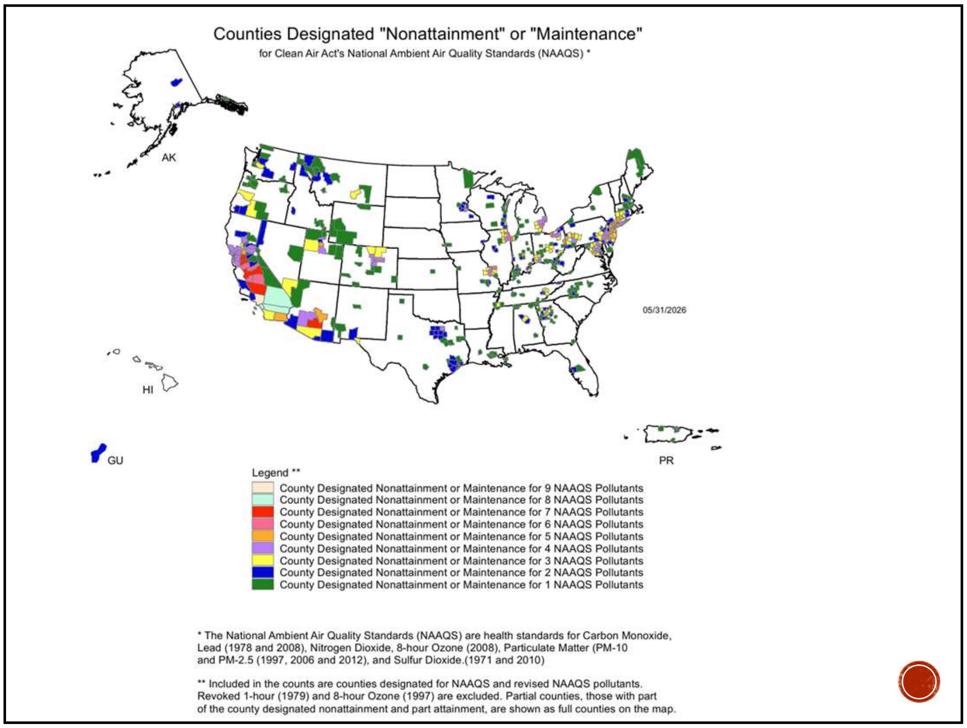
16


8-Hour Ozone Nonattainment Areas (2008 Standard)
10/31/2022
8-hour Ozone Classification
Extreme
Severe 15
Serious
Moderate
Marginal
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.

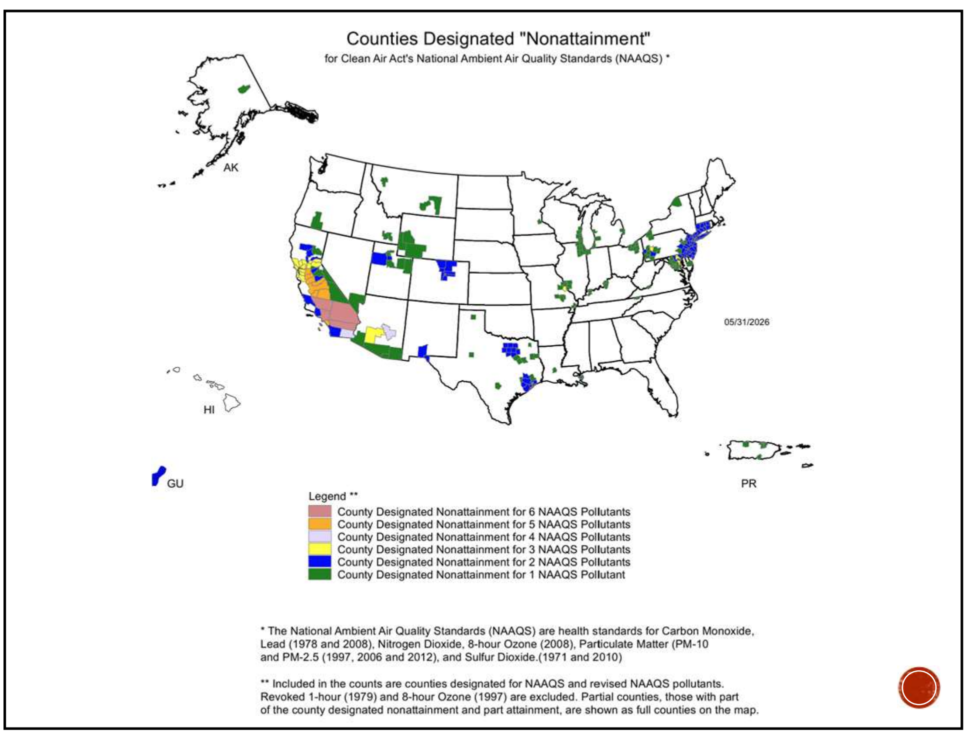
17


8-Hour Ozone Nonattainment Areas (2015 Standard)
10/31/2022
8-hour Ozone Classification
Extreme
Severe-17
Severe-15
Serious
Moderate
Marginal
Marginal (Rural Transport)
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.
For the Ozone-8Hr (2015) Cincinnati, OH-KY nonattainment area, the Ohio portion was redesignated on June 9, 2022. The Kentucky portion has not been redesignated.
For the Ozone-8Hr (2015) Louisville, KY-IN nonattainment area, the Ohio portion was redesignated on July 5, 2022. The Kentucky portion has not been redesignated.
The entire area is not considered in maintenance until all states in a multi-state area are redesignated.
https://www3.epa.gov/airquality/greenbook/map8hr_2015.html

18

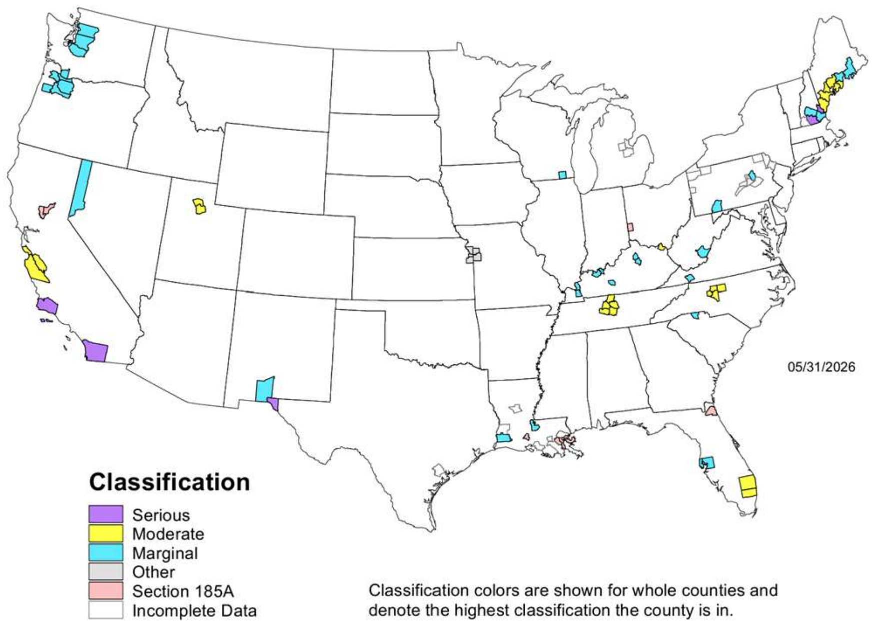

Counties Designated "Nonattainment" or "Maintenance"
for Clean Air Act's National Ambient Air Quality Standards (NAAQS) *
AK
HI
GU
PR
05/31/2026
Legend **
County Designated Nonattainment or Maintenance for 9 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 8 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 7 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 6 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 5 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 4 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 3 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 2 NAAQS Pollutants
County Designated Nonattainment or Maintenance for 1 NAAQS Pollutants
* The National Ambient Air Quality Standards (NAAQS) are health standards for Carbon Monoxide, Lead (1978 and 2008), Nitrogen Dioxide, 8-hour Ozone (2008), Particulate Matter (PM-10 and PM-2.5 (1997, 2006 and 2012), and Sulfur Dioxide.(1971 and 2010)
** Included in the counts are counties designated for NAAQS and revised NAAQS pollutants. Revoked 1-hour (1979) and 8-hour Ozone (1997) are excluded. Partial counties, those with part of the county designated nonattainment and part attainment, are shown as full counties on the map.

19

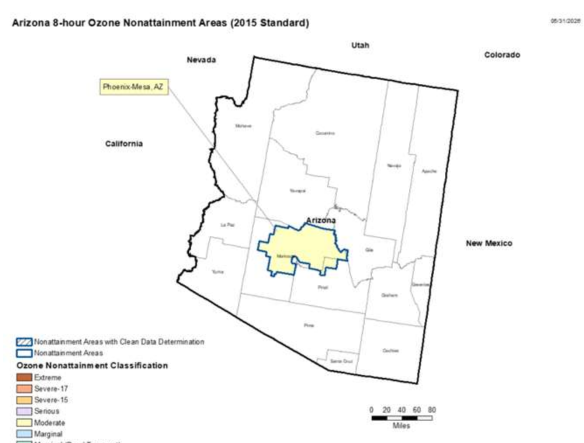

Counties Designated "Nonattainment"
for Clean Air Act's National Ambient Air Quality Standards (NAAQS) *
AK
HI
GU
PR
05/31/2026
Legend **
County Designated Nonattainment for 6 NAAQS Pollutants
County Designated Nonattainment for 5 NAAQS Pollutants
County Designated Nonattainment for 4 NAAQS Pollutants
County Designated Nonattainment for 3 NAAQS Pollutants
County Designated Nonattainment for 2 NAAQS Pollutants
County Designated Nonattainment for 1 NAAQS Pollutant
* The National Ambient Air Quality Standards (NAAQS) are health standards for Carbon Monoxide, Lead (1978 and 2008), Nitrogen Dioxide, 8-hour Ozone (2008), Particulate Matter (PM-10 and PM-2.5 (1997, 2006 and 2012), and Sulfur Dioxide.(1971 and 2010)
** Included in the counts are counties designated for NAAQS and revised NAAQS pollutants. Revoked 1-hour (1979) and 8-hour Ozone (1997) are excluded. Partial counties, those with part of the county designated nonattainment and part attainment, are shown as full counties on the map.

20

Maintenance Plan Under Section 110(a)(1) of the CAA

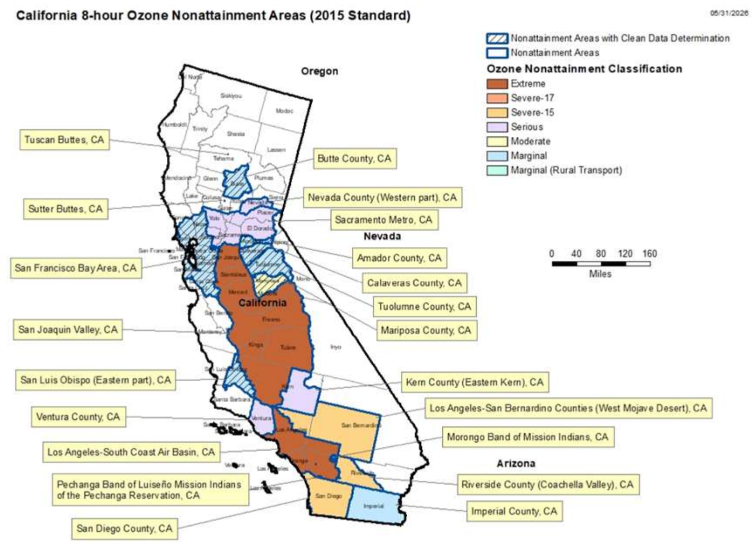


21



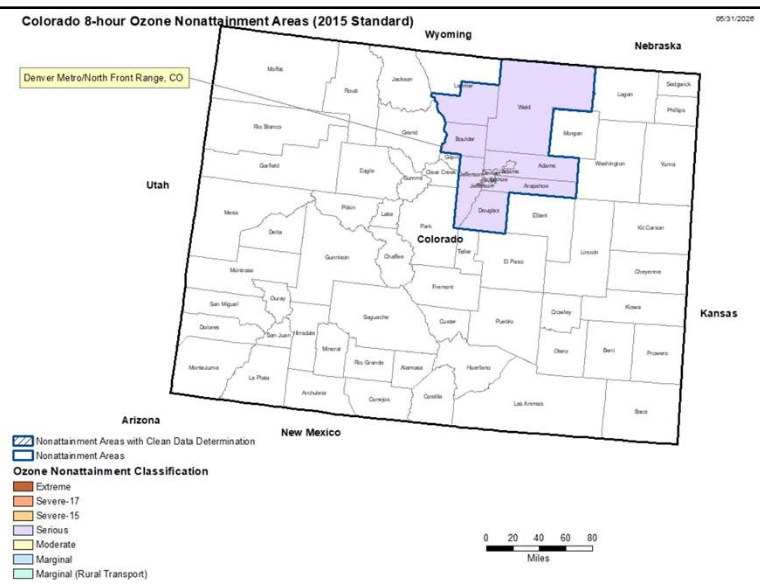
STATES WITH NON-ATTAINMENT COUNTIES

22



STATES WITH NON-ATTAINMENT COUNTIES

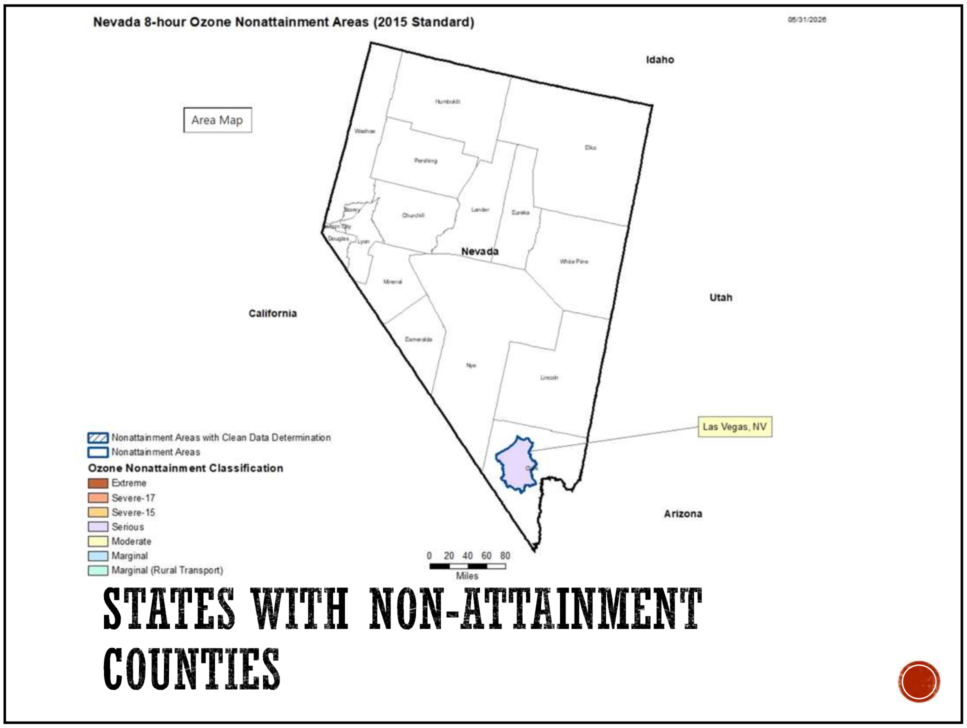
23



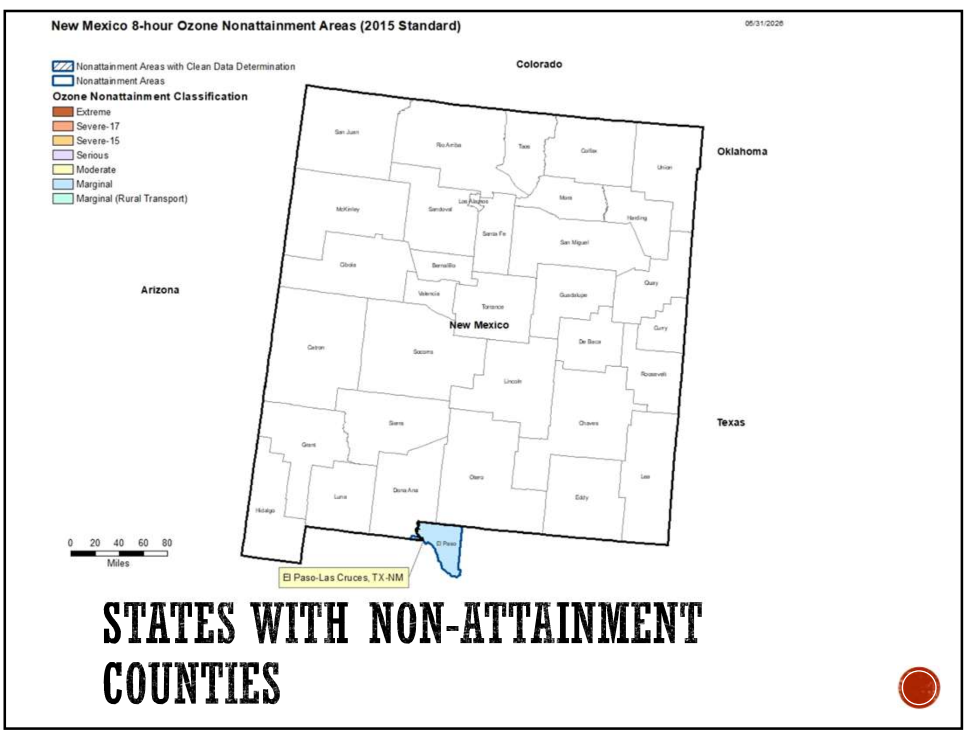
STATES WITH NON-ATTAINMENT COUNTIES

24

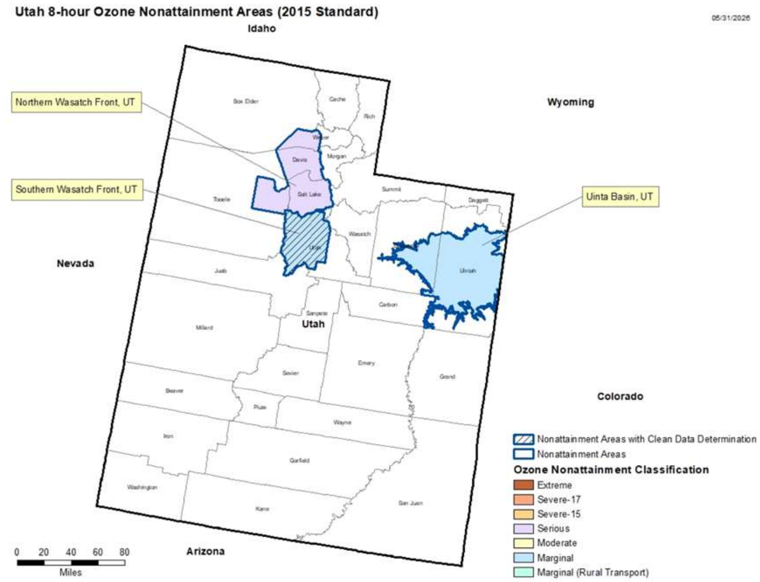
Presentation 3


Nevada 8-hour Ozone Nonattainment Areas (2015 Standard)
Idaho
Area Map
Nevada
Utah
California
Las Vegas, NV
Arizona
Nonattainment Areas with Clean Data Determination
Nonattainment Areas
Ozone Nonattainment Classification
Extreme
Severe-17
Severe-15
Serious
Moderate
Marginal
Marginal (Rural Transport)
0 20 40 60 80
Miles
STATES WITH NON-ATTAINMENT COUNTIES

25


New Mexico 8-hour Ozone Nonattainment Areas (2015 Standard)
Nonattainment Areas with Clean Data Determination
Nonattainment Areas
Ozone Nonattainment Classification
Extreme
Severe-17
Severe-15
Serious
Moderate
Marginal
Marginal (Rural Transport)
Colorado
Oklahoma
Arizona
New Mexico
Texas
0 20 40 60 80
Miles
El Paso-Las Cruces, TX-NM
STATES WITH NON-ATTAINMENT COUNTIES

26



STATES WITH NON-ATTAINMENT COUNTIES

27

EARLY ACTION COMPACT AREAS (HISTORICAL: 1-HOUR AND 1997 STANDARD ERA)

- Gave areas flexibility to develop their own approach to compliance
- Only areas meeting 1-hour standard were eligible
- Had to meet agreed upon milestones
- Certain CAA requirements were deferred
- Attainment deadline was December 31, 2007

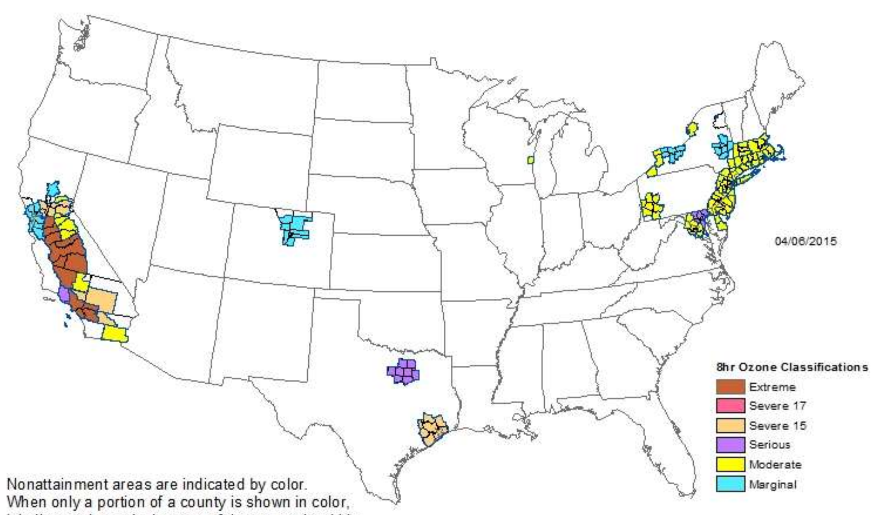
28

STATE IMPLEMENTATION PLAN (PHASE 2)

- Attainment demonstrations and modeling
- Reasonable further progress
- Reasonably available control measures
- Reasonable available control technology
- New source review requirements
- Reformulated gasoline regulation

29

8-Hour Ozone Nonattainment Areas (1997 Standard - Revoked)



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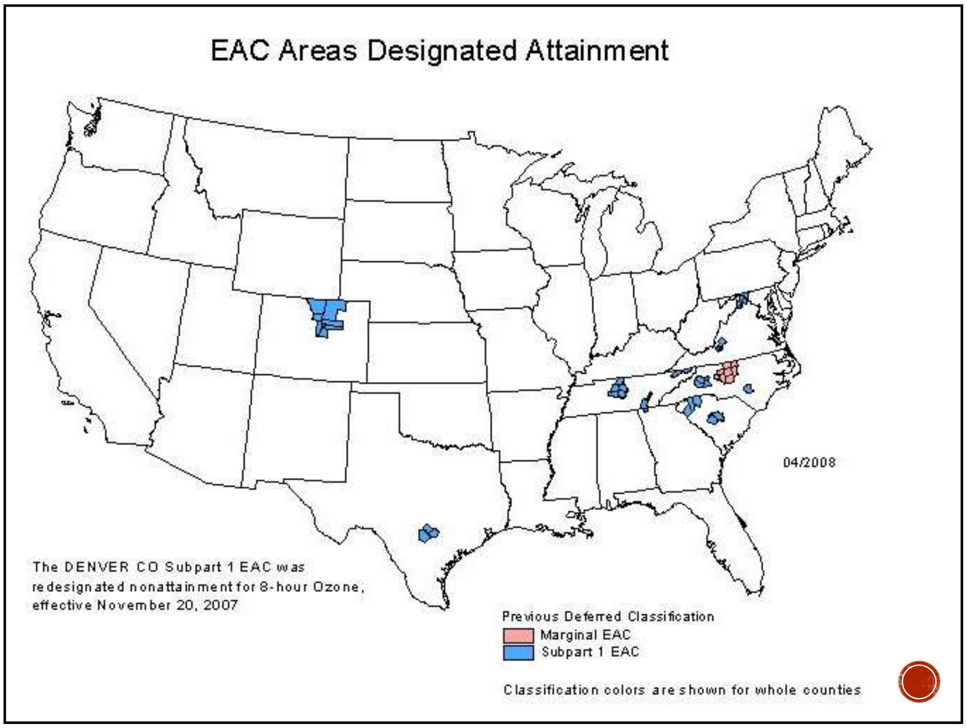
30



31

HISTORICAL OZONE IMPLEMENTATION STRATEGIES

- Focus
  - VOC controls
  - Metropolitan area
- 1991 NAS report recommended focus on NOx controls
- Ozone Transport Commission established by CAAA of 1990 https://www.epa.gov/air-quality-implementation-plans/nonattainment-and-ozone-transport-region-otr-sip-requirements

32

HISTORICAL OZONE IMPLEMENTATION STRATEGIES

Ozone Transport Assessment Group (OTAG) {Suppl. Matr.}

- Formed in 1995 by 37 states to address ozone regional transport
- Conducted 2-year comprehensive study
- Recommended regional NOx controls

33

NOX SIP CALL (1998)

- EPA used OTAG findings to require 22 states and DC to revise their SIPs to reduce NOx emissions
- Applied to large stationary sources, primarily power plants and industrial boilers
- States had to achieve reductions by May 2003 using a regional cap-and-trade approach
- Upheld by the DC Circuit in *Michigan v. EPA* (2000)

34

CLEAN AIR INTERSTATE RULE — CAIR (2005)

- Replaced the NOx SIP Call; addressed both NOx (ozone season) and SO_2 ($PM_{2.5}$)
- Covered 28 eastern states plus DC using cap-and-trade
- Vacated by DC Circuit in *North Carolina v. EPA* (2008); remanded and kept in place while EPA developed a replacement

35

CROSS-STATE AIR POLLUTION RULE — CSAPR (2011)

- Replaced CAIR; addressed Good Neighbor obligations under CAA §110(a)(2)(D)
- Covers annual SO_2, annual NOx, and ozone-season NOx for power plants in 28 states
- Upheld by the Supreme Court in *EPA v. EME Homer City* (2014)
- **Annual SO_2, annual NOx, and ozone-season NOx from CSAPR sources decreased 77%, 41%, and 15% respectively between 2009 and 2016**

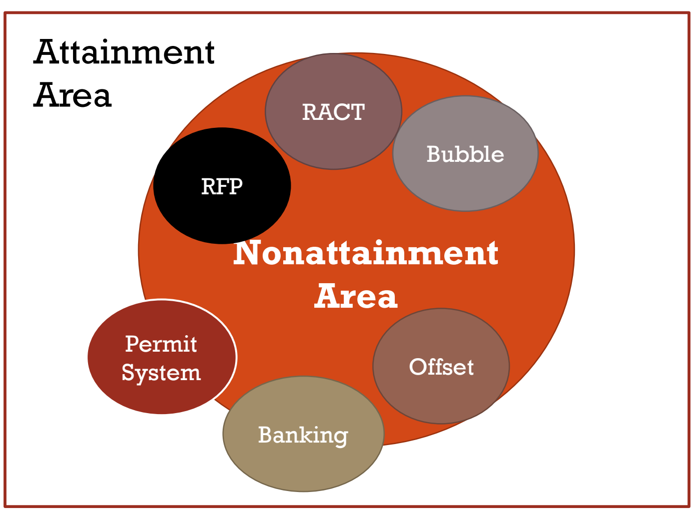
36

CSAPR UPDATES (2016, 2021) AND GOOD NEIGHBOR PLAN (2023)

- 2016 CSAPR Update: tightened ozone-season NOx budgets for 22 states for the 2008 ozone NAAQS
- 2021 Revised CSAPR Update: addressed DC Circuit remand (*Wisconsin v. EPA*, 2019)
- 2023 Good Neighbor Plan: addressed Good Neighbor obligations for the 2015 ozone NAAQS — **stayed by the Supreme Court in *Ohio v. EPA* (June 2024);** Trump administration has indicated it will not defend the rule; a replacement rulemaking is expected but will likely be less stringent
- **Current status (June 2026): Most states revert to CSAPR Update Group 2 budgets while the Good Neighbor Plan remains under legal and administrative review. Western states are largely outside CSAPR's geographic scope but face Good Neighbor obligations through their own SIP submissions.**

37

REGULATION OF EXISTING SOURCES



38

DETERMINING RACT

- RACT/BACT/LAER Clearinghouse (RBLC)
  https://cfpub.epa.gov/rblc
  - Control technology determinations
  - Regulation database
- Control Techniques Guideline Documents (CTGs)
  https://www.epa.gov/ground-level-ozone-pollution/control-techniques-guidelines-and-alternative-control-techniques
- Alternative Control Technology Documents (ACTs)

39

CONTROL TECHNIQUE GUIDELINE DOCUMENTS

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

40

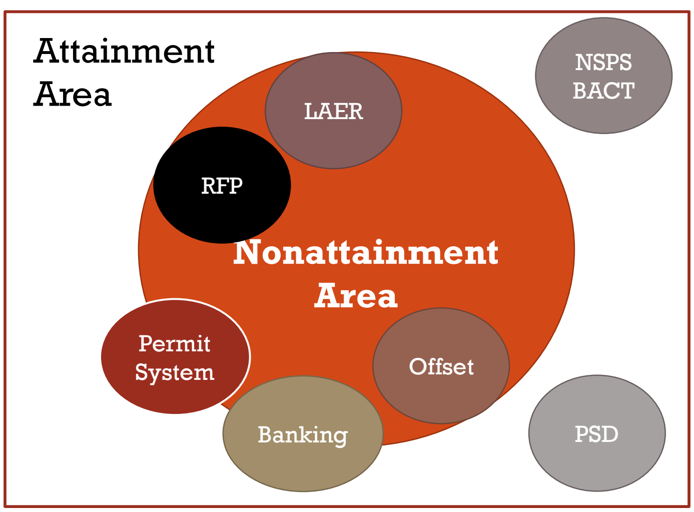
ALTERNATIVE CONTROL TECHNOLOGY DOCUMENTS

Promulgation of a CTG is a time intensive process. A draft document is prepared and published for review. Relevant comments on the draft are addressed and the final document promulgated. Although the CTG process is still alive, it has not been very active since the mid-1990s. EPA issued several new CTGs in 2006 and a batch of new and revised CTGs from 2016 to 2022 covering oil and natural gas, industrial cleaning solvents, and other categories.

- Issued without peer review
- Contain descriptions of alternative controls
- Do not recommend an RACT limit

41

REGULATION OF NEW AND MODIFIED SOURCES



42

DETERMINING BACT AND LAER

- RACT/BACT/LAER Clearinghouse (RBLC)
- New Source Performance Standards (40CFR60)

43

MACT STANDARDS FOR VHAP SOURCES (40CFR63)

44

REVIEW OF ORGANIC CHEMISTRY

Presentation: 4

Chapter 2 – Properties and Fundamentals

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

REVIEW OF ORGANIC CHEMISTRY

Presentation: 4

Chapter 2 – Properties and Fundamentals

2

REVIEW OF ORGANIC CHEMISTRY

- Chemistry of the compounds of carbon
- Number of organic compounds exceeds **8 million**
- Number of inorganic compounds is about 300,000

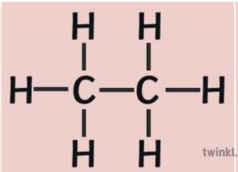
3

CHARACTERISTICS OF THE CARBON ATOM

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

4

MOLECULAR, STRUCTURAL & SEMI-STRUCTURAL FORMULAS

Molecular Formula	Structural Formula	Semi-Structural Formula
C_2H_6		CH_3-CH_3

5

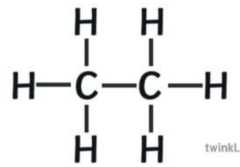
HYDROCARBONS

Compounds formed only from carbon and hydrogen

- Alkanes
- Alkenes
- Alkynes
- Cyclic Compounds

6

ALKANES



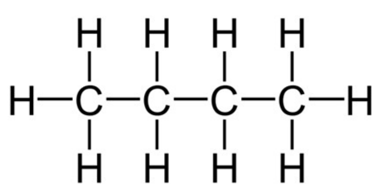
- Carbon atoms linked only by single bond

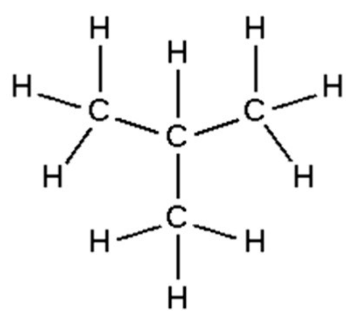
General Formula: C_nH_{2n+2}

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

7

ISOMERS OF BUTANE





n-butane

i-butane

8

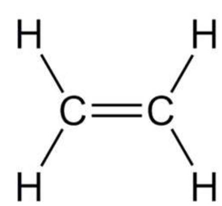
ISOMERS

Compounds with the same molecular formulas bit 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

9

ALKENES



- Carbon atoms linked at least by one double bond

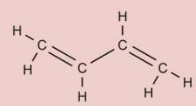
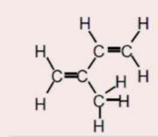
General Formula: C_nH_{2n}

Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8
Pentylene	C_5H_{10}

10

DIOLEFIN COMPOUNDS

- **Diolefin:** An olefin that has two double bonds; a diene
- **Olefin**: Any of a class of unsaturated open-chain hydrocarbons such as ethylene; an alkene with only one carbon-carbon double bond

Molecular Formula	Name	Structural Formula	Semi-structural Formula
C_4H_6	butadiene		$CH_2=CH-CH=CH_2$
C_5H_8	2-methyl butadiene		$CH_2=C-CH=CH_2$ $\vert$ CH_3

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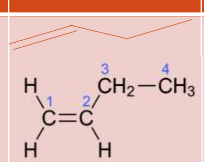
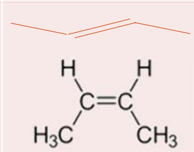
BUTYLENE ISOMERS

Molecula r Formula	Name	Structural Formula	Semi-structural Formula
C_4H_8	α-butylene		C=C-C-C
C_4H_8	Trans-β-butylene		CC=CC

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ALKYNES

H—C≡C—H

Hydrocarbons that contain at least 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)

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CYCLIC COMPOUNDS

- Cycloalkanes (aka naphthenes)
  - monocyclic saturated hydrocarbons consisting only of hydrogen and carbon atoms arranged in a structure containing a single ring. All the carbon-carbon bonds are single.
- Cycloparaffins
  - three or more of the carbon atoms in each molecule are united in a ring structure and each of the ring carbon atoms is joined to two hydrogen atoms or alkyl groups.
- Aromatic hydrocarbons
  - Containing one or more benzene rings

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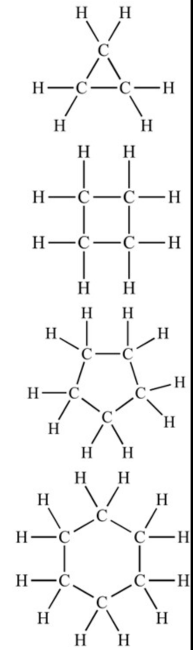
EXAMPLES OF CYCLOPARAFFIN COMPOUNDS

- Cyclopropane (C_3H_6): discovered in 1882 and was used as an anesthetic in 1933. It is extremely flammable and is thus no longer used clinically.
- Cyclobutane (C_4H_8): Although known for more than a century, their use as synthetic intermediates has only flourished in the last forty years.
- Cyclopentane (C_5H_{10}): preferred molecule for the manufacture of polyurethane insulation board as foaming material. Some of it remains in the foam cells.
- Cyclohexane (C_6H_{12}): Used to make nylon. Used as paint remover.



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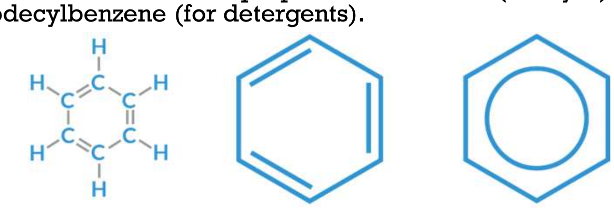
BENZENE STRUCTURE

- Benzene was first discovered by the English scientist Michael Faraday in 1825 in illuminating gas.
- August Kekulé visualized the ring structure of benzene in 1865.
- It is highly toxic and is a known carcinogen; exposure to it may cause leukemia.
- At one time, benzene was obtained almost entirely from coal tar; however since 1950 it is replaced by petroleum-based processes.
- More than half of the benzene produced each year is converted to ethylbenzene, then to styrene, and then to polystyrene.
- The next largest use of benzene is in the preparation of phenol. Other uses include the preparation of aniline (for dyes) and dodecylbenzene (for detergents).



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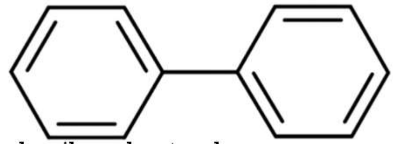
BIPHENYL



- Biphenyl occurs naturally in coal tar, crude oil, and natural gas.
- Biphenyl appears as a clear colorless insoluble liquid with a pleasant odor.
- Flash point 180 °F and vapors are heavier than air.
- It is used to manufacture other chemicals and as a fungicide.
- In workers, acute (short-term) exposure to high levels of biphenyl has been observed to cause eye and skin irritation and toxic effects on the liver, kidneys, and central and peripheral nervous systems.
- Kidney effects have been observed in chronically (long-term) exposed animals.
- EPA has classified biphenyl as a Group D, not classifiable as to human carcinogenicity.

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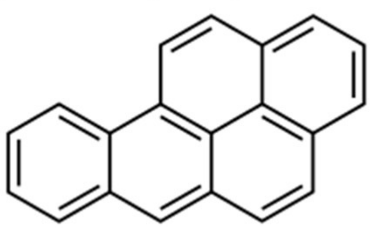
BENZO (A) PYRENE

- Results of incomplete combustion of organic matter at temperatures between 300°C (572°F) and 600°C (1,112 °F).
- Can be found in coal tar, tobacco smoke and many foods, especially grilled meats.
- It is listed as a Group 1 carcinogen by the IARC.
- In the 18th century a scrotal cancer of chimney sweepers, the chimney sweeps' carcinoma.



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NOMENCLATURE

# Carbon	Prefix	Formula	Alkane
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

These prefixes were invented by the IUPAC, deriving them from the pre-existing names for several compounds that it was intended to preserve in the new system:

•**methane** (via methyl which is in turn from the Greek word for wine),
•**ethane** (from ethyl coined by Justus von Liebig in 1834),
•**propane** (from propionic which is in turn from pro- and the Greek word for fat), and
•**butane** (from butyl which is in turn from butyric which is in turn from the Latin word for butter).

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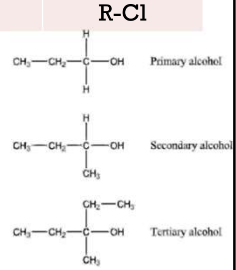
FUNCTIONAL GROUPS

Group	Substituent
Alcohols	R-OH
Amines	$R\text{-}NH_2$
Mercaptans (Thiol)	R-SH
Chlorides	R-Cl

- Molecules with similar functional groups tend to undergo similar reactions.
- A functional group is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds.
- The letter R is used in molecular structures to represent the "Rest of the molecule".
- Some thiol compounds have a distinctive smell similar to rotten eggs. They are often added to natural gas, which itself has no odor, as a way to detect leaks since its odor can be detected by humans in very small amounts.
- Amines serve a wide variety:
  - Diphenylamine acts as a stabilizer for certain types of explosives.
  - Amines are found in some lubricating materials and waterproofing textiles.
  - Some amines, such as novocaine, are used as anesthetics.
  - Many pharmaceutical compounds contain amines, including 8 of the 10 most prescribed medications in 2012.



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LOCATION OF SUBSTITUTION

- The location of the substitution of a functional group onto a hydrocarbon radical will also affect the properties of the resulting compound.
- The number of the carbon atom or atoms where the substitution is made is important as the type of functional group
- 1,1,1-trichloroethane: three chlorine atoms are substituted for the hydrogen atoms on the first carbon of an ethyl radical
- 2-propylamine: amine substitutes one hydrogen atom on the second carbon of a propyl radical
- If all hydrogen atoms are substituted by a functional group, the term "per" is used: 1,1,2,2-tetrachloroethylene is perchloroethylene

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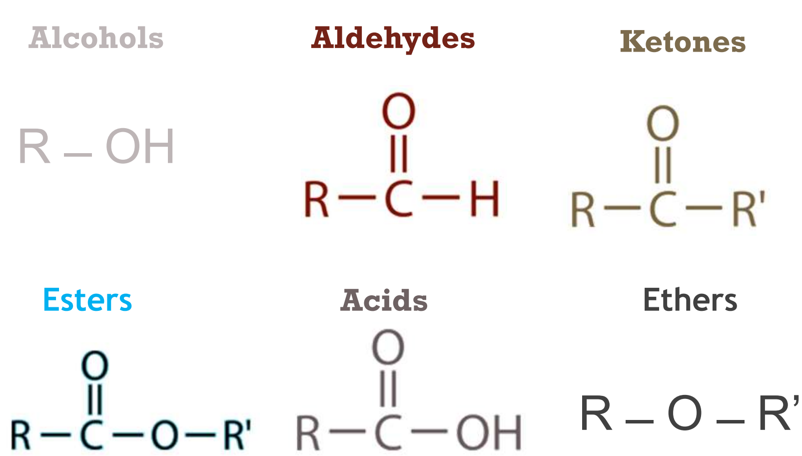
FUNCTIONAL GROUPS CONTAINING OXYGEN



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ALCOHOLS (R – OH)

- Common alcohols
- Phenols
- Polyhydric alcohols

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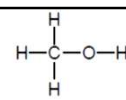

METHYL ALCOHOL (METHANOL)

Common Alcohols

- colorless liquid with a strong odor
- poisonous substance that can be absorbed through the eyes, skin, lungs, and digestive system
- Overexposure can cause death.
- Workers may be harmed by exposure to methyl alcohol.
- Methanol is primarily converted to formaldehyde, which is widely used in many areas, especially polymers
- Methanol and isobutene are combined to give methyl tert-butyl ether (MTBE). MTBE is a major octane booster in gasoline
- Condensation of methanol to produce hydrocarbons and even aromatic systems is the basis of several technologies related to gas to liquids.
- Methanol is used as a denaturant for ethanol, the product being known as "denatured alcohol" or "methylated spirit".
- Methanol is used as a solvent and as an antifreeze in pipelines and windshield washer fluid.
- In some wastewater treatment plants, a small amount of methanol is added to wastewater to provide a carbon food source for the denitrifying bacteria, which convert nitrates to nitrogen gas and reduce the nitrification of sensitive aquifers.

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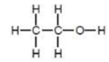

ETHYL ALCOHOL (ETHANOL)

Common Alcohols

- Ethanol is a volatile, flammable, colorless liquid with a characteristic wine-like odor and pungent taste.
- Ethanol is naturally produced by the fermentation process of sugars by yeasts or via petrochemical processes such as ethylene hydration.
- It is used as a chemical solvent and in the synthesis of organic compounds, and as a fuel source.
- Ethanol also can be dehydrated to make ethylene, an important chemical feedstock.

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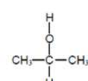

ISOPROPYL ALCOHOL

Common Alcohols

- Colorless, flammable organic compound with a strong alcoholic odor
- It is used in the manufacture of a wide variety of industrial and household chemicals and is a common ingredient in products such as antiseptics, disinfectants, hand sanitizer and detergents.
- Well over one million tons is produced worldwide annually used as solvent for coatings or for industrial processes..
- Used for household purposes and in personal care products.
- It is popular in pharmaceutical applications, due to its low toxicity.
- Some isopropyl alcohol is used as a chemical intermediate.
- Isopropyl alcohol may be converted to acetone

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Common Alcohols

N-PROPYL ALCOHOL

$CH_3—CH_2—CH_2—O—H$

- It is a colorless liquid used as a solvent in the pharmace industry, mainly for resins and cellulose esters, and, so as a disinfecting agent.
- It is formed naturally in small amounts during many fermentation processes
- Propanol has high octane number and is suitable for en fuel usage.

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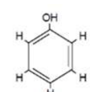
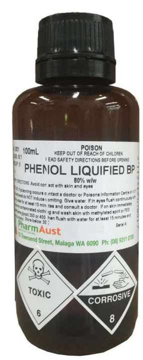
Phenols

PHENOLS



- It is a white crystalline solid that is volatile
- Mildly acidic, it requires careful handling because it can cause chemical burns.
- Phenol was first extracted from coal tar, but today is produced on a large scale (about 7 billion kg/year) from petroleum-derived feedstocks.
- It is an important industrial commodity as a precursor to many materials and useful compounds.
- It is primarily used to synthesize plastics and related materials.
- Phenol and its chemical derivatives are essential for production of polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and numerous pharmaceutical drugs.



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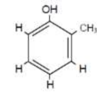
Presentation 4



Phenols

ORTHO-CRESOL (O-CRESOL)

- It is a colorless solid that is widely used intermediate in the production of other chemicals.
- Obtained from petroleum residue
- Large amount of supply is produced by methylation of phenol using methanol
- Cresols are skin irritants.
- When cresols are inhaled, ingested, or applied to the skin at very high levels, they can be harmful.
- Breathing high levels of cresols for a short time results in irritation of the nose and throat.

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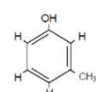

Phenols

META-CRESOL (M-CRESOL)

- It is a colorless, viscous liquid that is used as an intermediate in the production of other chemicals.
- m-Cresol is a precursor to numerous compounds. Important applications include:
  - pesticides such as fenitrothion and fenthion
  - synthetic vitamin E by methylation to give 2,3,6-trimethylphenol
  - antiseptics, such as amylmetacresol
  - a solvent for polymers.
  - preservatives in some insulin preparations

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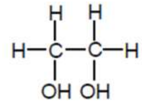

ETHYLENE GLYCOL

Polyhydric alcohols

- It is mainly used for two purposes, as a raw material in the manufacture of polyester fibers and for antifreeze formulations.
- It is an odorless, colorless, flammable, viscous liquid.
- Ethylene glycol has a sweet taste, but it is toxic in high concentrations.
- Ethylene glycol is produced from ethylene (ethene), via the intermediate ethylene oxide.

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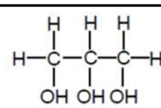

GLYCEROL

Polyhydric alcohols

- It is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic.
- Because it has antimicrobial and antiviral properties, it is widely used in FDA approved wound and burn treatments.
- It is also widely used as a sweetener in the food industry and as a humectant in pharmaceutical formulations.

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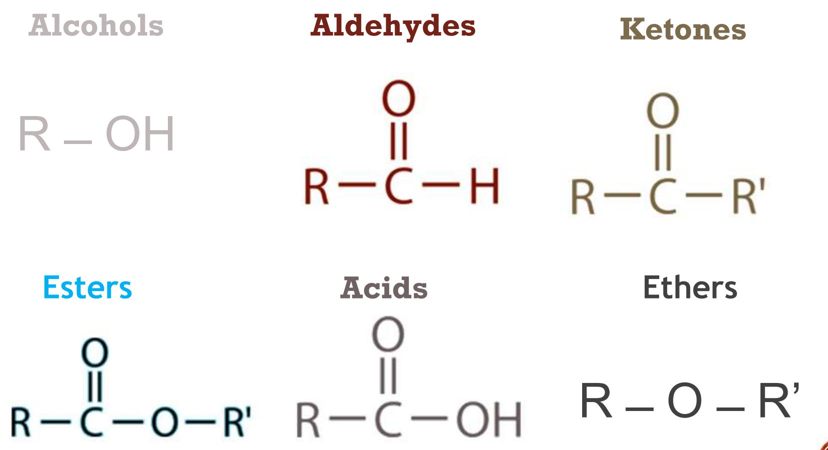
FUNCTIONAL GROUPS CONTAINING OXYGEN



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ETHERS

- Ethers are good solvents for other organic compounds because of their low reactivity.
- They readily dissolve nonpolar molecules.
- Diethyl ether is perhaps the best-known ether.
- It is widely used as a solvent and has been used as an inhalable anesthetic.
- Although ethers themselves are relatively unreactive, they can be converted to peroxides after prolonged exposure to oxygen.
- Peroxides are very reactive and are often explosive at elevated temperatures.
- Many commercially available ethers come with a small amount of a peroxide scavenger dissolved in them to help prevent this type of safety hazard.

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ETHER COMPOUNDS

Diethyl ether

CH_3CH_2-O-CH_2CH_3

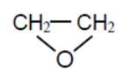
- Known anesthetic.

Methyl ethyl ether

CH_3-O-CH_2CH_3

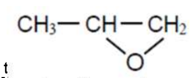
- important in the plastics industry for making epoxides and other compounds

Ethylene oxide



- Ethylene oxide is a colorless and flammable gas with a faintly sweet odor.

Propylene oxide



- Acutely t lorless volatile liquid with an odor.
- It is produced on a large scale industrially.

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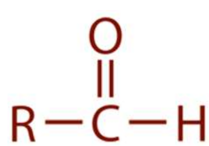
FUNCTIONAL GROUPS CONTAINING OXYGEN

Alcohols

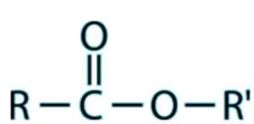
R – OH

Aldehydes

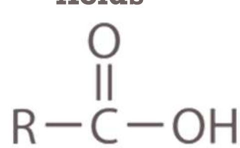


Ketones

Esters



Acids



Ethers

R – O – R’

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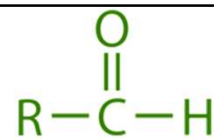

ALDEHYDES

- A very common structural component of organic structures is the **carbonyl**, which is simply a carbon atom and an oxygen atom connected by a double bond.
- The reactivity of carbonyls is primarily dictated by the polarization of the C=O bond, but the surrounding atoms also play a role in its specific reaction pathways.
- While carbonyl is a component of many functional groups, it is not itself a functional group.
- An aldehyde is a carbonyl in which the carbon atom is bonded to at least one hydrogen atom.
- The other group attached to the carbonyl may be an R -group or a hydrogen atom.
- Because the hydrogen atom is so small, the partial positive charge on the carbonyl carbon is very easy for other molecules to approach, making aldehydes a particularly reactive type of carbonyl.
- Aldehydes are versatile reactants for a wide variety of organic syntheses.
- Many aldehydes also have distinctive flavors and aromas.
  - Flavor of cinnamon is primarily due to the molecule cinnamaldehyde
  - Vanillin is the aldehyde responsible for the smell of vanilla extract.

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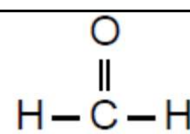

FORMALDEHYDE

Aldehydes

- A special aldehyde is the molecule in which the carbonyl is bonded to two hydrogen atoms.
- Formaldehyde has a wide variety of uses.
- It can be used as a tissue preservative or as a very harsh disinfectant.
- In 1996, the production of formaldehyde was estimated at 8.7 million tons per year.
- It is mainly used in the production of industrial resins, e.g., for particle board and coatings.

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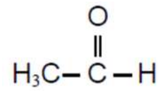
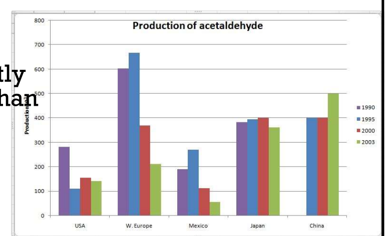


ACETALDEHYDE

Aldehydes

- It is a colorless liquid or gas, boiling near room temperature.
- Acetaldehyde occurs naturally in coffee, bread, and ripe fruit, and is produced by plants.
- It is produced by the partial oxidation of ethanol by the liver enzyme alcohol dehydrogenase
  - It is a contributing cause of hangover.
- Pathways of exposure include air, water, land, or groundwater, as well as drink and smoke.
- IARC listed acetaldehyde as a Group 1 carcinogen.
- Acetaldehyde is "one of the most frequently found air toxins with cancer risk greater than one in a million"



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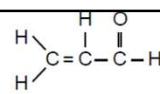
ACROLEIN



Aldehydes

- It is a colorless liquid with a piercing, acrid smell.
- The smell of burnt fat (as when cooking oil is heated to its smoke point) is caused by glycerol in the burning fat breaking down into acrolein.
- It is produced industrially from propylene and mainly used as a biocide and a building block to other chemical compounds, such as the amino acid methionine.
- In the 20th century, acrolein became an important intermediate for the industrial production of acrylic acid and acrylic plastics.
- Acrolein is toxic and is a strong irritant for the skin, eyes, and nasal passages.
- Connections exist between acrolein gas in the smoke from tobacco cigarettes and the risk of lung cancer.
- Acrolein is one of seven toxicants in cigarette smoke that are most associated with respiratory tract carcinogenesis.
- Found in **photochemical** smog and is quite reactive.

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FUNCTIONAL GROUPS CONTAINING OXYGEN

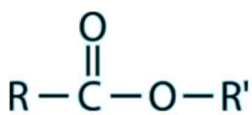
Alcohols

R – OH

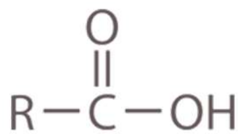
Aldehydes

Ketones

Esters



Acids



Ethers

R – O – R'

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KETONES

- A ketone involves a carbonyl in which the carbon atom makes single bonds with two R -groups.
- Ketones undergo most of the same reactions as aldehydes, but they tend to be slightly less reactive.
- Ketones are atmospherically reactive and contribute to the formation of photochemical smog
- Methyl ethyl ketone is used as a paint stripper and a solvent.
- Ketones are also used in the production of various polymers, either as a building block or as a solvent.
- The R -group in a ketone can be the same or different as seen in the example.

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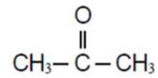
ACETONE



Ketones

- The simplest ketone is acetone, in which the carbonyl carbon is bonded to two CH_3 groups.
- It is a colorless, highly volatile and flammable liquid with a characteristic pungent odor.
- About 6.7 million tons were produced in 2010, mainly used as a solvent and production of methyl methacrylate and bisphenol A.
- This ketone is commonly used to remove fingernail polish and serves as an industrial solvent.

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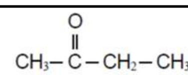
METHYL ETHYL KETONE (MEK)



Ketones

- Aka butanone
- sharp, sweet odor reminiscent of acetone
- It is produced industrially on a large scale but occurs in nature only in trace amounts.
- It is partially soluble in water and is commonly used as an industrial solvent.
- Common solvent used in processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films.
- Finds use in the manufacture of plastics, textiles, in the production of paraffin wax, and in household products such as lacquer, varnishes, paint remover, a denaturing agent for denatured alcohol, glues, and as a cleaning agent.

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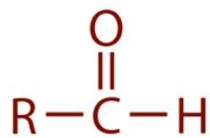
FUNCTIONAL GROUPS CONTAINING OXYGEN

Alcohols

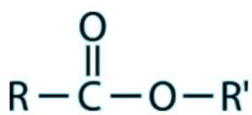
R – OH

Aldehydes

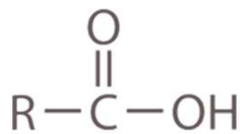


Ketones

Esters



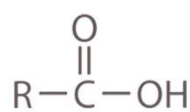
Acids



Ethers

R – O – R'

45



ACIDS

- Carboxylic acids are another carbonyl-containing functional group
  - carbon atom is bonded to an OH group on one side and
  - either a carbon or hydrogen atom on the other
- Carboxylic acids are weak acids
- An OH group that is directly connected to a carbonyl will ionize to a small extent when dissolved in water.
- The carboxylic acid and carboxylate ion are interchangeable.
- Carboxylate ions are often present in amino acids.

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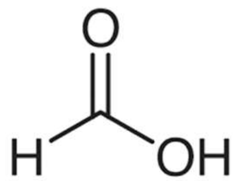
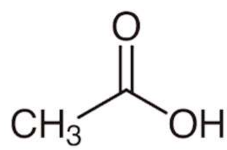
Acids

FORMIC- AND ACETIC ACIDS

- Formic acid acts as a protective chemical for many stinging insects and plants.
- Acetic acid gives vinegar its characteristic smell and flavor and is a fundamental biological and industrial building block.
- Carboxylic acids with longer carbon chains (fatty acids) are used by animals as a way of storing energy and are widely used in the manufacture of soaps.





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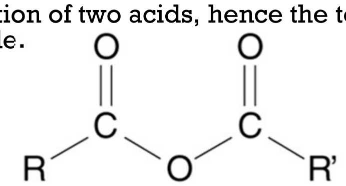
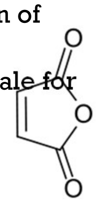
Acids

ACID ANHYDRIDES

- Acid anhydrides are derivatives of organic acids.
- They are formed from the intermolecular dehydration of two acids, hence the term anhydride.



- Maleic anhydride is an example of a cyclic anhydride and is used in the production of chemicals and plastics.
- It is produced industrially on a large scale for applications in coatings and polymers.



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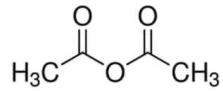
ACETIC ANHYDRIDE

Acids

- It is the simplest isolable anhydride of a carboxylic acid and is widely used as a reagent in organic synthesis.
- It is a colorless liquid that smells strongly of acetic acid, which is formed by its reaction with moisture in the air.
- Largest application is the conversion of cellulose to cellulose acetate
  - component of photographic film and other coated materials
  - manufacture of cigarette filters
- Used in the production of aspirin (acetylsalicylic acid) which is prepared by the acetylation of salicylic acid
- Active modification agent via autoclave impregnation and subsequent acetylation to make a durable and long-lasting timber.
- In starch industry, acetic anhydride is a common acetylation compound, used to produce modified starches
- Because of its use for the synthesis of heroin by the diacetylation of morphine, acetic anhydride is listed as a U.S. DEA List II precursor, and restricted in many other countries.
- Acetic anhydride is an irritant and combustible liquid; it is highly corrosive to skin and any direct contact will result in severe burns. Because of its reactivity toward water and alcohol, foam or carbon dioxide are preferred for fire suppression. The vapor of acetic anhydride is harmful.



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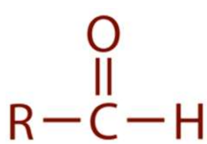
FUNCTIONAL GROUPS CONTAINING OXYGEN

Alcohols

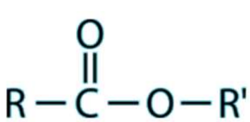
R – OH

Aldehydes

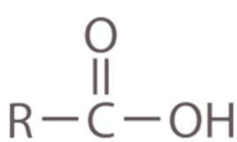


Ketones

Esters



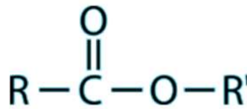
Acids



Ethers

R – O – R’

50



ESTERS

- An ester is like a carboxylic acid: contains a carbonyl where the carbon is bonded to one additional oxygen atom and one carbon or hydrogen atom
- The second oxygen atom is bonded to another carbon instead of to an acidic hydrogen atom.
- Structurally, carboxylic acids and esters are related to one another in the same way as alcohols and ethers.
- Esters can be formed by heating carboxylic acids and alcohols in the presence of an acid catalyst.
- This process is reversible, and the starting materials can be regenerated by reacting an ester with water in the presence of a weak base.
- Some esters have very pleasant odors, so they are used in the manufacture of many perfumes.
- Propyl acetate contributes to the odor of pears, while isoamyl acetate gives bananas their smell.
- This ester also serves as an alarm signal for honeybees.
- Esters are employed in the manufacture of fabrics (polyesters) and Plexiglass.
- Anesthetics such as procaine and benzocaine also contain esters.

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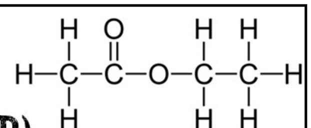

ETHYL ACETATE (ACETIC ESTER)

Esters

- This colorless liquid has a characteristic sweet smell (like pear drops)
- It is used in glues, nail polish removers, and in the decaffeination process of tea and coffee.
- Ethyl acetate is the ester of ethanol and acetic acid; it is manufactured on a large scale for use as a solvent.
- In 2004, an estimated 1.3 million tons were produced worldwide.
- The global ethyl acetate market was valued at $3.3 billion in 2018.
- Ethyl acetate is the most common ester in wine
- The aroma of ethyl acetate is most vivid in younger wines and contributes towards the general perception of "fruitiness" in the wine.
- Overexposure to ethyl acetate may cause irritation of the eyes, nose, and throat.
- Severe overexposure may cause weakness, drowsiness, and unconsciousness.

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ORGANIC COMPOUNDS CONTAINING HALIDES

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ORGANIC HALIDES

- Organic halides contain chlorine, fluorine, bromine and/or iodine
- They are widely used as solvents, refrigerants, propellants, anesthetics and as starting compounds for producing other chemicals.
- Many of them cause serious environmental problems and toxicological problems
- Some compounds in this class contribute to the depletion of the stratospheric ozone layer
- Main groups contain:
  - Chlorides of methane and ethane
  - Chlorides of ethylene
  - Double-bonded chlorides
  - Chlorides of benzene
  - Chloroflourocarbons
  - Compounds containing both oxygen and chloride

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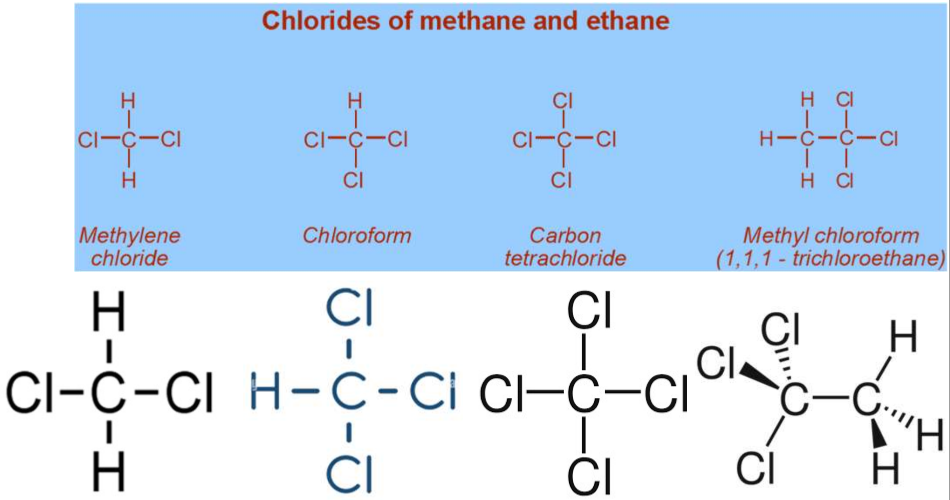
ORGANIC CHLORIDES



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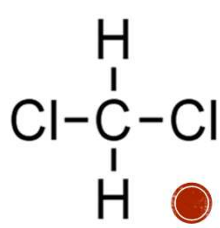
METHYLENE CHLORIDE

Chlorides of methane & ethane

- Methylene chloride aka Dichloromethane (DCM)
- Colorless, volatile liquid with a chloroform-like, sweet odor
- It is widely used as a solvent.
- Although it is not miscible with water, it is slightly polar, and miscible with many organic solvents
- In the food industry, it is used to decaffeinate coffee and tea as well as to prepare extracts of hops and other flavorings.
- Used as an aerosol spray propellant and as a blowing agent for polyurethane foams.



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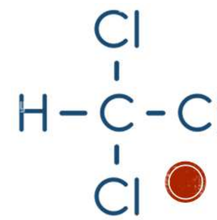
Chlorides of methane & ethane

CHLOROFORM

- Colorless, strong-smelling, dense liquid produced on a large scale as a precursor to PTFE.
- It is a precursor to various refrigerants.
- It is one of the four chloromethanes and a trihalomethane.
- It is a powerful anesthetic, euphoriant, anxiolytic, and sedative when inhaled or ingested.
- Chloroform is suspected of causing cancer (i.e., possibly carcinogenic, IARC Group 2B)
- It is classified as an extremely hazardous substance in the United States

It is nearly impossible to incapacitate someone using chloroform. It takes at least five minutes of inhaling an item soaked in chloroform to render a person unconscious.



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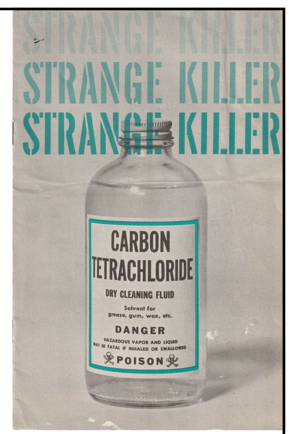
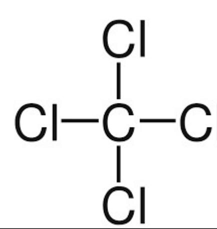
Chlorides of methane & ethane

CARBON TETRACHLORIDE

- It is a colorless liquid with a "sweet" smell that can be detected at low levels.
- It is practically incombustible at lower temperatures.
- It was formerly widely used in fire extinguishers, as a precursor to refrigerants and as a cleaning agent.
- It has since been phased out because of environmental and safety concerns.
- Exposure to high concentrations of carbon tetrachloride (including vapor) can affect the central nervous system and degenerate the liver and kidneys.
- Prolonged exposure can be fatal.





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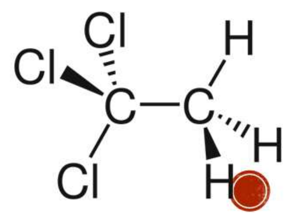
METHYL CHLOROFORM (1,1,1-TRICHLOROETHANE)

Chlorides of methane & ethane

- Colorless, sweet-smelling liquid was once produced industrially in large quantities for use as a solvent.
- It is regulated by the Montreal Protocol as an ozone-depleting substance and its use is being rapidly phased out.



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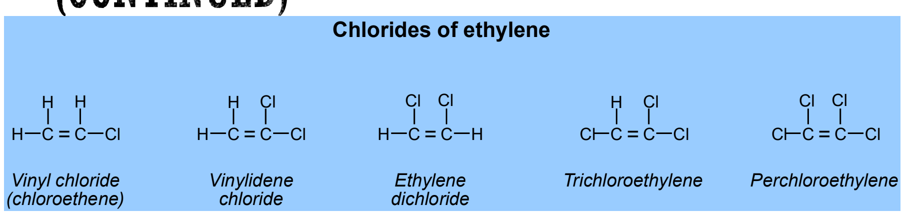
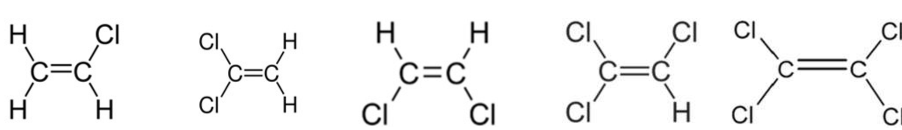
ORGANIC CHLORIDES (CONTINUED)





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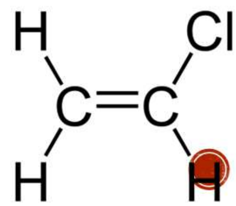
VINYL CHLORIDE (CHLOROETHENE)

Chlorides of ethylene

- Important industrial chemical
- Used to produce the polymer polyvinyl chloride (PVC)
- About 13 million metric tons are produced annually.
- Among the top twenty largest petrochemicals (petroleum-derived chemicals) in world production.
- The US currently remains the largest manufacturer because of its low-production-cost position in chlorine and ethylene raw materials.
- China is a large manufacturer and one of the largest consumers
- Vinyl chloride is a gas with a sweet odor.
- It is highly toxic, flammable, and carcinogenic.
- Vinyl chloride that is released by industries or formed by the breakdown of other chlorinated chemicals can enter the air and drinking water supplies.
- Vinyl chloride is a common contaminant found near landfills.
- In the past VCM was used as a refrigerant.

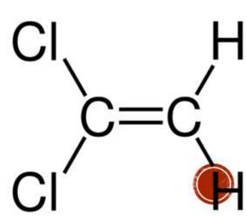


61

VINYLIDENE CHLORIDE (1,1-DICHLOROETHENE)

Chlorides of ethylene

- Colorless liquid with a sharp odor.
- Poorly soluble in water, but soluble in organic solvents.
- Was the precursor to the original clingwrap, Saran, for food, but this application has been phased out.
- Class 2B: possibly carcinogenic to humans.



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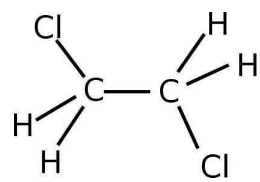
ETHYLENE DICHLORIDE (1,2-DICHLOROETHANE)

Chlorides of ethylene

- Colorless liquid with a chloroform-like odor.
- Most common use is in the production of vinyl chloride, which is used to make polyvinyl chloride (PVC) pipes, furniture and automobile upholstery, wall coverings, housewares, and automobile parts.
- Also used generally as an intermediate for other organic chemical compounds, and as a solvent.
- Has been used as degreaser and paint remover but is now banned from use due to its toxicity and possible carcinogenetic property.



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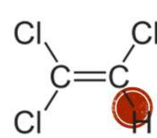
TRICHLOROETHYLENE

Chlorides of ethylene

- Commonly used as an industrial solvent.
- It is a clear, colorless non-flammable liquid with a chloroform-like sweet smell.
- Industrial abbreviations include TCE, trichlor, Trike, Tricky and tri.
- Used as a volatile anesthetic and as an inhaled obstetrical analgesic in millions of patients (tradename: Trimar and Trilene).
- Groundwater and drinking water contamination from industrial discharge is a major concern for human health and has precipitated numerous incidents and lawsuits.
- The 1998 film "A Civil Action" dramatizes the EPA lawsuit concerning trichloroethylene contamination that occurred in Woburn, Massachusetts in the 1980s.



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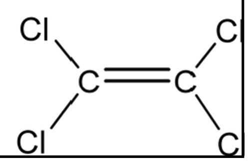
PERCHLOROETHYLENE (TETRACHLOROETHYLENE)

Chlorides of ethylene

- Known with many other names (and abbreviations such as "perc" or "PERC", and "PCE")
- Colorless liquid widely used for dry cleaning of fabrics,
- Sometimes called "dry-cleaning fluid".
- Used as an effective automotive brake cleaner.
- It has a sweet odor detectable by most people at a concentration of 1 part per million (1 ppm).
- Worldwide production was about 1 million metric tons in 1985



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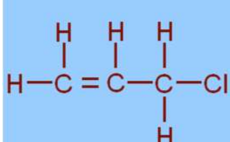
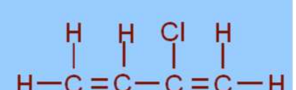
ORGANIC CHLORIDES (CONTINUED)

Other double-bonded chlorides



Allyl chloride



Chloroprene

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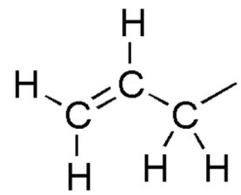
ALLYL CHLORIDE



Double bonded chlorides

- Colorless liquid insoluble in water but soluble in common organic solvents
- It is mainly converted to epichlorohydrin, used in the production of plastics.
- It is a chlorinated derivative of propylene.
- It is an alkylating agent, which makes it both useful and hazardous to handle.
- Highly toxic and flammable.
- Eye effects may be delayed and may lead to possible impairment of vision.

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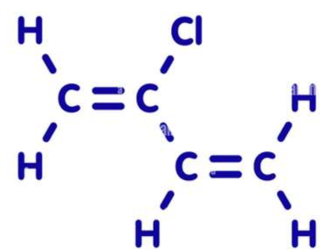
CHLOROPRENE



Double bonded chlorides

- Chloroprene is a colorless volatile liquid.
- It is almost exclusively used as a monomer to produce the polymer polychloroprene (neoprene), a type of synthetic rubber.

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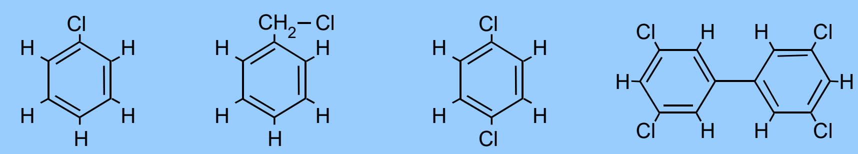
ORGANIC CHLORIDES (CONTINUED)

Chlorides of benzene



Chlorobenzene — *Benzylchloride* — *p-dichlorobenzene* — *Example of a polychlorinated biphenyl (PCB)*

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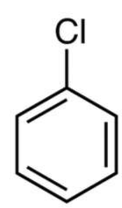
CHLOROBENZENE



Chlorides of benzene

- Colorless flammable liquid
- It is a common solvent and a widely used intermediate in the manufacture of other chemicals (paints).
- Permissible exposure limit at 75 ppm (350 mg/m3) over an eight-hour time-weighted average for workers handling chlorobenzene
- Chlorobenzene can persist in soil for several months, in air for about 3.5 days, and in water for less than one day.

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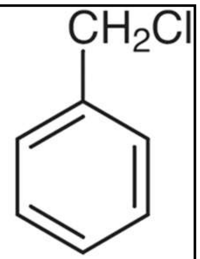
BENZYLCHLORIDE



Chlorides of benzene

- Colorless liquid
- Reactive organochlorine compound
- Widely used chemical building block
- It is classified as an extremely hazardous substance in the United States

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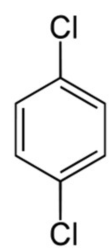
P-DICHLOROBENZENE (1,4-DICHLOROBENZENE)



Chlorides of benzene

- Colorless solid has a strong odor.
- It is used as a disinfectant, pesticide, and deodorant, most familiarly in mothballs in which it is a replacement for the more traditional naphthalene because of naphthalene's greater flammability (though both chemicals have the same NFPA 704 rating).
- It is also used as a precursor in the production of the chemically and thermally resistant polymer poly(p-phenylene sulfide).
- may reasonably be anticipated to be a carcinogen
- EPA set a target MCL of 75 µg/L but publishes no information on the cancer risk.
- EPA-registered pesticide.
- OSHA set a maximum level of 75 ppm in air for an 8-hour day, 40-hour workweek.

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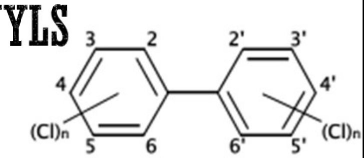
POLYCHLORINATED BIPHENYLS (PCB)



Chlorides of benzene

- Highly carcinogenic chemical compounds
- Formerly used in industrial and consumer products, however banned in the US by the Toxic Substances Control Act in 1979 and internationally by the Stockholm Convention on Persistent Organic Pollutants in 2001.
- Were widely used in the manufacture of carbonless copy paper, as heat transfer fluids, and as dielectric and coolant fluids for electrical equipment.
- Because of their longevity, PCBs are still widely in use, even though their manufacture has declined drastically since the 1960s.
- IARC rendered PCBs as definite carcinogens in humans.
- Many rivers and buildings, including schools, parks, and other sites, are contaminated with PCBs and there has been contamination of food supplies with the substances.
- Moreover, because of their use as a coolant in electric transformers, PCBs persist in built environments.
- An estimated 1.2 million tons have been produced globally.
- In 1988, 370,000 tons were in the environment globally and 780,000 tons were present in products, landfills and dumps or kept in storage.

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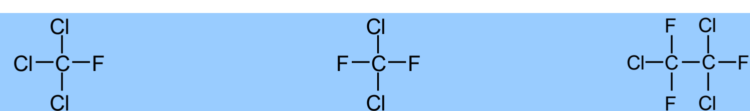
CHLOROFLUOROCARBONS



Trichlorofluormethane (Freon 11) *Dichlorodifluoromethane (Freon 12)* *Trichlorotrifluoroethane (Freon 13)*

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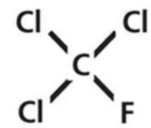
TRICHLOROFLUOROMETHANE (FREON 11)



Chloroflourocarbons

- It is a colorless, faintly ethereal, and sweetish-smelling liquid that boils around room temperature.
- Freon 11 (CFC-11) is a Class 1 ozone-depleting substance which damages Earth's protective stratospheric ozone layer.
- Prior to the knowledge of the ozone depletion potential of chlorine in refrigerants and other possible harmful effects on the environment, trichlorofluoromethane was sometimes used as a cleaning/rinsing agent for low-pressure systems.

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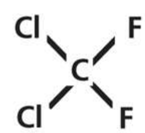
DICHLORODIFLUOROMETHANE (FREON 12)



Chloroflourocarbons

- Colorless and odorless gas.
- It is produced by fluorination of chloroform using a catalyst such as antimony trifluoride
- Dichlorofluoromethane was used as a propellant and refrigerant.
- Due to its role in ozone depletion, dichlorofluoromethane has been largely phased out.
- It has ozone depletion potential 1.
- Production and consumption has been since 2004 reduced to 15% of level from 1989 and it is to be phased out in 2015 according to Montreal Protocol.

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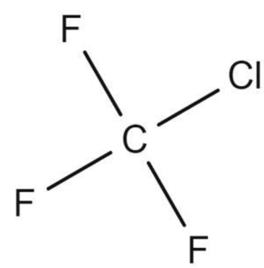
CHLOROTRIFLUOROMETHANE (FREON 13)

Chloroflourocarbons

- It is a man-made substance used primarily as a refrigerant.
- When released into the environment, CFC-13 has a high ozone depletion potential, high global warming potential, and long atmospheric lifetime.



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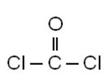
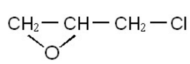
COMPOUNDS CONTAINING BOTH OXYGEN AND CHLORINE



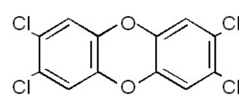
Phosgene

(a)



Epichlorohydrin

(b)



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

(c)

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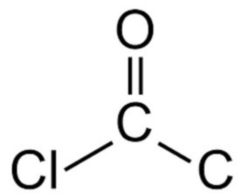
PHOSGENE

Compounds containing both oxygen & chloride

- It is a toxic, colorless gas; in low concentrations, its musty odor resembles that of freshly cut hay or grass.
- Phosgene is a valued and important industrial building block, especially to produce precursors of polyurethanes and polycarbonate plastics.
- Phosgene is extremely poisonous and was used as a chemical weapon during World War I, where it was responsible for 85,000 deaths.
- It was a highly potent pulmonary irritant and quickly filled enemy trenches due to it being a heavy gas.
- It is classified as a Schedule 3 substance under the Chemical Weapons Convention.
- In addition to its industrial production, small amounts occur from the breakdown and the combustion of organochlorine compounds, such as chloroform.



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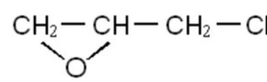
EPICHLOROHYDRIN



Compounds containing both oxygen & chloride

- Epichlorohydrin (ECH) is an organochlorine compound and an epoxide.
- It is a colorless liquid with a pungent, garlic-like odor, moderately soluble in water, but miscible with most polar organic solvents.
- ECH is a highly reactive electrophilic compound and is used in the production of glycerol, plastics, epoxy glues and resins, epoxy diluents and elastomers.
- Probable or likely carcinogen in humans.

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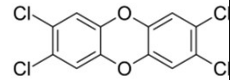
DIOXIN 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN (TCDD)



Compounds containing both oxygen & chloride

- TCDD is a polychlorinated dibenzo-p-dioxin
- shortened to simply 'dioxin'
- Pure TCDD is a colorless solid with no distinguishable odor at room temperature.
- It is usually formed as an unwanted product in burning processes of organic materials or as a side product in organic synthesis.
- TCDD is a potent compound
- It is known as a contaminant in Agent Orange, a herbicide used in the Vietnam War
- TCDD was released into the environment in the Seveso disaster
- It is a persistent organic pollutant.

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ORGANIC COMPOUNDS CONTAINING NITROGEN

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ORGANIC COMPOUNDS INCLUDING NITROGEN

- The simplest organic nitrogen compounds are the amines (derivatives of ammonia NH_3)
- Amines are odorous materials and have often been the subject of nuisance complaints.
- The organic nitrates are end products in photochemical oxidation reactions and are responsible for many of the adverse effects of photochemical smog.
- Nitrogen has the capability of sharing either three or five electrons with either carbon or hydrogen.
- When one hydrogen atom of NH_3 is replaced by a hydrocarbon radical, the resulting compound is called a primary amine and is represented by the general formula RNH_2: methyl amine (CH_3NH_2) and ethyl amine ($C_2H_5NH_2$)
- When two hydrogen atoms are replaced by hydrocarbon radicals, the compound is called a secondary amine and has the general formula R_2NH: methyl ethyl amine ($(CH_3)(C_2H_5)NH$) and diethylamine ($(C_2H_5)_2NH$)
- The replacement of all 3 hydrogen atoms with hydrocarbon radicals forms a tertiary amine of the general formula R_3N: methyl diethyl amine ($(CH_3)(C_2H_5)_2N$) and triethyl amine ($(C_2H_5)_3N$)
- More complicated organic nitrogen compounds shares five electrons: organic nitro compounds ($R\text{-}NO_2$) and the organic nitrates ($R\text{-}ONO_2$): nitroethane ($CH_3CH_2\text{-}NO_2$) and ethyl nitrate ($CH_3CH_2\text{-}ONO_2$) are found in photochemical smog.
- Two important photochemical oxidants from this group are peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN), which are **strong eye irritants** and cause plant damage.

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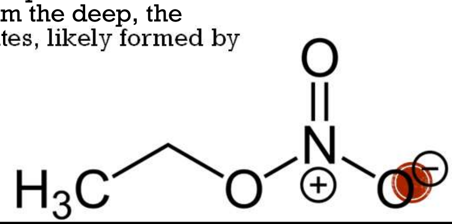
ETHYL NITRATE

Nitroparaffins

- Ethyl nitrate is the ethyl ester of nitric acid
- Colorless, volatile, explosive, and highly flammable liquid
- It is used in organic synthesis and as an intermediate in the preparation of some drugs, dyes, and perfumes.
- Ethyl nitrate is found in the atmosphere, where it can react with other gases to form smog
- Originally thought to be a pollutant, formed mainly by the combustion of fossil fuels
- Recent analysis of ocean water samples reveal that in places where cool water rises from the deep, the water is saturated with alkyl nitrates, likely formed by natural processes.



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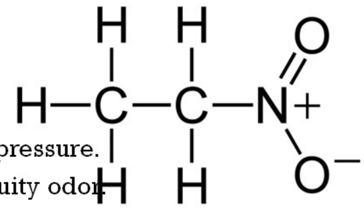
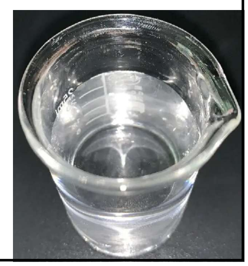
NITROETHANE



Nitroparaffins

- Oily liquid at standard temperature and pressure.
- Pure nitroethane is colorless and has a fruity odor.
- Like some other nitrated organic compounds, nitroethane is also used as a fuel additive and a precursor to Rocket propellants
- Nitroethane is suspected to cause genetic damage and be harmful to the nervous system
- Skin contact causes dermatitis in humans.
- In animal studies, nitroethane exposure was observed to cause lacrimation, dyspnea, pulmonary rales, edema, liver and kidney injury, and narcosis.
- Children have been poisoned by accidental ingestion of artificial nail remover.



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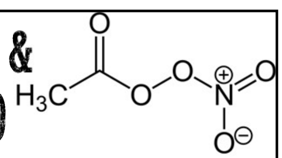
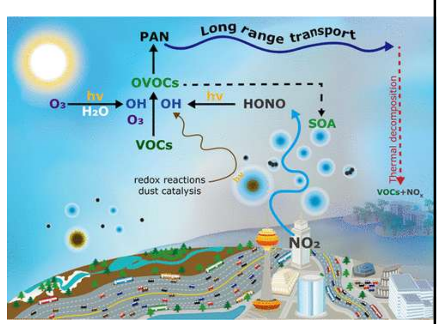
PEROXYACETYL NITRATE (PAN) & PEROXYBENZOYL NITRATE (PBN)

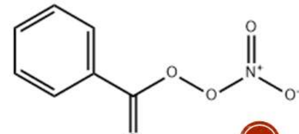


PAN & PBN Compounds

PAN:

- It is a secondary pollutant present in photochemical smog
- It is thermally unstable and decomposes into peroxyethanoyl radicals and nitrogen dioxide gas
- It irritates the lungs and eyes
- Peroxyacetyl nitrate, or PAN, is an oxidant that is more stable than ozone.
- Hence, it is more capable of long-range transport than ozone.
- It serves as a carrier for oxides of nitrogen (NOx) into rural regions and causes ozone formation in the global troposphere
- PAN is a greenhouse gas.





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ORGANIC COMPOUNDS CONTAINING SULFUR

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ORGANIC COMPOUNDS INCLUDING SULFUR

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

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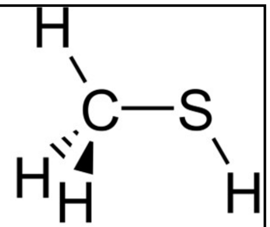
METHYL MERCAPTAN (METHANETHIOL)



Organic Sulfur

- It is a colorless gas with a distinctive putrid smell
- It is a natural substance found in the blood, brain and feces of animals (including humans), as well as in plant tissues.
- It also occurs naturally in certain foods, such as some nuts and cheese.
- It is one of the chemical compounds responsible for bad breath and the smell of flatus.
- It is very flammable.
- In 2001 an explosion of 25,000 US gallons left 3 people dead and 9 injured.
- In 2014 (Dupont's La Porte facility), a deadly release of Methyl Mercaptan occurred in a confined space, killing 4 and injuring 1 other.

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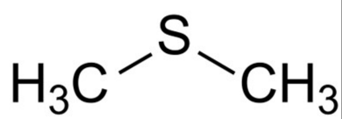
DIMETHYL SULFIDE



Organic Sulfur

- Dimethyl sulfide is a flammable liquid that boils at 37 °C
- Has a characteristic disagreeable odor.
- It is a component of the smell produced from cooking of certain vegetables, notably maize, cabbage, beetroot, and seafoods.
- It is also an indication of bacterial contamination in malt production and brewing.
- It is a breakdown product of dimethylsulfoniopropionate (DMSP)
- It is also produced by the bacterial metabolism of methanethiol

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FORMATION OF OZONE AND PHOTOCHEMICAL SMOG

Presentation: 5

Chapter 2 – Properties and Fundamentals

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

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WESTAR
Western States Air Resources Council

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FORMATION OF OZONE AND PHOTOCHEMICAL SMOG

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SCIENCE OF SMOG

3

PHOTOCHEMICAL REACTIONS

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

- Photochemical reactions are initiated by the absorption of a photon of energy (h) by an atom, molecule, free radical or ion.

Where A* is an excited state of A.

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

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

- The energy for atmospheric photochemical dissociation reactions comes from the sun.
- In the troposphere, the wavelength range of interest is approximately **280 nm to 730 nm**

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PHOTOCHEMICAL REACTIONS (CONT'D)

- Stratospheric oxygen and ozone block out most of the ultraviolet radiation below 280 nm
- No photochemical reactions of interest take place at wavelengths above 730 nm
- **NO_2 is the most important energy absorbing molecule**:
  - absorbing energy over the entire visible and ultraviolet range of the solar spectrum in the lower atmosphere.
  - Between 300 nm and 370 nm, this energy absorption results in over 90 percent of the NO_2 dissociating to NO and O.
- Other molecules that can undergo photochemical dissociation include O_3, H_2O_2, HNO_2, NO_3, aldehydes and ketones.
- These photochemical dissociation reactions are important because of the products (mainly free radicals) that result from them.
- These products then initiate or participate in many other reactions responsible for the conversion of primary air pollutants into ozone and photochemical smog.

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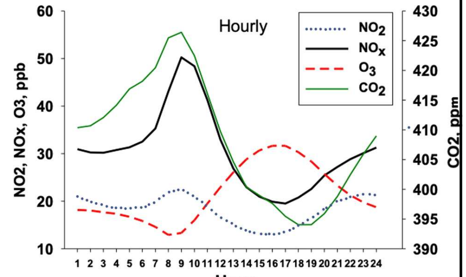
BASIC PHOTOCHEMICAL CYCLE

- The steady-state O_3 concentration can be calculated as a function of initial NO_2 concentration.
- Typical urban NO_2 concentration = 0.1 ppm → O_3 concentration = 0.027 ppm
- Peak 1-hour O_3 concentration as high as 0.5 ppm have been measured in some urban areas
- Evidently, some other mechanism must be involved.
- It is equally clear that mechanism must result in the conversion of NO to NO_2 without consuming O_3.

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

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

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



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ROLE OF VOCS

- At wavelengths below about 315 nm, O_3 dissociates into an excited oxygen atom and an oxygen molecule
- Most of the time O* collides with N_2 or O_2, removing the excess energy and quenching the O* to its ground state.
- Occasionally, however, O* collides with H_2O and produces two hydroxyl radicals
- This radical, unlike many radicals formed from organic molecules, does not react with oxygen.
- Instead, it survives to react with most atmospheric compounds, including carbon monoxide, hydrocarbons and aldehydes.

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

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

Understanding **OH· reactions** is key

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OZONE FORMATION REGIMES: VOC-LIMITED VS NOX-LIMITED

- Ozone formation depends on **both VOC and NOx**, but the ratio determines which one is the rate-limiting reactant **VOC-limited regime** (low VOC : NOx ratio): Typical of dense urban cores with heavy traffic
- Cutting VOC reduces ozone
- Cutting NOx alone can **increase** ozone (NOx titration effect)
- **NOx-limited regime** (high VOC : NOx ratio): Typical of suburbs, rural areas, downwind regions, and forested areas with high biogenic VOC background
- Cutting NOx reduces ozone
- Cutting VOC has limited effect (background biogenic VOCs dominate)
- The **ridge line** — roughly VOC : NOx of 8:1 — separates the two regimes **Why this matters:** the same emission reduction can have very different effects depending on which regime your area is in. SIP planners and modelers determine the local regime before recommending control strategies.

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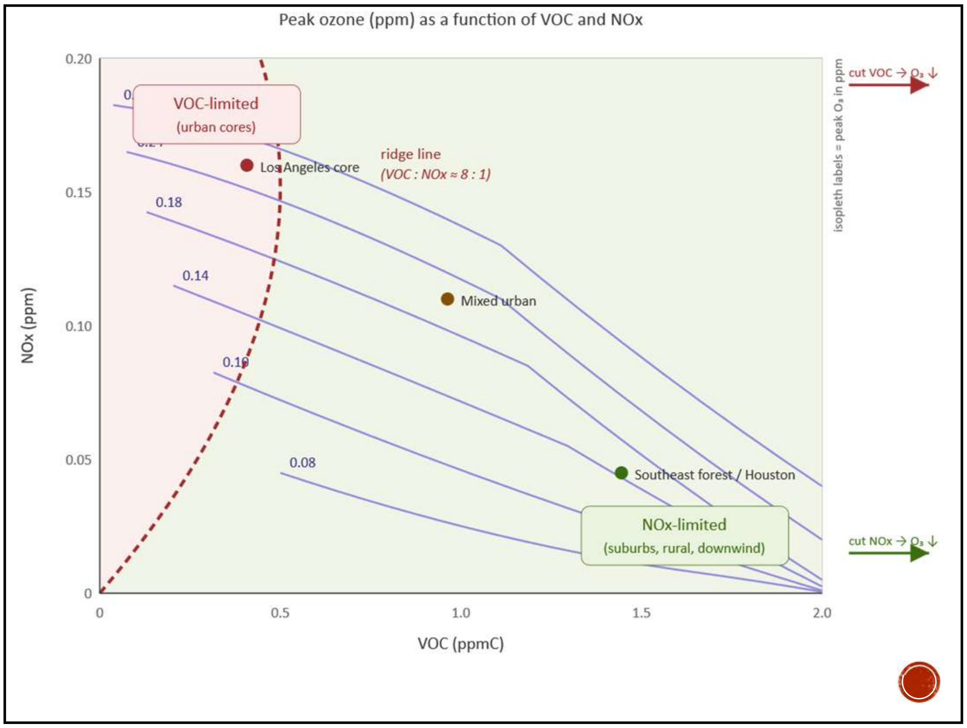

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REACTIONS OF FORMALDEHYDE

Photolysis:

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

Reaction with OH:

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

Forming hydroperoxyl:

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

Forming more hydroperoxyl:

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

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REACTIONS OF FORMALDEHYDE (CONT'D)

- The hydroperoxyl radical then reacts with NO to form NO_2 and regenerate the OH radical
- OH and NO_2 may react to form nitric acid

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

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

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REACTIONS OF ACETALDEHYDE

Photolysis:

$$CH_3CHO \xrightarrow{h\nu} CH_3 \cdot + HCO \cdot$$

Reaction with OH:

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

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

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

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

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REACTIONS OF ACETALDEHYDE (CONT'D)

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

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

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

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

Formation of PAN

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SUMMARY

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

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

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

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

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PHOTOLYSIS OF ALDEHYDES

$$RCHO \xrightarrow{h\nu} R\cdot + HCO\cdot$$

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

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

$$RCHO + OH\cdot \rightarrow RCO\cdot + H_2O$$

$$RCO\cdot + O_2 \rightarrow RCOO_2\cdot$$

$$RCOO_2\cdot + NO \rightarrow NO_2 + RCOO\cdot$$

$$RCOO\cdot \rightarrow R\cdot + CO_2$$

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

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REACTION OF OH WITH HYDROCARBONS

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

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

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

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

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

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

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PROPERTIES OF ORGANIC VAPORS

Presentation: 6

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PROPERTIES OF ORGANIC VAPORS

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Chapter 2 – Properties and Fundamentals

2

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

3

GAS AND VAPOR DEFINITIONS

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.

4

MOLECULAR WEIGHT

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

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

χ_i = mole fraction of component I

MW_i = molecular weight of component i

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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 gram-mole is the mass of material that contains Avogadro's number of molecules.

6

EQUATION OF STATE

The ideal gas law:

$$PV = nRT$$

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

7

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 Pa-m^3/kg-mole-K

8

Volume Correction

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

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

9

MOLAR VOLUME

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

At 68°F and 1 atm:

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

10

GAS DENSITY

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

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

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VAPOR PRESSURE

Antoine equation:

$$Log_{10}(p^*) = A - \frac{B}{T + C}$$

p^* = vapor pressure

T = temperature

A,B,C = constants

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PARTIAL PRESSURE

Dalton stated that the total pressure of a gas mixture is the sum of the individual pressures of each component

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

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PARTIAL VOLUME

Amagat stated that the total volume of a gas mixture is the sum of the individual volumes of each component

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

14

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

15

CONCENTRATION EXPRESSIONS

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

$$ppmv_i = \left(\frac{\nu_i}{V_T}\right) x\, 10^6$$

- Mass per unit volume

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Conversion Equation

$$1\,\text{ppmv} = \frac{1\,\text{ft}^3\ \text{VOC}}{10^6\,\text{ft}^3}\left(\frac{1}{V_{molar}}\frac{\text{lb}-\text{mole VOC}}{\text{ft}^3\ \text{VOC}}\right)\left(MW_{VOC}\frac{\text{lb VOC}}{\text{lb}-\text{mole VOC}}\right)$$

$$1\,\text{ppmv} = \frac{MW_{VOC}}{V_{molar}\,x\,10^6}\frac{\text{lb VOC}}{\text{ft}^3}$$

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EXPLOSIVE LIMITS

- LEL is the concentration of VOC below which combustion will not be self-sustaining
- UEL is the concentration of VOC that produces a non-burning mixture because of the lack of oxygen

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EXPLOSIVE LIMITS OF SELECTED VOCS

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

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SOURCE MEASUREMENT TECHNIQUES

Presentation: 7

Chapter 3 – Source Measurement Techniques

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SOURCE MEASUREMENT TECHNIQUES

Presentation: 7

Chapter 3 – Source Measurement Techniques

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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 21

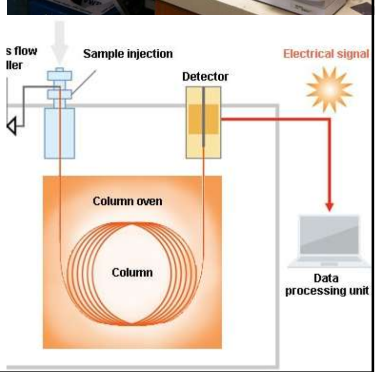
- Determination of volatile organic compound leaks

3

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

https://www.epa.gov/emc/method-18-volatile-organic-compounds-gas-chromatography



4

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

5

PRE-SURVEY SAMPLING TECHNIQUES

The minimum detectable concentration is determined during the presurvey calibration for each compound.

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

6

FINAL SAMPLING TECHNIQUES

- Direct interface
- Dilution interface
- Adsorption tubes
- Flexible bags

7

DIRECT OR DILUTION INTERFACE SAMPLING

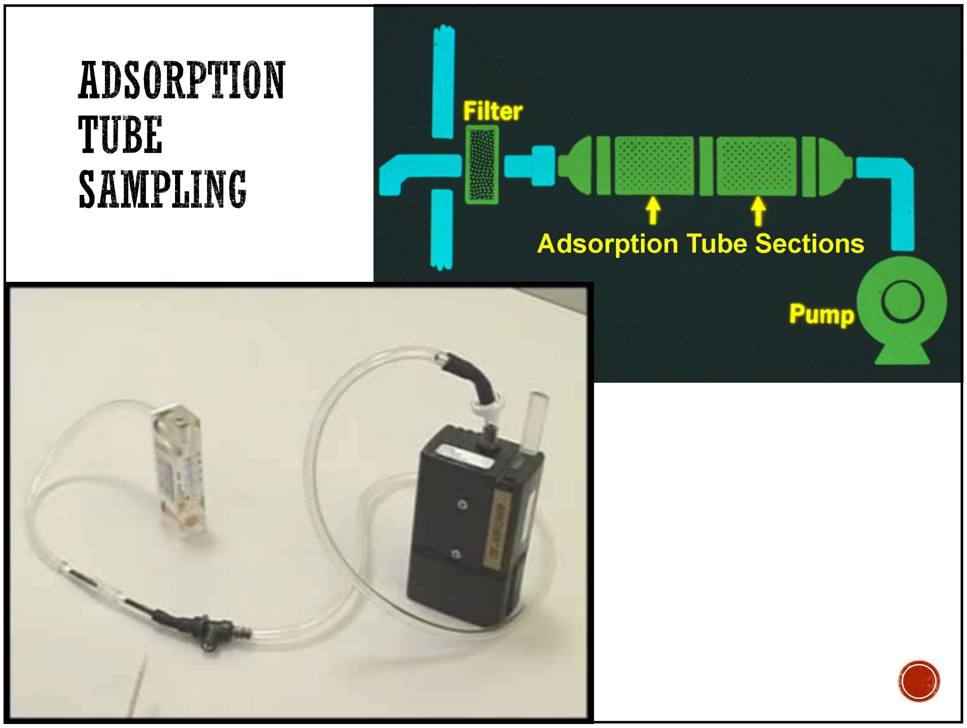
Strengths

- No loss or alteration of compounds
- Method of choice when temperature is below 100°C and **VOC concentrations are suitable**

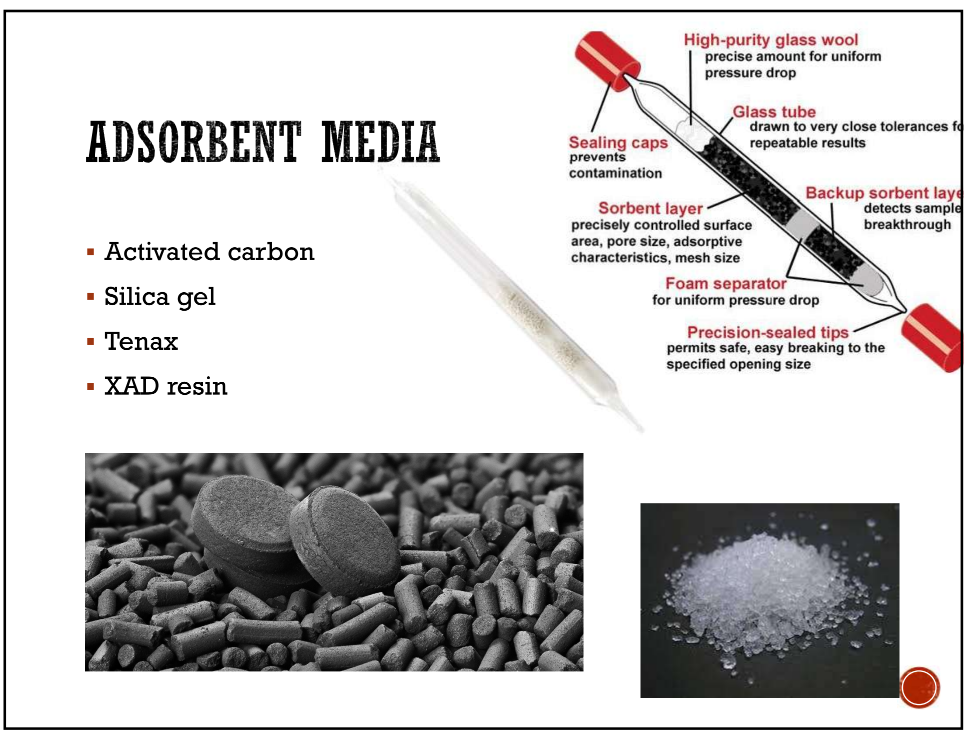
Weaknesses

- GC must be located at sampling site
- Cannot sample proportionally or obtain time integrated sample

8


ADSORPTION TUBE SAMPLING
Filter
Adsorption Tube Sections
Pump

9


ADSORBENT MEDIA
▪ Activated carbon
▪ Silica gel
▪ Tenax
▪ XAD resin
High-purity glass wool
precise amount for uniform pressure drop
Glass tube
drawn to very close tolerances fo
repeatable results
Sealing caps
prevents contamination
Backup sorbent laye
detects sample
breakthrough
Sorbent layer
precisely controlled surface area, pore size, adsorptive characteristics, mesh size
Foam separator
for uniform pressure drop
Precision-sealed tips
permits safe, easy breaking to the specified opening size

10

ADSORPTION TUBE SAMPLING

Strengths

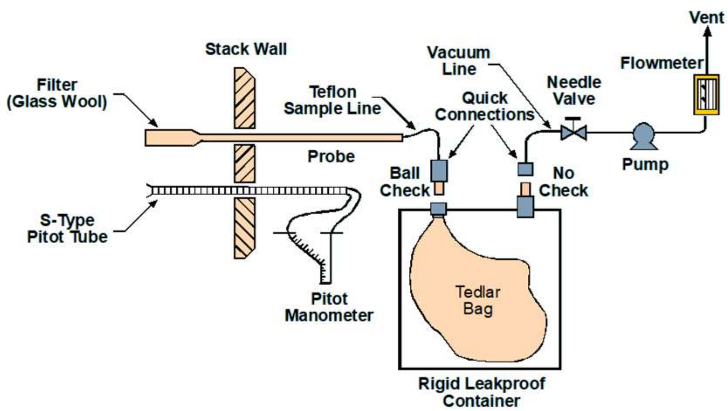
- Samples are compact and easy to handle
- Samples returned to lab for analysis
- Can be stored up to a week at 0°C

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

11

FLEXIBLE BAG SAMPLING



12

FLEXIBLE BAG SAMPLING

Strengths

- Samples approximate form in stack
- Samples are returned to lab for analysis
- Samples <u>may be collected proportionally</u>

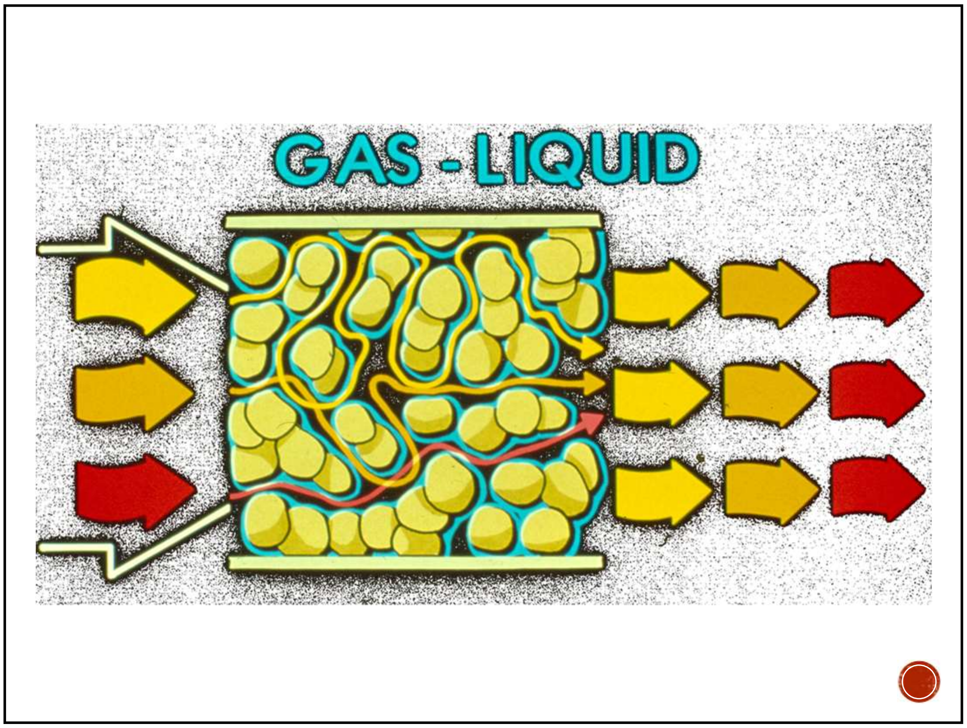
Weaknesses

- 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

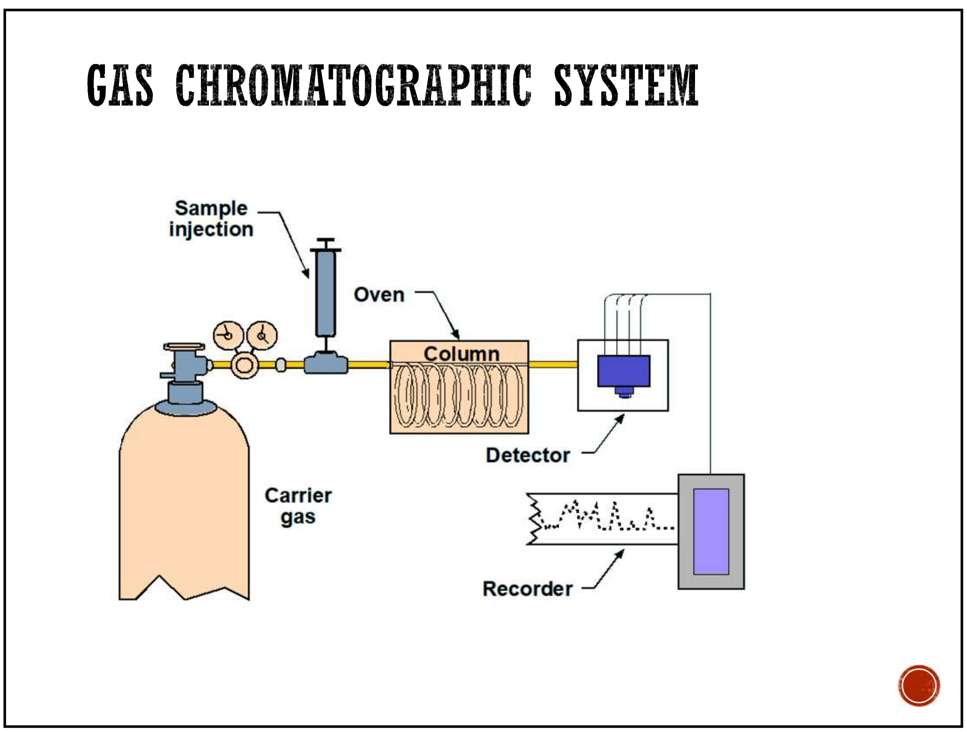
13

LABORATORY ANALYSIS

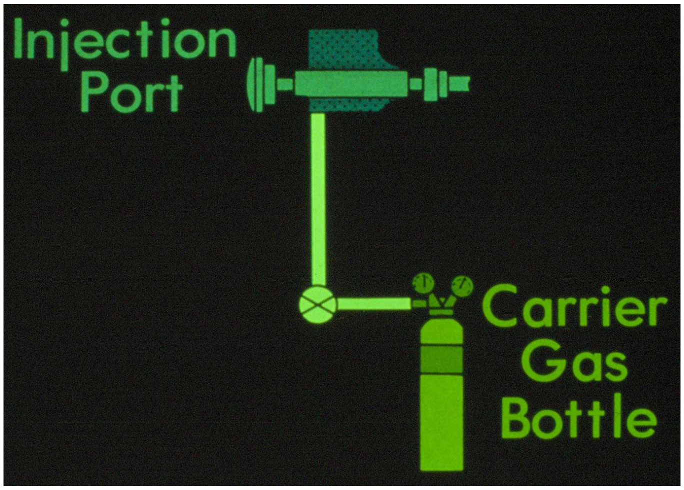
14


GAS - LIQUID

15


GAS CHROMATOGRAPHIC SYSTEM
Sample injection
Oven
Column
Detector
Carrier gas
Recorder

16



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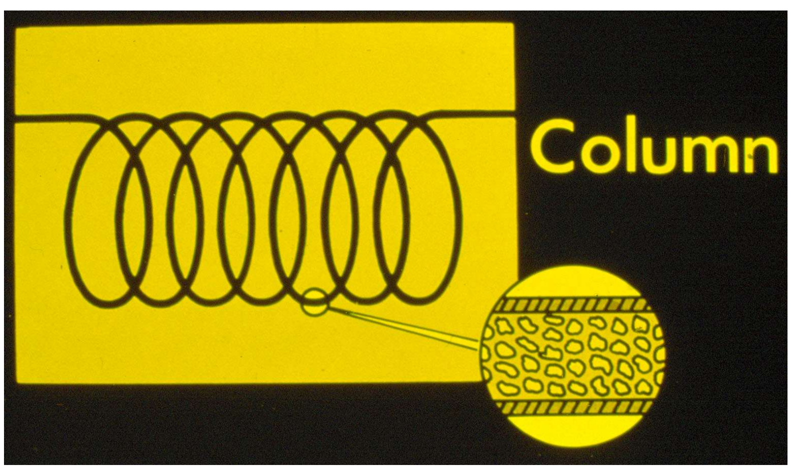

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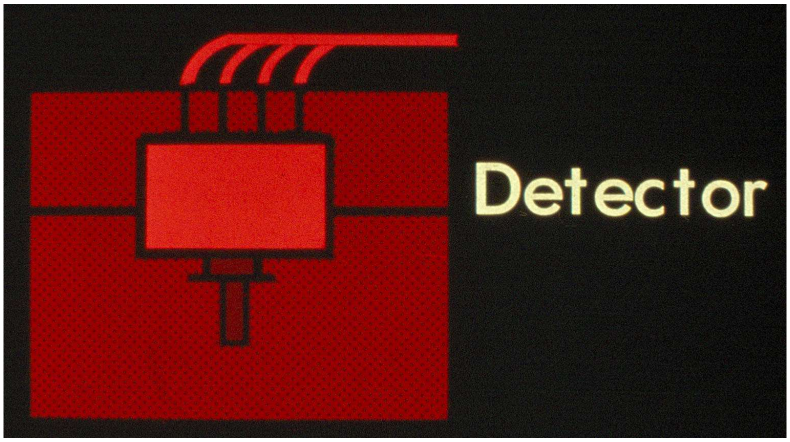
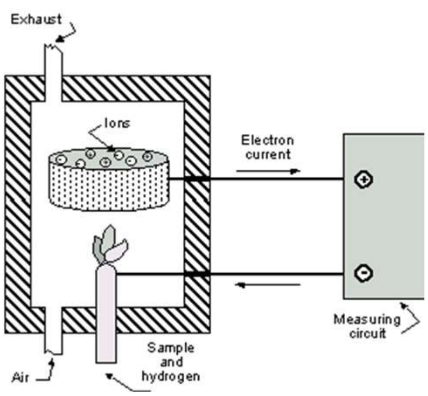
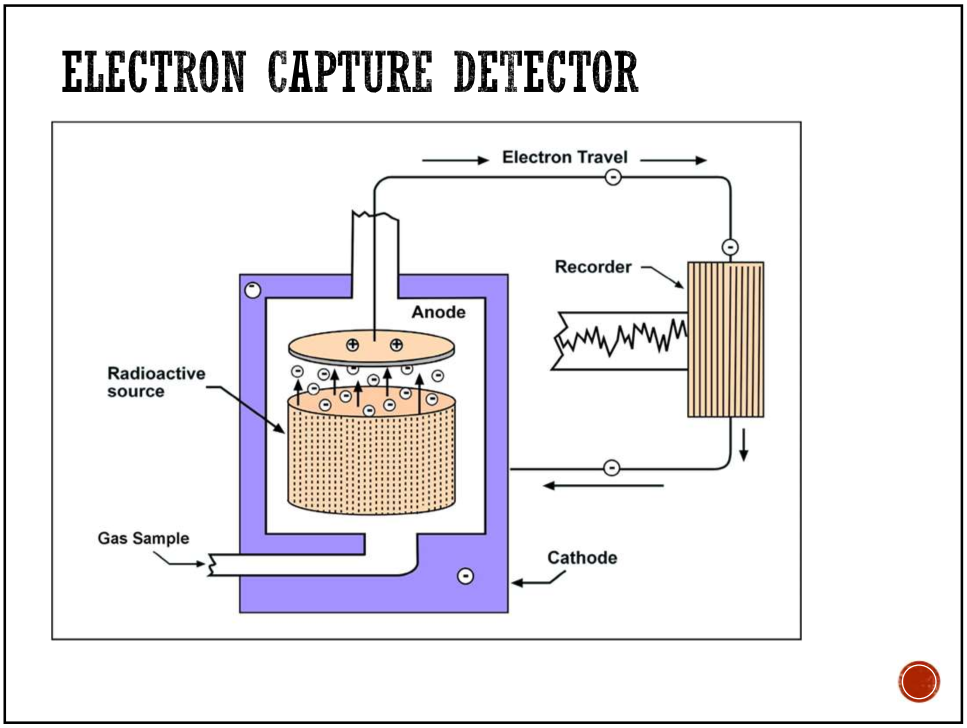


19

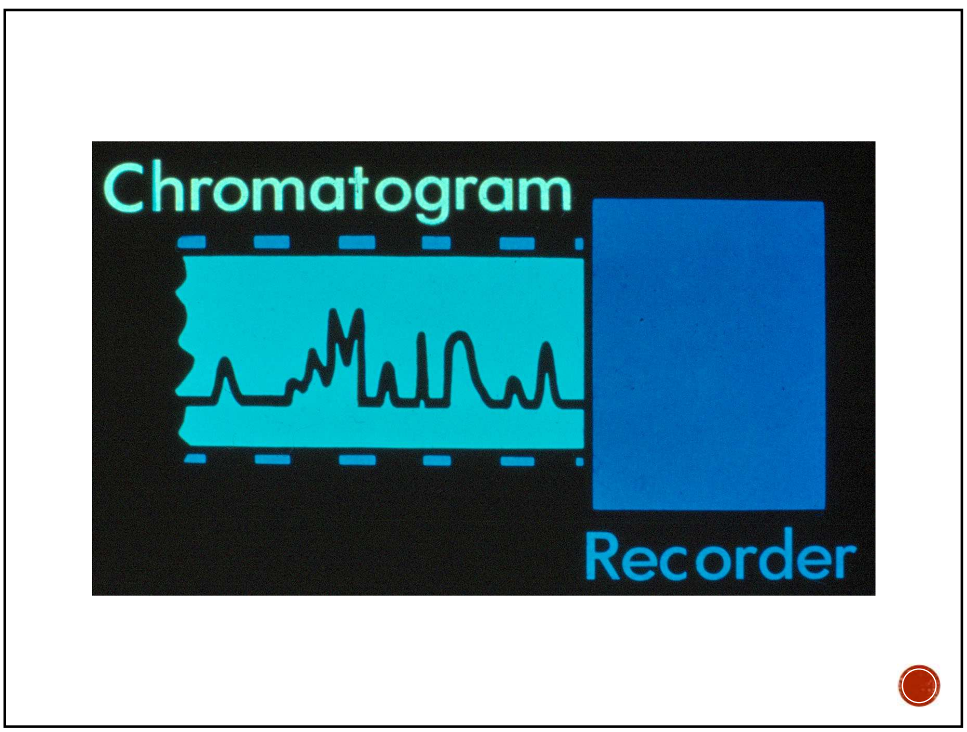


FLAME IONIZATION DETECTOR

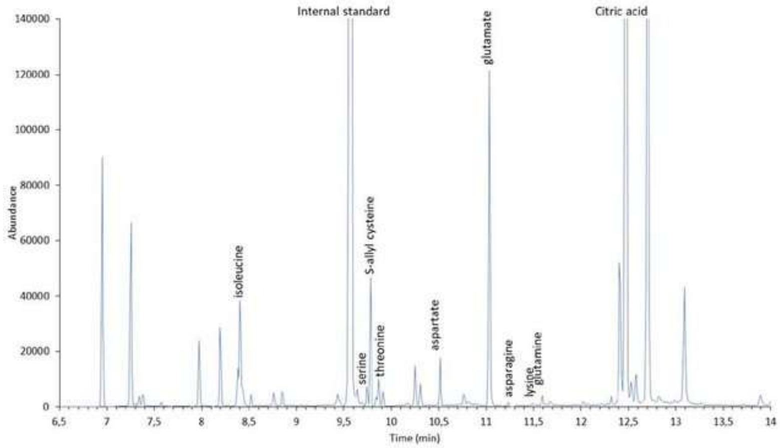
20


ELECTRON CAPTURE DETECTOR
Electron Travel
Recorder
Anode
Radioactive source
Gas Sample
Cathode

21


Chromatogram
Recorder

22



23

METHOD 25: GASEOUS NONMETHANE ORGANIC EMISSIONS

- Method applicable for the determination of VOC: measured as total gaseous nonmethane organics (TGNMO) and reported as carbon
- Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams.
- Proper judgment is required in determining the most applicable VOC test method

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METHOD 25: GASEOUS NONMETHANE ORGANIC EMISSIONS

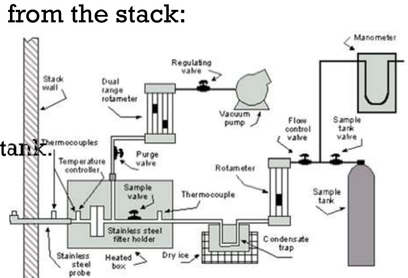
- Sample is extracted from a single point at a rate proportional to gas velocity
- Sample is separated into condensable and non-condensable fractions
- Analysis yields total gaseous non-methane organic emissions as carbon

https://www.epa.gov/emc/method-25-gaseous-nonmethane-organic-emissions

25

METHOD SUMMARY

- An emission sample is withdrawn from the stack:
  - constant rate
  - through a heated filter and
  - a chilled condensate trap
  - by means of an evacuated sample tank.
- **TGNMO** is determined by:
  - analyzing the condensate trap,
    - oxidizing the NMO to CO_2
    - quantitatively collecting in the effluent in an evacuated vessel;
    - then a portion of the CO_2 is reduced to CH_4 and measured by an FID
  - sample tank fractions and
    - injecting a portion of the sample into a GC column
    - separate the NMO from CO, CO_2, and CH_4
    - the NMO are oxidized to CO_2, reduced to CH_4, and
    - measured by an FID
  - combining the analytical results



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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

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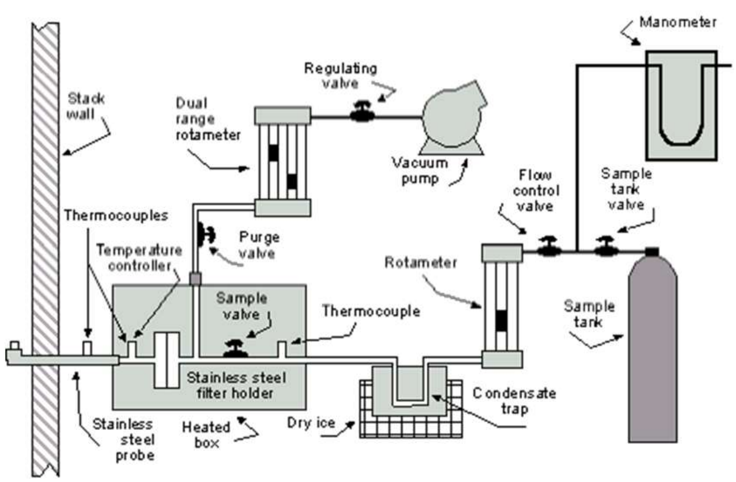
METHOD 25 SAMPLING TRAIN



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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

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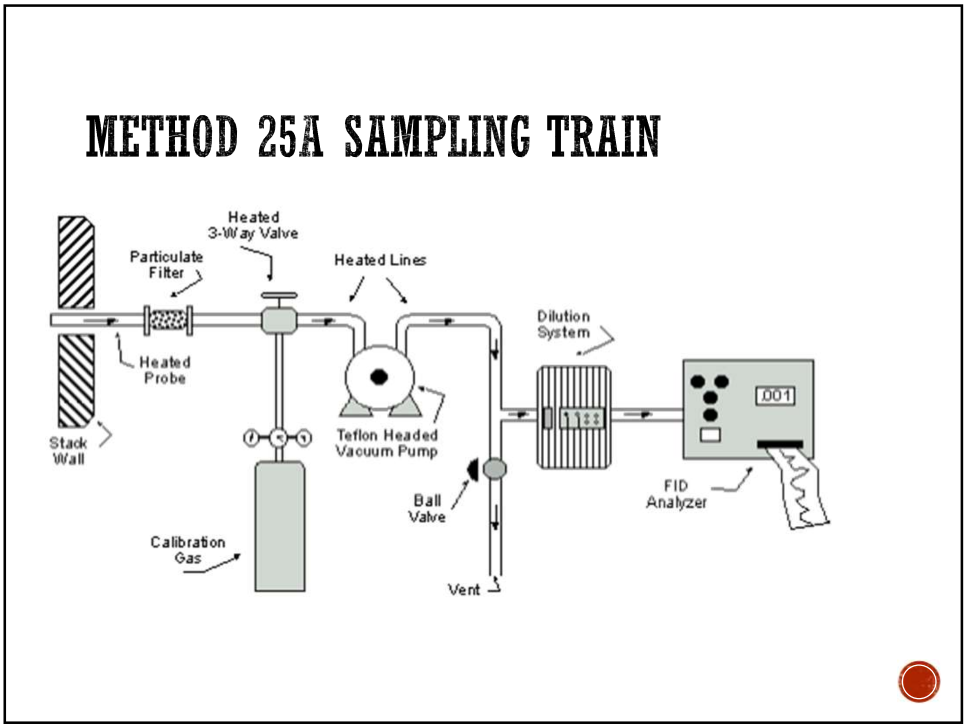
METHOD 25A: GASEOUS ORGANIC CONCENTRATION - FLAME IONIZATION

- 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**

https://www.epa.gov/emc/method-25a-gaseous-organic-concentration-flame-ionization

30


METHOD 25A SAMPLING TRAIN
Heated 3-Way Valve
Particulate Filter
Heated Lines
Dilution System
Heated Probe
.001
Stack Wall
Teflon Headed Vacuum Pump
Ball Valve
FID Analyzer
Calibration Gas
Vent

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SURFACE COATING

Presentation: 8

Chapter 5 – Surface Coating

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

SURFACE COATING

Presentation: 8

Chapter 5 – Surface Coating

2

SURFACE COATING

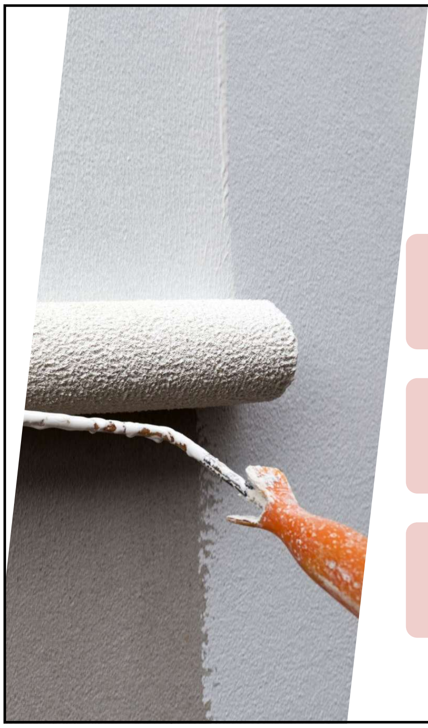
The application of a wet or dry coating material to the surface of another material, either for decoration or for protection against damage or corrosion.

3

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

4



PROCESS DESCRIPTION

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

5

Preparation of the surface to be coated is necessary to insure proper bonding between the coating and the surface.

1. Cleaning
   1. detergent or aqueous alkaline solution
   2. remove dirt, oil, grease & others
   3. organic degreasers may be used
   4. In automotives solvent wipe is used after the initial cleaning step to remove any traces of oil and grease
2. Acid etching, Phosphate treatment, or chromate conversion coating
   1. promote good coating adhesion
   2. provide for corrosion resistance
3. Drying

6

TYPES OF COATINGS

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

Except for powder and radiation-cured coatings, all coatings are composed of solid resins, pigments and additives that are dispersed in a volatile carrier.

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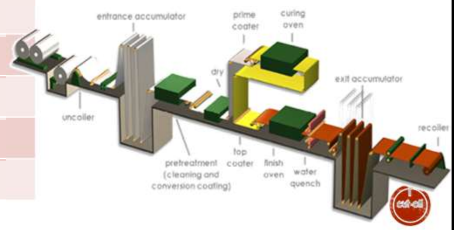
CONVENTIONAL COATINGS

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

8

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%



9

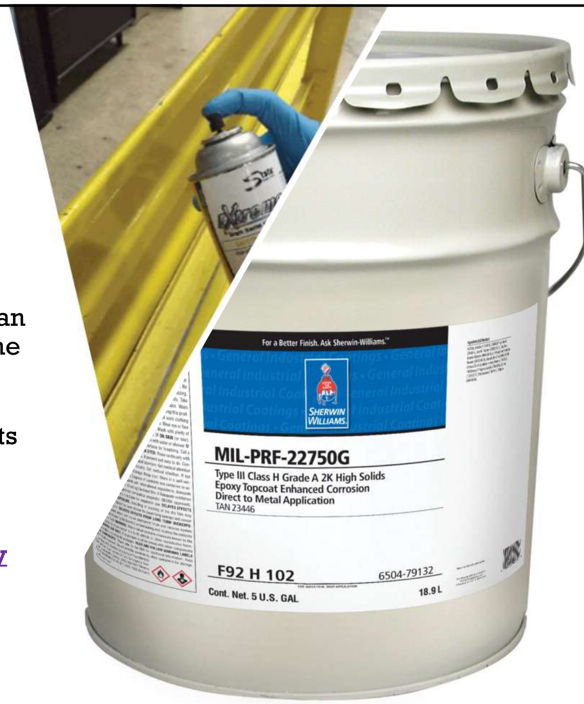
TYPICAL SOLVENT CONTENT OF CONVENTIONAL COATINGS USED IN VARIOUS INDUSTRIES

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%

10

HIGH-SOLIDS COATINGS

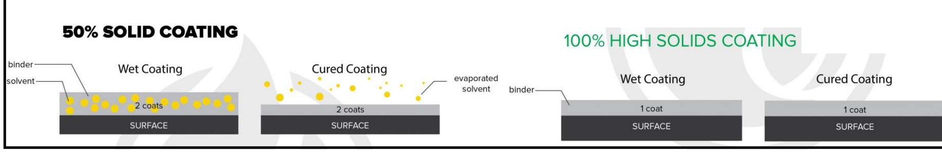
- Typically, greater than 60% solids by volume
- Less drum handling
- Reduced freight costs
- Reduced solvent removal energy
- **Increased viscosity**



11

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%



12

WATERBORNE COATINGS

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

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WATERBORNE COATINGS

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

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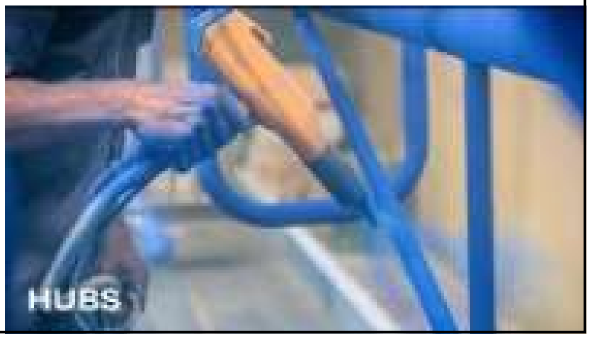
EMISSION REDUCTIONS FOR WATERBORNE COATINGS

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%

15

POWDER COATINGS

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



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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

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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%

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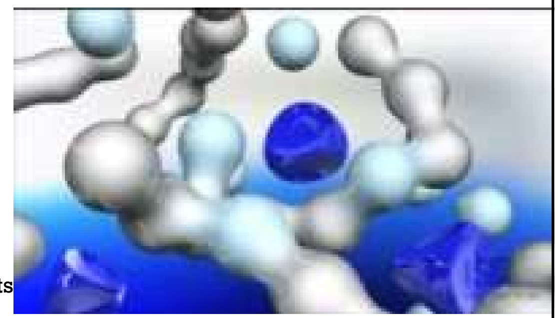
RADIATION-CURED COATINGS

- 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



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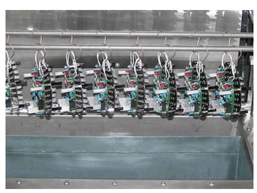
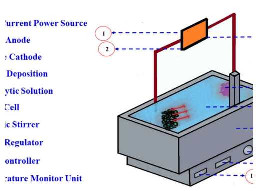
COATING APPLICATION

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





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TRANSFER EFFICIENCY

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

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SPRAY COATING

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

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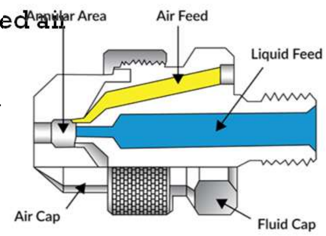
SPRAY COATING

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

- Coating is atomized and propelled by forced air
- Spray gun (two-fluid gun) is supplied with
  - compressed air at pressures up to 60 psi and
  - coating at pressures of 10 to 30 psi
- High-pressure air mixes with the coating
- It is atomized into small droplets
- It propels in a turbulent mist toward the part to be coated



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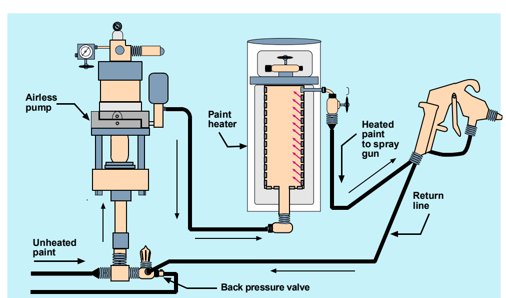
AIRLESS SPRAY GUN

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

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



24

SPRAY COATING

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

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

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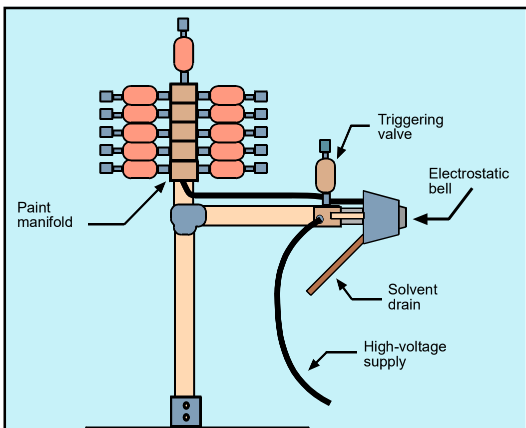

- The surface of the bell or disk is negatively charged,
- Gives a negative charge to the coating particles passing across it.
- Atomization occurs primarily because of the repelling forces between the individual particles and between the particles and the applicator surface.
- Some atomization occurs because of the centrifugal forces imparted by the rapidly spinning bell or disk.
- The atomized coating particles are attracted to the positively grounded parts.
- The bell or disk may reciprocate up and down or back and forth to allow complete coating of the part.

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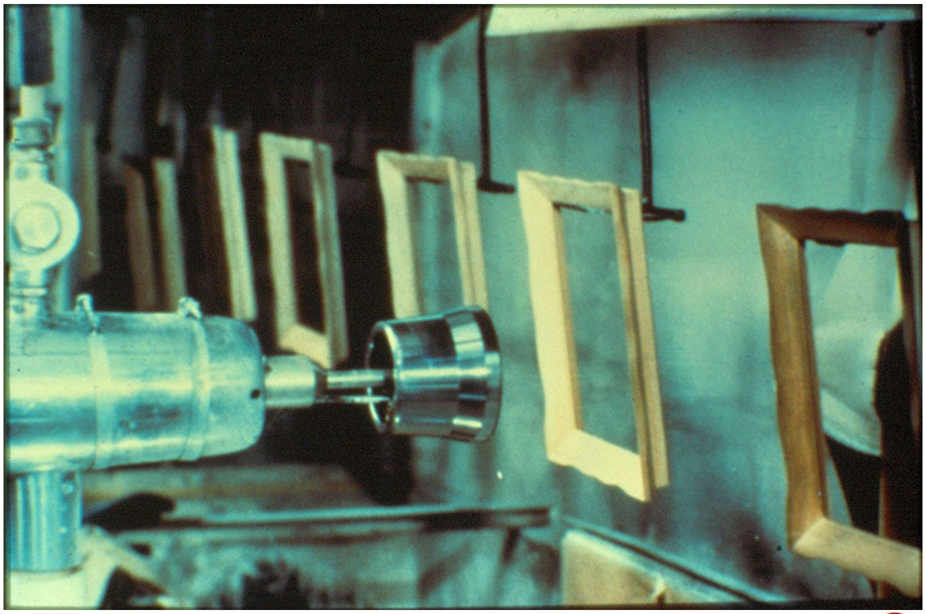

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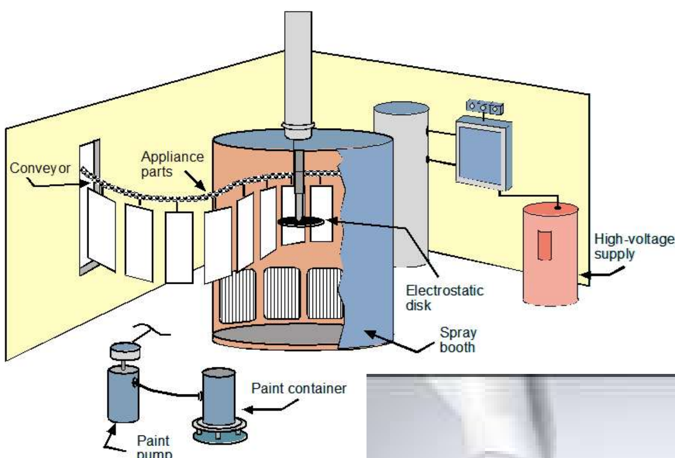

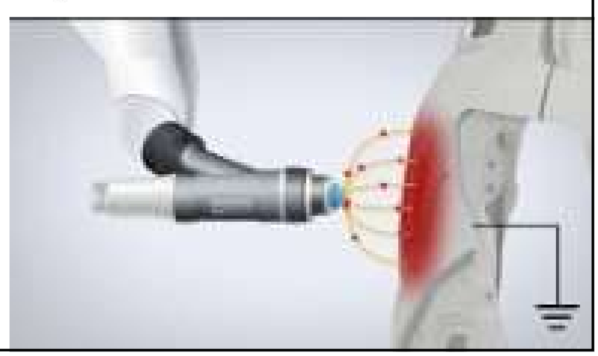

RECIPROCATING DISK

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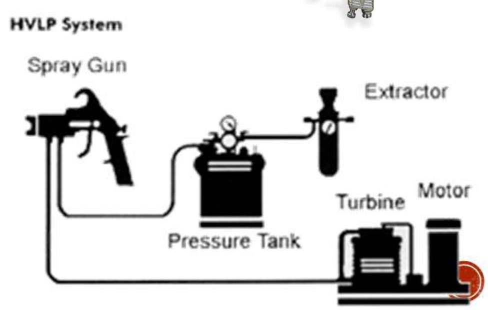
SPRAY COATING

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

- AKA turbine spray gun
- Turbine is used to generate and deliver the atomizing air.
- Turbine draws in filtered air and drives it through several stages that rotate at up to 10,000 rpm.
- This results in a high volume of warm, dry atomizing air that is delivered to the spray gun at pressures of 4 to 6 psi.
- This low-pressure air gives greater control over the spray, with less of the overspray and fogging that accompanies the blasting effect common with conventional high-pressure systems.
- Transfer efficiencies of 60% to 70%



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SPRAY COATING

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

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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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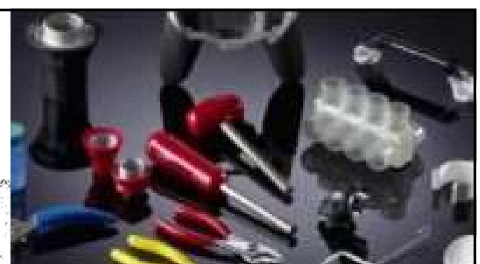

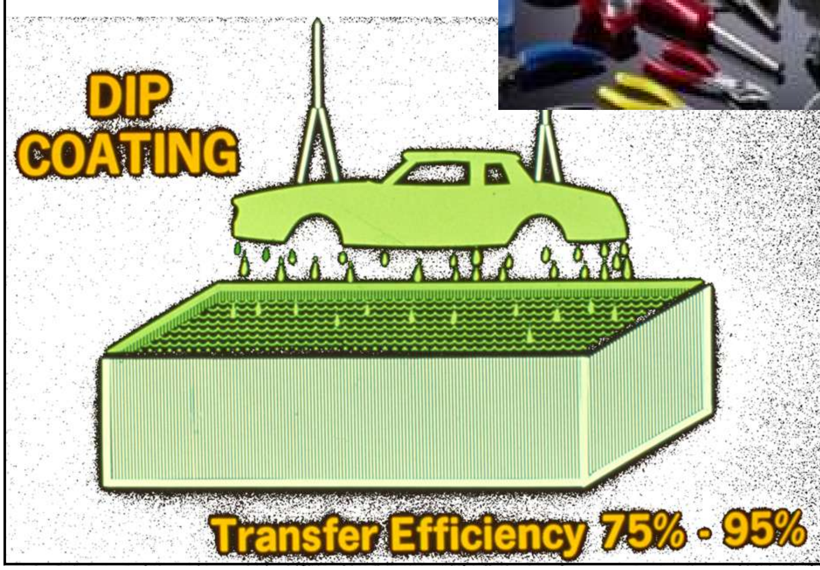

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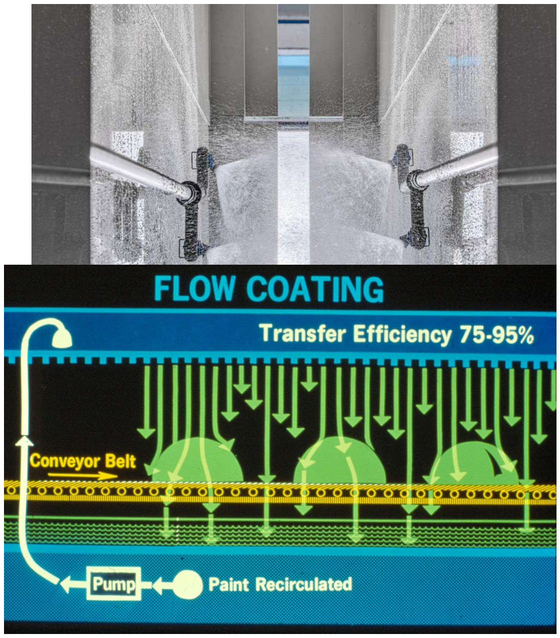
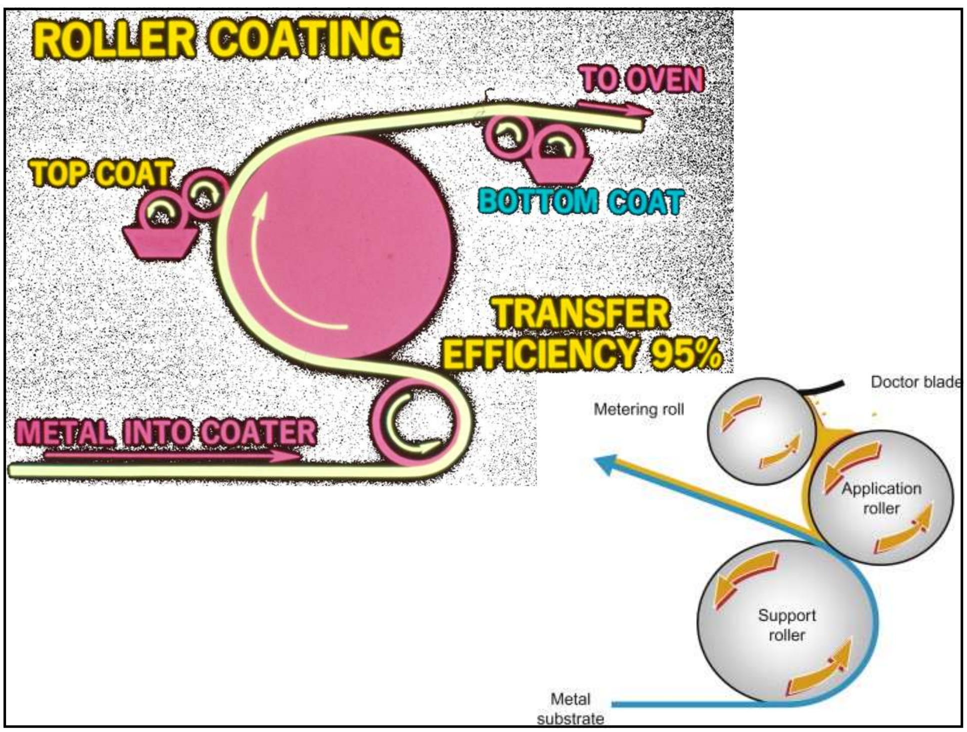

FLOW COATING
Transfer Efficiency 75-95%
Conveyor Belt
Pump
Paint Recirculated

33


ROLLER COATING
TO OVEN
TOP COAT
BOTTOM COAT
TRANSFER EFFICIENCY 95%
METAL INTO COATER
Doctor blade
Metering roll
Application roller
Support roller
Metal substrate

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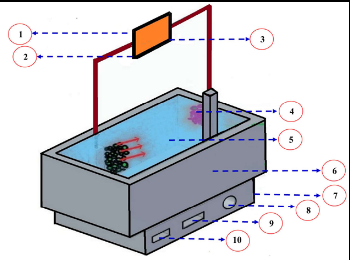
ELECTRODEPOSITION COATING

1. Direct Current Power Source
2. Positive Anode
3. Negative Cathode
4. Coating Deposition
5. Electrolytic Solution
6. Plating Cell
7. Magnetic Stirrer
8. Voltage Regulator
9. Speed Controller
10. Temperature Monitor Unit



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

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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

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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					

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CURING

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

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EMISSION CONTROL TECHNIQUES

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

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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

40

RECENT AND EMERGING VOC-REDUCTION TECHNOLOGIES

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OVERSPRAY-FREE ROBOTIC APPLICATION

- Uses robotic jetting or print-head technology instead of conventional atomized spray.
- Applies coating only to the target area.
- Can reduce overspray, masking, paint waste, booth filter loading, and rework.
- Most applicable to high-volume automated lines and two-tone/decorative applications.
- Limitation: high capital cost and not yet universal for all coating types, part geometries, or production scales.

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ADVANCED RADIATION CURING: UV-LED AND EXCIMER

- UV-LED curing uses LED lamps rather than conventional mercury UV lamps.
- Benefits may include instant on/off operation, lower heat load, lower energy use, and no mercury lamps.
- Excimer curing can be used for specialty surface effects such as low-gloss or textured finishes.
- Coating chemistry, photoinitiator package, line speed, and substrate geometry must be matched to the curing source.
- Worker shielding and radiation-safety controls are still required.

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PLASMA SURFACE PRETREATMENT

- Uses ionized gas to clean and activate the surface before coating.
- Can improve adhesion on plastics, metals, glass, and composites.
- May reduce or replace some solvent-wipe or chemical pretreatment steps.
- Can be integrated into automated production lines.
- Limitation: does not replace all cleaning needs; process validation is required for each substrate and coating system.

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UPDATED SURFACE PRETREATMENT OPTIONS

- Chrome-free zirconium/titanium pretreatments can replace some chromate or phosphate systems.
- Main benefit is reduction of hazardous metals, sludge, and wastewater burden, not VOC reduction.
- Important for facilities with coating, pretreatment, and wastewater compliance obligations.

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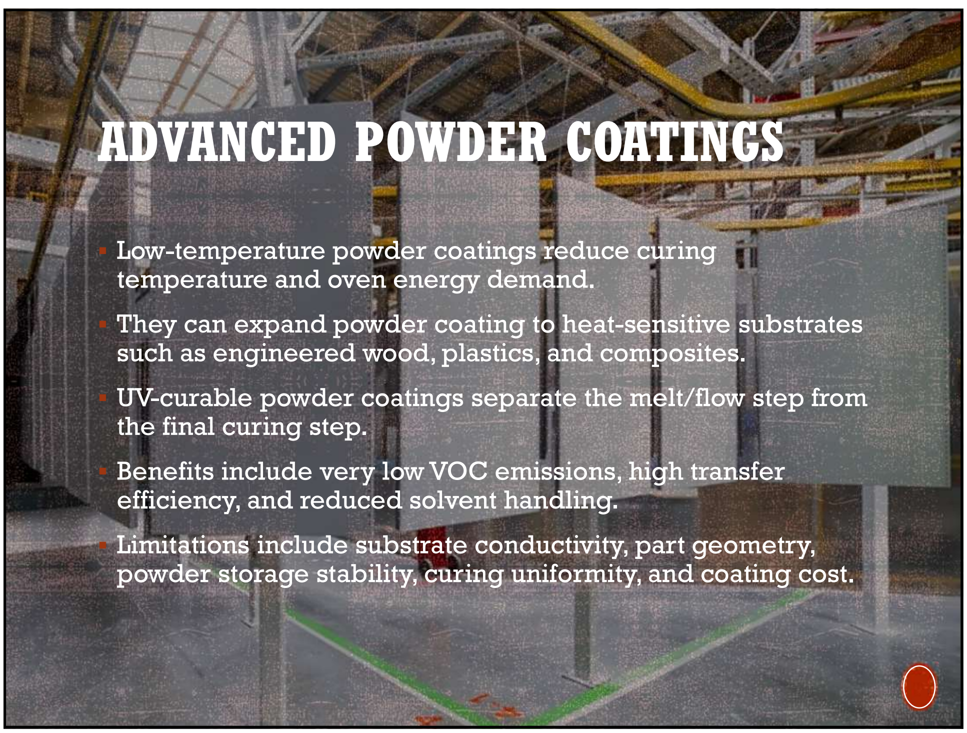

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EMISSION REGULATION

Emission Regulation — Large Appliance Surface Coating

{Suppl. Matr.}

https://www.epa.gov/stationary-sources-air-pollution/clean-air-act-guidelines-and-standards-solvent-use-and-surface

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EMISSION REGULATION — LARGE APPLIANCE SURFACE COATING

- Surface Coating of Large Appliances, Control Technique Guideline Document, EPA-453/R-07-004 {Suppl. Matr.}

Recommended standard:

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

- Standards of Performance for Industrial Surface Coating: Large Appliances, 40CFR60, Subpart SS {Suppl. Matr.}

Applicability Date: December 24, 1980

Applicability Size: All

Standard:

An emission limit of 7.51 lbs of VOC per gallon of solids applied

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VOC / RACT GUIDANCE — EPA CTG EPA-453/R-07-004

- Applies as guidance for state/local RACT rules in ozone nonattainment areas. Recommended control options include:
  - Low-VOC coatings.
  - Equivalent VOC limits based on coating solids and/or add-on controls.
  - 90% overall control efficiency for add-on controls.
- VOC limits are expressed **excluding water and exempt compounds, as applied**.
- General coating limits:
  - **One-component coatings:** 2.3 lb VOC/gal coating.
  - **Multi-component baked coatings:** 2.3 lb VOC/gal coating.
  - **Multi-component air-dried coatings:** 2.8 lb VOC/gal coating.
- Specialty coatings may have separate limits.

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FEDERAL NSPS — 40 CFR PART 60, SUBPART SS

- Applies to new, modified, or reconstructed large-appliance surface coating operations that commenced after **December 24, 1980**.
- VOC emission limit:
  0.90 kg VOC/L applied coating solids
  ≈ 7.51 lb VOC/gal applied coating solids

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FEDERAL NESHAP — 40 CFR PART 63, SUBPART NNNN

- Applies to **major HAP sources** that coat large appliance parts or products.
- Organic HAP limits:
  - **Existing affected sources:** 1.1 lb organic HAP/gal coating solids used.
  - **New or reconstructed affected sources:** 0.18 lb organic HAP/gal coating solids used.
- Compliance determinations include coatings, thinners, and cleaning materials.

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COMPLIANCE REMINDER

- State/local rules and permit limits may be more stringent.
- Coating composition may be determined using manufacturer data and/or **EPA Method 24**, where required.
- Check current electronic reporting requirements for applicable NESHAP reports.

Requirement	**Main point**
EPA CTG EPA-453/R-07-004	RACT guidance for VOC controls. Limits vary by coating type and are expressed excluding water and exempt compounds, as applied. General limits include 2.3 lb VOC/gal for one-component coatings and multi-component baked coatings, and 2.8 lb VOC/gal for multi-component air-dried coatings.
NSPS — 40 CFR 60 Subpart SS	Applies to new, modified, or reconstructed large-appliance coating operations after Dec. 24, 1980. Limit: 0.90 kg VOC/L applied coating solids, approximately 7.51 lb VOC/gal applied coating solids.
NESHAP — 40 CFR 63 Subpart NNNN	Applies to major HAP sources. Limits: 1.1 lb organic HAP/gal coating solids used for existing sources; 0.18 lb/gal for new or reconstructed sources.

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PROCESS INSPECTION

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

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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

55

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

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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

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OBSERVE PRE-DRYING AREA

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

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OBSERVE CURING AREA

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

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GRAPHIC ARTS (AKA PRINTING, PUBLISHING, AND PACKAGING)

Presentation: 9

Chapter 6 – Graphic Arts

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

GRAPHIC ARTS (AKA PRINTING, PUBLISHING, AND PACKAGING)

Presentation: 9

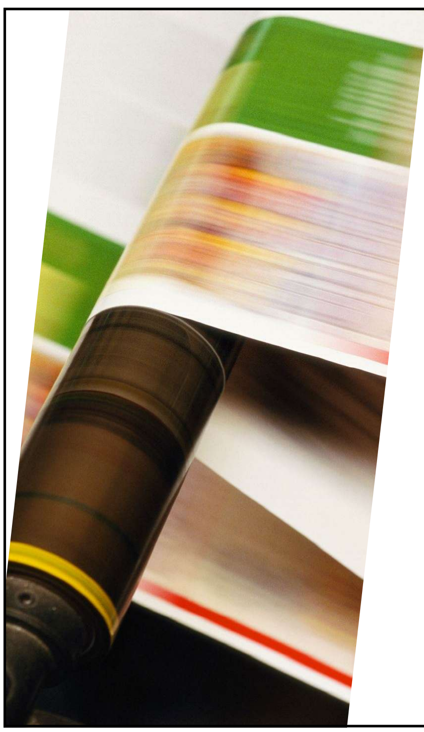
Chapter 6 – Graphic Arts

2

MAJOR EMISSION POINTS IN GRAPHIC ARTS OPERATIONS

- Ink fountain / ink pan / chamber.
- Printing unit.
- Between-color dryers.
- Main dryers or curing units.
- Fountain solution system.
- Press cleaning and blanket washing.
- Ink mixing and viscosity adjustment.
- Solvent storage and waste containers.
- Post-press adhesives, laminating, coating, and finishing.

3



PRINTING OPERATIONS

- Offset lithography
- Flexography
- Rotogravure
- Screen

4

Process	Image carrier	Typical substrates	Common ink type	Main VOC concern	Common controls
Offset lithography	Planographic plate and blanket	Paper, paperboard	Paste inks, fountain solution	Fountain solution, heatset dryer, cleaning solvent	Low-IPA fountain solution, low-VOC cleaning, dryer oxidizer
Flexography	Flexible raised plate	Packaging films, paper, foil, labels	Solvent, water-based, UV/EB	Solvent ink evaporation in dryers	Low-VOC inks, enclosed ink systems, oxidizer, carbon adsorption
Rotogravure	Engraved cylinder	Publication and packaging webs	Solvent-based inks	High solvent loading from dryers	Carbon adsorption/solvent recovery, oxidizer
Screen printing	Stencil screen	Broad substrate range	Solvent, water-based, UV, plastisol	Thick ink films, drying/curing, cleaning	Low-VOC inks, UV curing, ventilation, oxidizer where needed

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OFFSET LITHOGRAPHY

- **Offset lithography**
- Flexography
- Rotogravure
- Screen

- Offset printing: the inked image is transferred (or "offset") from a plate to a rubber blanket and then to the printing surface
- Lithographic process is based on the repulsion of oil and water, the offset technique employs a flat (planographic) image carrier.
- Ink rollers transfer ink to the image areas of the image carrier, while a water roller applies a water-based film to the non-image areas.
- The modern "web" process feeds a large reel of paper through a large press machine in several parts, typically for several meters, which then prints continuously as the paper is fed through.

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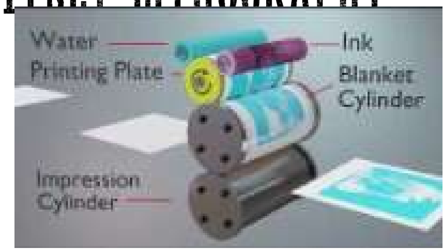
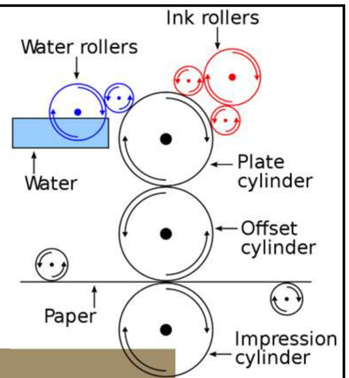
OFFSET LITHOGRAPHY





Uses a planographic printing surface

Printing unit components:

Inking system	Dampening system	Plate cylinder	Blanket cylinder	Impression cylinder

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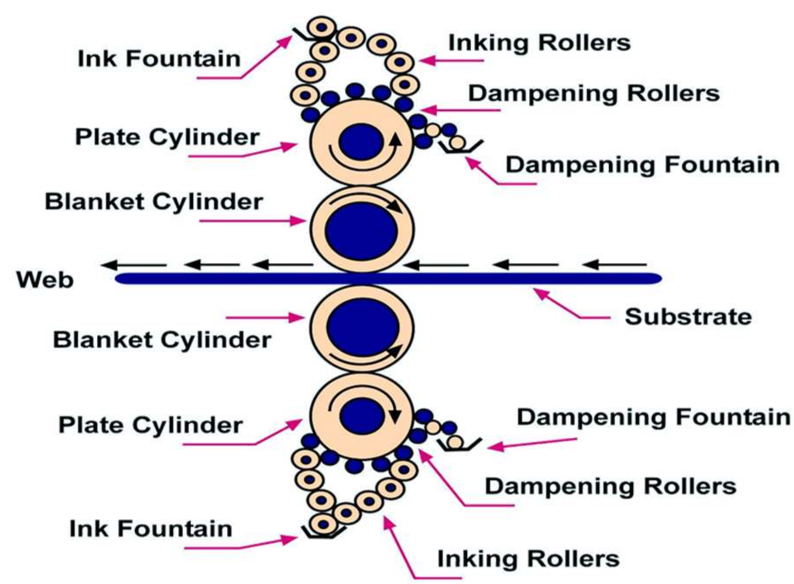
OFFSET LITHOGRAPHY PRINTING UNIT



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OFFSET LITHOGRAPHY PROCESSES

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

9

NON-HEATSET WEB PRINTING

- Prints on continuous web of paper
- Typically used for lower quality print output.
- It is typical of newspaper production
- 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

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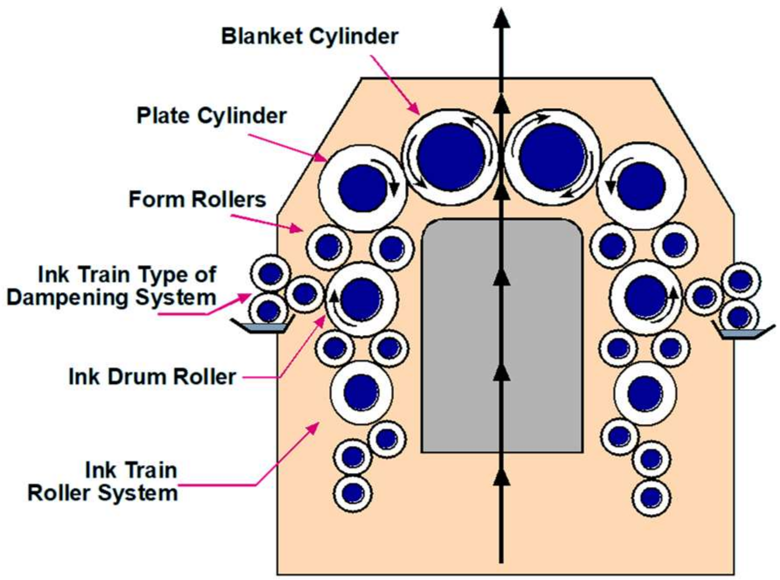
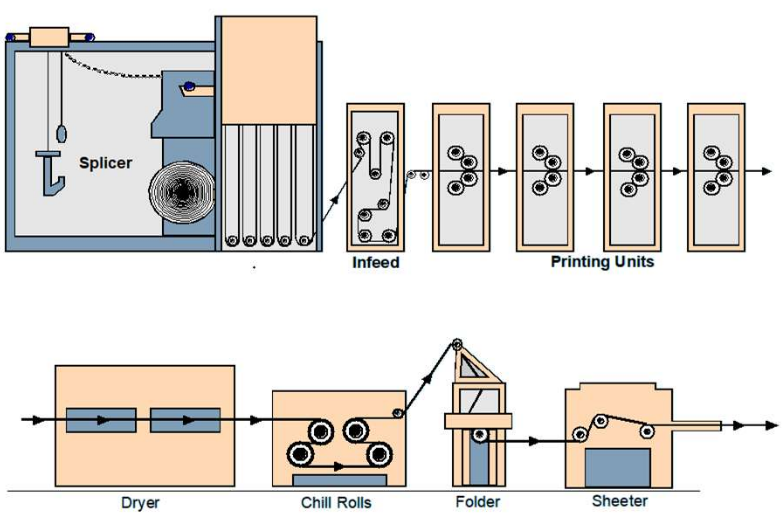
NON-HEATSET WEB PRINTING UNIT



11

HEATSET WEB PRINTING PRESS



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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% Isopropyl alcohol 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

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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

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EMISSION CONTROL TECHNIQUES

INKS

FOUNTAIN SOLUTION

PRESS CLEANING

16

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

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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

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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

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FOUNTAIN SOLUTION

- Most volatile additive is IPA
- Use low volatility dampening agents
- Refrigerate fountain solution to 55-60°F
- For nonheatset 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

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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

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2006 CTG FOR OFFSET LITHOGRAPHY AND LETTERPRESS

22

- Offset lithography
- **Flexography**
- Rotogravure
- Screen

FLEXOGRAPHY

- Flexography (flexo) is a form of printing process which utilizes a flexible relief plate.
- It is essentially a modern version of letterpress, evolved with high-speed rotary functionality
- Can be used for printing on almost any type of substrate, including plastic, metallic films, cellophane, and paper.
- It is widely used for printing on the non-porous substrates required for various types of food packaging (it is also well suited for printing large areas of solid color).

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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

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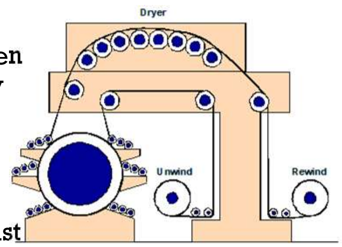
CENTRAL IMPRESSION PRESS

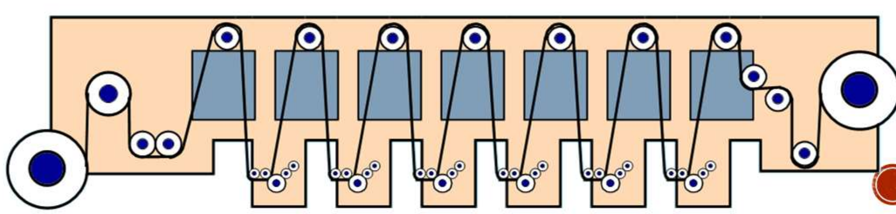
- The central impression design uses one common impression cylinder,
- Two to eight printing stations distributed around it.
- Design has the advantages of compactness, excellent registration of multi-color images and excellent control of the web.
- In between each printing station, a between color dryer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



25

IN-LINE PRESS

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



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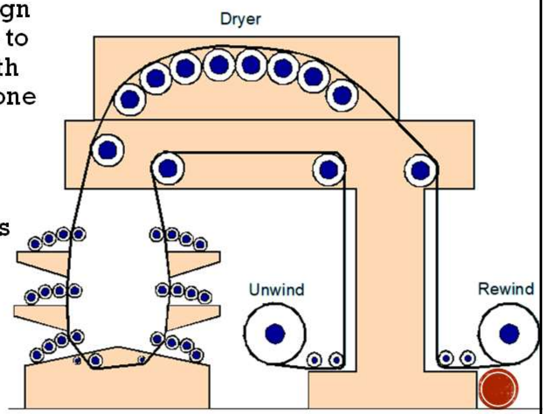
STACK PRESS

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



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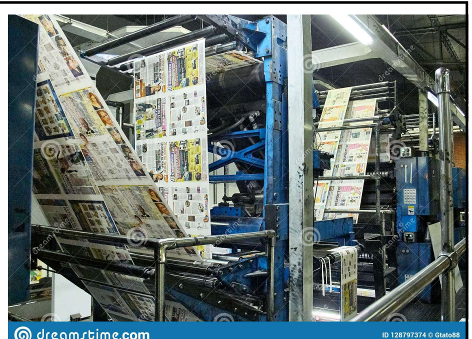
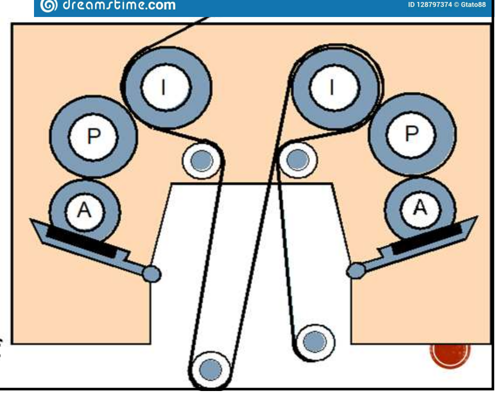
NEWSPAPER PRINTING UNIT

- Consists of 2 printing stations located back-to-back in a common pair of frames.
- Arrangement permits printing of black images on both sides.
- Multiple units are arranged in a pressline to print the many pages required of a large newspaper.
- Color decks, each consisting of one printing station, are placed above those positions where the publisher wants to add a single color.
- Occasionally, double decks, stacked units or multiple color units are added where single colors are wanted on both sides of the web or for multiple color





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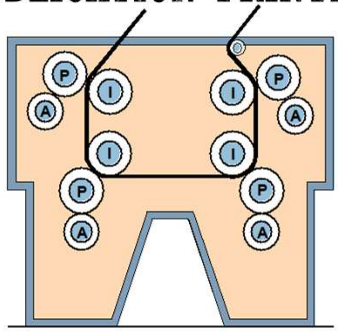
PUBLICATION PRINTING UNIT



- Use dedicated four-color units
- Two units are typically combined into one press for printing four colors on both sides of the web.
- The advantages of this design include wide web capability, high operating speed and compact design.
- Dryers, usually infrared, are used to ensure adequate drying of the ink after each side of the web is printed

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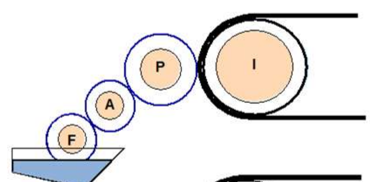
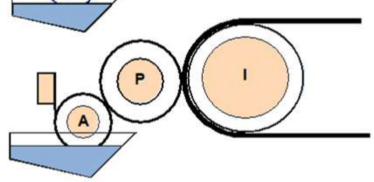
INKING SYSTEMS (ANILOX ROLL)

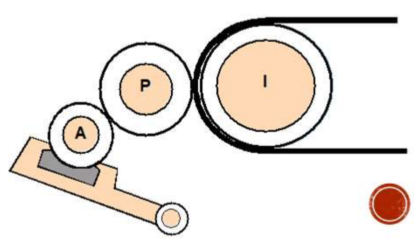
- Fountain Roller Style Printing Station



- Single Doctor Blade Style Printing Station



- Double Doctor Blade Style Printing Station



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Types of Inks

- Organic solvent-based inks represent a little more than half of all flexographic inks.
- Low solvent boiling point and quick solvent release from the ink film layer result in higher production speed
- Water-based inks require higher airflow rates for drying, typically 6,000 cfm to 12,000 cfm.
- Radiation-cured inks are set by exposure to **ultraviolet or electron beam radiation**.
- They are very fast drying and have high quality image formation.

ORGANIC SOLVENT BASED

WATER BASED

RADIATION CURABLE

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EMISSION CONTROL TECHNIQUES

Reduced-VOC ink

Reduced-VOC cleaning

Add-on control equipment
- Incineration
- Adsorption
- Condensation

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ROTOGRAVURE

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

- Offset lithography
- Flexography
- **Rotogravure**
- Screen

33

EMISSION CONTROL TECHNIQUES

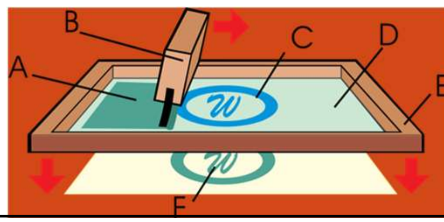
- Reduced-VOC ink
- Reduced-VOC cleaning
- Add-on control equipment
  - Incineration
  - Adsorption
  - Condensation

34

SCREEN PRINTING

- Offset lithography
- Flexography
- Rotogravure
- **Screen**

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



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SCREEN PRINTING

Ink flows through screen with stencil bonded to it

Types of inks:

Solvent based	Water based	UV curable	Plastisols

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DRYING UNITS

- HOT-AIR OVENS
- INFRARED RADIATION
- UV RADIATION

37

SCREEN RECLAMATION

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

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EMISSION CONTROL TECHNIQUES

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

39

VOC RACT GUIDANCE: OFFSET LITHOGRAPHY & LETTERPRESS

EPA CTG EPA-453/R-06-002

- Applies as VOC RACT guidance for state/local rules.
- Covers:
  - Offset lithography: inks, fountain solution, cleaning materials.
  - Letterpress: inks and cleaning materials.
- Recommended applicability:
  - Cleaning/fountain-solution controls: **≥15 lb/day actual VOC before controls**.
  - Heatset dryer controls: **≥25 tpy potential VOC before controls**.
- Heatset dryer control:
  - **90% control efficiency** for older control devices.
  - **95% control efficiency** for newer control devices.
  - Alternative: **20 ppmv as hexane, dry basis**.
- Key work practices:
  - Lower-IPA or alcohol-substitute fountain solution.
  - Low-VOC or low-vapor-pressure cleaners.
  - Closed containers for cleaning materials and used wipes.

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VOC RACT GUIDANCE: FLEXIBLE PACKAGE PRINTING

EPA CTG EPA-453/R-06-003

- Applies as VOC RACT guidance for flexible package printing.
- Covers:
  - Inks.
  - Coatings.
  - Adhesives.
  - Cleaning materials.
- Cleaning work practices apply at **≥15 lb/day actual VOC before controls**.
- Ink/coating/adhesive controls apply to presses with **≥25 tpy potential dryer VOC before controls**.
- Recommended overall control levels: **65% to 80%**, depending on press and control-device installation dates.
- Equivalent limits:
  - **0.8 kg VOC/kg solids applied**, or
  - **0.16 kg VOC/kg materials applied**.
- Cleaning work practices:
  - Keep cleaning materials and used shop towels in closed containers.
  - Convey cleaning materials in closed containers or pipes.

41

NESHAP: PRINTING AND PUBLISHING INDUSTRY

40 CFR Part 63, Subpart KK

- Applies to **major HAP sources** with:
  - Publication rotogravure presses.
  - Product and packaging rotogravure presses.
  - Wide-web flexographic presses.
- Publication rotogravure:
  - Limit organic HAP to **≤8% of total volatile matter used each month**, or
  - Achieve **≥92% overall organic HAP control**.
- Product/packaging rotogravure and wide-web flexography:
  - Limit organic HAP emissions using low-HAP materials, emission-rate limits, equivalent allowable mass, or capture/control.
  - One compliance option is **≥95% overall organic HAP control**.
- Inspection focus:
  - HAP content of inks, coatings, adhesives, solvents, reducers, and thinners.
  - Monthly usage records.
  - Capture-system and control-device monitoring.

42

NSPS FOR GRAPHIC ARTS OPERATIONS

40 CFR Part 60, Subparts QQ and FFF

Subpart QQ — Publication Rotogravure

- Applies to publication rotogravure presses constructed, modified, or reconstructed after **October 28, 1980.**
- Does not apply to proof presses.
- VOC limit: emissions may not exceed **16% of the total mass of VOC solvent and water used** during the performance averaging period.

Subpart FFF — Flexible Vinyl and Urethane Coating/Printing

- Applies to rotogravure printing lines used to print or coat flexible vinyl or urethane products.
- Applies to affected facilities constructed, modified, or reconstructed after **January 18, 1983.**
- Compliance options:
  - Use inks with weighted average VOC content **<1.0 kg VOC/kg ink solids**, or
  - Reduce VOC emissions by **85%**.

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TEXTILE AND FABRIC PRINTING APPLICABILITY

40 CFR Part 63, Subpart OOOO

- May apply when graphic arts operations include printing or coating fabric/textile substrates.
- Covers major-source operations involving:
  - Printing.
  - Coating.
  - Slashing.
  - Dyeing.
  - Finishing of fabric and other textiles.
- The coating and printing subcategory includes operations that coat or print fabric or other textiles.
- Examples include apparel, luggage, tents, military fabrics, sheets, rainwear, and industrial fabrics.
- Do not assume all screen printing is covered.
- Confirm:
  - Substrate type.
  - HAP source status.
  - Organic HAP content.
  - Applicable exemptions.

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ELECTRONIC REPORTING UPDATE

CEDRI / ERT Reporting Awareness

- Check current electronic reporting requirements for each applicable federal rule and permit.
- EPA's 2024 Cross-Media Electronic Reporting notice allows many paper-format reports, notifications, and submissions under **40 CFR Parts 59–63** to be submitted electronically through **CEDRI/CDX.**
- CEDRI may be used for:
  - Performance test reports.
  - Notification of compliance status reports.
  - Periodic and semiannual compliance reports.
  - Other rule-specific reports.
- ERT is used to prepare electronic stationary-source test plans and test reports.
- Inspection reminder:
  - Ask whether the facility submits through CEDRI.
  - Verify submitted reports against permit records and operating data.

45

PROCESS INSPECTION

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

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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

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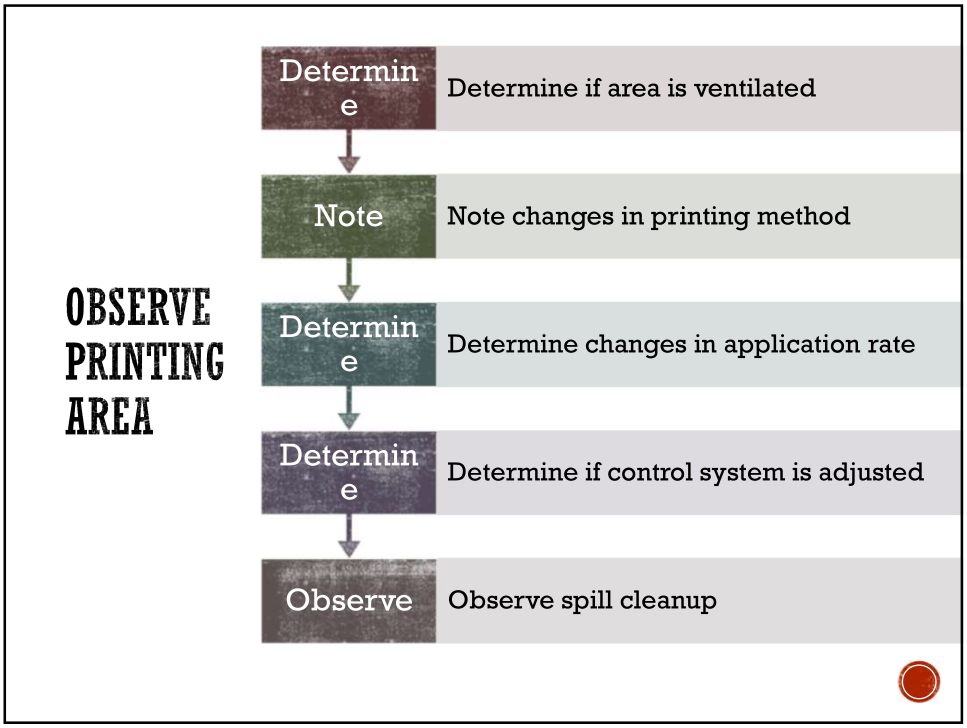
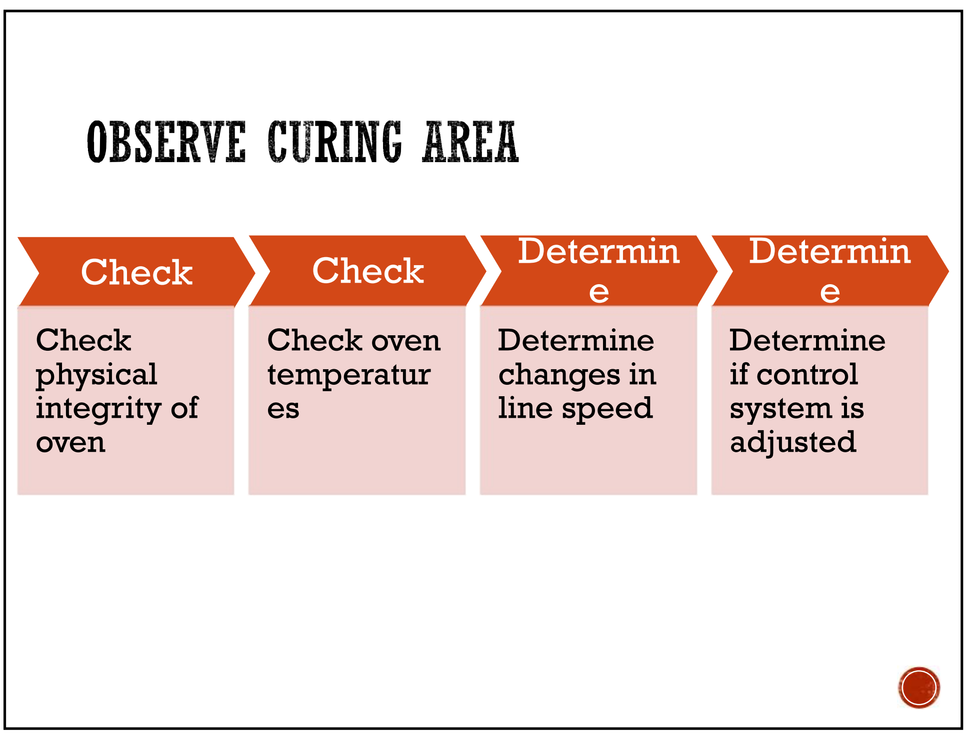
OBSERVE INK PREPARATION

- 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

48


OBSERVE PRINTING AREA
Determin e
Determine if area is ventilated
Note
Note changes in printing method
Determin e
Determine changes in application rate
Determin e
Determine if control system is adjusted
Observe
Observe spill cleanup

49


OBSERVE CURING AREA
Check
Check physical integrity of oven
Check
Check oven temperatur es
Determin e
Determine changes in line speed
Determin e
Determine if control system is adjusted

50

GRAPHIC ARTS CONTROL STRATEGY

Material substitution

Process changes

Capture and add-on control

Compliance records

51

MATERIAL SUBSTITUTION

- Low-VOC or no-VOC inks.
- Water-based inks.
- UV/UV-LED/EB-curable inks.
- Low-VOC cleaning materials.
- Low-IPA or alcohol-free fountain solution.

52

PROCESS CHANGES

- Enclosed/chambered doctor-blade systems.
- Automatic viscosity control.
- Improved dryer balance.
- Reduced press cleaning frequency.
- Good container and wipe-management practices.

53

CAPTURE AND ADD-ON CONTROL

- Permanent total enclosure or local capture.
- Thermal oxidizer or catalytic oxidizer.
- Regenerative thermal oxidizer for suitable solvent loading.
- Carbon adsorption with solvent recovery.
- Condenser systems where appropriate.

54

COMPLIANCE RECORDS

- Ink and solvent usage.
- VOC/HAP content.
- As-applied formulation.
- Dryer temperature and line speed.
- Control-device operating parameters.
- Capture-system checks.
- Cleaning-material and wipe-management records

55

NEW TECHNOLOGIES IN GRAPHIC ARTS

56

NEW TECHNOLOGIES IN GRAPHIC ARTS

Newer approaches focus on reducing VOC/HAP emissions by:

- Reducing solvent-containing materials.
- Reducing exposed ink and solvent surface area.
- Reducing makeready, changeover waste, and rework.
- Improving curing efficiency.
- Improving capture, monitoring, and process control.

Technologies covered in this section:

- Digital and hybrid printing.
- UV-LED and electron beam curing.
- Enclosed/chambered doctor-blade systems.
- Processless plates and low-/zero-IPA offset operation.
- Solventless laminating and low-VOC post-press materials.
- Smart process control and closed material handling.

57

DIGITAL AND HYBRID PRINTING

What it is

- Digital printing applies the image directly using inkjet or electrophotographic systems.
- Hybrid systems combine conventional flexographic, offset, or gravure stations with digital print units.

Why it matters

- Useful for short runs, labels, packaging, variable data, regional products, and frequent artwork changes.
- Can reduce makeready waste, plate-related waste, obsolete printed inventory, and changeover losses.

VOC/HAP considerations

- Digital printing may use water-based, UV-curable, UV-LED-curable, EB-curable, or solvent-based inks.
- Do not assume digital printing is automatically VOC-free.
- Include ink purging, printhead cleaning, maintenance fluids, dryers, and curing units in the emissions review.

Inspection questions

- What ink chemistry is used?
- Are there dryers or curing lamps?
- Are cleaning/purging fluids included in emission calculations?
- Is digital printing replacing or supplementing an existing press?

58

UV-LED AND ELECTRON BEAM CURING

Update to radiation-curable inks

- UV and EB curing are already used in graphic arts printing and varnishing.
- Newer systems increasingly include UV-LED curing and improved EB curing for packaging, labels, and specialty printing.

Potential benefits

- Fast curing.
- High-solids/reactive ink systems.
- Reduced evaporative VOC compared with solvent-based inks.
- Lower heat load for some UV-LED applications.
- Good fit for labels, packaging, overprint varnishes, and specialty finishes.

Limitations

- Ink chemistry must match the curing source.
- UV-LED wavelength, lamp intensity, and line speed must be controlled.
- EB and UV systems require shielding and worker-safety controls.
- Food-packaging applications may require low-migration formulations and documentation.

Inspection questions

- Is the system mercury UV, UV-LED, or EB?
- Are lamp intensity, dose, and line speed monitored?
- Were inks changed when the curing system changed?
- Are uncured ink waste and cleanup materials included in the inventory?

59

ENCLOSED / CHAMBERED DOCTOR-BLADE SYSTEMS

What it is

- Used mainly on flexographic and rotogravure presses.
- Replaces open ink pans or partially open ink-feed systems with an enclosed ink chamber.
- Typically uses two doctor blades to meter ink onto the anilox roll or gravure cylinder.

VOC/HAP benefit

- Reduces exposed solvent-containing ink surface area.
- Reduces fugitive solvent evaporation at the printing station.
- Improves ink metering and viscosity stability.
- Can reduce cleanup losses and improve print consistency.

Important limitation

- This reduces fugitive emissions at the ink station.
- It does not eliminate dryer emissions or cleaning-solvent emissions.

Inspection questions

- Are ink chambers sealed and maintained?
- Are covers used on ink reservoirs and return containers?
- Are solvent additions and viscosity adjustments recorded?
- Are dryers and capture systems still included in the emissions calculation?

60

PROCESSLESS PLATES AND LOW-/ZERO-IPA OFFSET OPERATION

Processless lithographic plates

- Reduce or eliminate separate wet plate-processing steps.
- Can reduce prepress chemicals, water use, processor waste, and maintenance.
- Best treated as a pollution-prevention update rather than a direct stack-control technology.

Low-/zero-IPA fountain solution

- Reduces VOC emissions from offset lithography.
- Uses lower alcohol levels, alcohol substitutes, refrigeration, and tighter dampening control.
- Requires careful control of pH, conductivity, temperature, ink/water balance, and press conditions.

Inspection questions

- What fountain solution is used and what is the IPA percentage?
- Is the fountain solution refrigerated?
- Are pH, conductivity, and temperature recorded?
- Are plate-processing chemicals still used?
- Are cleaning solvents controlled separately?

61

SOLVENTLESS LAMINATING AND LOW-VOC POST-PRESS MATERIALS

Why add this topic

- Packaging operations may include printing, coating, laminating, adhesives, and finishing.
- VOC emissions may come from more than the printing press itself.

Technology options

- Solventless laminating adhesives.
- Water-based adhesives.
- Hot-melt adhesives.
- UV/EB-curable adhesives and coatings.
- Lower-VOC coatings and overprint varnishes.

VOC/HAP benefit

- Reduces solvent evaporation from laminating and post-press operations.
- May reduce dryer loading and add-on control demand.
- Can reduce solvent handling and waste solvent generation.

Inspection questions

- Are adhesives, coatings, and overprint varnishes included in emission calculations?
- Are laminating dryers vented or controlled?
- Are mix ratios and usage records available?
- Are cleaning solvents used on laminators or coating stations?
- Are post-press operations covered by the same permit limits?

62

SMART PROCESS CONTROL AND CLOSED MATERIAL HANDLING

Technology examples

- Closed ink and solvent delivery systems.
- Closed return lines and covered reservoirs.
- Automatic viscosity control.
- Automatic pH, conductivity, and temperature monitoring.
- Inline web inspection and defect detection.
- Digital logs from dryers, oxidizers, carbon systems, and capture systems.

VOC/HAP benefit

- Reduces open-container evaporation.
- Reduces solvent additions caused by poor viscosity control.
- Reduces scrap, rework, and press-cleaning frequency.
- Improves compliance documentation.

Inspection questions

- Are containers, reservoirs, and used-wipe containers kept closed?
- Are automatic control systems calibrated and maintained?
- Are setpoints and alarms documented?
- Do material-use records match production and control-device records?
- Are bypasses, downtime, and maintenance periods recorded?

63

CALCULATING THE VOC CONTENT OF COATINGS AND INKS

Presentation: 10

Chapter 7 – Calculating the VOC Content of Coatings and Inks

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

CALCULATING THE VOC CONTENT OF COATINGS AND INKS

Presentation: 10

Chapter 7 – Calculating the VOC Content of Coatings and Inks

2

CHAPTER 7

Calculating the VOC Content of Coatings and Inks

3

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.

4

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

5

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

6

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

7

COATING AND INK DATA

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

8

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

9

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: ____________

10

Presentation 10

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: ______

11

COATING AND INK DATA

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

12

TRANSFER EFFICIENCY

Baseline transfer efficiencies are specified in some CTG documents and NSPS

Enhanced transfer efficiencies are determined under actual operating conditions

13

CAPTURE AND CONTROL EFFICIENCIES

Claimed efficiencies can be determined from manufacturer's information

Actual efficiencies are determined by performance testing on the specific source

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PROCESS RECORDS

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

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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

EMISSION CALCULATIONS

AN EMISSION LIMIT OF 2.8 LBS OF VOC PER GALLON OF COATING LESS WATER

AN EMISSION LIMIT OF 7.51 LBS OF VOC PER GALLON OF SOLIDS APPLIED

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CALCULATION ROADMAP

- Select a basis, usually **100 lb coating** or **1 gal coating**.
- Determine mass of solids, water, VOC, and exempt compounds.
- Convert masses to volumes using density.
- Calculate coating density and volume fractions.
- Calculate VOC content in the required regulatory format.
- Apply transfer efficiency if the limit is based on **applied solids**.
- Apply capture/control efficiency if calculating controlled emissions.
- Compare the result with the applicable emission limit.

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CALCULATION OF MIXED SOLVENT DENSITY

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

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

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

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

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CALCULATION OF COATING DENSITY

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

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

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

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

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CALCULATION OF COATING DENSITY (CONTINUED)

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

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

Coating composition by volume:

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

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CALCULATION OF VOC CONTENT BASED ON COATING VOLUME

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

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

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CALCULATION OF VOC CONTENT BASED ON COATING VOLUME (CONTINUED)

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

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

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

22

CALCULATION OF VOC CONTENT BASED ON COATING VOLUME (CONTINUED)

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

23

CALCULATION OF VOC CONTENT BASED ON 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

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

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CALCULATION OF VOC CONTENT BASED ON SOLIDS VOLUME (CONTINUED)

Assume a transfer efficiency of 75%:

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

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GRAPHIC ARTS CALCULATIONS

Consider the following ink:

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

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VOLUME PERCENT VOC IN THE VOLATILE FRACTION

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

27

VOLUME PERCENT WATER IN THE VOLATILE FRACTION

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

28

VOLUME PERCENT SOLIDS IN THE INK LESS WATER

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

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THE PETROLEUM INDUSTRY

Presentation: 11

-

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THE PETROLEUM INDUSTRY

Presentation: 11

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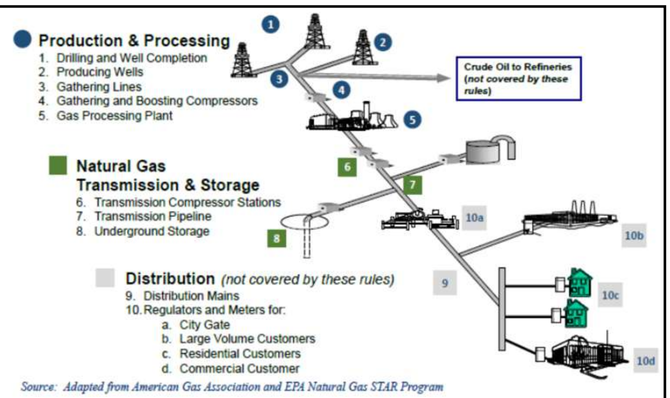
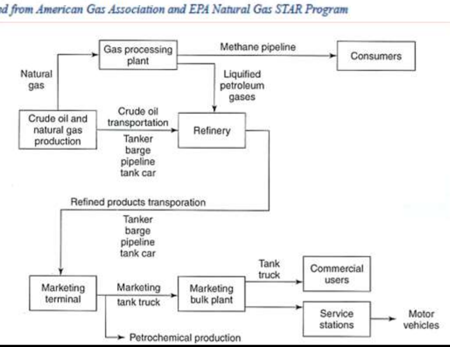
2

3

INDUSTRY SEGMENTS

- Exploration and production
- Transportation
- Refining
- Distribution





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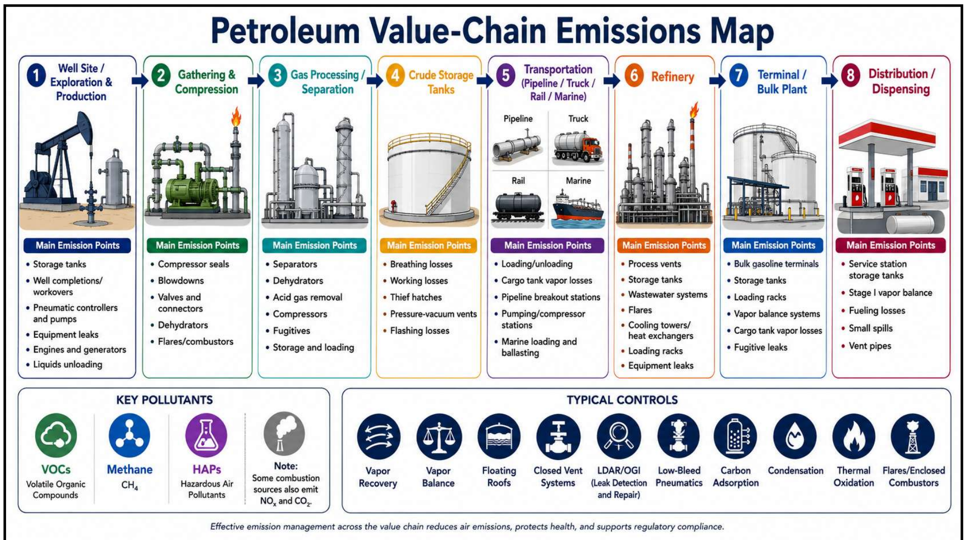
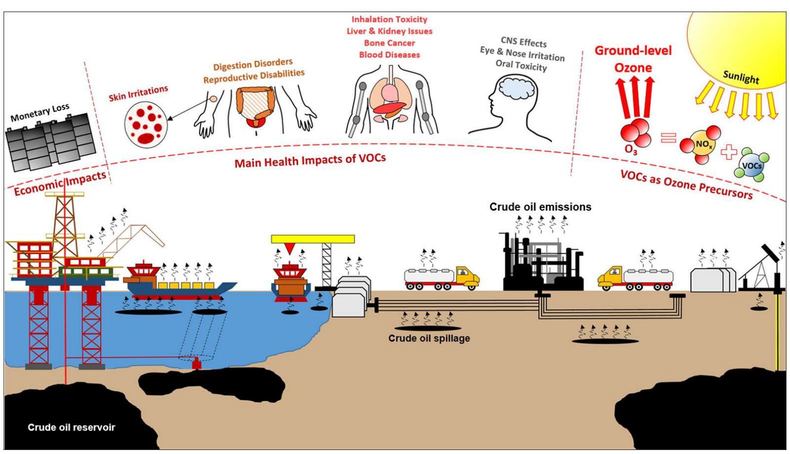


INDUSTRY SEGMENTS

5



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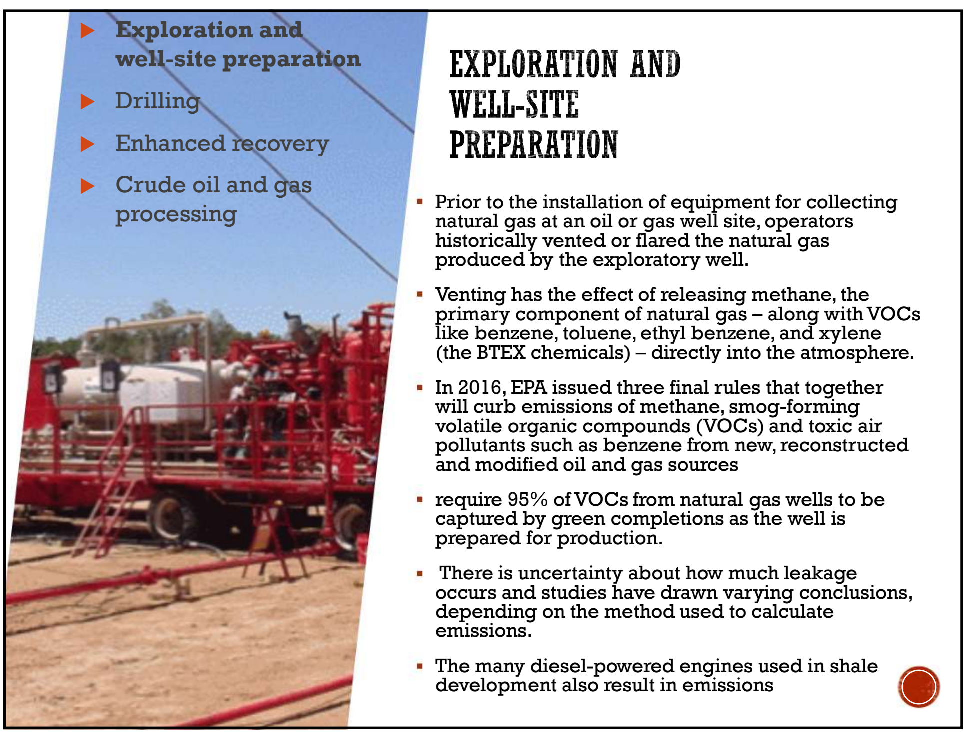
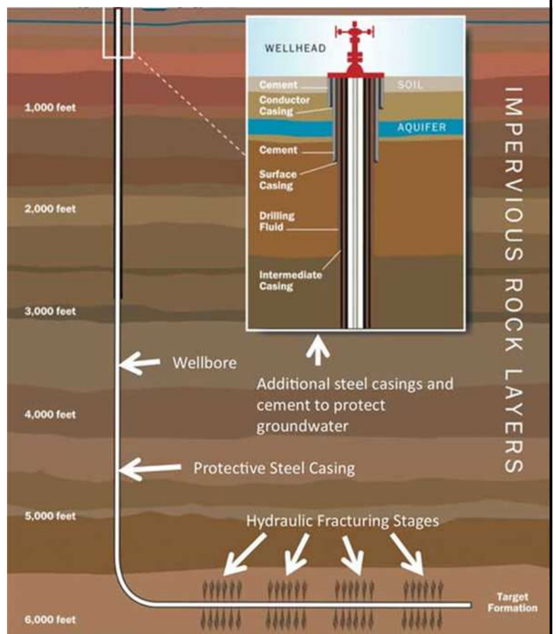
6


EXPLORATION AND PRODUCTION
Exploration and well-site preparation
Drilling
Enhanced recovery
Crude oil and gas processing

7

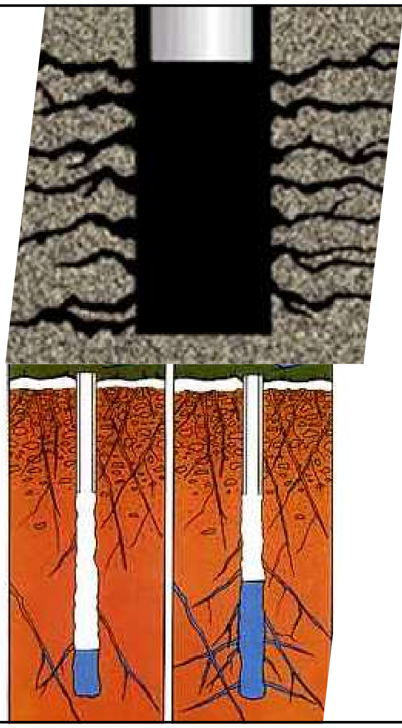

Exploration and well-site preparation
Drilling
Enhanced recovery
Crude oil and gas processing
EXPLORATION AND WELL-SITE PREPARATION
Prior to the installation of equipment for collecting natural gas at an oil or gas well site, operators historically vented or flared the natural gas produced by the exploratory well.
Venting has the effect of releasing methane, the primary component of natural gas – along with VOCs like benzene, toluene, ethyl benzene, and xylene (the BTEX chemicals) – directly into the atmosphere.
In 2016, EPA issued three final rules that together will curb emissions of methane, smog-forming volatile organic compounds (VOCs) and toxic air pollutants such as benzene from new, reconstructed and modified oil and gas sources
require 95% of VOCs from natural gas wells to be captured by green completions as the well is prepared for production.
There is uncertainty about how much leakage occurs and studies have drawn varying conclusions, depending on the method used to calculate emissions.
The many diesel-powered engines used in shale development also result in emissions

8


WELLHEAD
Cement
SOIL
Conductor Casing
AQUIFER
Cement
Surface Casing
Drilling Fluid
Intermediate Casing
IMPERVIOUS ROCK LAYERS
1,000 feet
2,000 feet
3,000 feet
4,000 feet
5,000 feet
6,000 feet
Wellbore
Additional steel casings and cement to protect groundwater
Protective Steel Casing
Hydraulic Fracturing Stages
Target Formation

9

10



ACIDIZING AND FRACTURING

11

Additive Type	Main Compound(s)	Purpose
Acid	hydrochloric or muriatic acid	Helps dissolve minerals and initiate cracks in the rock
Antibacterial agent	Glutaraldehyde	Eliminates bacteria in the water that produce corrosive byproducts
Breaker	Ammonium persulfate	Allows a delayed breakdown of the fracturing gel
Clay stabilizer	Potassium chloride	Brine carrier fluid
Corrosion Inhibitor	N,n-dimethyl formamide	Prevents the corrosion of pipes
Crosslinker	Borate salts	Maintains fluid viscosity
Defoamer	Polyglycol	Lowers surface tension and allows gas to escape
Foamer	Acetic acid (with NH4and NaNO2)	Reduces fluid volume and improves proppant carrying capacity
Friction Reducer	Petroleum distillate	Minimizes friction in pipes
Gel guar gum	Hyroxyethyl	Helps suspend the sand in water
Iron Control	Citric Acid	Prevents precipitation of metal oxides
Oxygen Scavenger	Ammonium bisulfate	Maintains integrity of steel casing of wellbore; protects pipes from corrosion by removing oxygen from fluid
pH Adjusting Agent	Sodium or potassium carbonate	Adjusts and controls pH of fluid
Proppant	Silica, sometimes ceramic particles	Holds open (props) fractures to allow fluids (oil and/or natural gas) to escape from shale
Scale Inhibitor	Ethylene glycol	Reduces scale deposits in pipe
Solvents	Stoddard solvent, various aromatic hydrocarbons	Improve fluid wettability or ability to maintain contact between the fluid and the pipes
Surfactant	Isopropanol	Increases the viscosity of the fracture fluids and prevents emulsions

12

ENHANCED RECOVERY

- Water injection
- Gas injection
- Thermal processes
- Chemical injection

- Exploration and well-site preparation
- Drilling
- **Enhanced recovery**
- Crude oil and gas processing

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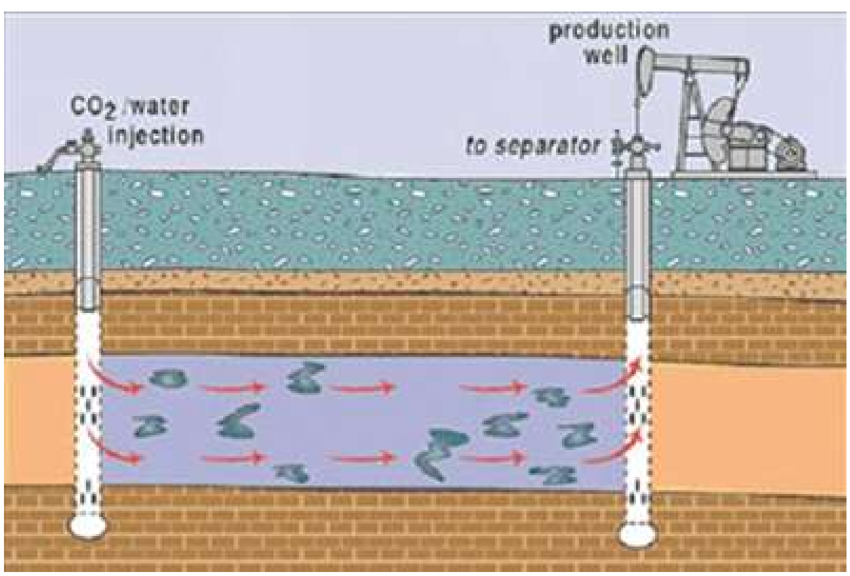

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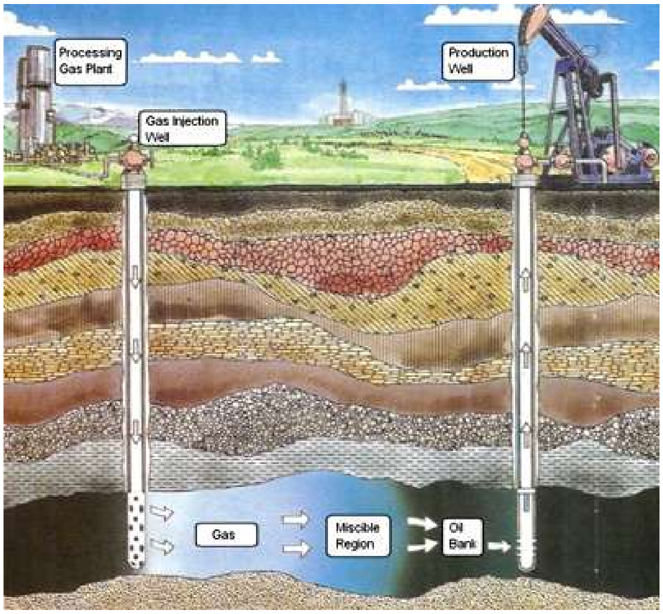

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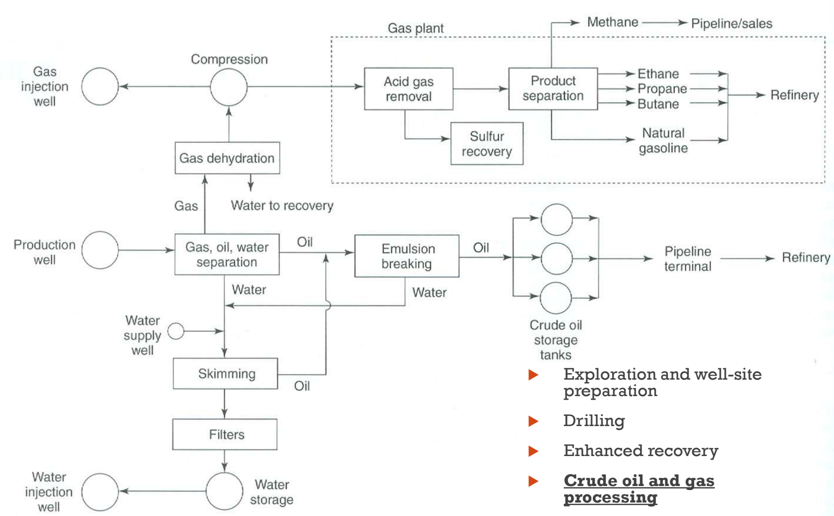
CRUDE OIL AND GAS PROCESSING



- Exploration and well-site preparation
- Drilling
- Enhanced recovery
- **Crude oil and gas processing**

16

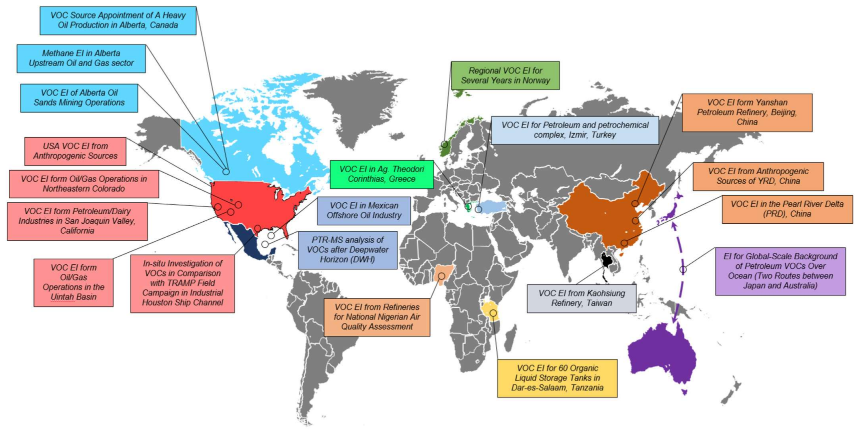
EMISSION SOURCES

17

PRODUCTION EMISSION SOURCES

- Storage tanks
- Loading operations
- Liquid unloading
- Pneumatic controllers
- Leaks
- Engine operations

18



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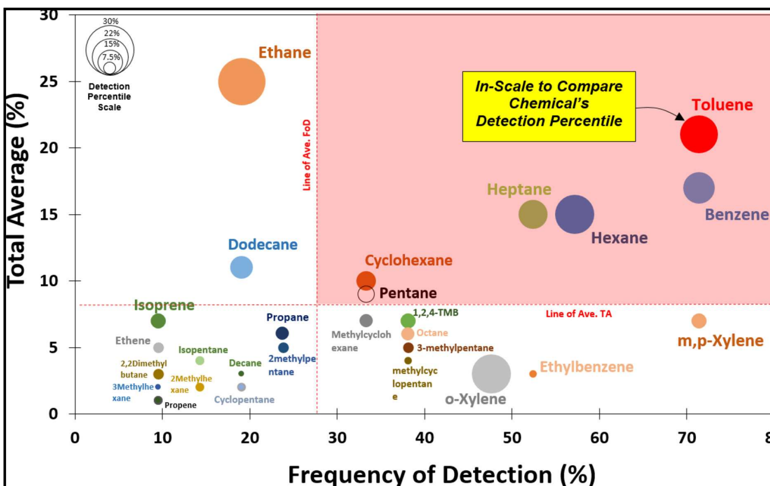

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- Benzene May be released during well unloadings or other maintenance
- Xylene: issuing from the well during the fracturing process
- Toluene: might be present in chemicals used during the drilling and fracking process

20

Presentation 11

CONTROL TECHNIQUES

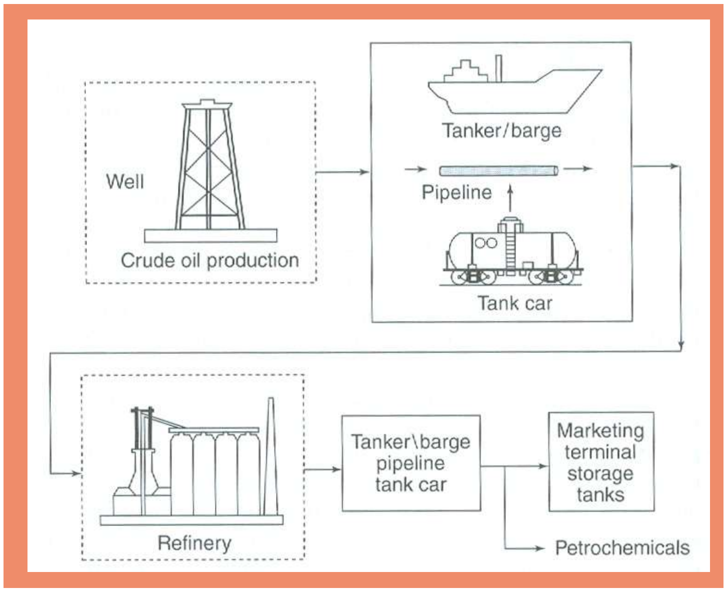
21

EMISSION CONTROL TECHNIQUES

- Vent collection system
  - Carbon adsorption
  - Refrigeration condensation
  - Thermal oxidation
- Combustion controls
- Storage tank controls
- Inspection and maintenance

22

TRANSPORTATION



23

TRANSPORTATION EMISSION SOURCES

- Loading
- Transit
- Marine vessel ballasting operations
- Storage

24

EMISSION CONTROL TECHNIQUES

- Loading controls
- Vent collection or vapor balance system
  - Carbon adsorption
  - Refrigeration condensation
  - Thermal oxidation
- Product refrigeration
- Inspection and maintenance
- Storage tank controls

25

SUMMARY OF CONTROL MATRIX

Emission source	Main pollutants	Typical controls	Inspection focus
Storage tanks	VOC, methane, HAP	Internal/external floating roof, pressure-vacuum vents, vapor recovery, routing to control	Tank design, throughput, liquids stored, control status, pressure records
Loading operations	VOC, HAP	Vapor balance, vapor recovery unit, carbon adsorption, thermal oxidizer	Loading rate, vapor collection, truck/tank vapor tightness
Pneumatic controllers/pumps	Methane, VOC	Zero-bleed/low-bleed devices, instrument air, electric actuation	Device inventory, gas supply, maintenance logs
Equipment leaks	Methane, VOC, HAP	LDAR, OGI, Method 21, alternative monitoring	Monitoring frequency, repair timing, delay-of-repair records
Liquids unloading	Methane, VOC	Plunger lift, reduced-emission unloading, routing to control	Event logs, venting/flaring records
Flares/combustors	VOC, methane, HAP	Proper design, pilot monitoring, NHV monitoring, maintenance	Pilot flame, visible emissions, assist gas, monitoring data
Wastewater/oil-water systems	VOC, HAP	Covers, closed vent systems, control devices	Open drains, seals, covers, inspection logs

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CURRENT REGULATIONS

27

FIRST EPA RULES – THE OBAMA ADMINISTRATION

- During the Obama administration, EPA set standards for VOCs and methane emissions for new oil and gas production sources (including production, processing, transmission, and storage).
- This was the first rule expressly targeting methane emissions.
- EPA also issued Control Technique Guidelines to states with moderate nonattainment areas for ozone, requiring them to amend their State Implementation Plans (SIPs) to address VOCs from existing sources via a set of controls that would also reduce methane emissions.

28

REVOKING EPA RULES – THE TRUMP ADMINISTRATION

- The Trump Administration revoked nearly all actions
- only some of the standards controlling VOCs in new sources are left in place
- It eliminated methane standards for all segments of the oil and gas industry and left in place some VOC standards only for production and processing facilities.
- It also rolled back the efforts to develop a rule covering existing sources, having eliminated the legal predicate for doing so.

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REINSTATING EPA RULES – THE BIDEN ADMINISTRATION

- In June 2021, President Biden signed a joint resolution of Congress disapproving of the Trump administration's rollback of VOC and methane standards regarding transmission and storage facilities along with other operations (the "Review Rule") in 2021
- technical standards are left for Biden's EPA to address through rulemaking.
- On November 15, 2021, EPA proposed new performance standards and emissions guidelines for new and existing oil and gas facilities,
- On November 11, 2022 EPA issued a supplemental proposal that would further strength EPA's requirements for facilities.
- Comments on the supplemental proposal are due by February 13, 2023.

30

WHERE DO WE STAND TODAY?

The Biden EPA finalized three rules regulating methane from the oil and gas sector:

- regulations for VOCs and methane from the oil and gas (NSPS OOOOb/EG OOOOc),
- revisions to the Greenhouse Gas Reporting Program Subpart W, and
- implementation of the Waste Emissions Charge in the Inflation Reduction Act, which has been repealed by the Congressional Review Act.

The Trump EPA announced it is reconsidering these Biden-era regulations for the oil and gas industry.

In September 2025 EPA proposed to delay the program until 2034.

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LATEST UPDATE

- • **March 8, 2024**: NSPS OOOOb/EG OOOOc published (89 FR 16820), effective May 7, 2024
  • **August 5, 2025**: First annual reporting deadline under OOOOb
  • **March 12, 2025**: EPA Administrator Zeldin announced comprehensive reconsideration
  • **July 31, 2025**: Interim final rule extending compliance deadlines (90 FR 36716)
  • **November/December 2025**: Final rule made extensions permanent
  • **April 4, 2026**: Final reconsideration rule

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CURRENT REGULATORY SNAPSHOT — PETROLEUM VOC/METHANE SOURCES

Area	Rules/guidance to mention	Why it matters
Oil and natural gas production/process/transmission/storage	NSPS OOOOb and EG OOOOc	Methane and VOC standards for affected sources
Existing oil and gas VOC RACT	2016 Oil & Gas CTG	State/local RACT rules in ozone nonattainment areas
Methane reporting	GHGRP Subpart W	GHG reporting and methane data
Waste Emissions Charge	CRA disapproval; rule no longer in effect	Do not present the 2024 WEC rule as active
Refineries	NESHAP Subpart CC, Subpart UUU, NSPS J/Ja	HAP, flares, process vents, benzene fenceline monitoring
Gasoline distribution	NESHAP Subparts R and BBBBBB; NSPS XX/XXa	Loading racks, vapor collection, cargo tanks, storage, LDAR
Marine loading	NESHAP Subpart Y	Petroleum liquid loading to marine vessels

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PETROLEUM REFINING

Presentation: 12

Chapter 8 – Petroleum Refining

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

PETROLEUM REFINING

Presentation: 12

Chapter 8 – Petroleum Refining

2

3

CATEGORIES OF REFINING OPERATIONS

Separation processes

Conversion processes

Treatment processes

Auxiliary processes

4

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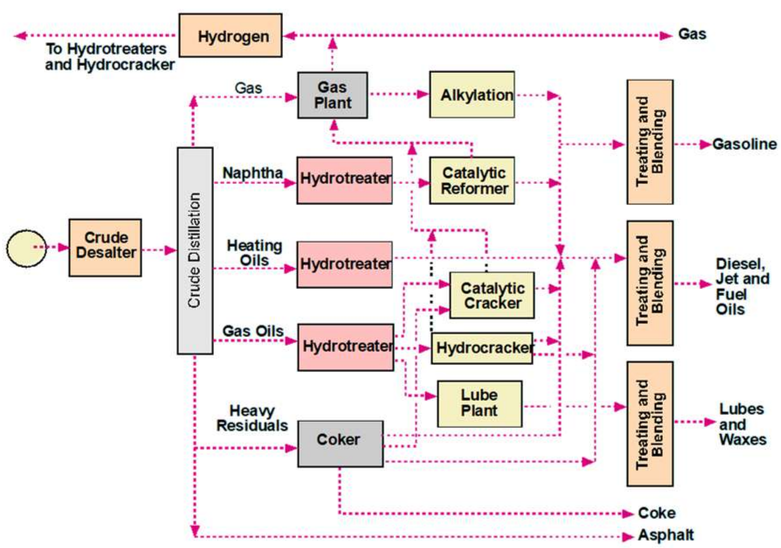
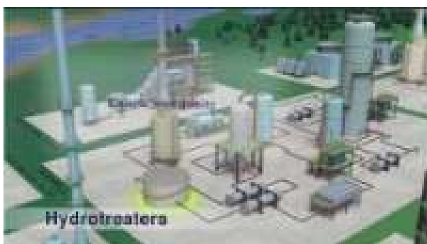


TYPICAL PROCESSING STEPS

6

SEPARATION PROCESSES

- Desalting
- **Distillation**
- Deasphalting



7

DESALTING

Electrical desalting

Crude, water and demulsifier heated under pressure and subjected to electrostatic field. Salt-containing water droplets agglomerate, settle and are removed.

Chemical desalting

Crude, water and demulsifier heated under pressure. Salt-containing water droplets agglomerate, settle and are removed.

8

DISTILLATION

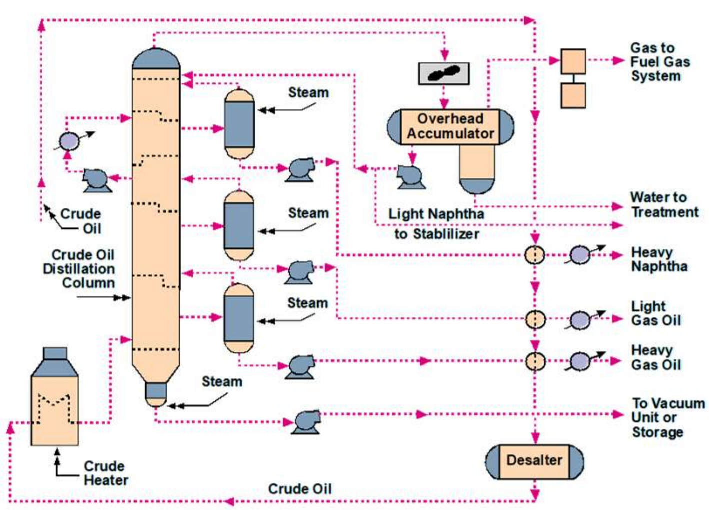
Atmospheric distillation

Vacuum distillation

- The temperatures required for atmospheric distillation of the heavier fractions of crude oil are so high that thermal cracking would occur, resulting in lost product and equipment fouling.
- Therefore, these materials are further distilled under vacuum, since the boiling temperature decreases with decreasing pressure

9

ATMOSPHERIC DISTILLATION UNIT



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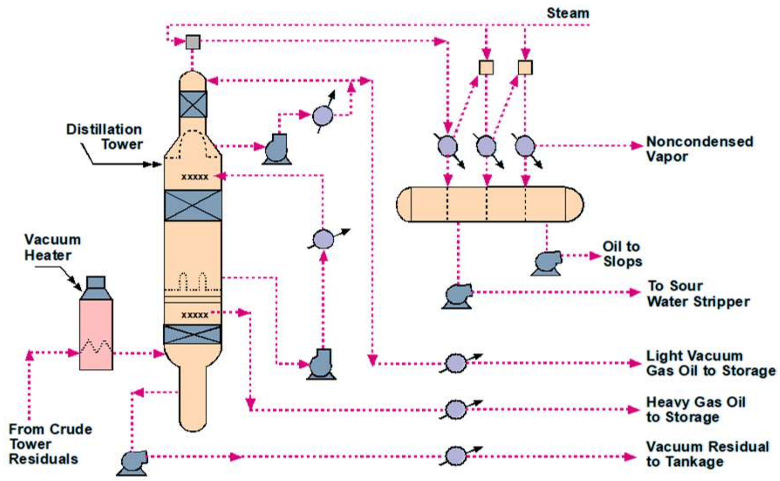
VACUUM DISTILLATION



11

DEASPHALTING

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

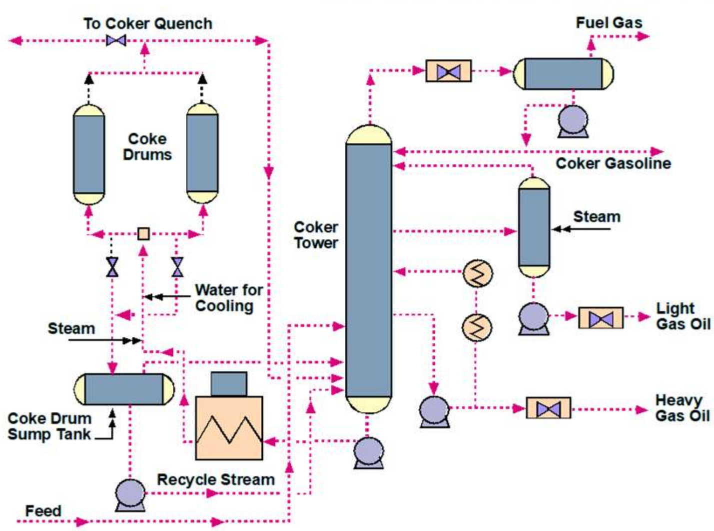
12

CONVERSION PROCESSES

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

13

DELAYED COKING UNIT



14

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

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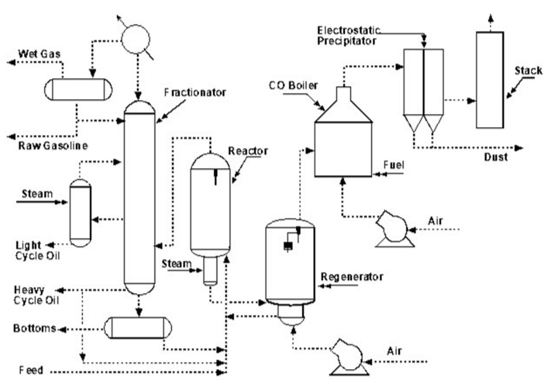

16

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

17

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

18

ALKYLATION PROCESSES

- Sulfuric acid alkylation
  - Olefin and isobutane are mixed and contacted with sulfuric acid in a refrigerated reactor. Emulsion is formed, recovered and separated to obtain alkylate
- Hydrofluoric acid alkylation
  - Olefin, isobutane and hydrofluoric acid are mixed and react to form an emulsion that is recovered and separated to obtain alkylate

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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
- Feedstock is mixed with hydrogen and passed over a fixed-bed noble metal catalyst
- Reactor effluent is separated to recover the hydrogen and the branched-chain isomers

20

REFORMING

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

Platforming

- Naphtha feed is mixed with hydrogen and passed over a fixed-bed noble metal catalyst
- Reactor effluent is separated to recover the hydrogen and the reformate product
- Catalyst regeneration cycle varies from once a day to less than once a year, depending on pressure and hydrogen-naphtha ratio

21

TREATMENT PROCESSES

- Hydrotreating
- Amine treating
- Chemical sweetening
- Asphalt blowing

22

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

23

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

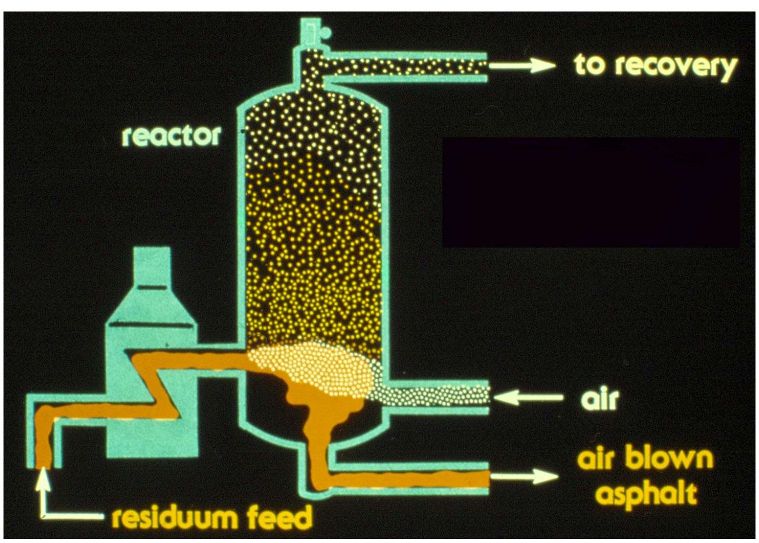
24

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 mercaptans recovered as alkyl disulfides

25

ASPHALT BLOWING



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AUXILIARY PROCESSES

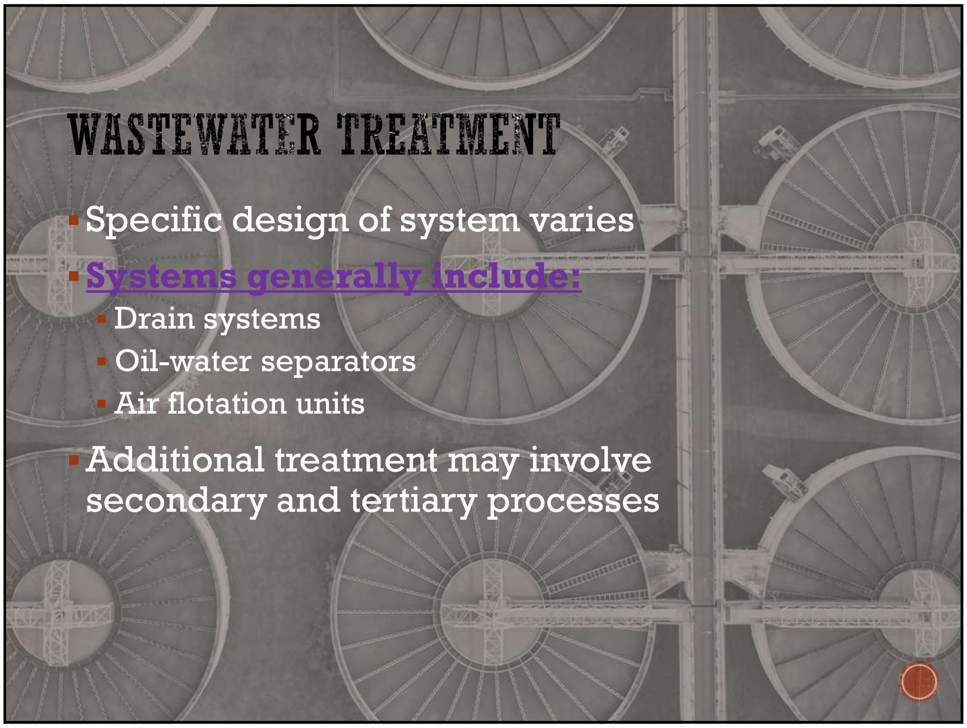
- Sulfur recovery
- Wastewater treatment
- Fuel gas recovery
- Blowdown systems

27

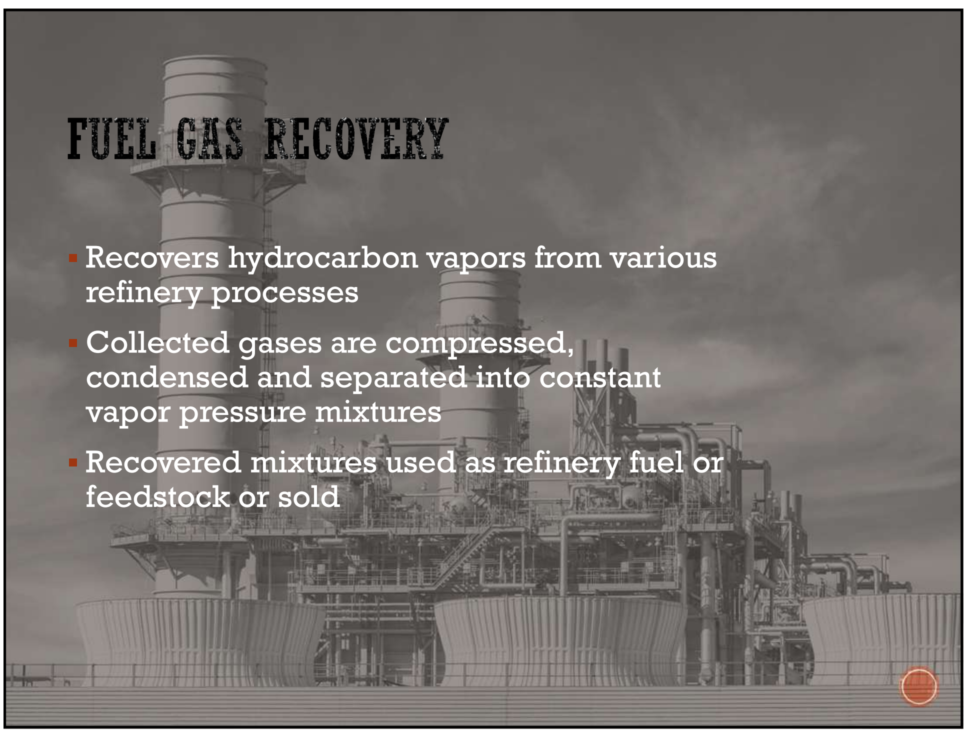
SULFUR RECOVERY

- 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**

28


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

29


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

30

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

31

EMISSION CONTROL TECHNIQUES

- Flares
- Incinerators
- Process heaters
- Covers
- Fugitive emission control
- catalytic cracking units MACT (Subpart UUU)

32

Emission Regulation

33

Control of Refinery Vacuum Producing Systems, Wastewater Separators and Process Unit Turnarounds, Control Technique Guideline Document, EPA-450/2-77-025 {Suppl Materials}

Recommended standard:

- Incinerate, or compress and add to the refinery fuel gas system, non-condensable vapors from the vacuum producing system.
- Cover the forebay and separator sections of wastewater separators.
- Vent all vapors to a flare or vapor recovery system when a process unit is shut down for a turnaround.

34

Applicability Date: May 4, 1987

Standard: Individual Drain Systems

- Each drain shall be equipped with water seal controls.
- Junction boxes shall be equipped with a tightly sealed cover and may have an open vent pipe.
- Sewer lines shall be covered or enclosed.
- Wastewater routed through new process drains and a new first common downstream junction box shall not be routed through a downstream catch basin.
- Modified or reconstructed drain systems that had a catch basin in the existing configuration are exempt from the provisions of this section.
- An alternative standard allows for a completely closed drain system.

35

Standard: Oil-Water Separators

- Each separator shall be equipped with a fixed roof that completely covers the separator with no separation between the roof and wall. An alternative standard allows for the use of a floating roof.
- Separators treating greater than 250 gallons per minute shall be equipped with a closed vent system and control device with at least 95 percent efficiency. Modified or reconstructed separators handling less than 600 gallons per minute that were equipped with a fixed roof are exempt from this requirement.
- Slop oil and oily wastewater shall be collected, stored, transported, recycled, reused or disposed of in an enclosed system.
- Separator tanks, slop oil tanks, storage vessels and other required auxiliary equipment may be equipped with a pressure control valve set at the maximum pressure for proper system operation but may not vent continuously.
- Storage vessels subject to 40CFR60, subparts K, Ka or Kb are not subject to this section.

36

Standard: Closed Vent Systems and Control Devices

- Combustion devices shall be at least 95 percent efficient or have a minimum residence time of 0.75 seconds at 1,500°F.
- Vapor recovery system shall be at least 95 percent efficient.
- Closed vent systems shall operate with no detectable emissions, be equipped with a flow indicator, and direct the vapors to a control device.

37

NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS FROM PETROLEUM REFINERIES, 40CFR63, SUBPART CC

Applicability: All process vents, storage vessels, wastewater streams and treatment operations, equipment leaks, gasoline loading racks and marine vessel loading racks that are located at major sources and that handle one or more HAPs listed in the subpart.

Standard: Process Vents (Group 1)

- Reduce emissions using a flare that operates with no visible emissions and meets 40CFR63.11(b); or
- Reduce emissions using a control device by 98 percent by weight or to an outlet concentration of 20 ppmv, whichever is less stringent.

Standard: Storage Vessels (Group 1)

- The provisions for Group 1 storage vessels are essentially the same as 40CFR60, Subpart Kb, and are summarized in Chapter 9.

38

NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS FROM PETROLEUM REFINERIES, 40CFR63, SUBPART CC

Standard: Wastewater (Group 1)

- **Comply with the provisions of 40CFR61, Subpart FF, for tanks, surface impoundments, containers, individual drain systems, oil-water separators, treatment processes, and closed vent systems and control devices.**

Standard: Equipment Leaks

- **Existing sources shall comply with 40 CFR 60, Subpart VV.**
- **New sources shall comply with 40 CFR 63, Subpart H.**

Standard: Gasoline Loading Racks

- **Comply with 40 CFR 63, Subpart R. The provisions of this standard are summarized in Chapter 9.**

Standard: Marine Tank Vessel Loading

- **Comply with 40CFR63, Subpart Y.**

39

2024 REFINERY SECTOR RULE AMENDMENTS AND CURRENT RECONSIDERATION

- **2015 Refinery Sector Rule:** First introduced benzene fenceline monitoring (9 μg/m^3 action level), enhanced flare controls, delayed coker decoking limits, and storage tank requirements
- **April 2024 amendments:** Strengthened standards under both NESHAP Subpart CC and Subpart UUU; D.C. Circuit litigation initially held in abeyance
- **March 12, 2025:** EPA Administrator Zeldin announced reconsideration of the refinery NESHAPs; administration considering a 2-year Section 112(i)(4) compliance exemption
- **April 10, 2025:** D.C. Circuit returned litigation to active docket (American Chemistry Council et al. v. EPA)

40

BENZENE FENCELINE MONITORING ENFORCEMENT PUSH

This is currently the most active refinery enforcement area and deserves a dedicated slide:

- **September 2023:** EPA OIG report criticized fenceline monitoring oversight
- **February 2024:** EPA enforcement alert on Benzene Waste Operations NESHAP (BWON, 40 CFR 61 Subpart FF)
- **October 2025:** EPA enforcement alert specifically on benzene fenceline monitoring
- **Recent settlements:** BP Products NA (2023), Lima Refining (2024), HF Sinclair Navajo Refining (January 2025, ~$35M penalty) — these are real-world cases your audience will reference

41

PROCESS INSPECTION

42

PETROLEUM PRODUCT STORAGE AND DISTRIBUTION

Presentation: 13

Chapter 9 – Petroleum Product Storage and Distribution

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
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Western States Air Resources Council

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PETROLEUM PRODUCT STORAGE AND DISTRIBUTION

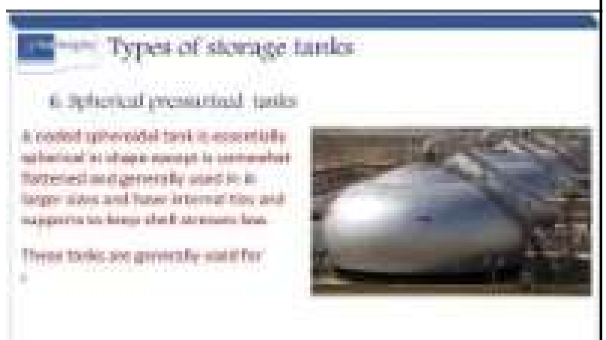
Presentation: 13

Chapter 9 – Petroleum Product Storage and Distribution

2

PETROLEUM PRODUCT STORAGE

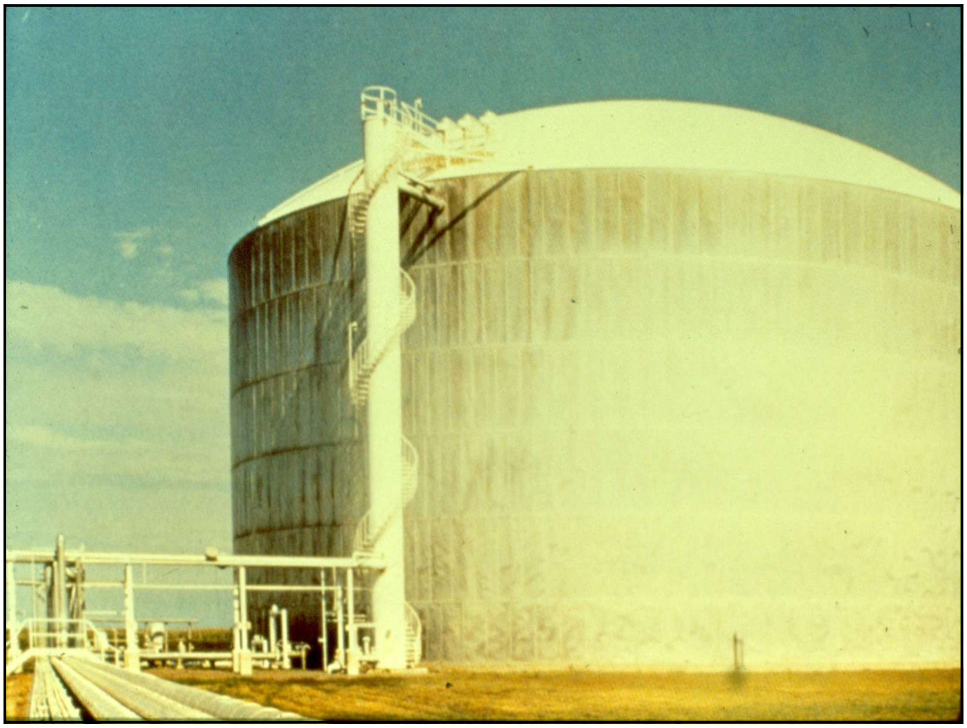
- Fixed roof tanks
- Internal floating roof tanks
- External floating roof tanks



3

Product	Volatility	VP Range	Tank Type
Crude, lube oils	Low	<1.5 psia	Fixed
Kerosene, gasoline, fuel oils	Moderate	1.5-11.1 psia	Float
Butane, propane	High	>11.1 psia	Pressure

4



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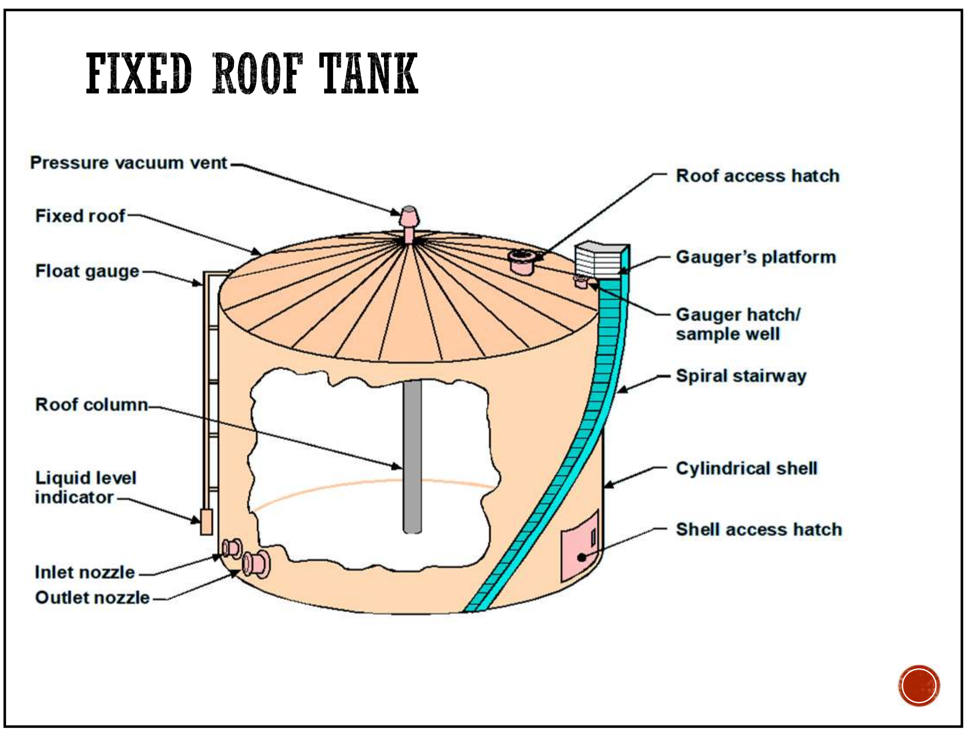
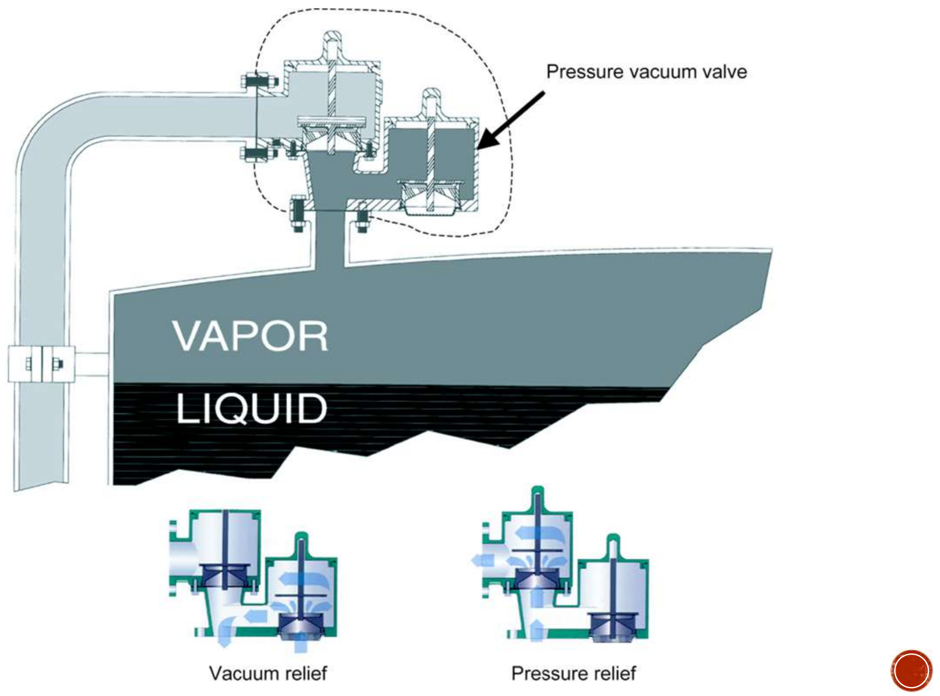

FIXED ROOF TANK
Pressure vacuum vent
Fixed roof
Float gauge
Roof column
Liquid level indicator
Inlet nozzle
Outlet nozzle
Roof access hatch
Gauger's platform
Gauger hatch/ sample well
Spiral stairway
Cylindrical shell
Shell access hatch

6



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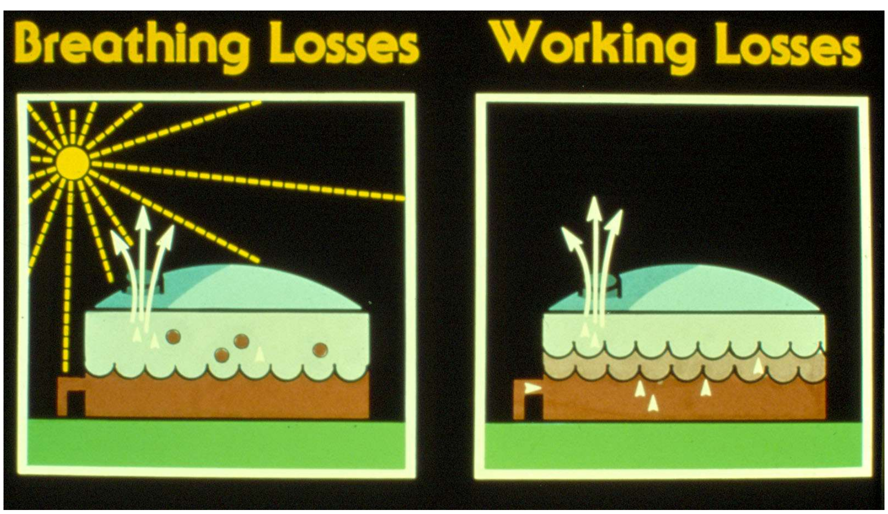


Emissions from fixed roof tanks are a result of:

- Evaporative losses during storage (known as breathing losses or standing losses) and
- Evaporative losses during filling operations (known as working losses)

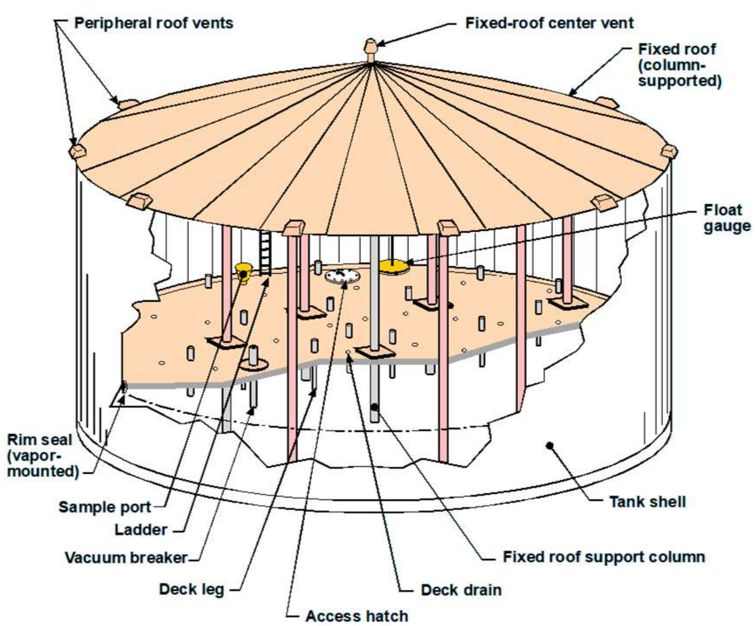
8

INTERNAL FLOATING ROOF TANK

- An internal floating roof tank has both a fixed roof and a roof that floats inside the tank
  - on the liquid surface (contact roof)
  - or is supported on pontoons several inches above the liquid surface (non-contact roof) and rises and falls with the liquid level.
- There are two basic types of internal floating roof tanks:
  - tanks where the fixed roof is supported by vertical columns within the tank; and
  - tanks with a self-supporting fixed roof.
- Tanks initially constructed with both a fixed roof and an internal floating roof may be of either type

9

INTERNAL FLOATING ROOF TANK



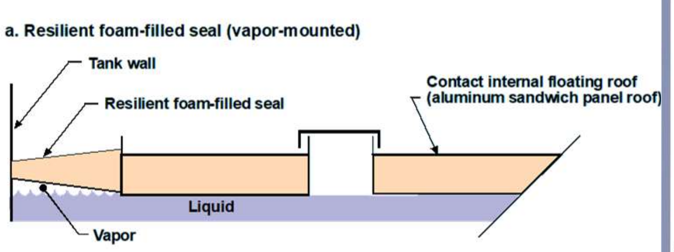
10

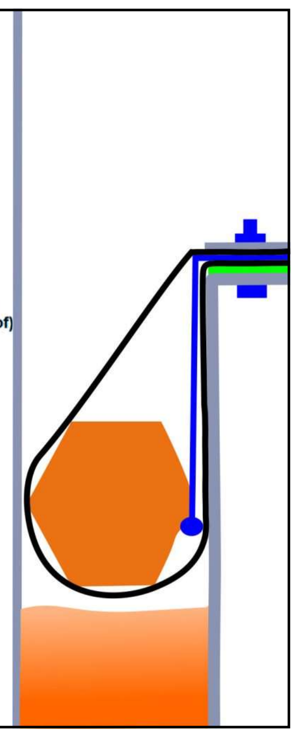
FLOATING ROOF CONSTRUCTION

- Aluminum panel with honeycombed core
- Aluminum deck on aluminum framework
- Fiberglass reinforced polyester (FRP) panel
- Steel pan

11

VAPOR MOUNTED FOAM SEAL





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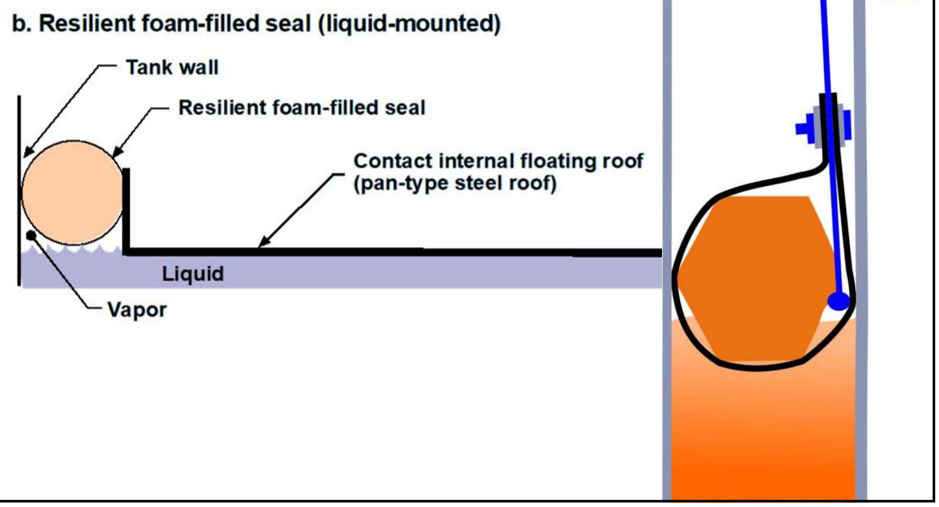
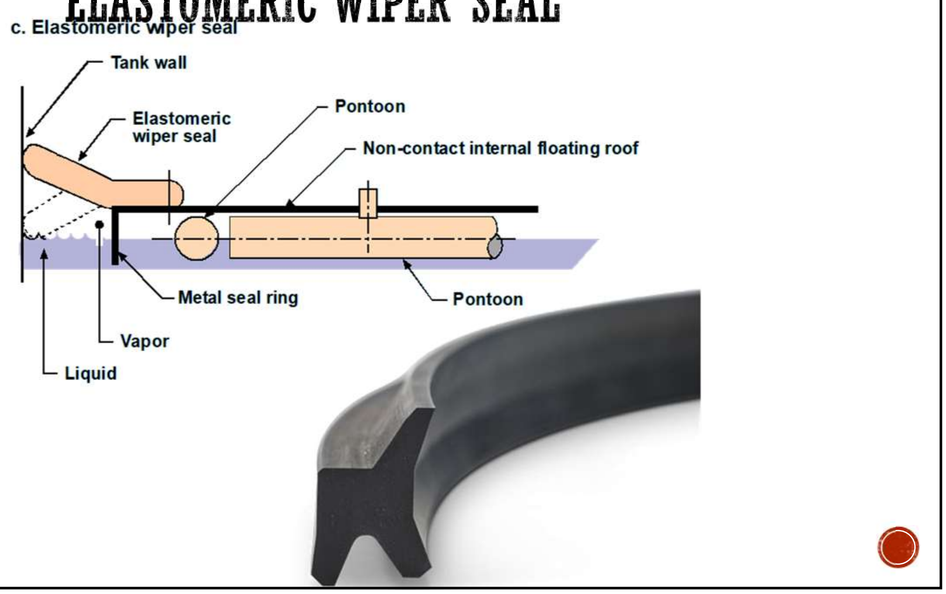
LIQUID MOUNTED FOAM SEAL



13

ELASTOMERIC WIPER SEAL



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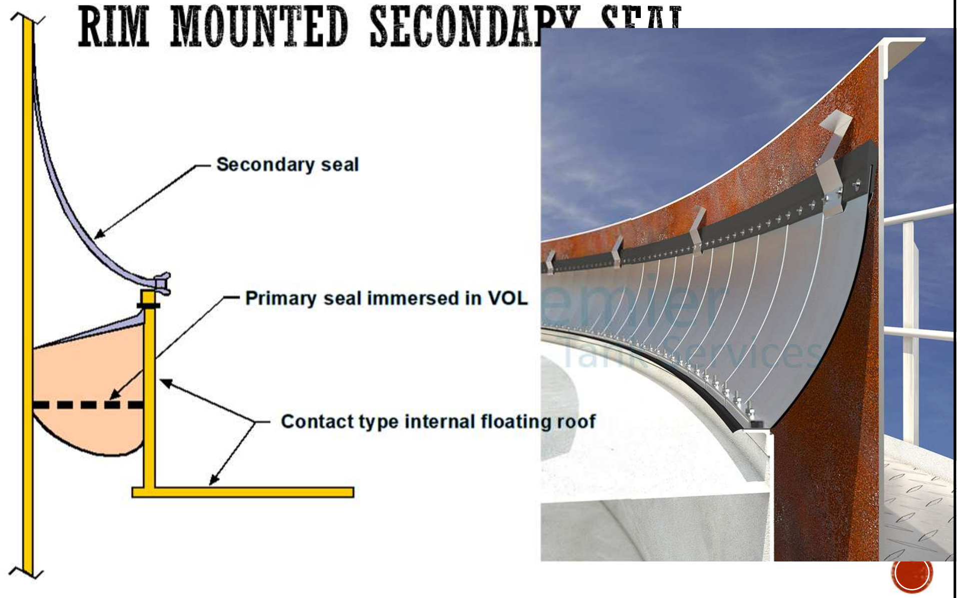
RIM MOUNTED SECONDARY SEAL

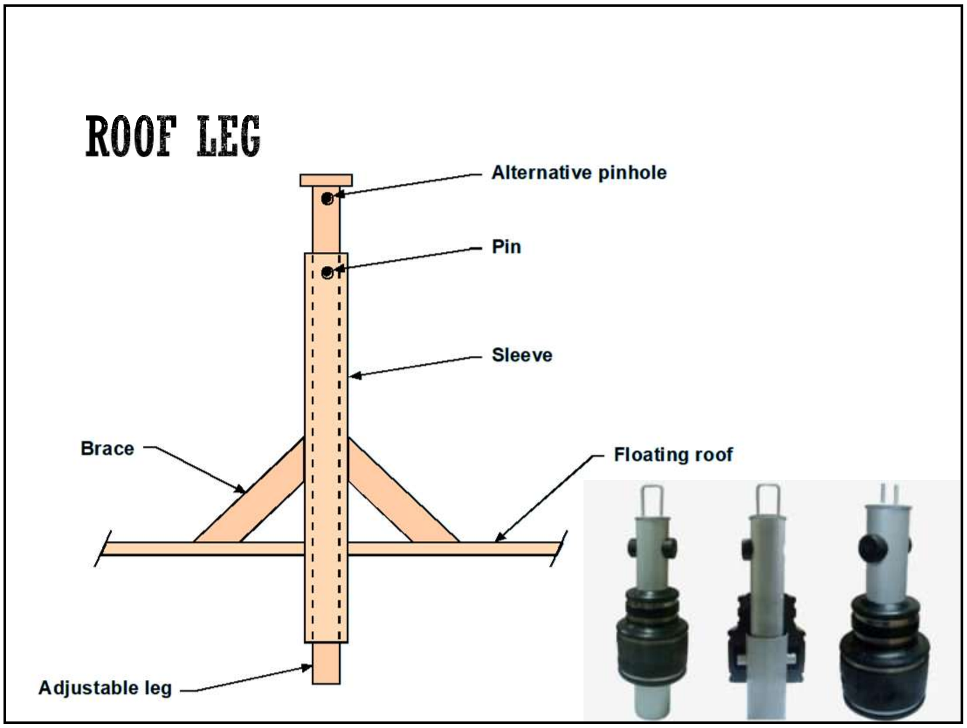


15

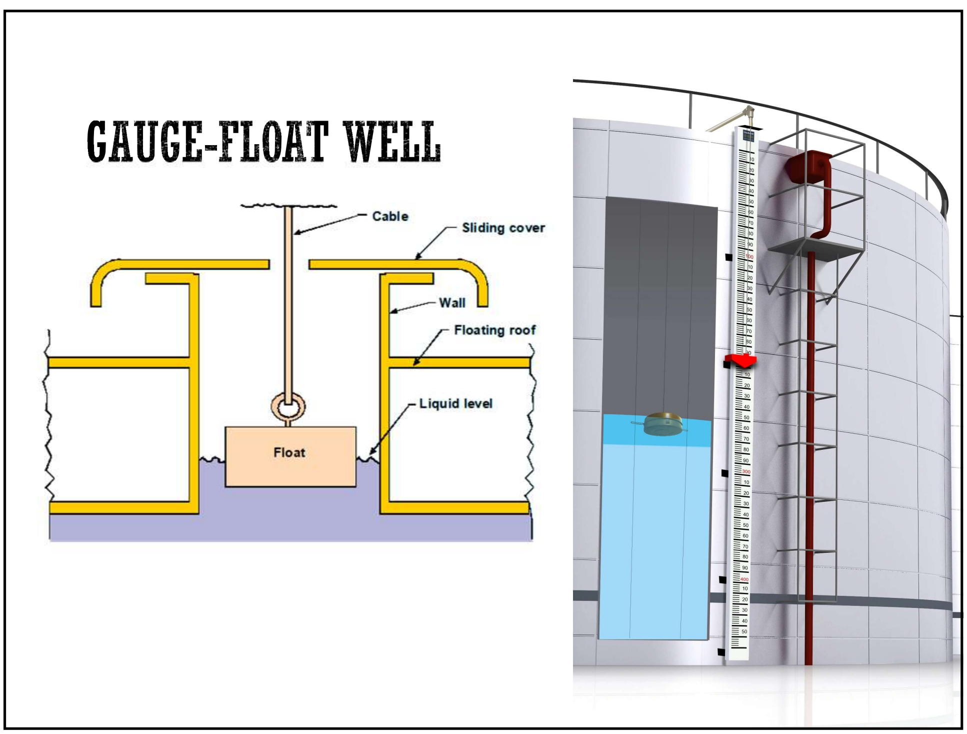
ROOF PENETRATIONS

- Numerous fittings penetrate or are attached to an internal floating roof.
- These fittings serve to accommodate structural support members or to allow for operational functions.
- Those fittings requiring penetration through the floating roof can be a source of VOC emissions.
  - Column wells
  - Roof legs
  - Vacuum breakers
  - Gauge-float wells
  - Sample wells
  - Access hatches
  - Ladder wells

16


ROOF LEG
Alternative pinhole
Pin
Sleeve
Brace
Floating roof
Adjustable leg

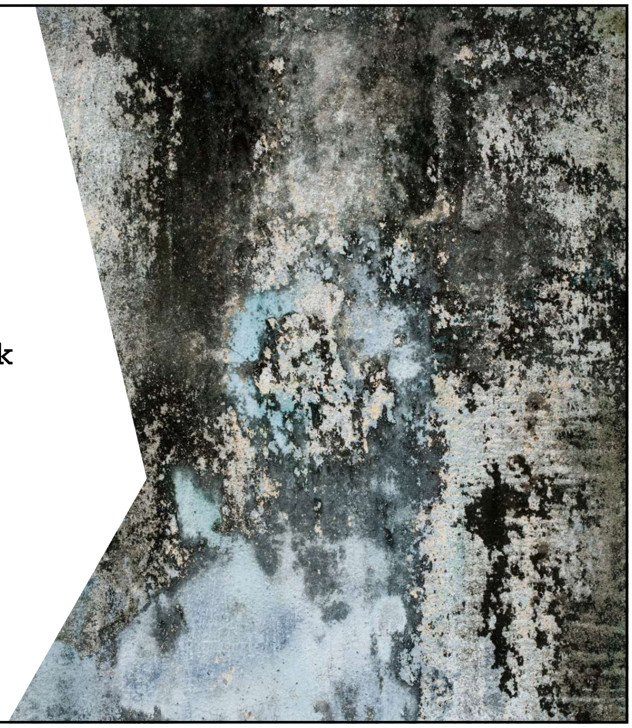
17


GAUGE-FLOAT WELL
Cable
Sliding cover
Wall
Floating roof
Liquid level
Float

18

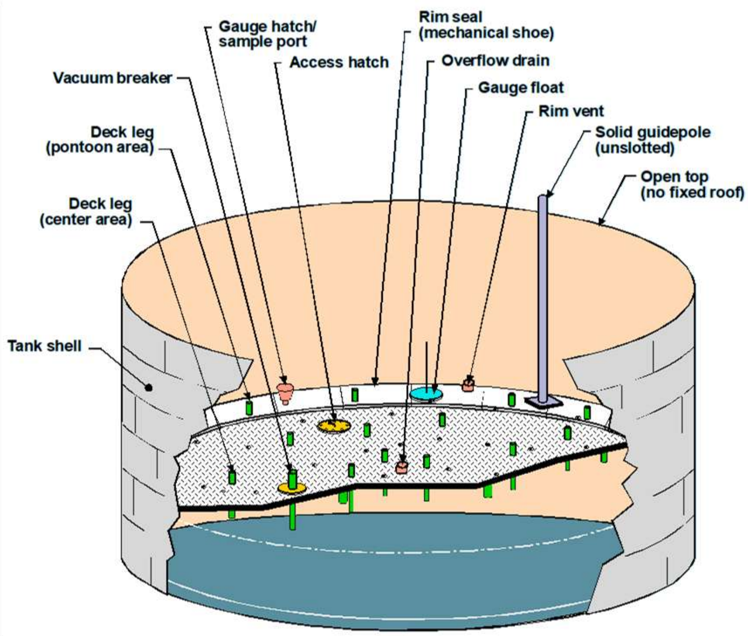
SOURCES OF VOC LOSSES

- Rim seal
- Roof fittings
- Non-welded deck seams
- Wet tank wall



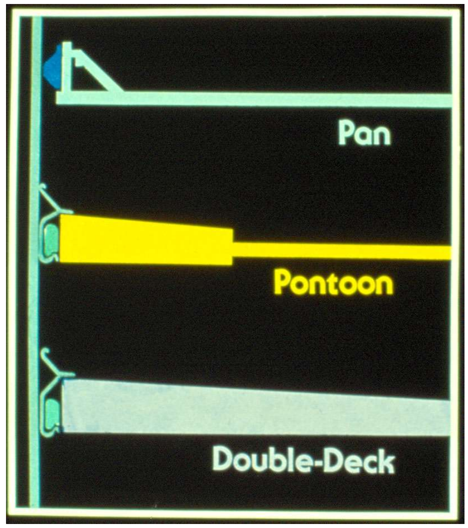
19

EXTERNAL FLOATING ROOF TANK



20

Types of External Floating Roofs



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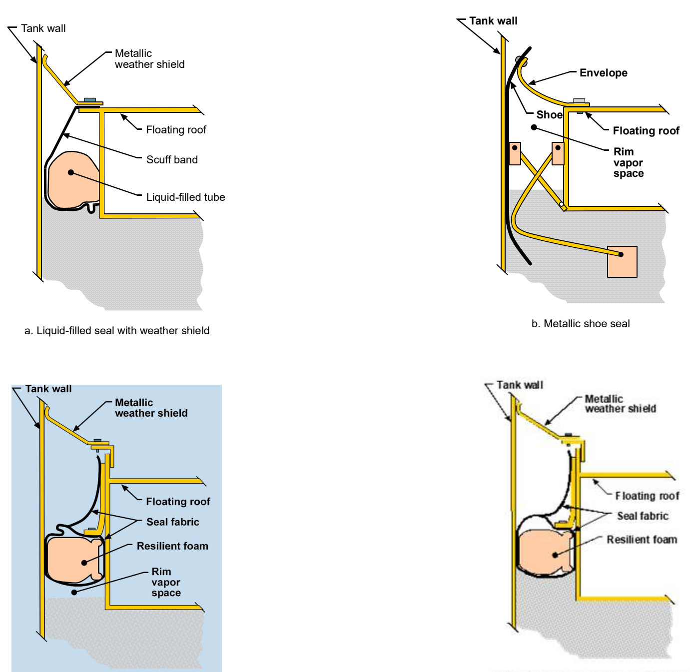


a. Liquid-filled seal with weather shield

b. Metallic shoe seal

c. Vapor-mounted resilient foam-filled seal with weather shield

d. Liquid-mounted resilient foam-filled seal with weather shield

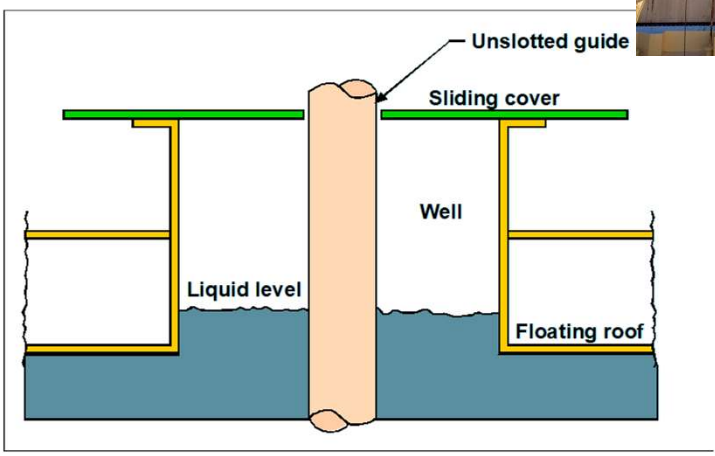
22

ROOF PENETRATIONS

- Guide-pole wells
- Sample wells
- Roof drains
- Rim vents

23

UNSLOTTED GUIDE POLE WELL



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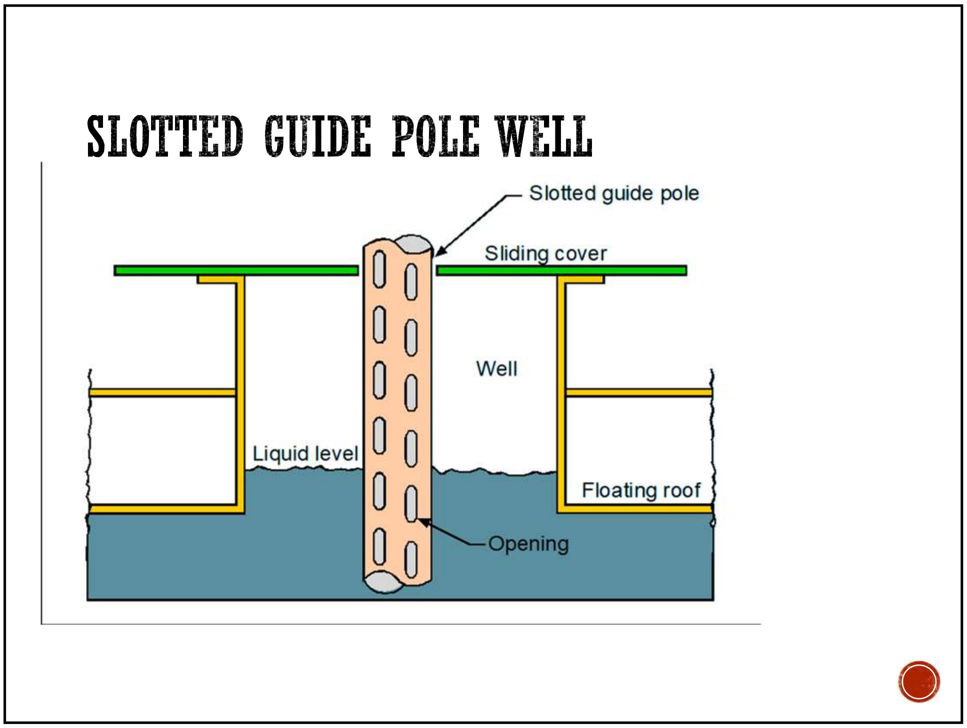
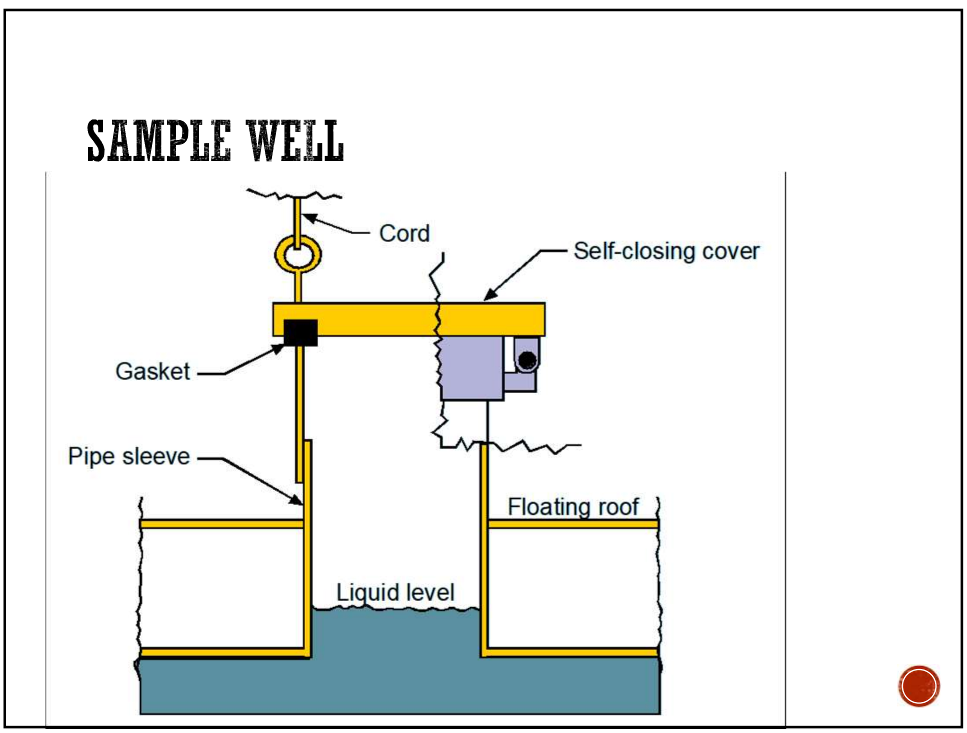
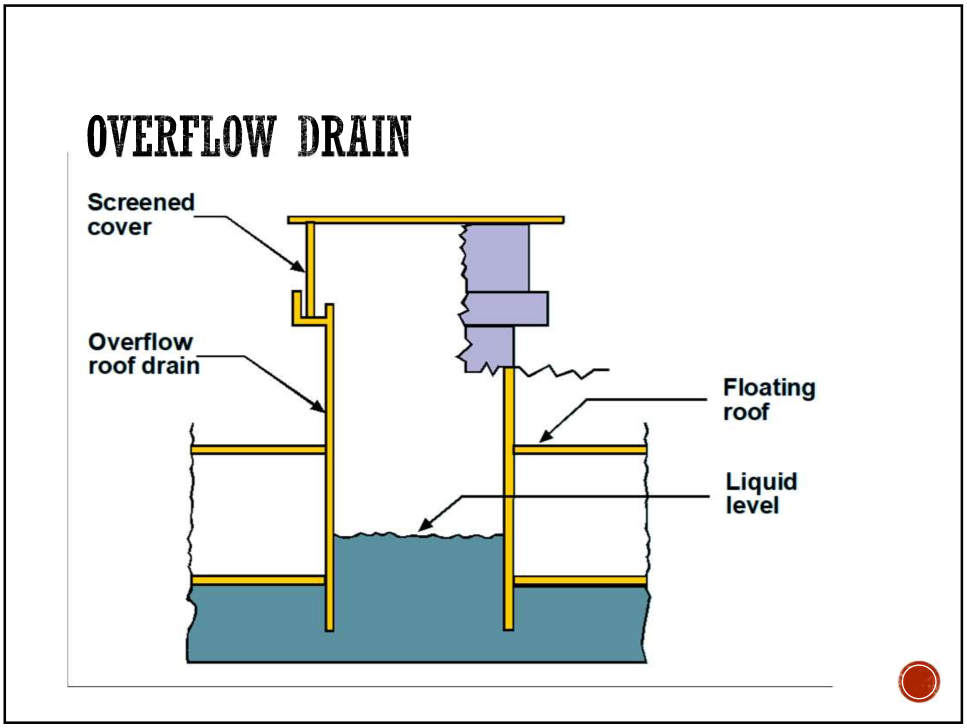

SLOTTED GUIDE POLE WELL
Slotted guide pole
Sliding cover
Well
Liquid level
Floating roof
Opening

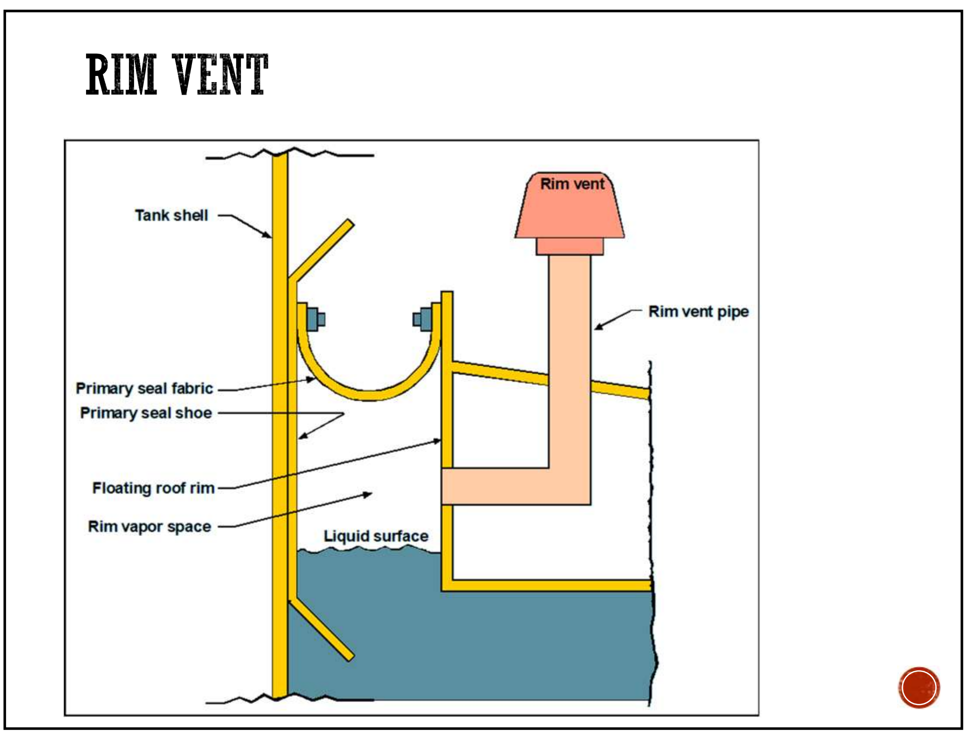
25


SAMPLE WELL
Cord
Self-closing cover
Gasket
Pipe sleeve
Floating roof
Liquid level

26


OVERFLOW DRAIN
Screened cover
Overflow roof drain
Floating roof
Liquid level

27


RIM VENT
Rim vent
Tank shell
Rim vent pipe
Primary seal fabric
Primary seal shoe
Floating roof rim
Rim vapor space
Liquid surface

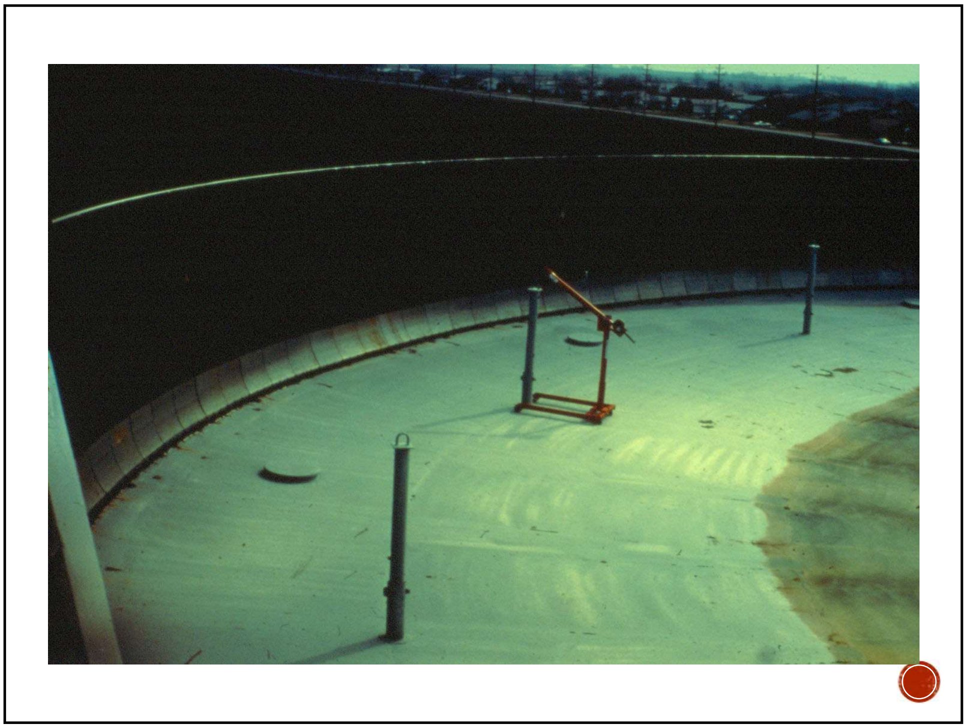
28

SOURCES OF VOC LOSSES

- Rim seal
- Roof fittings
- Wet tank wall

29

30



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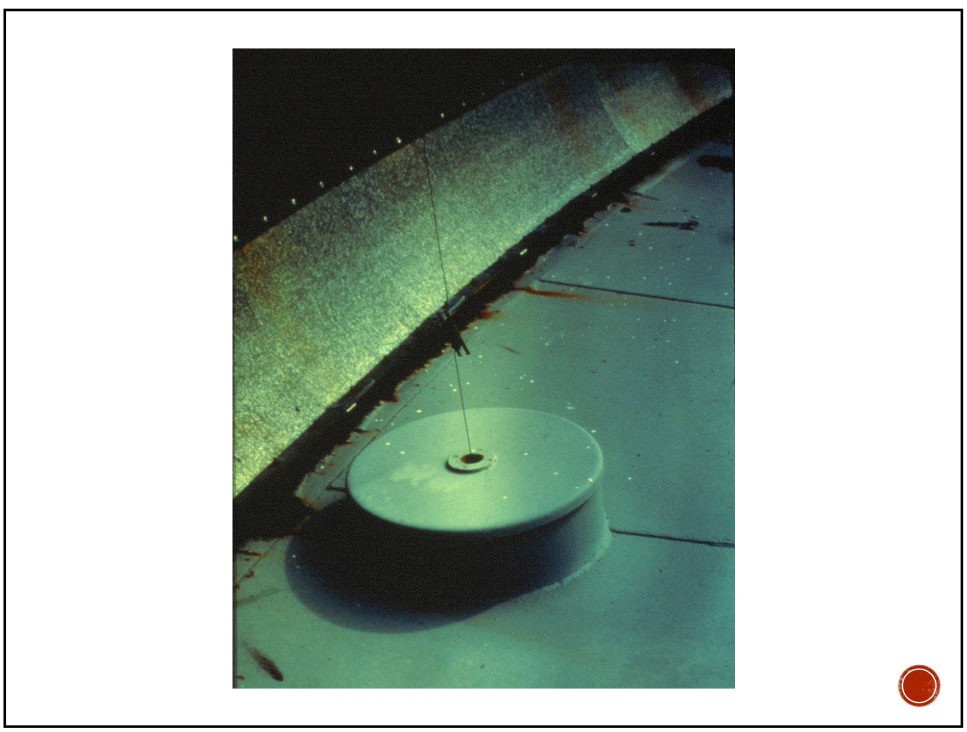

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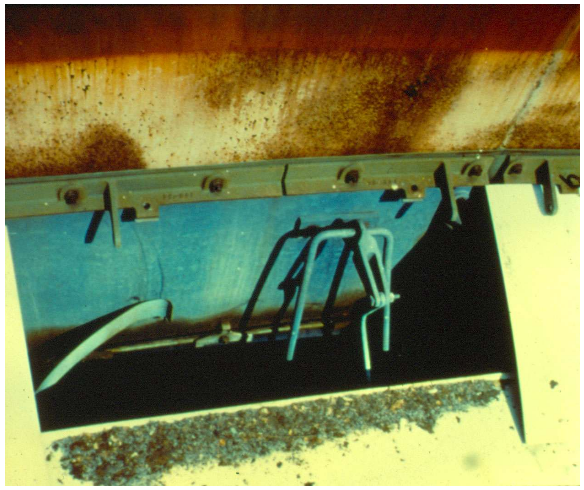

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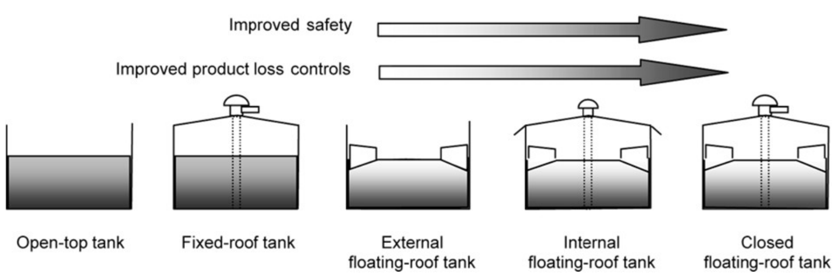
Emission **Control** Techniques



38

FIXED ROOF TANKS

INTERNAL FLOATING ROOF

VAPOR RECOVERY SYSTEM

39

BASIC INTERNAL FLOATING ROOF DESIGN

- Non-contact bolted roof
- Primary vapor mounted wiper seal
- Uncontrolled fittings

40

DISTRIBUTION OF VOC LOSSES FOR INTERNAL FLOATING ROOF TANKS

Rim seal losses	35%
Fitting losses	35%
Deck seam losses	18%
Withdrawal losses	12%

41

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**

42

CONTROLLED AND UNCONTROLLED INTERNAL FLOATING ROOF DECK FITTINGS (CONTINUED)

Deck Fitting Type	Equipment Description	
	Uncontrolled	Controlled
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

43

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%

44

BASIC EXTERNAL FLOATING ROOF DESIGN

- Welded steel roof
- Mechanical shoe primary seal
- Uncontrolled fittings

45

DISTRIBUTION OF VOC LOSSES FOR EXTERNAL FLOATING ROOF TANKS

Rim seal losses	68%
Fitting losses	28%
Withdrawal losses	4%

46

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

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CONTROLLED AND UNCONTROLLED EXTERNAL FLOATING ROOF DECK FITTINGS (CONTINUED)

Deck Fitting Type	Equipment Description	
	Uncontrolled	Controlled
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

48

EXTERNAL FLOATING ROOF RIM SEAL SYSTEM CONTROL EFFICIENCY

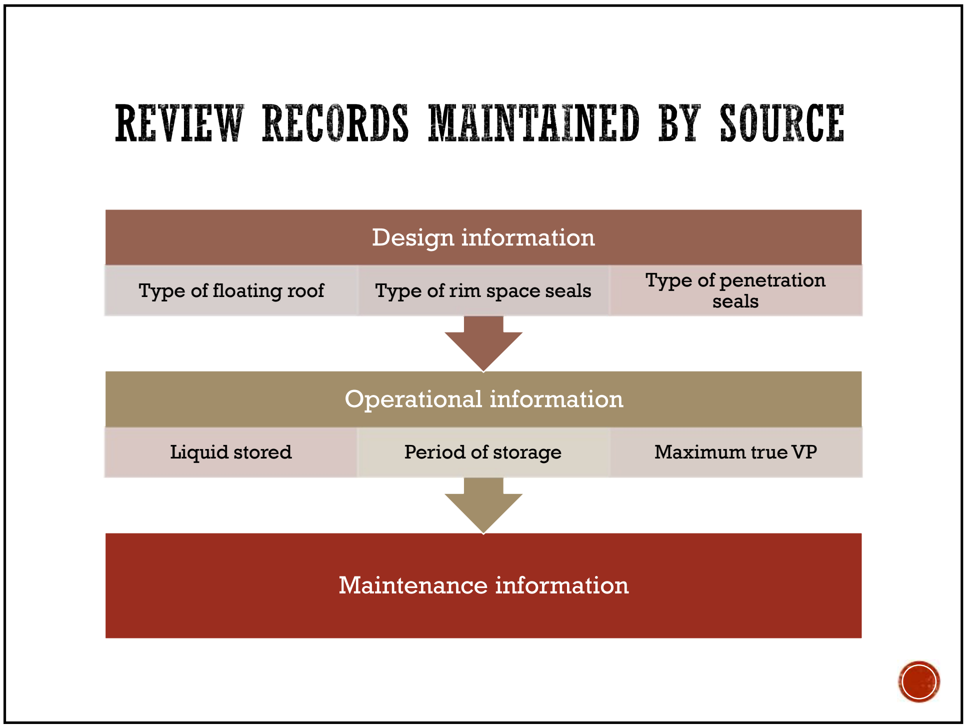
Seal System Description	Efficiency Relative to Baseline
Vapor mounted primary seal only	Baseline
Vapor mounted primary seal with secondary seal	66%
Mechanical shoe primary seal only	84%
Mechanical shoe primary seal with shoe mounted secondary seal	95%
Liquid mounted primary seal only	95%
Mechanical shoe primary seal with rim mounted secondary seal	99%
Liquid mounted primary seal with rim mounted secondary seal	99%

49

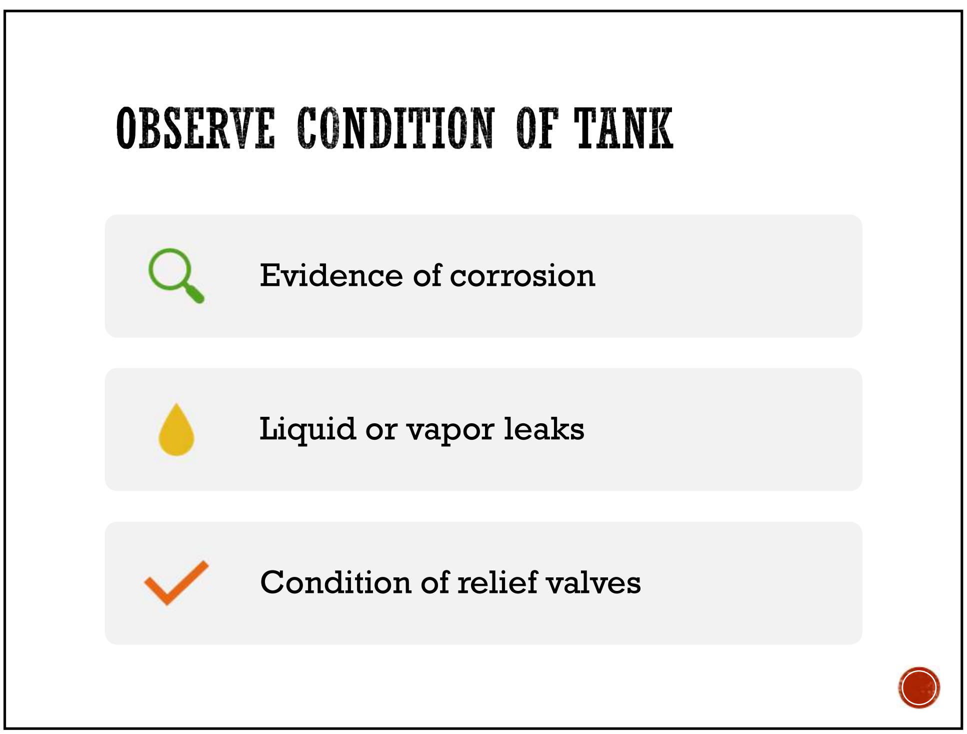
PROCESS INSPECTION

- Review records maintained by source
- Observe condition of tank
- Observe floating roof
- Measure rim seal gap areas

50


REVIEW RECORDS MAINTAINED BY SOURCE
Design information
Type of floating roof
Type of rim space seals
Type of penetration seals
Operational information
Liquid stored
Period of storage
Maximum true VP
Maintenance information

51


OBSERVE CONDITION OF TANK
Evidence of corrosion
Liquid or vapor leaks
Condition of relief valves

52

OBSERVE FLOATING ROOF

- SAFETY
- General condition
- Roof floating on liquid
- Liquid accumulation on roof
- Condition of rim space seals
- Roof penetrations

53

PROCESS INSPECTION

REVIEW RECORDS MAINTAINED BY SOURCE

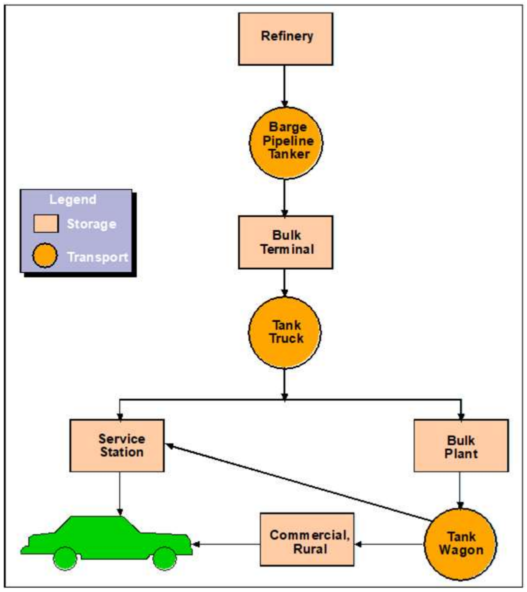
OBSERVE CONDITION OF TANK

OBSERVE FLOATING ROOF

MEASURE RIM SEAL GAP AREAS

54

GASOLINE MARKETING SYSTEM



55

EMISSION CONTROL TECHNIQUES

Collect vapors emitted at end of chain and transport to beginning of chain for recovery or destruction

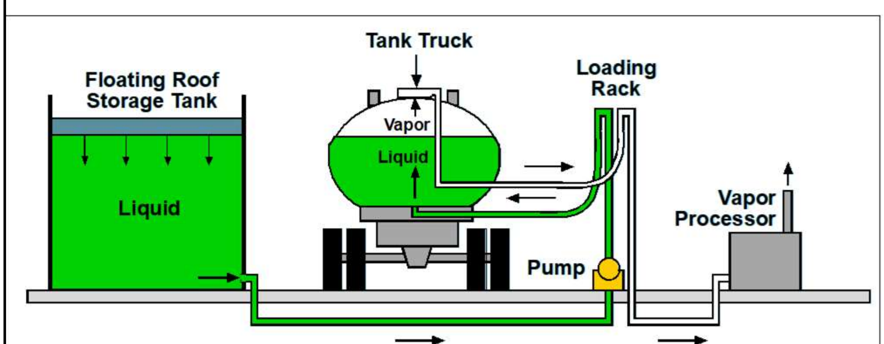
56

TANK TRUCKS

- Must be equipped with vapor return piping
- System must be free of significant leaks

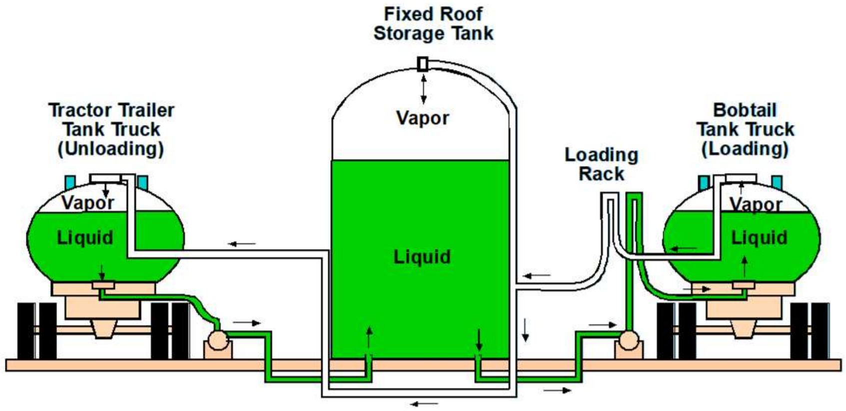
57

BULK TERMINALS



58

BULK PLANTS



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SERVICE STATIONS

STAGE I CONTROLS

STAGE II CONTROLS

60

MAY 2024 NESHAP/NSPS UPDATE FOR GASOLINE DISTRIBUTION

On **May 8, 2024**, EPA finalized major changes affecting approximately **9,500 facilities**:

- **New NSPS Subpart XXa** (40 CFR Part 60) — for bulk gasoline terminals that commenced construction, modification, or reconstruction after June 10, 2022; effective July 8, 2024
- **Revised NESHAP Subpart R** (major sources, 40 CFR 63) and **Subpart BBBBBB / "6B"** (area sources) — compliance deadline May 10, 2027
- Key changes the rules impose:
  • Lower loading rack emission limits
  • Strengthened cargo tank vapor-tightness requirements
  • Additional storage tank controls under both major and area source NESHAP
  • Tighter equipment leak detection and repair requirements
  • New performance testing and compliance reporting

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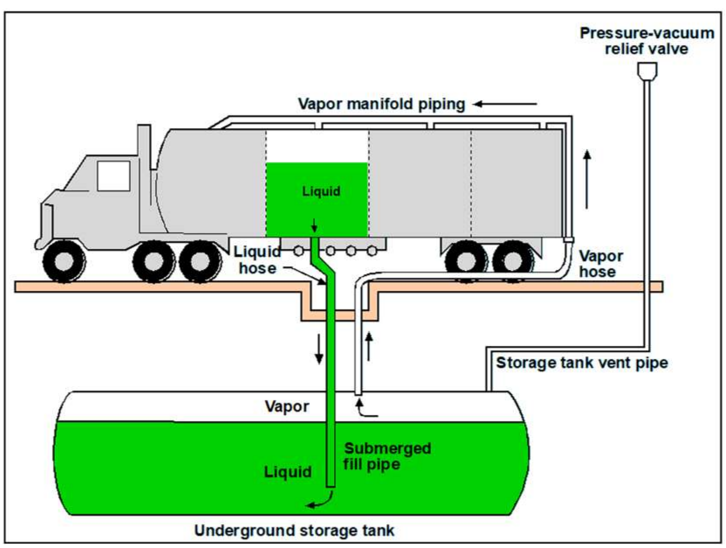
STAGE I CONTROL



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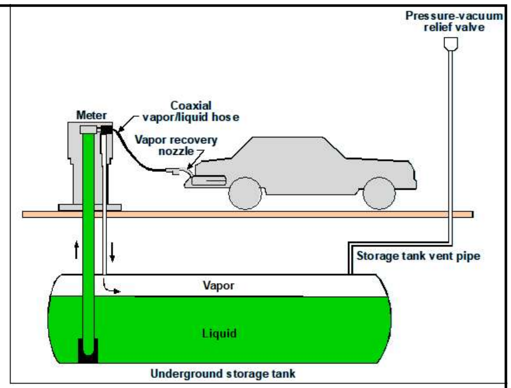
STAGE II CONTROL



- **May 16, 2012:** EPA finalized a rule allowing decommissioning of Stage II since ORVR was found to be in "widespread use"
- **Since 2006:** All new vehicles, light/medium-duty trucks have ORVR
- **Most states have decommissioned Stage II:** Texas (2014 onward), Pennsylvania (by Dec 2022), most New England states, etc.
- Some states (e.g. California) retain Stage II under separate state authority

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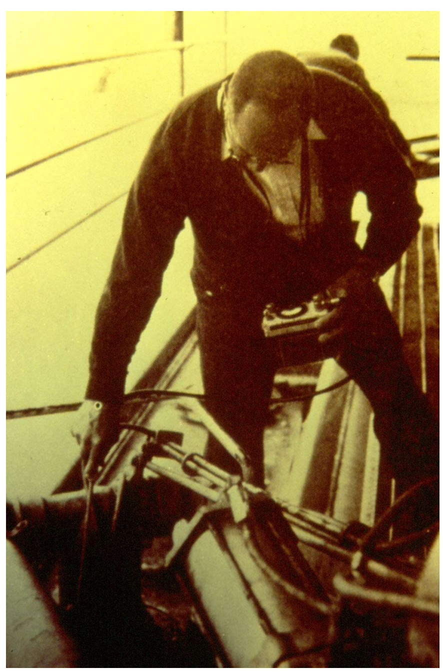
ONBOARD REFUELING VAPOR RECOVERY (ORVR)

- Displaced vapors sent to onboard carbon adsorber
- Carbon regenerated while vehicle is in operation
- Recovered vapors sent to engine air intake and burned

- **1998:** ORVR required on new passenger cars (phased in)
- **2006:** All new passenger cars, light/medium trucks have ORVR
- **2026:** Effectively full ORVR penetration of the on-road light-duty fleet (older non-ORVR vehicles essentially retired)

64

65



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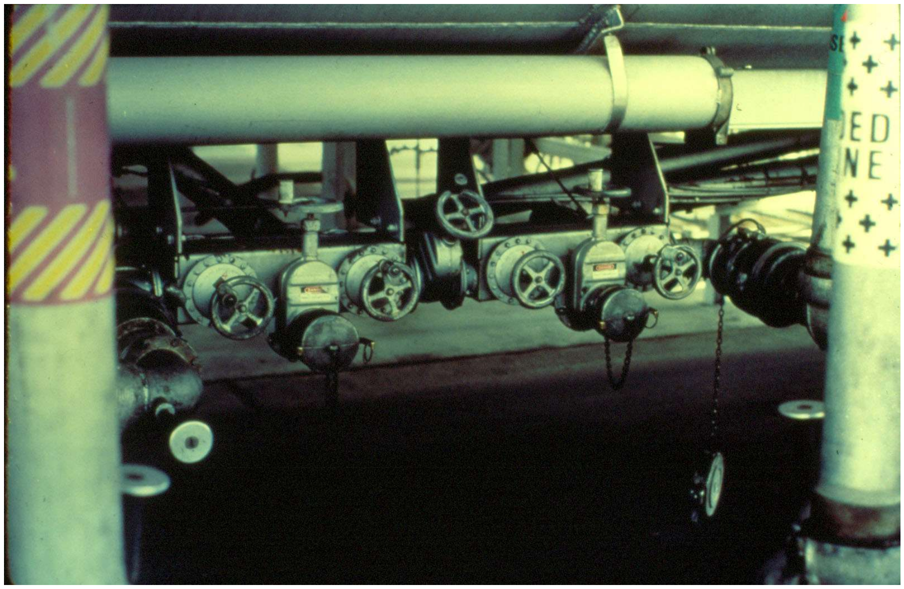

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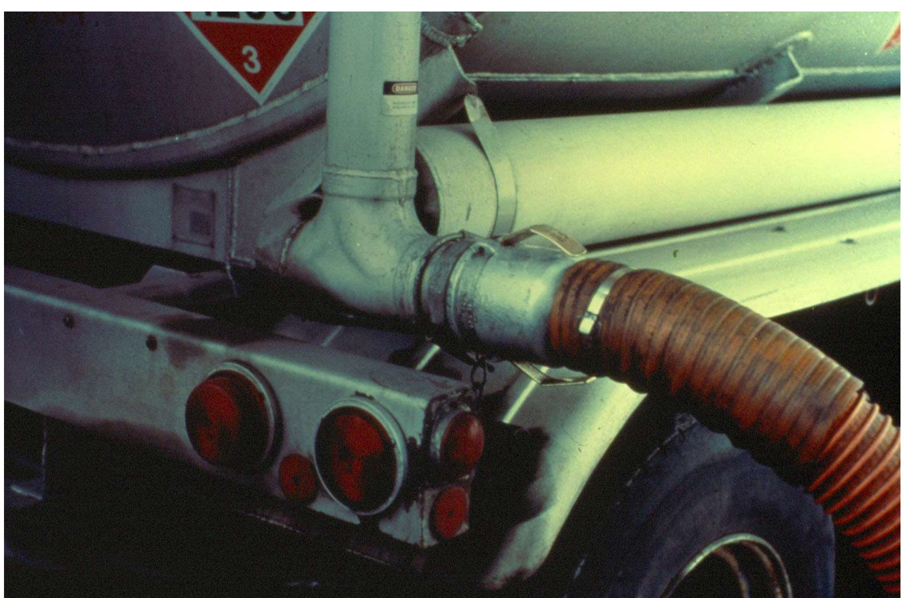

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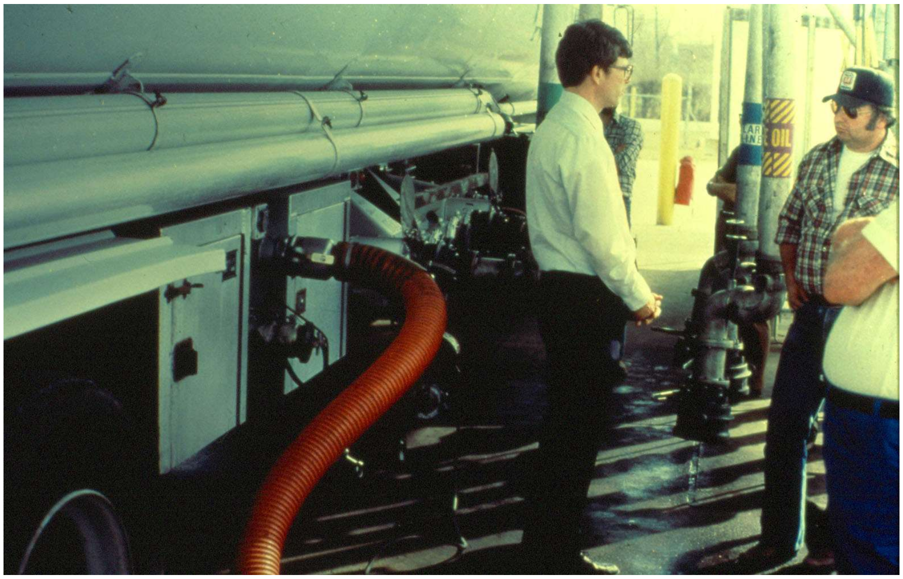

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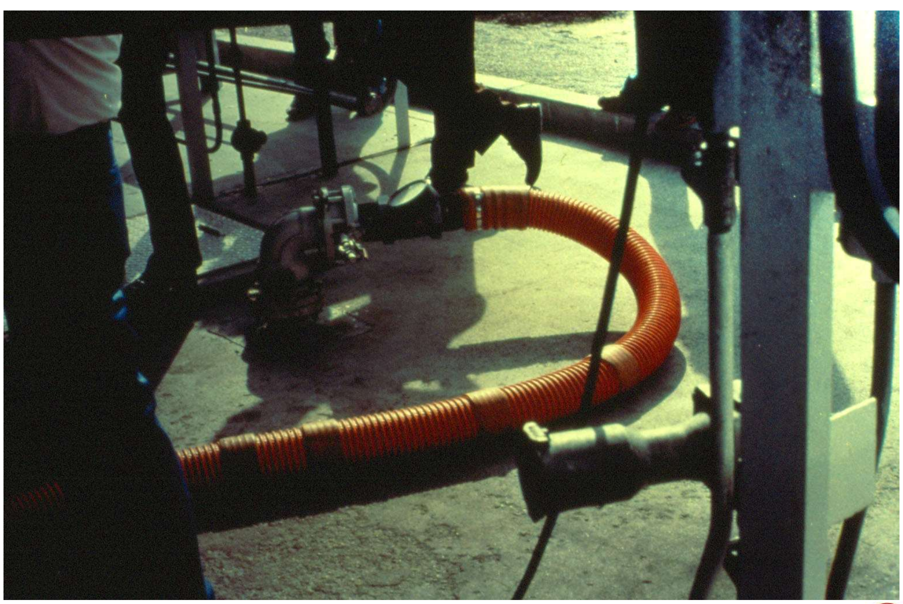

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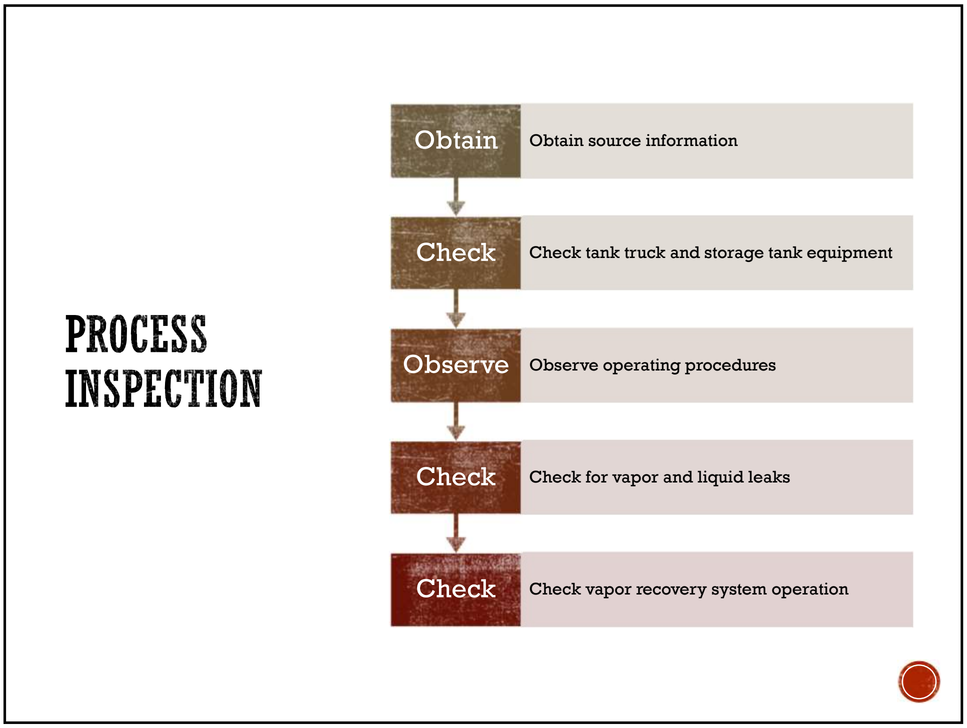
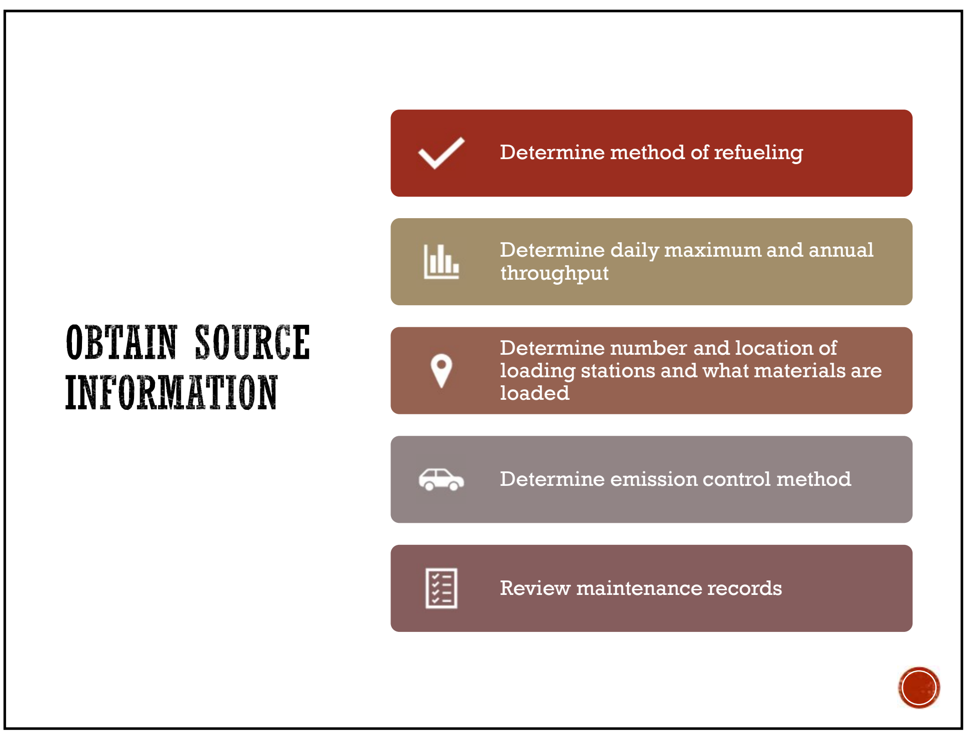

PROCESS INSPECTION
Obtain
Obtain source information
Check
Check tank truck and storage tank equipment
Observe
Observe operating procedures
Check
Check for vapor and liquid leaks
Check
Check vapor recovery system operation

71


OBTAIN SOURCE INFORMATION
Determine method of refueling
Determine daily maximum and annual throughput
Determine number and location of loading stations and what materials are loaded
Determine emission control method
Review maintenance records

72

CHECK TANK TRUCK AND STORAGE TANK EQUIPMENT

- **Determine** – Determine if properly equipped for vapor recovery
- **Determine** – Determine if tank truck has valid leak-tightness certification
- **Verify** – Verify submerged fill

73

OBSERVE OPERATING PROCEDURES

- **Verify** – Verify that vapor return line is connected
- **Verify** – Verify that other return lines are closed
- **Verify** – Verify that overfill sensor is connected
- **Verify** – Verify that relief valves do not open
- **Check** – Check for switch loading

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CHECK FOR VAPOR AND LIQUID LEAKS

- **Check**: Check piping, hoses, connectors, covers and relief valves for vapor leaks
- **Check**: Check piping, hoses, connectors, covers and tank shell for liquid leaks
- **Verify**: Verify no spills or excessive drips when lines are disconnected

75

CHECK VAPOR RECOVERY SYSTEM OPERATION

01 Verify system is operating during loading or when accumulator is full

02 If not operating, verify accumulator is filling

03 Verify that pressure relief valves are closed

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DEGREASING

Presentation: 14

Chapter 10 – Degreasing

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

DEGREASING

Presentation: 14

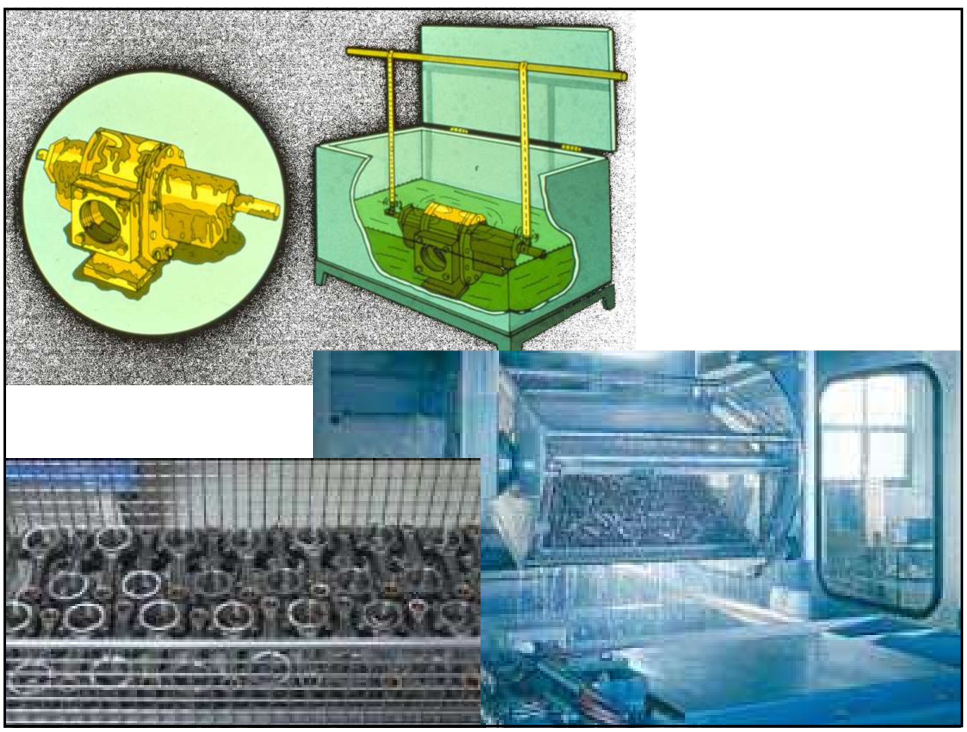
Chapter 10 – Degreasing

2

DEGREASING

- Degreasers, or organic solvent cleaners, use organic solvents or their vapors to remove grease, oil, wax, tar, carbon deposits and fluxes from metal, plastic, printed circuit boards, and other surfaces.
- This cleaning is typically done prior to such processes as painting, plating, heat treating and machining, or as part of maintenance operations.

3



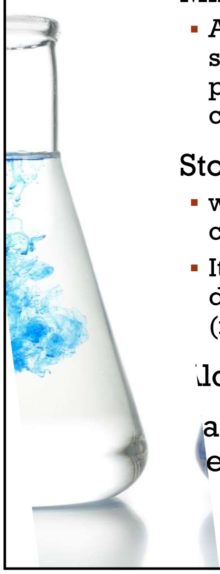
4

TYPES OF DEGREASING EQUIPMENT

- Cold cleaners: 2M
- Open top vapor cleaners: 35K
- In-line cleaners: 6K

5

DEGREASING SOLVENTS



- Mineral spirits
  - Aka mineral turpentine, turpentine substitute, and petroleum spirits, is a petroleum-derived clear liquid used as a common organic solvent in painting
- Stoddard solvents
  - widely used synthetic, organic solvent that comes from the refining of crude oil.
  - It is a petroleum mixture made from distilled alkanes, cycloalkanes (naphthenes), and aromatic compounds.
- lcohols
- alogenated solvents (carburetor eaners and vapor cleaners)

6

HALOGENATED SOLVENTS

- Methylene chloride
- Perchloroethylene
- Trichloroethylene
- Hydrochlorofluorocarbons

7

SOLVENT SELECTION HAS CHANGED

Traditional vapor degreasing relied heavily on halogenated solvents because they were effective, nonflammable, and had dense vapors.

However, many traditional solvents now raise major regulatory, health, and environmental concerns:

- **Methylene chloride** — EPA finalized a TSCA rule banning consumer uses and most industrial/commercial uses, with limited critical-use exemptions and worker-protection requirements.
- **Trichloroethylene, TCE** — EPA finalized a TSCA rule in December 2024 addressing unreasonable risk, restricting or prohibiting many uses with transition periods and limited exemptions.
- **Perchloroethylene, PCE/perc** — should be flagged as a high-concern chlorinated solvent; verify current use restrictions before presenting as a routine option.
- **1,1,1-trichloroethane and many HCFCs** — largely obsolete because of ozone-depletion phaseout concerns.
- **Aqueous, semi-aqueous, modified alcohol, hydrocarbon, and enclosed vacuum-vapor systems** are increasingly used as alternatives.

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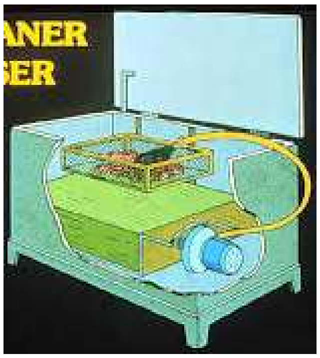
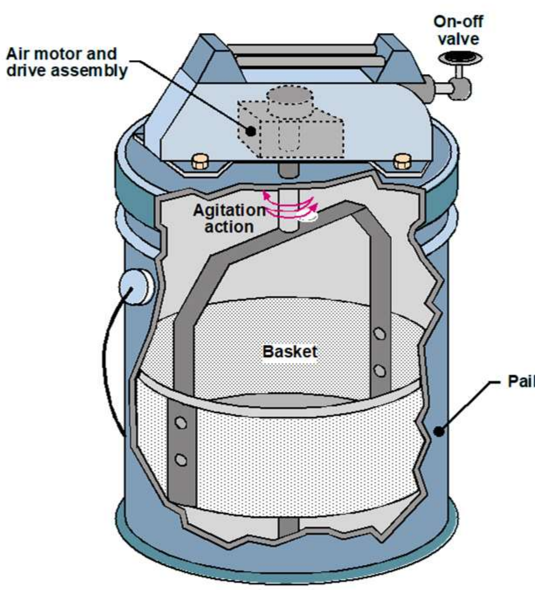


COLD CLEANERS

9

CARBURETOR CLEANER



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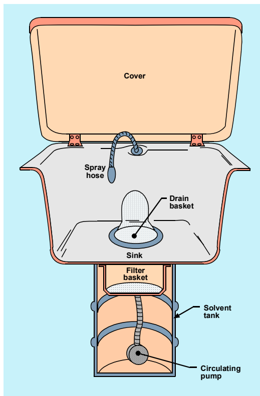
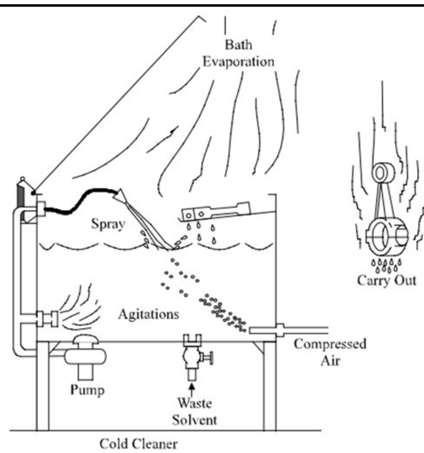
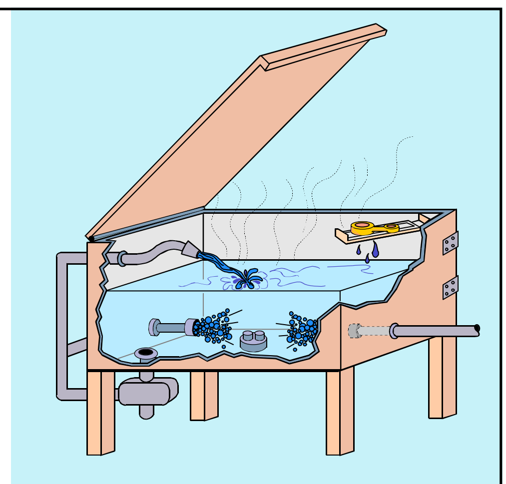


SPRAY SINK

11





DIP TANK COLD CLEANER

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POTENTIAL SOURCES OF EMISSIONS

- Waste solvent disposal
  - greatest potential source of emissions
- Solvent carryout
- Bath evaporation
  - the greatest actual source of emissions

Table 4.6-1 (Metric And English Units). NONMETHANE VOC EMISSIONS FROM SMALL COLD CLEANING DEGREASING OPERATIONS[a]

EMISSION FACTOR RATING: C

Operating Period		Per Capita Emission Factor
Annual	25 percent 1,1,1 trichloroethane, methylene chloride, and trichlorotrifluoroethane.	1.8 kg 4.0 lb
Daily[b]		5.8 g 0.013 lb

[a] Reference 3.
[b] Assumes a 6-day operating week (313 days/yr).

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Open Top Vapor Cleaners

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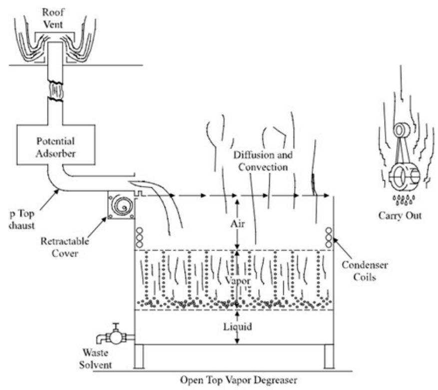
OPEN TOP VAPOR CLEANER

- Open top vapor cleaners are used primarily in metalworking and other manufacturing operations.
- Tank equipped with a heating system to boil the liquid solvent.
- As the solvent boils, dense vapors rise to the level of the primary condensing coils.
- Coolant, usually chilled water, is circulated through the coils in order to condense the rising solvent vapors and create a controlled vapor zone that reduces losses from the tank.



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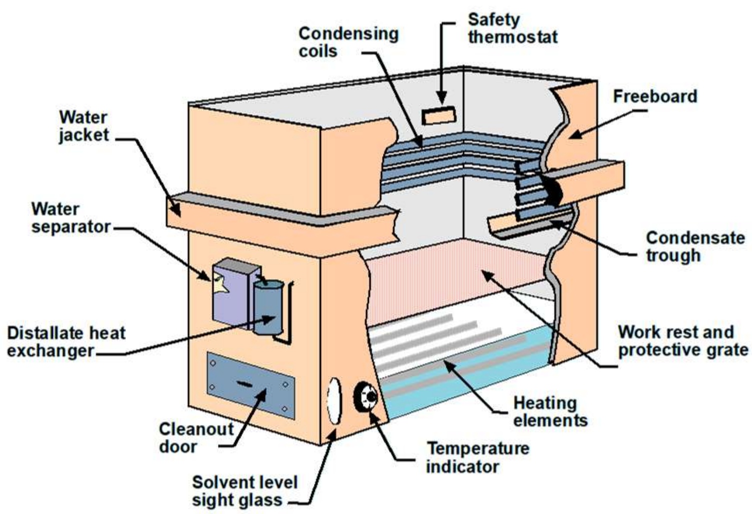
OPEN TOP VAPOR CLEANER



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POTENTIAL SOURCES OF EMISSIONS

- Waste solvent disposal
- Solvent carryout
- Bath evaporation

Table 4.6-2 (Metric And English Units). SOLVENT LOSS EMISSION FACTORS FOR DEGREASING OPERATIONS

EMISSION FACTOR RATING: C

Type Of Degreasing	Activity Measure	Uncontrolled Organic Emission Factor[a]	
All[b]	Solvent consumed	1,000 kg/Mg	2,000 lb/ton
Cold cleaner			
Entire unit[c]	Units in operation	0.30 Mg/yr/unit	0.33 tons/yr/unit
Waste solvent loss		0.165 Mg/yr/unit	0.18 tons/yr/unit
Solvent carryout		0.075 Mg/yr/unit	0.08 tons/yr/unit
Bath and spray evaporation		0.06 Mg/yr/unit	0.07 tons/yr/unit
Entire unit	Surface area and duty cycle[d]	0.4 kg/hr/m^2	0.08 lb/hr/ft^2
Open top vapor			
Entire unit	Units in operation	9.5 Mg/yr/unit	10.5 ton/yr/unit
Entire unit	Surface area and duty cycle[e]	0.7 kg/hr/m^2	0.15 lb/hr/ft^2
Conveyorized, vapor			
Entire unit	Units in operation	24 Mg/yr/unit	26 tons/yr/unit
Conveyorized, nonboiling			
Entire unit	Units in operation	47 Mg/yr/unit	52 tons/yr/unit

[a] 100% Nonmethane VOC.
[b] Solvent consumption data will provide much more accurate emission estimates than any of the other factors presented.
[c] Emissions generally would be higher for manufacturing units and lower for maintenance units.
[d] Reference 4, Appendix C-6. For trichloroethane degreaser.
[e] For trichloroethane degreaser. Does not include waste solvent losses.

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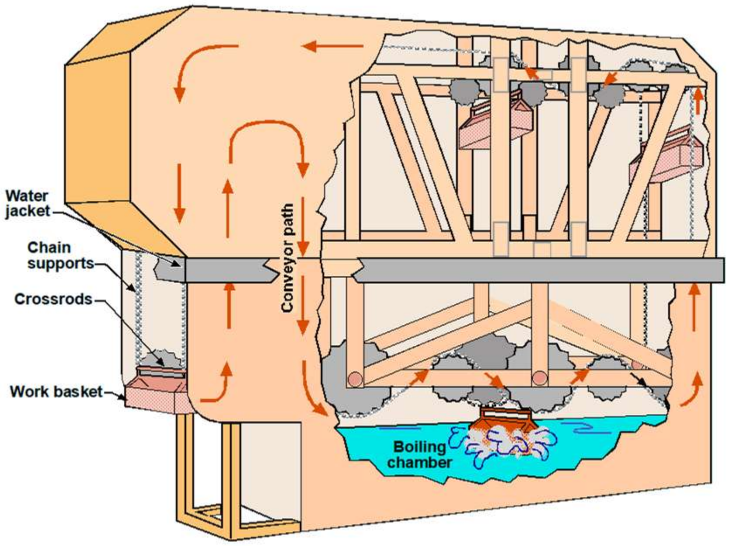
CROSS-ROD CLEANER



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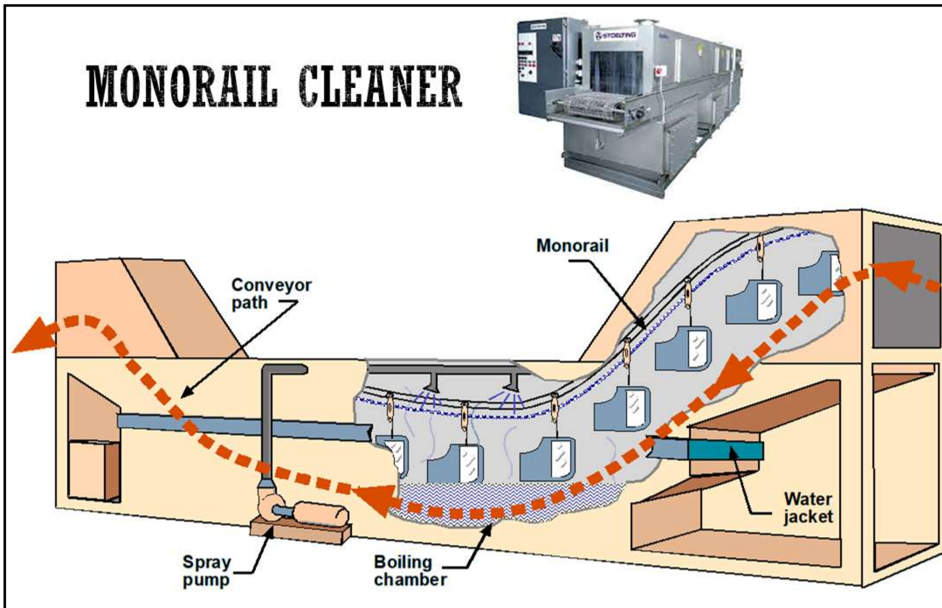
MONORAIL CLEANER



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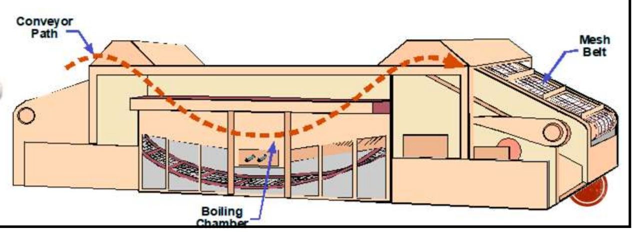
MESH BELT CLEANER

- Production of printed circuit boards is a common application of the mesh belt cleaner.
- The circuit pattern is produced by projecting ultraviolet rays through an artwork film onto a copper sheet covered with resist, causing the exposed areas to harden.
- A developer, such as 1,1,1-trichloroethane, is used to dissolve the unexposed resist, and then an acid is used to remove the copper not covered by the hardened resist.
- Next, a stripping agent, such as methylene chloride, is used to remove the hardened resist, exposing the circuit pattern.
- Finally, molten solder is bonded to the copper circuit and a defluxer, is used to dissolve the solder flux.



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EMISSION CONTROL TECHNIQUES (COLD CLEANERS AND OPEN TOP VAPOR CLEANERS)

- Water cover (cold cleaner only)
- Manual or powered cover
- Refrigerated freeboard device
  - second set of cooling coils located above the primary condenser.
  - cool the air immediately above the vapor zone,
  - creating a temperature inversion that reduces the mixing of air and solvent vapors
- Refrigerated primary condenser
  - operates at a temperature of 40°F to 50°F.
- Increased freeboard ratio
- Reduced room draft
- Enclosed designs
- Mechanically assisted parts handling
- Carbon adsorption
- Operation and maintenance

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Table 4.6-3. PROJECTED EMISSION REDUCTION FACTORS FOR SOLVENT DEGREASING[a]

System	Cold Cleaner		Vapor Degreaser		Conveyorized Degreaser	
	A	B	A	B	A	B
Control devices						
Cover or enclosed design	X	X	X	X	X	X
Drainage facility	X	X	X			X
Water cover, refrigerated chiller, carbon adsorption or high freeboard[b]		X		X		X
Solid, fluid spray stream[c]		X		X		
Safety switches and thermostats				X		X
Emission reduction from control devices (%)	13-38	NA[d]	20-40	30-60		40-60
Operating procedures						
Proper use of equipment	X	X	X	X	X	X
Waste solvent reclamation	X	X	X	X	X	X
Reduced exhaust ventilation			X	X	X	X
Reduced conveyor or entry speed			X	X	X	X
Emission reduction from operating procedures (%)	15-45	NA[d]	15-35	20-40	20-30	20-30
Total emission reduction (%)	28-83[e]	55-69[f]	30-60	45-75	20-30	50-70

[a] Reference 2. Ranges of emission reduction present poor to excellent compliance. X indicates devices or procedures that will produce the given reductions. Letters A and B indicate different control device circumstances. See Appendix B of Reference 2.

[b] Only one of these major control devices would be used in any degreasing system. Cold cleaner system B could employ any of them. Vapor degreaser system B could employ any except water cover. Conveyorized degreaser system B could employ any except water cover and high freeboard.

[c] If agitation by spraying is used, the spray should not be a shower type.

[d] Breakout between control equipment and operating procedures is not available.

[e] A manual or mechanically assisted cover would contribute 6 - 18% reduction; draining parts 15 seconds within the degreaser, 7 - 20%; and storing waste solvent in containers, an additional 15 - 45%.

[f] Percentages represent average compliance.

23

OPERATION AND MAINTENANCE

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

24

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

25

EMISSIONS AND CONTROL SUMMARY

Emission source	Why emissions occur	Controls / good practices
Bath evaporation	Solvent exposed to air	Covers, higher freeboard, low-vapor-pressure solvent, refrigerated freeboard
Solvent carryout	Solvent trapped on parts	Drain parts, rotate baskets, slow hoist speed, drying tunnel
Spray losses	Spraying above vapor zone or splashing	Spray only below vapor level, low-pressure spray, avoid splashing
Waste solvent handling	Open waste containers and transfers	Closed containers, closed transfer, proper disposal/recycling
Vapor-zone disturbance	Drafts and rapid part movement	Reduce room drafts, hoist speed limits, covers
Leaks	Pumps, hoses, drains, fittings	Inspection, prompt repair, maintenance records
Poor operation	Covers left open, overloading, water contamination	Operator training, labels, safety interlocks, water separator maintenance

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EMISSION REGULATION

27

REGULATORY SUMMARY

Regulatory area	Applies to	Main idea
Industrial Cleaning Solvents CTG	Industrial cleaning solvent operations	Low-VOC cleaning materials, low vapor pressure alternatives, work practices, or add-on control
Solvent Metal Cleaning CTG	Cold cleaners, open-top vapor cleaners, in-line cleaners	RACT operating practices and equipment controls
40 CFR Part 63, Subpart T	Halogenated solvent cleaning machines	NESHAP requirements for machines using listed halogenated HAP solvents
TSCA chemical-specific rules	Certain solvents such as methylene chloride and TCE	Restrictions, phaseouts, worker-protection requirements, and allowed-use limits
State/local rules and permits	Facility-specific	May be more stringent than federal guidance

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INDUSTRIAL CLEANING SOLVENTS , CONTROL TECHNIQUE GUIDELINE DOCUMENT, EPA-HQ-OAR-2006-0535 {SUPPL. MATR}

These unit operations are identified below together with the VOC emission distribution based on the system material balance data:

1. Spray Gun Cleaning (50 percent);
2. Spray Booth Cleaning (14 percent);
3. Large Manufactured Components Cleaning (14 percent);
4. Parts Cleaning (7.0 percent);
5. Equipment Cleaning (6.9 percent);
6. Line Cleaning (3.6 percent);
7. Floor Cleaning (2.9 percent);
8. Tank Cleaning (0.82 percent); and
9. Small Manufactured Components Cleaning (0.44 percent)

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INDUSTRIAL CLEANING SOLVENTS , CONTROL TECHNIQUE GUIDELINE DOCUMENT, EPA-HQ-OAR-2006-0535

- Recommend a generally applicable VOC content limit of 50 grams VOC per liter (0.42 1b/gal) of cleaning material
- unless emissions are controlled by an emission control system with an overall control efficiency of at least 85 percent.

Alternative Composite Vapor Pressure Limit

- EPA is recommending inclusion of a composite vapor pressure limit of 8 millimeters of mercury (mmHg) at 20 degrees Celsius, as

1) a replacement for the 50 g/l VOC content limit entirely; or
2) an alternative limit that may be used in lieu of the 50 g/l VOC content limit for specific operations as determined by the State or local agency.

30

SOLVENT METAL CLEANING, CONTROL TECHNIQUE GUIDELINE DOCUMENT, EPA-450/2-77-022 {SUPPL. MATR}

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.

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Recommended standard: Cold cleaners

System A:

- Cover
- Facility for draining cleaned parts
- Label summarizing operating requirements
  - Proper disposal of waste solvent
  - Close degreaser when not handling parts
  - Drain cleaned parts for 15 seconds or until dripping stops

System B:

- Cover (operate with one hand if VP >0.3 psi at 100°F or agitated)
- Facility for draining cleaned parts (must be internal if VP >0.6 psi at 100°F
- Solid spray at pressure minimizing splashing
- Major control device (if VP >0.6 psi at 100°F or solvent is >120°F
  - Freeboard ratio greater than 0.7
  - Water cover
  - Other equivalent control

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Recommended standard: Open top vapor cleaners

System A:

- Cover, closed except when processing
- Minimize solvent carryout
  - Rack parts for drainage
  - Move parts in and out at less than 11 ft/min
  - Degrease for 30 seconds or until condensation stops
  - Tip out pools of solvent
  - Dry parts within degreaser for 15 seconds or until visually dry
- No porous or absorbent materials
- Work load not over half of open top area
- Vapor level drop should be less than 4 inches when parts enter
- Never spray above vapor level
- Repair leaks immediately
- Dispose of waste solvent properly
- Exhaust ventilation less than 65 cfm/ft2
- No water in solvent exiting separator

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Recommended standard: Open top vapor cleaners (continued)

System B:

- Powered cover if degreaser opening is greater than 10 ft^2
- Safety switches
  - Condenser flow switch and thermostat
  - Spray safety switch
- Major control device
  - Freeboard ratio greater than 0.75
  - Refrigerated chiller
  - Enclosed design
  - Carbon adsorption system or equivalent, with ventilation less than 50 cfm/ft^2 and exhausting less than 25 ppm
- Label summarizing operating procedures

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Recommended standard: In-line cleaners

System A:

- Exhaust ventilation less than 65 cfm/ft^2
- Minimize solvent carryout
  - Rack parts for drainage
  - Move parts in and out at less than 11 ft/min
- Dispose of waste solvent properly
- Repair leaks immediately
- No water in solvent exiting separator

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Recommended standard: In-line cleaners (continued)

System B:

- Major control device
  - Refrigerated chiller
  - Carbon adsorption system or equivalent, with ventilation less than 50 cfm/ft^2 and exhausting less than 25 ppm
- Drying tunnel or other means to prevent solvent carryout
- Safety switches
  - Condenser flow switch and thermostat
  - Spray safety switch
  - Vapor level control thermostat
- Minimize entrance and exit openings
- Down-time covers

Open top vapor degreasers with area <10.76 ft^2 and in-line cleaners with area <21.53 ft^2 should be exempted from major control device requirement. Facilities in rural non-attainment areas emitting <100 tons per year should also be exempt.

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NATIONAL EMISSION STANDARDS FOR HALOGENATED SOLVENT CLEANING, 40 CFR 63, SUBPART T {SUPPL MATR}

Applicability: Batch vapor, in-line vapor, in-line cold and batch cold cleaning machines that contain methylene chloride, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride or chloroform or any combination thereof in a total concentration greater than 5 percent by weight.

Standard: Batch cold cleaning machines

- Employ tight fitting cover and water layer at least 1 inch thick; or employ tight fitting cover and freeboard ratio of 0.75 or greater.
- Collect and store waste solvent in closed containers.
- Spray only within the freeboard area.
- Drain parts for 15 seconds or until dripping stops.
- Solvent level shall not exceed the fill line.
- Use agitation that produces a rolling action with no observable splashing.
- Do not expose machine to drafts greater than 132 fpm when the cover is open.
- Wipe up spills immediately.

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Standard: Batch vapor and in-line cleaning machines

- Employ idling and downtime mode cover or reduced room draft (50 fpm).
- Have a freeboard ratio of 0.75 or greater.
- Use automated system to move parts at 11 fpm or less.
- Shut off sump heat if solvent level drops to heater coils.
- Shut off sump heat if vapor level rises above primary condenser.
- Employ a primary condenser.
- Spray within the vapor zone.
- Parts shall not occupy more than half of cross-sectional area unless they are introduced at 3 fpm or less.
- Orient parts so that solvent drains freely.
- Employ one of the following control combinations or demonstrate idling emissions <0.045 pounds per hour per square foot for a batch vapor machine or <0.020 pounds per hour per square foot for an in-line machine.

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OPTION	CONTROL COMBINATION
1	Cover, freeboard ratio of 1.0, superheated vapor
2	Freeboard refrigeration device, superheated vapor
3	Cover, freeboard refrigeration device
4	Reduced room draft, freeboard ratio of 1.0, superheated vapor
5	Freeboard refrigeration device, reduced room draft

CONTROL COMBINATIONS FOR BATCH VAPOR MACHINES LESS THAN 13 FT^2 IN AREA

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OPTION	CONTROL COMBINATION
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

CONTROL COMBINATIONS FOR BATCH VAPOR MACHINES LESS THAN 13 FT^2 IN AREA

*Dwell is holding parts in the freeboard area above the vapor zone for drainage. Dwell time is calculated as 35% of the time required for parts in the vapor zone to stop dripping.

40

OPTION	CONTROL COMBINATION
1	Freeboard refrigeration device, freeboard ratio of 1.0, superheated vapor
2	Freeboard refrigeration device, dwell, reduced room draft
3	Cover, freeboard refrigeration device, superheated vapor
4	Freeboard ratio of 1.0, reduced room draft, superheated vapor

CONTROL COMBINATIONS FOR BATCH VAPOR MACHINES GREATER THAN 13 FT^2 IN AREA

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OPTION	CONTROL COMBINATION
5	Freeboard refrigeration device, reduced room draft, superheated vapor
6	Freeboard refrigeration device, freeboard ratio of 1.0, reduced room draft
7	Freeboard refrigeration device, carbon adsorber, superheated vapor

CONTROL COMBINATIONS FOR BATCH VAPOR MACHINES GREATER THAN 13 FT^2 IN AREA

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OPTION	CONTROL COMBINATION
1	Superheated vapor, freeboard ratio of 1.0
2	Freeboard refrigeration device, freeboard ratio of 1.0
3	Freeboard refrigeration device, dwell
4	Dwell, carbon adsorber

CONTROL COMBINATIONS FOR EXISTING IN-LINE MACHINES

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OPTION	CONTROL COMBINATION
1	Superheated vapor, freeboard refrigeration device
2	Freeboard refrigeration device, carbon adsorber
3	Superheated vapor, carbon adsorber

CONTROL COMBINATIONS FOR NEW IN-LINE MACHINES

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TECHNOLOGY UPDATES: LOWER-EMISSION CLEANING

Modern alternatives and improvements include:

- Aqueous alkaline cleaning systems.
- Semi-aqueous cleaning systems.
- Modified alcohol cleaning in enclosed vacuum systems.
- Enclosed vapor degreasers with automated handling.
- Solvent distillation and closed-loop recycling.
- Low-vapor-pressure cleaning materials.
- Ultrasonic cleaning to reduce solvent intensity.
- Automated covers and hoists to reduce dragout and evaporation.
- Carbon adsorption or refrigerated condensation for captured solvent vapors.

45

INSPECTION

46

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

47

REVIEW RECORDS MAINTAINED BY SOURCE

- Design information
- Operational information
- Maintenance information

48

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

49

REVIEW RECORDS MAINTAINED BY SOURCE

Operational information

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

50

REVIEW RECORDS MAINTAINED BY SOURCE

- Design information
- Operational information
- Maintenance information

51

CHECK EQUIPMENT OPERATION

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

52

DEGREASING INSPECTION CHECKLIST

Records to review

- Solvent type and SDS.
- Solvent purchase and usage records.
- Waste solvent shipment/recycling records.
- Degreaser dimensions and freeboard ratio.
- Cover type and operating condition.
- Control equipment type and operating records.
- Hoist or conveyor speed.
- Refrigerated condenser or chiller temperature.
- Carbon adsorber records, if used.
- Leak repair and maintenance logs.
- Applicable permit and Subpart T applicability.

Field observations

- Is the cover closed when parts are not being handled?
- Are parts drained before removal?
- Is spraying limited to the vapor zone?
- Are solvent containers and waste containers closed?
- Are there visible leaks, spills, or solvent odors?
- Is the vapor zone stable?
- Are drafts disturbing the vapor zone?
- Are operators following posted work-practice instructions?

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DRY CLEANING

Presentation: 15

Chapter 11 – Dry Cleaning

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

DRY CLEANING

Presentation: 15

Chapter 11 – Dry Cleaning

2

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

3

DRY CLEANING STEPS

WASHING

EXTRACTION

DRYING

4

DRY CLEANING SOLVENTS

PERCHLOROETHYLENE

PETROLEUM SOLVENTS

“Dry cleaning historically used perchloroethylene, but the industry is transitioning away from PCE because of health, environmental, and regulatory restrictions.”

5

EPA TSCA RULE FOR PERCHLOROETHYLENE

- EPA finalized a TSCA rule in December 2024 to address unreasonable risks from perchloroethylene.
- The rule bans or restricts many uses of PCE.
- For dry cleaning and spot cleaning, EPA’s rule includes a phaseout rather than treating PCE as a routine long-term solvent.
- Some remaining allowed uses may require a Workplace Chemical Protection Program or other prescriptive worker-protection controls.
- The rule is separate from the Clean Air Act dry-cleaning NESHAP.
- Always check the current EPA TSCA compliance dates, exemptions, and state requirements before inspecting PCE dry cleaners.

6

TECHNOLOGY UPDATES — ALTERNATIVES TO PCE DRY CLEANING

Alternative systems include:

- **Professional wet cleaning**
  - Uses water, detergents, computer-controlled washers, humidity-controlled dryers, and finishing equipment.
  - Very low VOC emissions.
  - Requires operator training and fabric-care expertise.
- **High-flashpoint hydrocarbon solvents**
  - Lower odor and lower volatility than traditional petroleum solvents.
  - Still VOC-containing and combustible.
  - Requires fire-safety controls and solvent management.
- **Silicone-based solvents**
  - Lower odor and different fabric compatibility profile.
  - Still requires review of SDS, emissions, waste, and local approval.
- **Liquid CO_2 cleaning**
  - Uses pressurized CO_2 as the cleaning medium.
  - Low VOC potential, but higher equipment complexity and capital cost.
- **Enclosed dry-to-dry machines**
  - Reduce transfer emissions and operator exposure.
  - Use refrigerated condensers, carbon adsorption, leak controls, and solvent recovery.

7

INDUSTRY CLASSES

- Commercial
- Industrial
- Coin operated

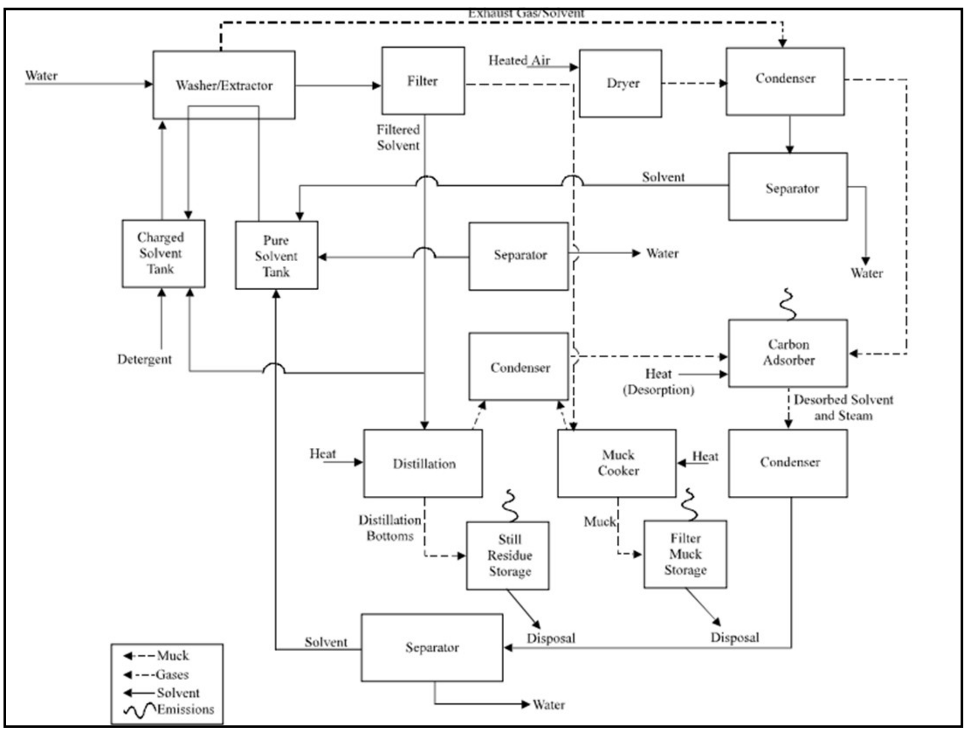
8

EQUIPMENT TYPES

TRANSFER

DRY-TO-DRY

9



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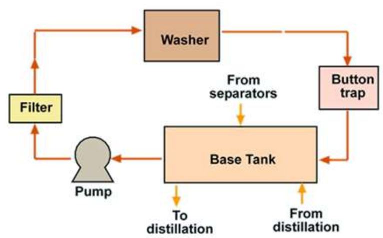
WASHING PROCESS



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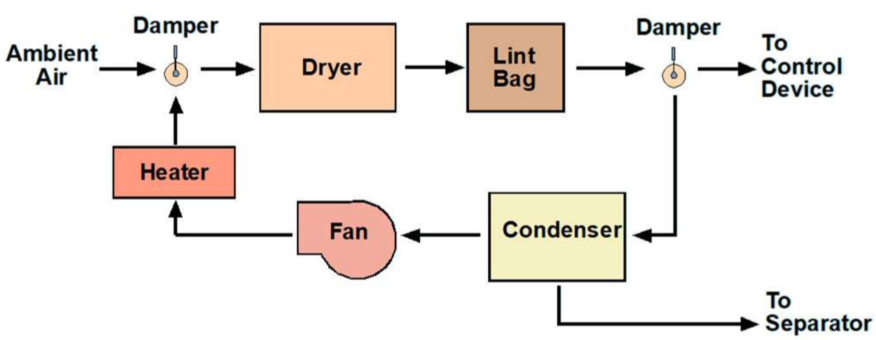
DRYING PROCESS



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SOLVENT FILTERING

- Powder filters
- Cartridge filters

13

SOLVENT DISTILLATION

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

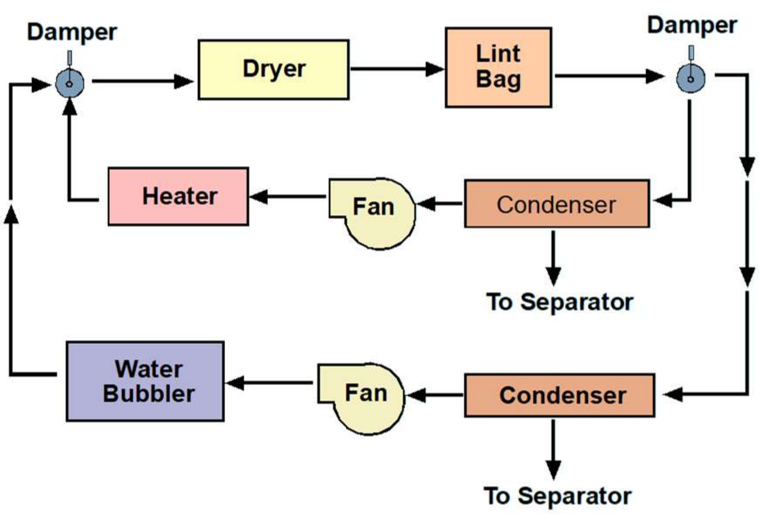
14

EMISSION CONTROL TECHNIQUES

- Fugitive emission control
- Carbon adsorption
- Condensation
- Azeotropic vapor recovery

15

AZEOTROPIC DRYING PROCESS



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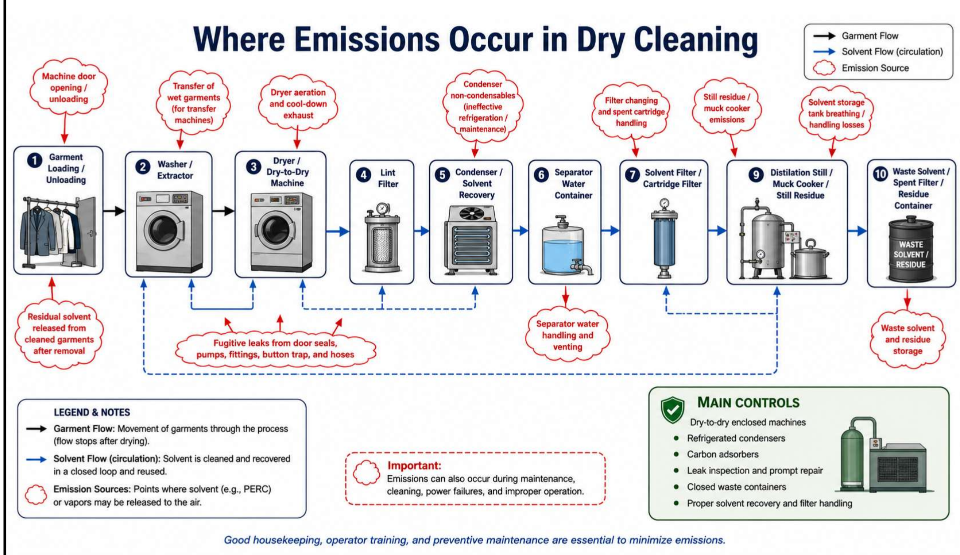

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Table 4.1-2 (Metric And English Units). PER CAPITA SOLVENT LOSS EMISSION FACTORS FOR DRY CLEANING PLANTS[a]

EMISSION FACTOR RATING: B

Operation	Emission Factors	
	kg/yr/capita (lb/year/cap)	g/day/capita[b] (lb/day/cap)
Commercial	0.6 (1.3)	1.9 (0.004)
Coin-operated	0.2 (0.4)	0.6 (0.001)

[a] References 2-4. All nonmethane VOC.
[b] Assumes a 6-day operating week (313 days/yr).

Emission Regulation

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Table 4.1-1 (Metric And English Units). SOLVENT LOSS EMISSION FACTORS FOR DRY CLEANING OPERATIONS

EMISSION FACTOR RATING: B

Solvent Type (Process Used)	Source	Emission Rate[a] Typical System, kg/100 kg (lb/100 lb)	Well-Controlled System, kg/100 kg (lb/100 lb)
Petroleum	Washer/dryer[b]	18	2[c]
(transfer process)	Filter disposal		
	Uncooked (drained)	8	
	Centrifuged		0.5 - 1
	Still residue disposal	1	0.5 - 1
	Miscellaneous[d]	1	1
Perchloroethylene	Washer/dryer/still/muck cooker	8[e]	0.3[c]
(transfer process)	Filter disposal		
	Uncooked muck	14	
	Cooked muck	1.3	0.5 - 1.3
	Cartridge filter	1.1	0.5 - 1.1
	Still residue disposal	1.6	0.5 - 1.6
	Miscellaneous[d]	1.5	1
Trichlorotrifluoroethane	Washer/dryer/still[f]	0	0
(dry-to-dry process)	Cartridge filter disposal	1	1
	Still residue disposal	0.5	0.5
	Miscellaneous[d]	1 - 3	1 - 3

[a] References 1-4. Units are in terms of weight solvent per weight of clothes cleaned (capacity x loads). Emissions also may be estimated by determining the amount of solvent consumed. Assuming that all solvent input is eventually evaporated to the atmosphere, an emission factor of 1000 kg/Mg (2000 lb/ton) of solvent consumed can be applied.

[b] Different materials in wash retain a different amount of solvent (synthetics, 10 kg/100 kg [10 lb/100 lb]; cotton, 20 kg/100 kg [20 lb/100 lb]; leather, 40 kg/100 kg [40 lb/100 lb]).

[c] Emissions from washer, dryer, still, and muck cooker are passed collectively through a carbon adsorber.

[d] Miscellaneous sources include fugitives from flanges, pumps, pipes, and storage tanks, and fixed losses such as opening and closing dryers, etc.

[e] Uncontrolled emissions from washer, dryer, still, and muck cooker average about 8 kg/100 kg (8 lb/100 lb). About 15% of solvent emitted is from washer, 75% dryer, 5% each from still and muck cooker.

[f] Based on the typical refrigeration system installed in fluorocarbon plants.

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PERCHLOROETHYLENE DRY CLEANING SYSTEMS CONTROL TECHNIQUE GUIDELINE DOCUMENT, EPA-450/2-78-047 {SUPPL. MATR.}

Recommended standard:

- Vent dryer exhaust through a carbon adsorber or equivalent device with an outlet concentration ≤100 ppmv (Coin operated dry cleaners are exempt).
- Reduce filter residue to ≤25% perchloroethylene and still residue to ≤60% perchloroethylene.
- Drain filter cartridges for ≥24 hours or until dry before disposal.
- Immediately repair liquid and vapor leaks.

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LARGE PETROLEUM DRY CLEANERS CONTROL TECHNIQUE GUIDELINE DOCUMENT, EPA-450-3-82-009

Recommended standard:

- Use a solvent recovery dryer to reduce emissions by 81%.
- Use a cartridge filter.
- Improve operation of distillation unit.
- Repair liquid and vapor leaks within 3 working days.

21

STANDARDS OF PERFORMANCE FOR PETROLEUM DRY CLEANERS, 40CFR60, SUBPART JJJ {SUPPL. MATR.}

- ***Applicability Date:*** December 14, 1982
- ***Applicability Size:*** $\geq$84 pound capacity

Standard:

- Use a solvent recovery dryer.
- Use a cartridge filter. Drain in sealed housing for at least 8 hours prior to removal.
- Inspect every 15 days and repair all vapor and liquid leaks within the subsequent 15 day period.

22

NATIONAL PERCHLOROETHYLENE AIR EMISSION STANDARDS FOR DRY CLEANING FACILITIES, 40 CFR 63, SUBPART M {SUPPL. MATR.}

- ***Applicability:*** Each dry cleaning facility that uses perchloroethylene, except coin-operated machines. An existing transfer plant installed before December 9, 1991, or a new plant installed between December 9, 1991, and September 22, 1993, is exempt from all but recordkeeping and maintenance requirements if it uses less than 200 gallons of perchloroethylene per year. An existing dry-to-dry plant, or a new plant installed between December 9, 1991, and September 22, 1993, is similarly exempted if it uses less than 140 gallons of perchloroethylene per year.

23

Standard: **Existing systems**

- Route gas stream within dry cleaning machine through a **refrigerated condenser** or equivalent control device or through a carbon adsorber installed prior to September 22, 1993.
- Contain transfer machines located at a major source in a room enclosure under negative pressure.

Standard: **New systems**

- Route gas stream within dry cleaning machine through a refrigerated condenser or equivalent control device.
- Eliminate emissions during transfer of articles between washer and dryer.
- If at a major source, route gas stream within dry cleaning machine through a carbon adsorber or equivalent device before or as the **door is opened.**

24

Standard: **Refrigerated condensers on dry-to-dry, dryer or reclaimer**

- Shall not release gas stream within machine while machine drum is rotating.
- Shall have an outlet temperature less than 45°F.
- Shall have a diverter valve that prevents air drawn in when the door is open from passing through the refrigerated condenser.

Standard: **Refrigerated condensers on a washer**

- Shall not vent gas stream within machine until door opens.
- Shall have a temperature drop of at least 20°F.
- Shall not use the same condenser coil that is used by a dry-to-dry machine, dryer or reclaimer.

25

Standard: **Carbon adsorber**

- Shall not be bypassed.
- If used on an existing machine or on a new machine immediately upon door opening, outlet concentration at the end of the last cycle before regeneration must be equal to or less than 100 ppmv.
- If used on a new machine prior to door opening, the concentration inside the drum at the end of the cycle must be equal to or less than 300 ppmv.

Standard: **Room enclosure**

- Shall vent all air through a carbon adsorber or equivalent control device.
- Carbon adsorber can not be the same one used for the dry cleaning machine.

Standard: **Additional requirements**

- Use a cartridge filter. Drain in sealed housing for at least 24 hours prior to removal.
- Inspect system weekly and repair leaks within 24 hours.

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PROCESS INSPECTION

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

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LIQUID ASPHALT

Presentation: 16

Chapter 12 – Liquid Asphalt

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

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Western States Air Resources Council

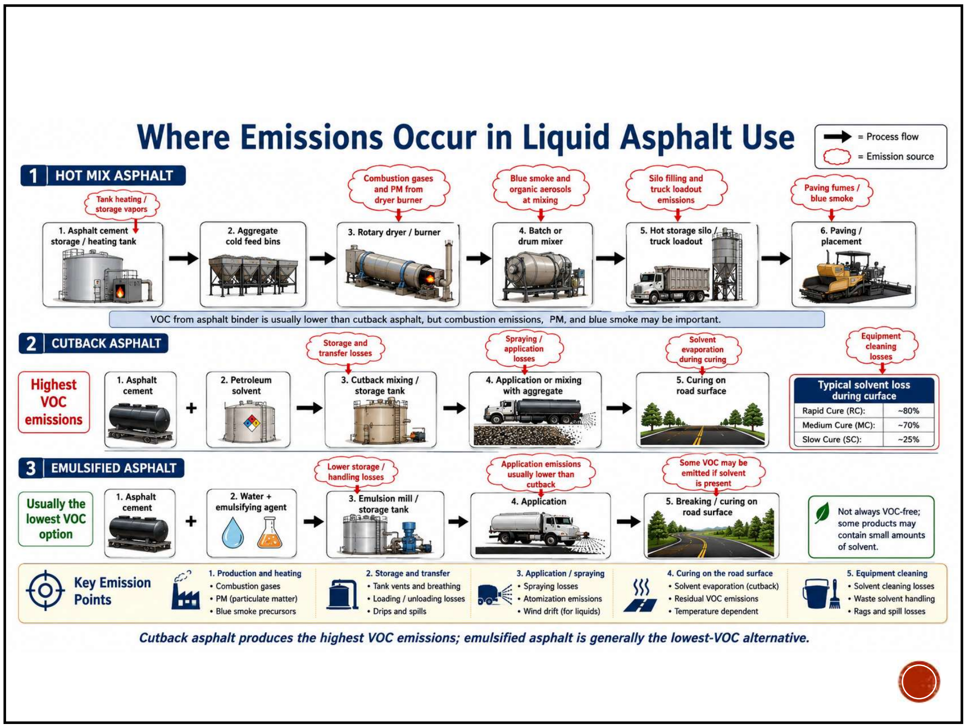
1

LIQUID ASPHALT

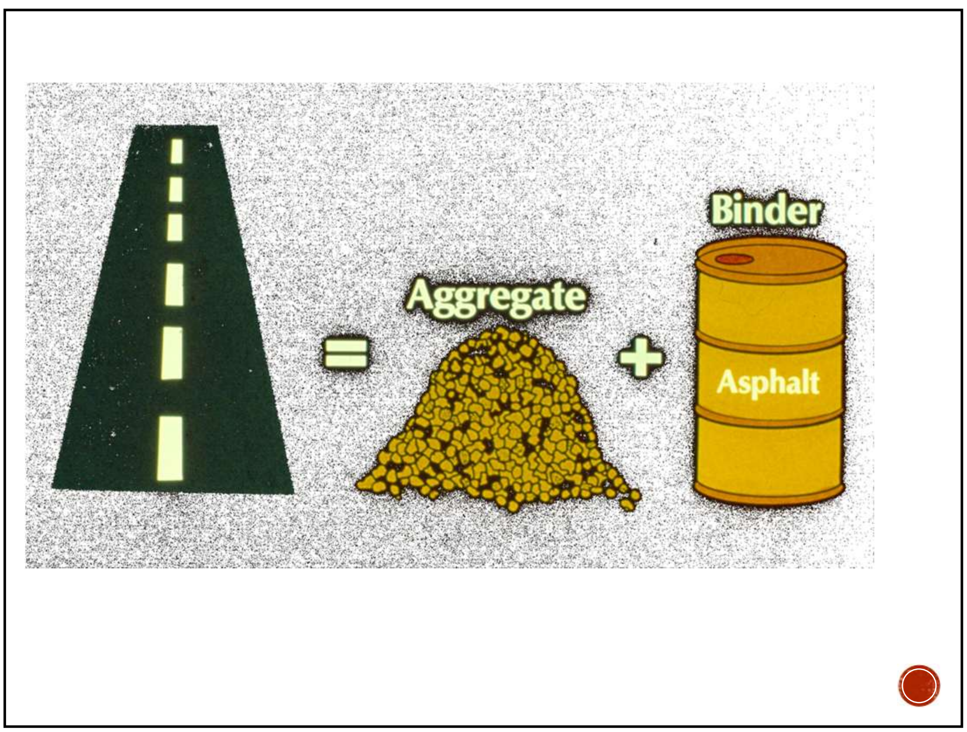
Presentation: 16

Chapter 12 – Liquid Asphalt

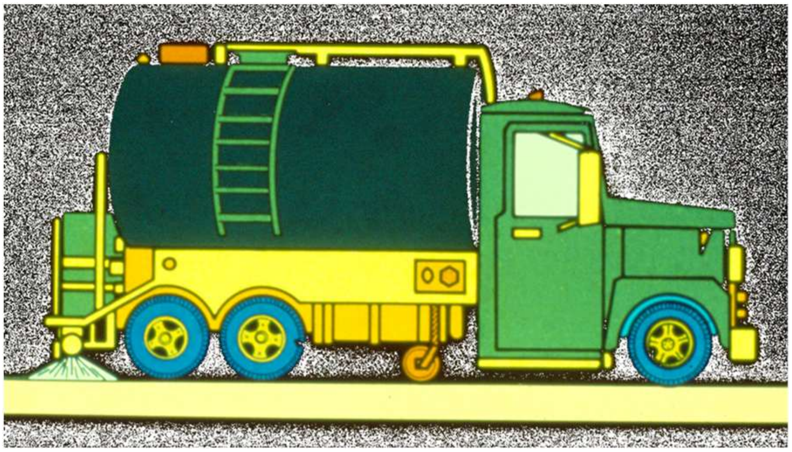
2


Where Emissions Occur in Liquid Asphalt Use
= Process flow
= Emission source
1 HOT MIX ASPHALT
Tank heating / storage vapors
Combustion gases and PM from dryer burner
Blue smoke and organic aerosols at mixing
Silo filling and truck loadout emissions
Paving fumes / blue smoke
1. Asphalt cement storage / heating tank
2. Aggregate cold feed bins
3. Rotary dryer / burner
4. Batch or drum mixer
5. Hot storage silo / truck loadout
6. Paving / placement
VOC from asphalt binder is usually lower than cutback asphalt, but combustion emissions, PM, and blue smoke may be important.
2 CUTBACK ASPHALT
Highest VOC emissions
Storage and transfer losses
Spraying / application losses
Solvent evaporation during curing
Equipment cleaning losses
1. Asphalt cement
2. Petroleum solvent
3. Cutback mixing / storage tank
4. Application or mixing with aggregate
5. Curing on road surface
Typical solvent loss during curface
Rapid Cure (RC): ~80%
Medium Cure (MC): ~70%
Slow Cure (SC): ~25%
3 EMULSIFIED ASPHALT
Usually the lowest VOC option
Lower storage / handling losses
Application emissions usually lower than cutback
Some VOC may be emitted if solvent is present
1. Asphalt cement
2. Water + emulsifying agent
3. Emulsion mill / storage tank
4. Application
5. Breaking / curing on road surface
Not always VOC-free; some products may contain small amounts of solvent.
Key Emission Points
1. Production and heating • Combustion gases • PM (particulate matter) • Blue smoke precursors
2. Storage and transfer • Tank vents and breathing • Loading / unloading losses • Drips and spills
3. Application / spraying • Spraying losses • Atomization emissions • Wind drift (for liquids)
4. Curing on the road surface • Solvent evaporation (cutback) • Residual VOC emissions • Temperature dependent
5. Equipment cleaning • Solvent cleaning losses • Waste solvent handling • Rags and spill losses
Cutback asphalt produces the highest VOC emissions; emulsified asphalt is generally the lowest-VOC alternative.

3


Binder
Aggregate
Asphalt

4



5

LIQUEFACTION METHODS

- Heating
- Blending with petroleum solvents
- Emulsifying with water

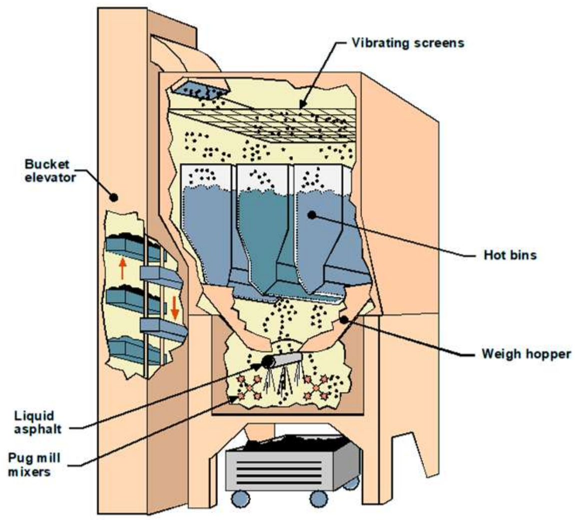
6

7

Material	How it is made usable	Main use	VOC potential	Key issue
Hot mix asphalt	Asphalt cement is heated and mixed with hot aggregate	Durable paving	Low from asphalt binder; plant combustion/PM may matter	Requires heating and plant controls
Cutback asphalt	Asphalt cement blended with petroleum solvent	Prime coat, tack coat, patching, some maintenance	Highest	Solvent evaporates during curing
Emulsified asphalt	Asphalt cement emulsified in water with emulsifier	Prime/tack coats, surface treatments, cold mix, maintenance	Lower, but not always zero	May contain small VOC fraction
Warm mix asphalt	Uses additives, foaming, or process changes to lower mixing temperature	Paving with lower production temperature	Lower energy and potentially lower emissions	Requires mix-design and performance verification

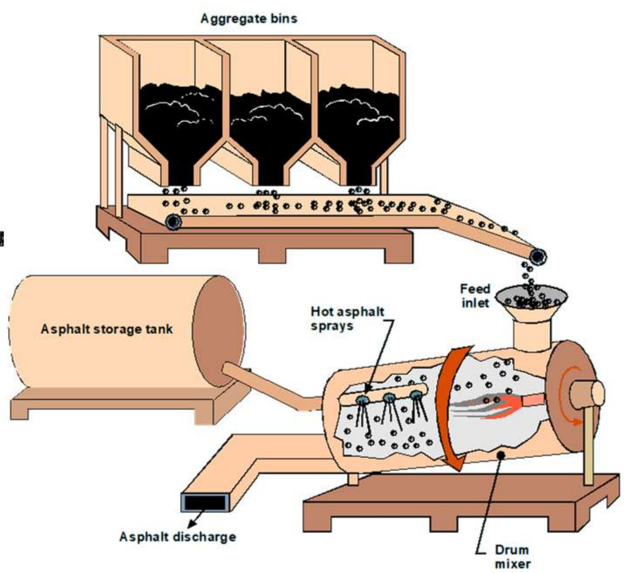
8

HOT MIX PLANT



9

DRUM MIX PLANT



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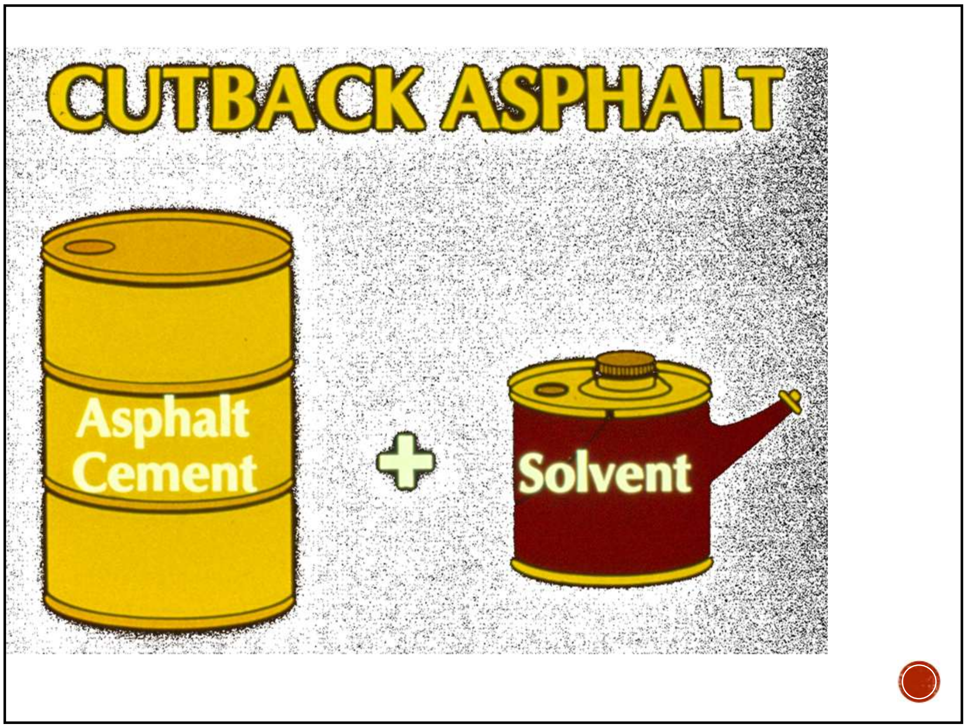
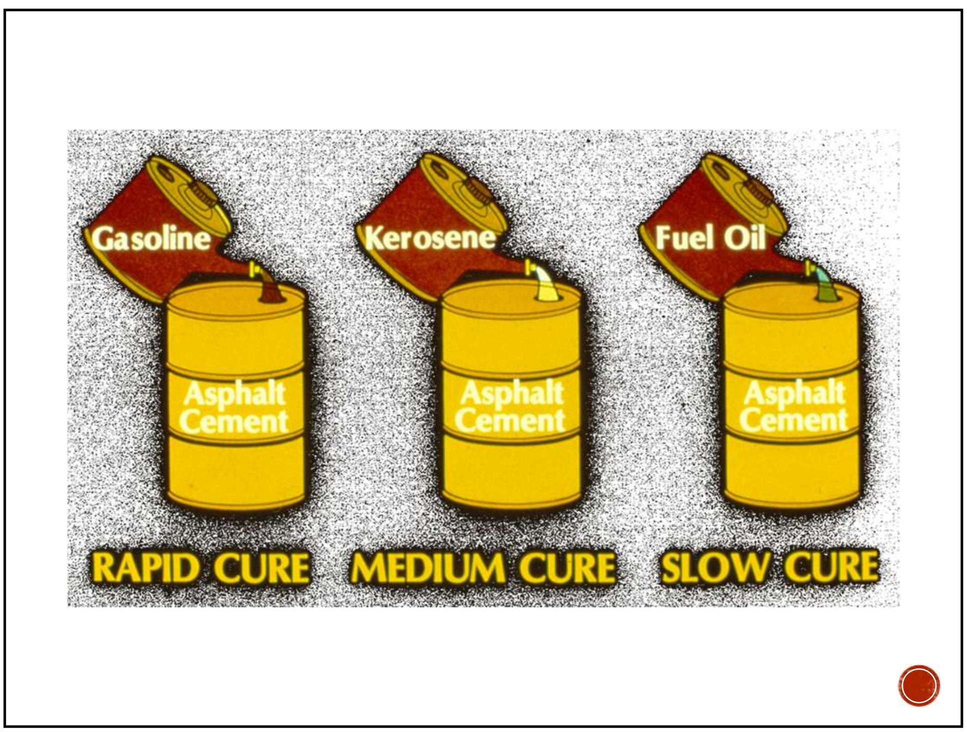
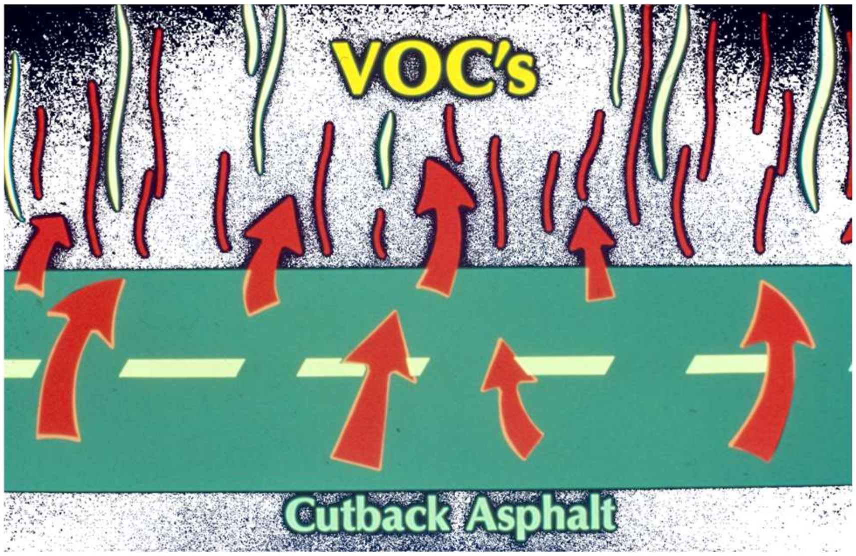

CUTBACK ASPHALT
Asphalt Cement
Solvent

11


Gasoline
Kerosene
Fuel Oil
Asphalt Cement
Asphalt Cement
Asphalt Cement
RAPID CURE
MEDIUM CURE
SLOW CURE

12



13

VOC LOSSES

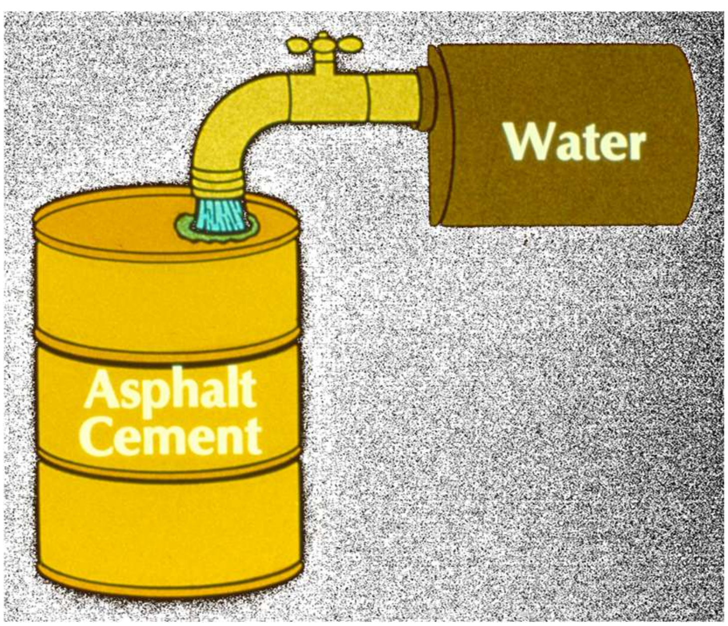
	Solvent Loss	Curing Period
Rapid cure	80%	2-3 hours
Medium cure	70%	2-3 days
Slow cure	25%	~2-3 weeks

14

WHY CUTBACK ASPHALT HAS HIGH VOC EMISSIONS

Cutback type	Typical solvent	Curing time	Approximate solvent loss
Rapid Cure — RC	Gasoline/naphtha	2–3 hours	~80%
Medium Cure — MC	Kerosene	2–3 days	~70%
Slow Cure — SC	Fuel oil / low-volatility solvent	2–3 weeks	~25%

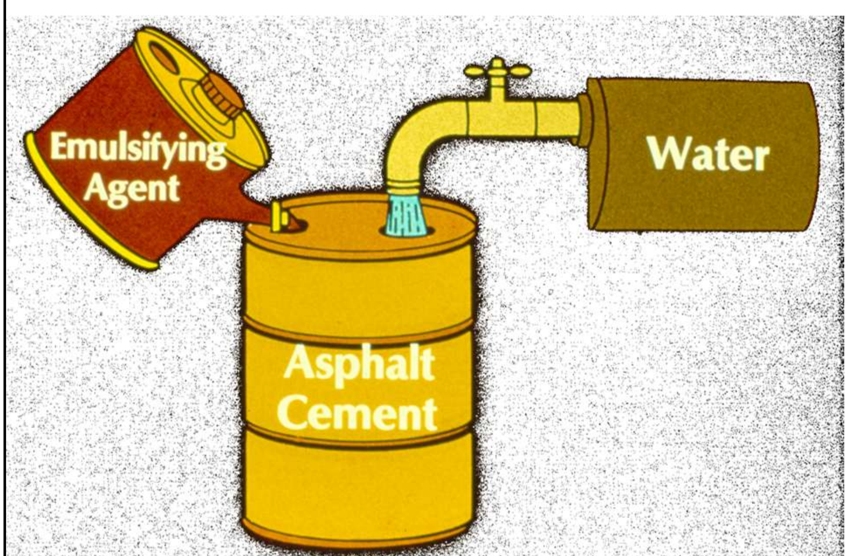
15



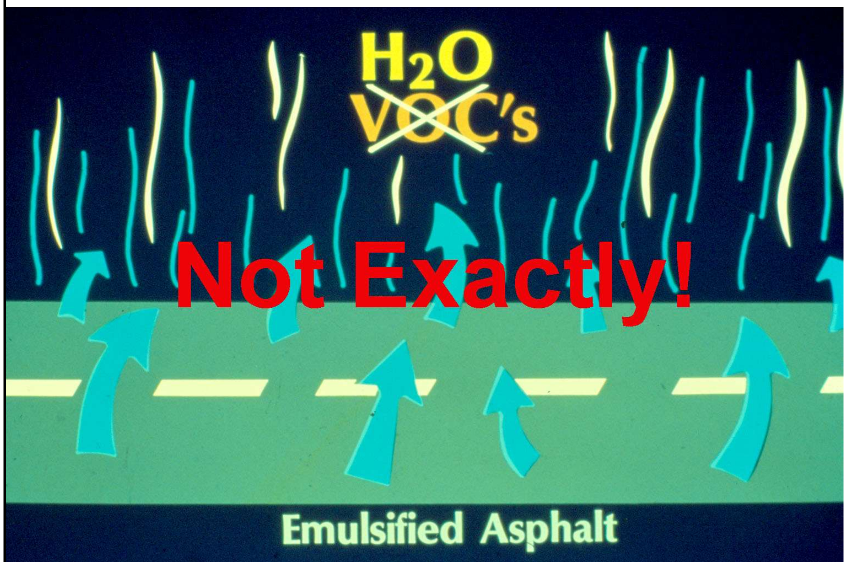
16


Water
Asphalt
Cement
IMMISCIBLE

17


Emulsifying
Agent
Water
Asphalt
Cement

18



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REGULATORY UPDATE: CUTBACK AND EMULSIFIED ASPHALT

Common regulatory approach

- Restrict or prohibit cutback asphalt during ozone season.
- Limit VOC content of cutback asphalt and emulsified asphalt.
- Encourage or require substitution of emulsified asphalt or other low-VOC materials.
- Require records of asphalt type, quantity used, VOC content, and application dates.
- Allow exemptions for certain uses, depending on state/local rules.

Inspection focus

- Was cutback asphalt used?
- What type: rapid cure, medium cure, or slow cure?
- Was it used during ozone season?
- What was the VOC content?
- Was an emulsified asphalt or other low-VOC substitute available?
- Are purchase and usage records available?

20

TECHNOLOGY AND PRACTICE UPDATES

Lower-emission options include:

- **Emulsified asphalt** instead of cutback asphalt.
- **Warm mix asphalt** to reduce production temperature and fuel use.
- **Cold mix / cold patch with low-VOC binder** for maintenance applications.
- **Reclaimed asphalt pavement (RAP)** to reduce virgin material demand.
- **Cold in-place recycling and full-depth reclamation** for roadway rehabilitation.
- **Improved storage and transfer practices** to reduce handling losses.
- **Blue-smoke capture/control** at asphalt plants where applicable.

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INSPECTION CHECKLIST: LIQUID ASPHALT

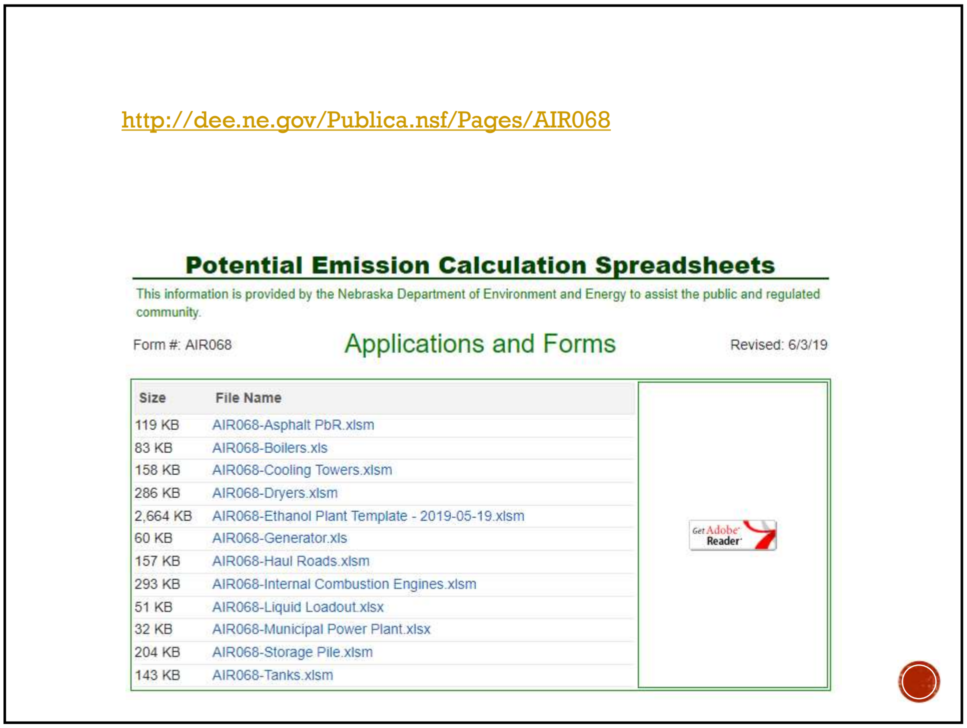
Records to review

- Asphalt product type: hot mix, cutback, emulsified, warm mix.
- Cutback type: RC, MC, or SC.
- VOC content or solvent content.
- Quantity used and dates of use.
- Ozone-season restrictions.
- Product SDS and technical data sheet.
- Storage tank records.
- Mixing/application logs.
- Permit or state/local rule applicability.

Field observations

- Is cutback asphalt being sprayed or mixed?
- Is there visible blue smoke or strong solvent odor?
- Are storage tanks heated or vented?
- Are loading and transfer practices controlled?
- Is emulsified asphalt being used as a substitute?
- Are trucks covered and loaded properly?
- Are asphalt plant dryer, baghouse, and fuel-combustion controls operating properly?

22


http://dee.ne.gov/Publica.nsf/Pages/AIR068

Potential Emission Calculation Spreadsheets

This information is provided by the Nebraska Department of Environment and Energy to assist the public and regulated community.

Form #: AIR068 — Applications and Forms — Revised: 6/3/19

Size	File Name
119 KB	AIR068-Asphalt PbR.xlsm
83 KB	AIR068-Boilers.xls
158 KB	AIR068-Cooling Towers.xlsm
286 KB	AIR068-Dryers.xlsm
2,664 KB	AIR068-Ethanol Plant Template - 2019-05-19.xlsm
60 KB	AIR068-Generator.xls
157 KB	AIR068-Haul Roads.xlsm
293 KB	AIR068-Internal Combustion Engines.xlsm
51 KB	AIR068-Liquid Loadout.xlsx
32 KB	AIR068-Municipal Power Plant.xlsx
204 KB	AIR068-Storage Pile.xlsm
143 KB	AIR068-Tanks.xlsm

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23

INTRODUCTION TO CONTROL TECHNOLOGY

Presentation: 17

Chapter 13 – Introduction to Control Technology

AIR POLLUTION TRAINING INSTITUTE (APTI 482)

SOURCES AND CONTROL OF VOLATILE ORGANIC AIR POLLUTANTS

Ashraf Aly Hassan, Ph.D., P.E.
Convironment, LLC

Online
June 9-12, 2026

WESTAR
Western States Air Resources Council

1

INTRODUCTION TO CONTROL TECHNOLOGY

Presentation: 17

Chapter 13 – Introduction to Control Technology

2

INTRODUCTION TO CONTROL TECHNOLOGY

- Carbon adsorption
- Oxidation
- Condensation
- Bioreaction

3

VOC CONTROL TECHNOLOGY SELECTION

Gas-stream condition	Better-fit technology	Why
Low to moderate VOC concentration; valuable solvent	Carbon adsorption or condensation	Allows solvent recovery
High VOC concentration; high heating value	Thermal oxidizer, RTO, or flare	Destruction may be self-sustaining
Low VOC concentration; high flow	RTO or concentrator + oxidizer	Heat recovery or concentration improves economics
Water-soluble and biodegradable compounds	Biofilter, biotrickling filter, bioscrubber	Biological destruction at low energy cost
Halogenated, sulfur-containing, or corrosive VOCs	Careful oxidation with acid-gas control	Oxidation can form HCl, HF, SO_2, etc.
High humidity	Adsorption may need more carbon or pretreatment	Water competes for adsorption sites
Particulate-laden gas	Pretreatment required	PM fouls carbon, heat exchangers, catalysts, and bio-media

4

Carbon Adsorption

5

ACTIVATED CARBON

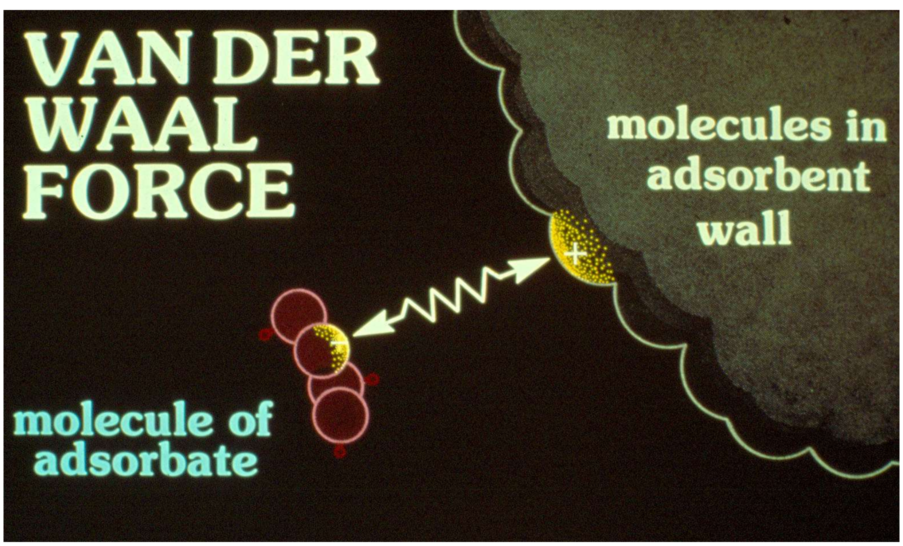
- A class of materials
- Produced from coal, wood, nut shells and petroleum-based products
- Activation process
  - Heat material to ~1,100°F without oxygen
  - Use stream, air or CO_2 to increase pore structure

6

TYPES OF ADSORPTION PROCESSES

- Chemical adsorption
- **Physical adsorption**

7



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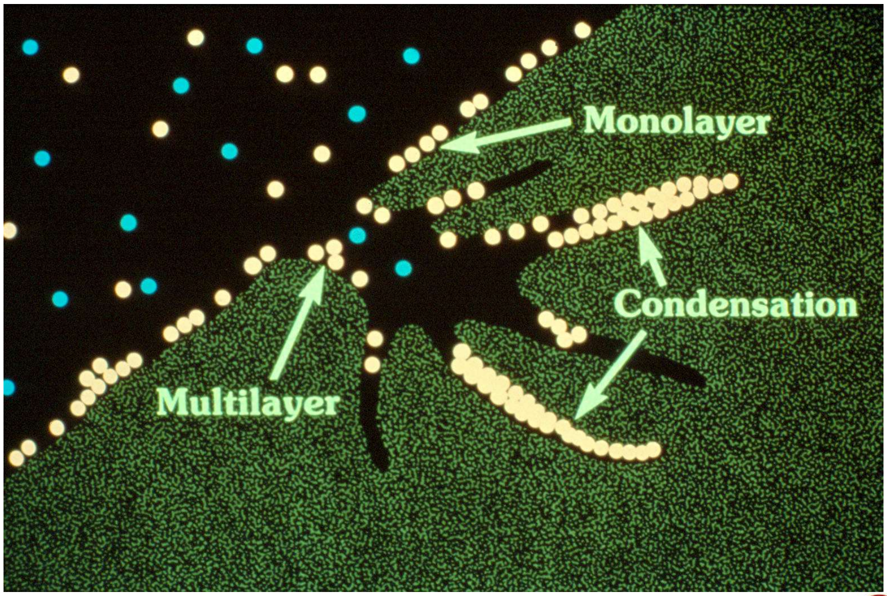

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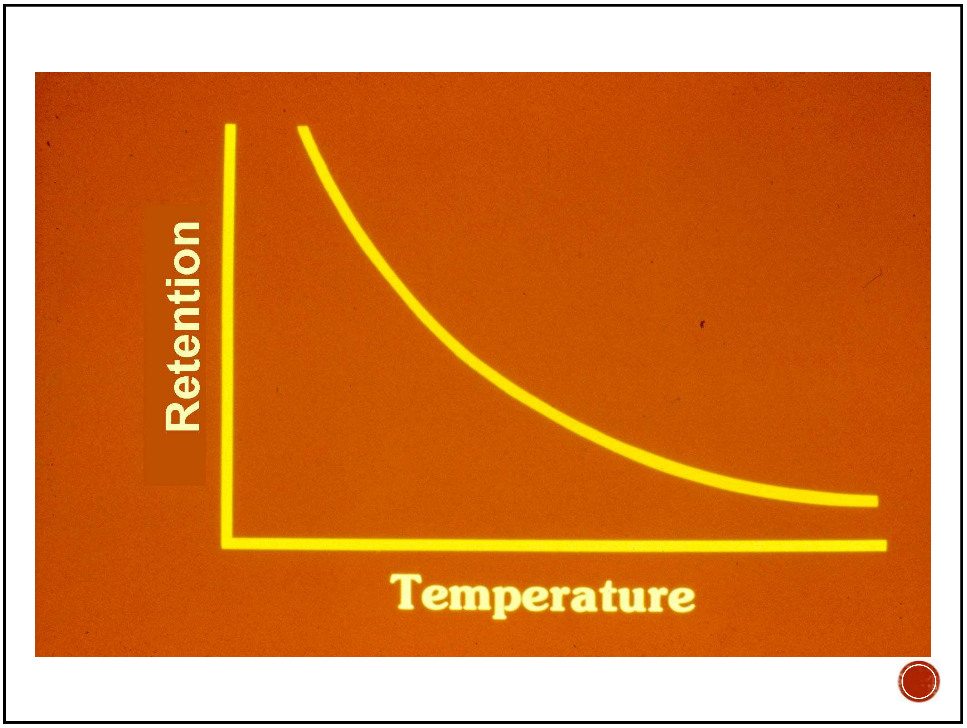
ADSORPTION CAPACITY

Retention

- Lbs of VOC adsorbed per 100 lbs of carbon
- Weight percent

10



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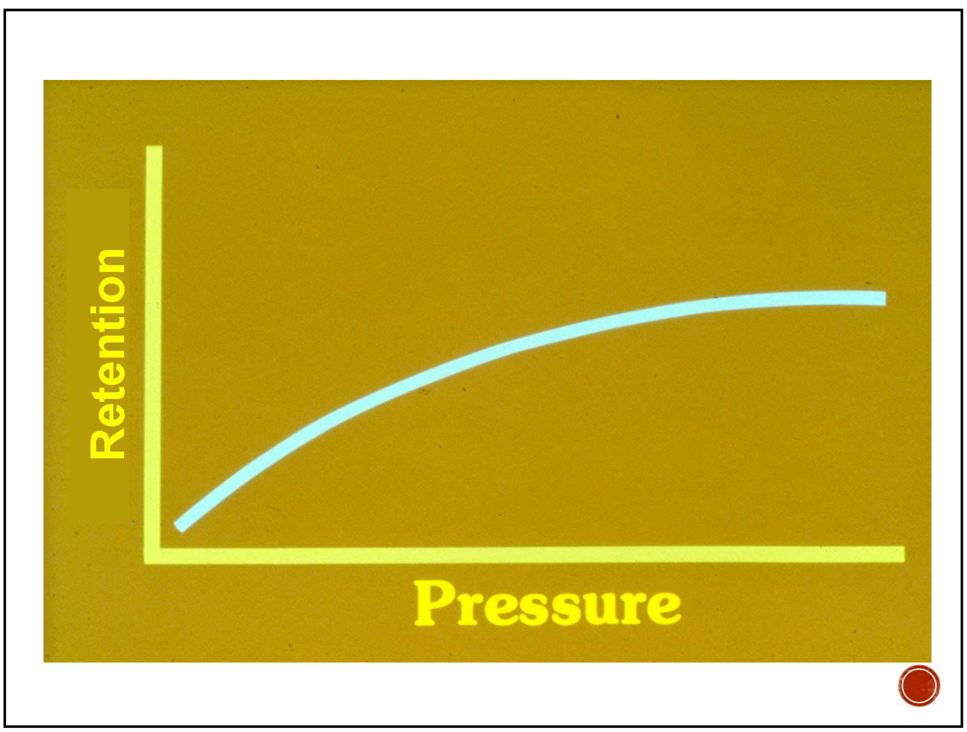

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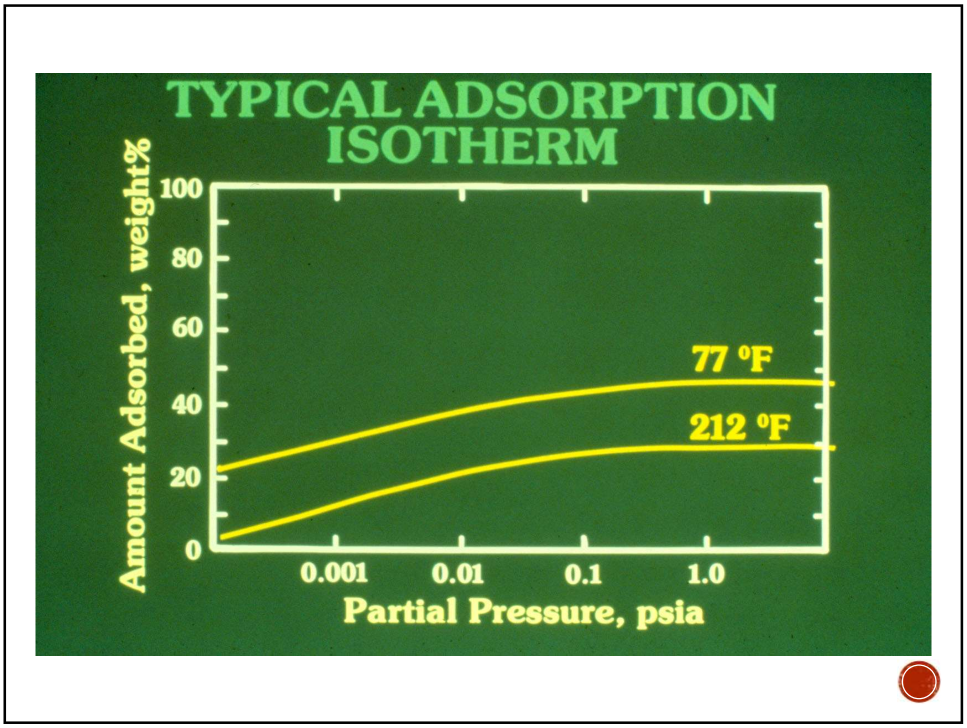
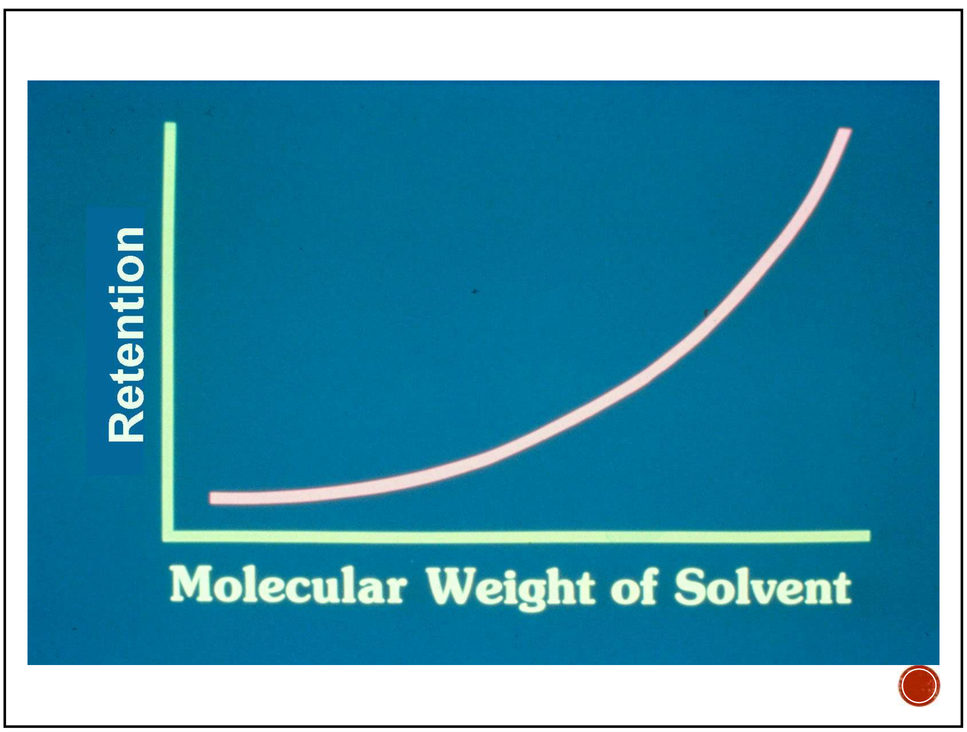
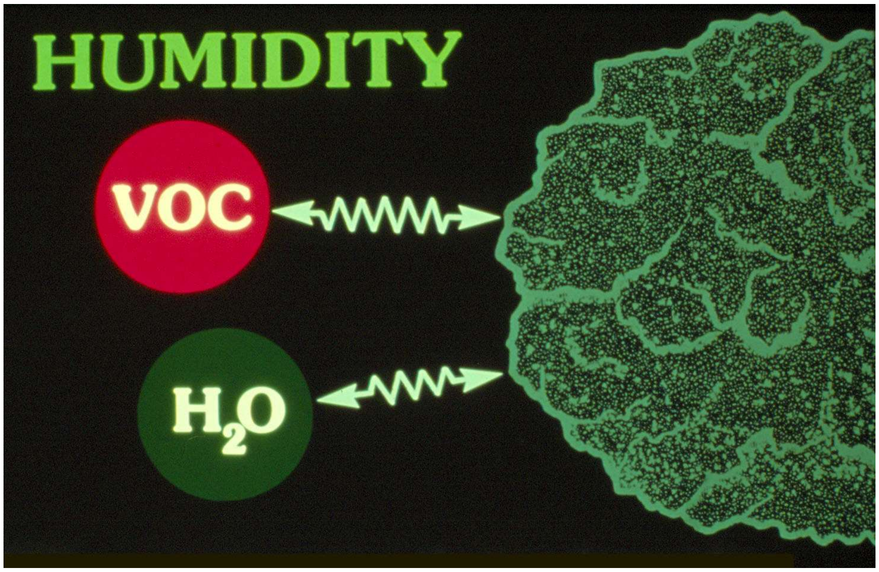

TYPICAL ADSORPTION ISOTHERM
Amount Adsorbed, weight%
100
80
60
40
20
0
77 °F
212 °F
0.001
0.01
0.1
1.0
Partial Pressure, psia

13


Retention
Molecular Weight of Solvent

14



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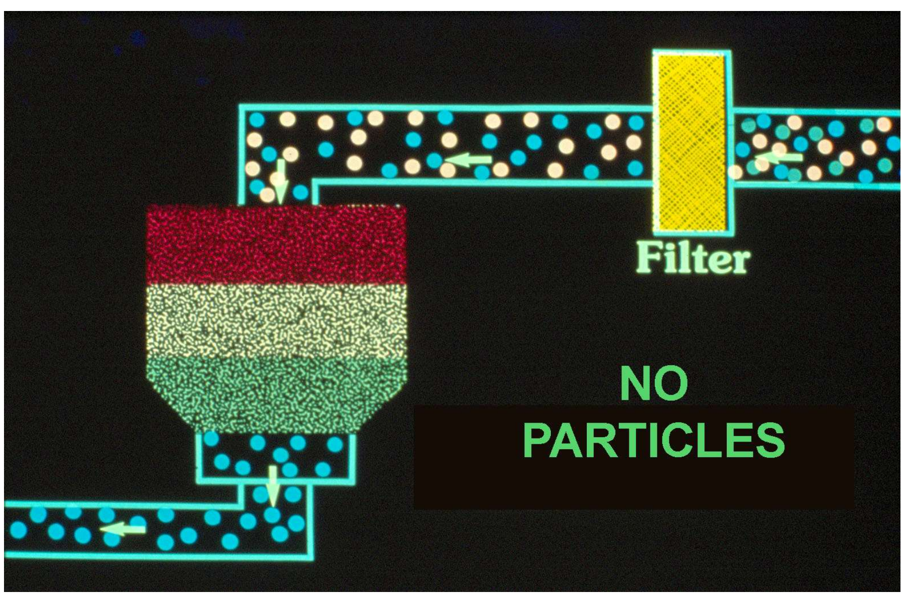
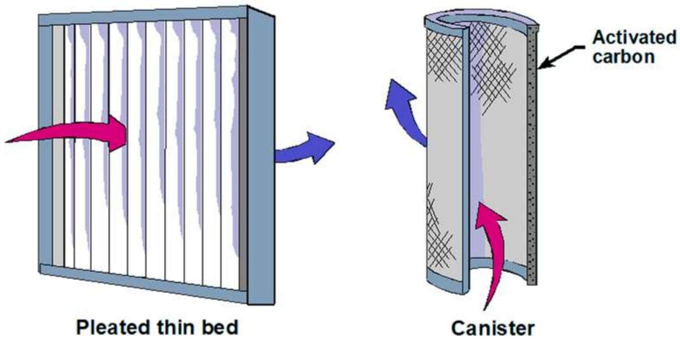


16

TYPES OF ADSORPTION SYSTEMS

- On-site regeneration
- Off-site regeneration



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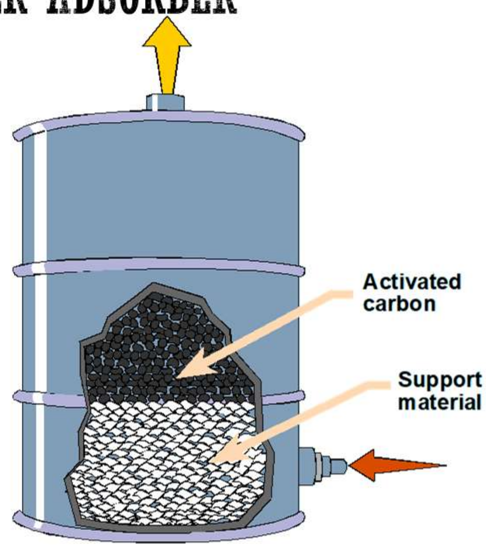
CANISTER ADSORBER



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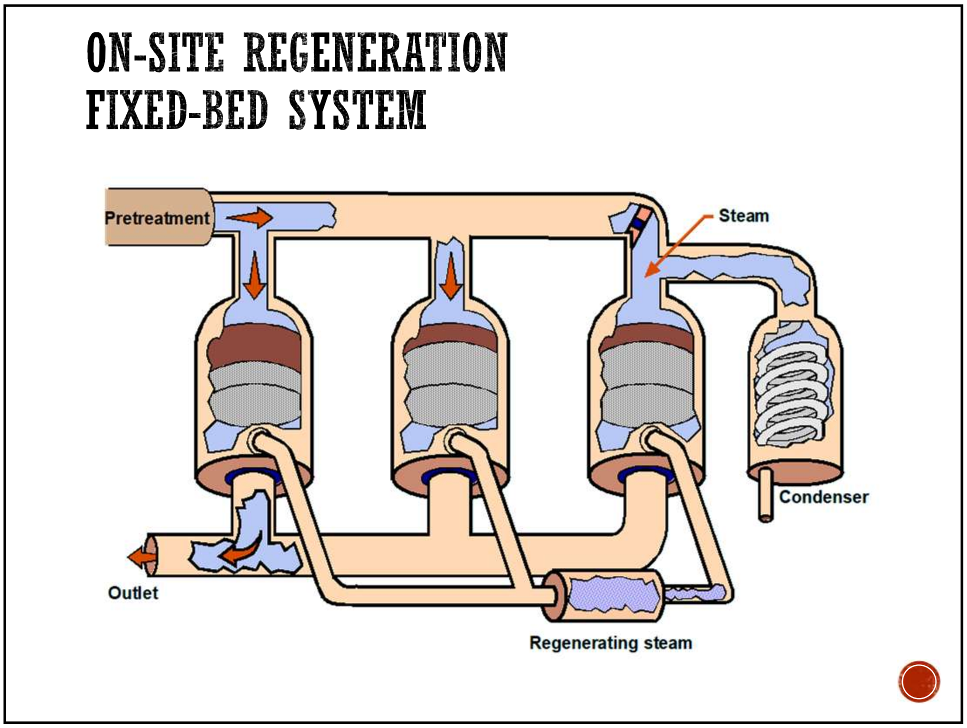
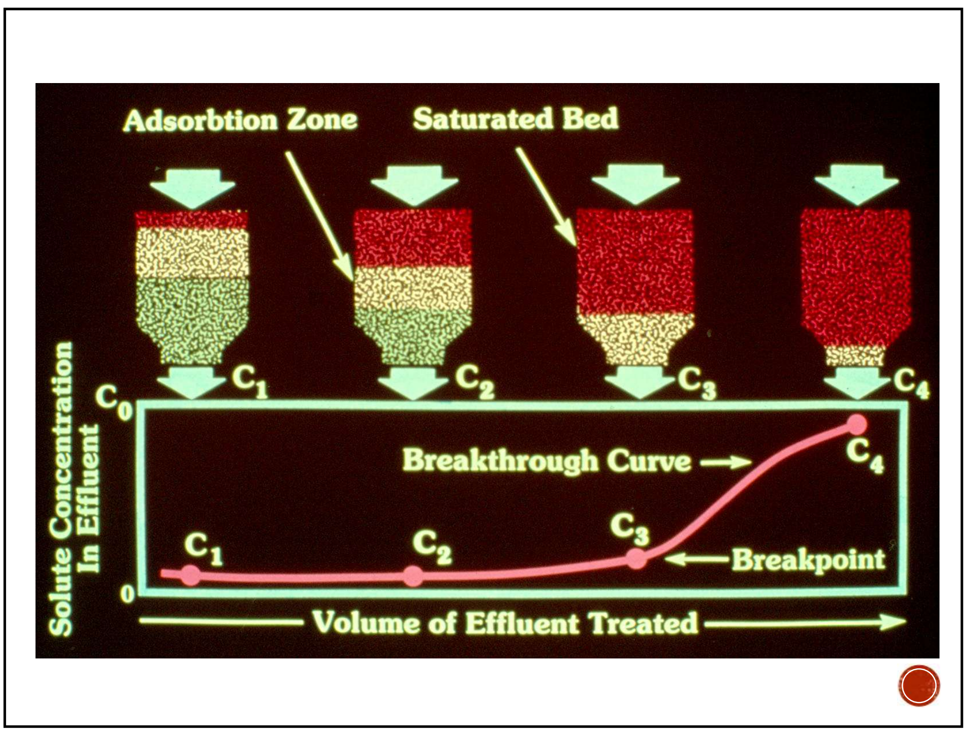

ON-SITE REGENERATION
FIXED-BED SYSTEM
Pretreatment
Steam
Condenser
Outlet
Regenerating steam

19


Adsorbtion Zone
Saturated Bed
C1
C2
C3
C4
C0
Breakthrough Curve
Breakpoint
0
Solute Concentration In Effluent
Volume of Effluent Treated

20

REGENERATION METHODS

- Thermal swing
  - Steam
  - Hot gas
- Pressure swing

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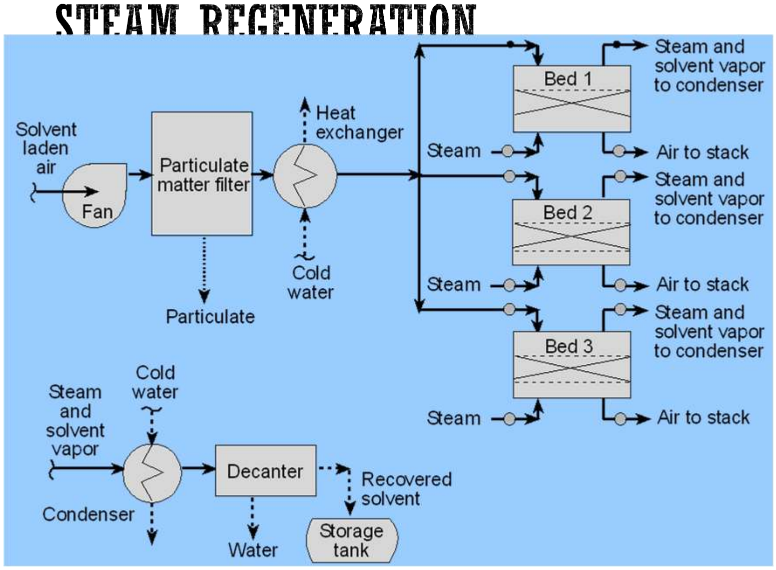
STEAM REGENERATION



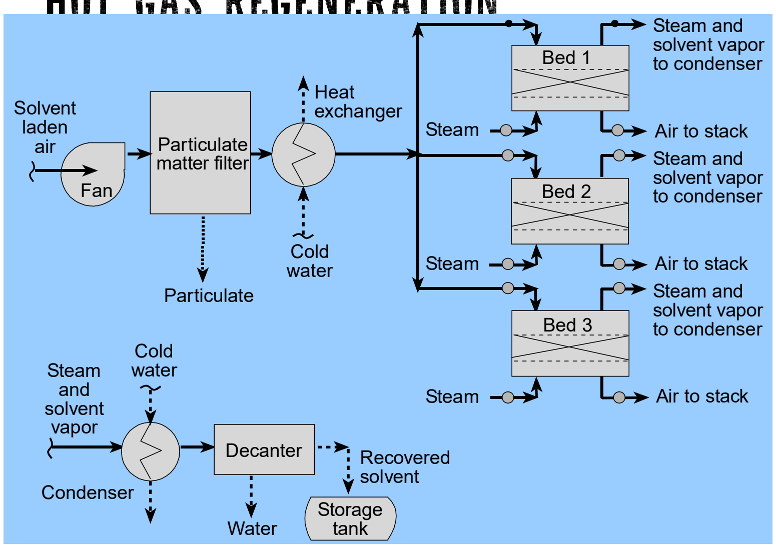
22

REGENERATION METHODS

- **Thermal swing**
  - Steam
  - **Hot gas**
- Pressure swing

23

HOT GAS REGENERATION



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REGENERATION METHODS

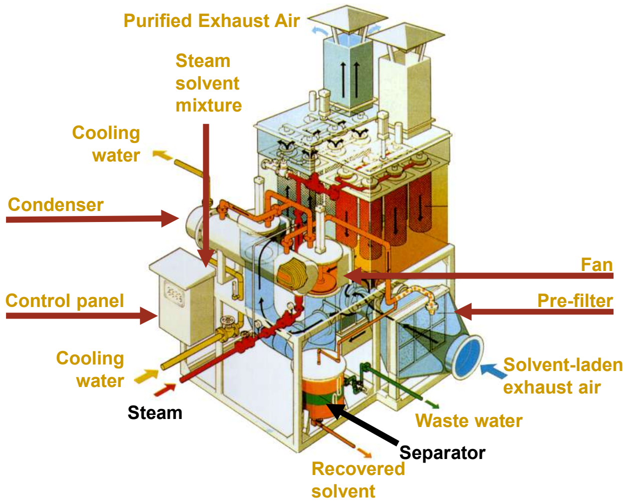
- Thermal swing
  - Steam
  - Hot gas
- **Pressure swing**

25

Other Adsorber Designs

26

CARBON FIBER ADSORBER



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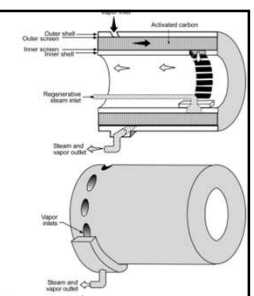
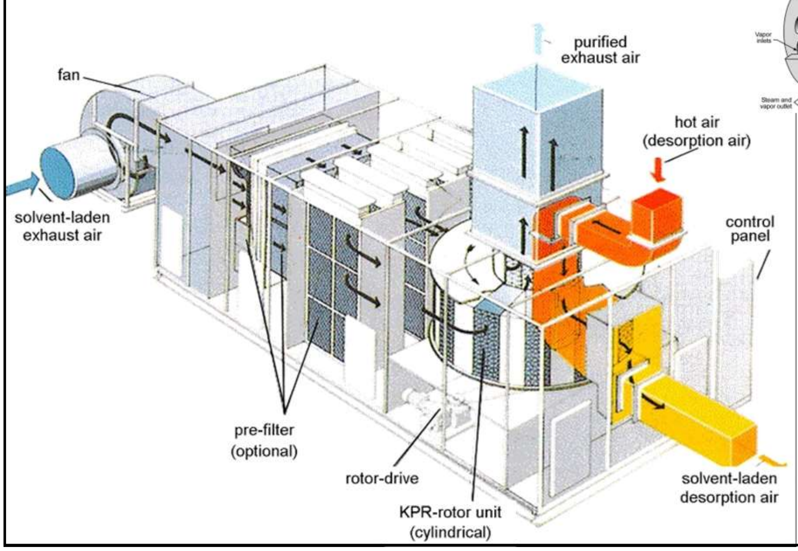
ROTARY BED ADSORBER





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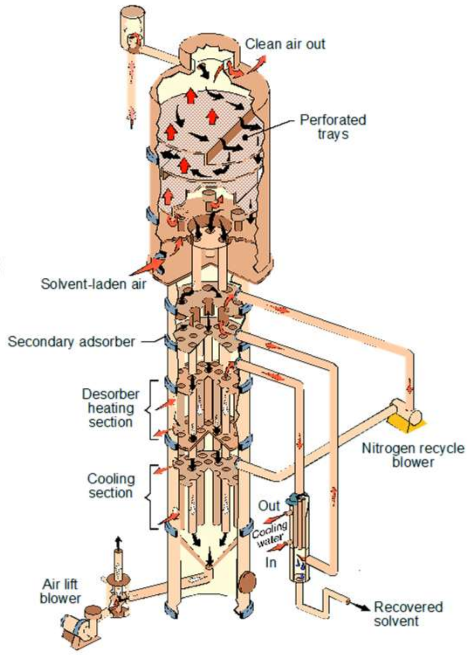
FLUIDIZED BED ADSORBER



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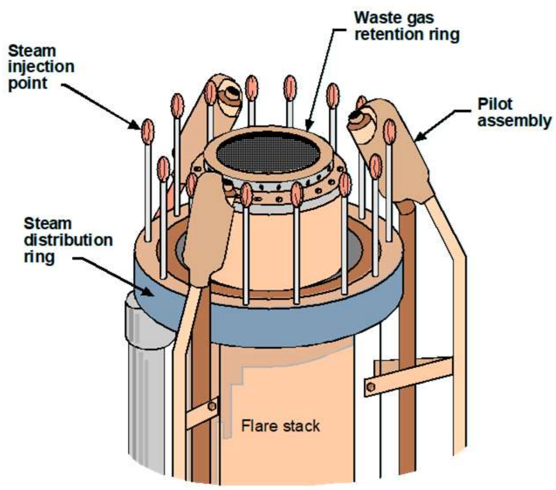
OXIDATION

- Flares
- Thermal oxidizers
- Catalytic oxidizers

30

FLARE



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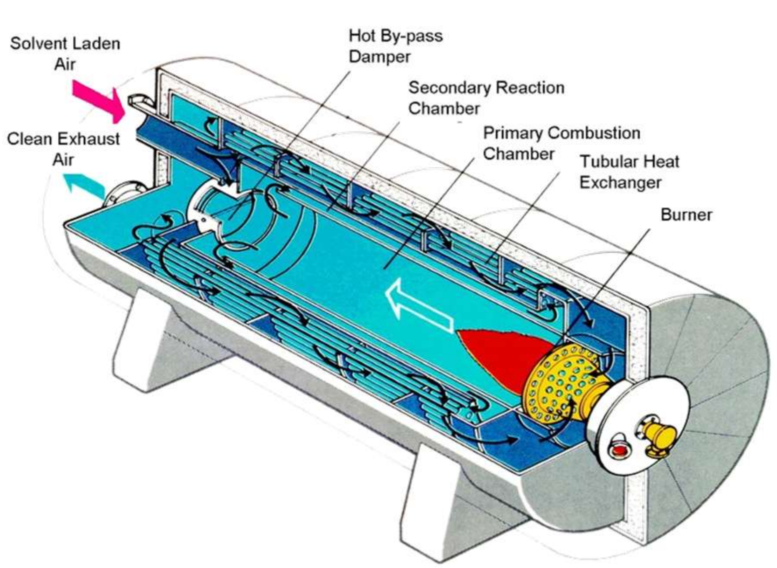
THERMAL OXIDIZER

- Refractory-brink lined chamber with one or more oil or gas burners
- Temperature: 1,300-1,800°F
- Residence time: 0.3-0.5 seconds

32

RECUPERATIVE THERMAL OXIDIZER



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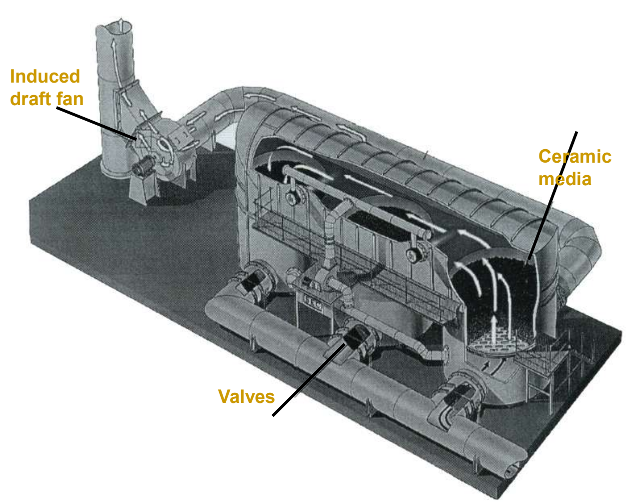
REGENERATIVE THERMAL OXIDIZER



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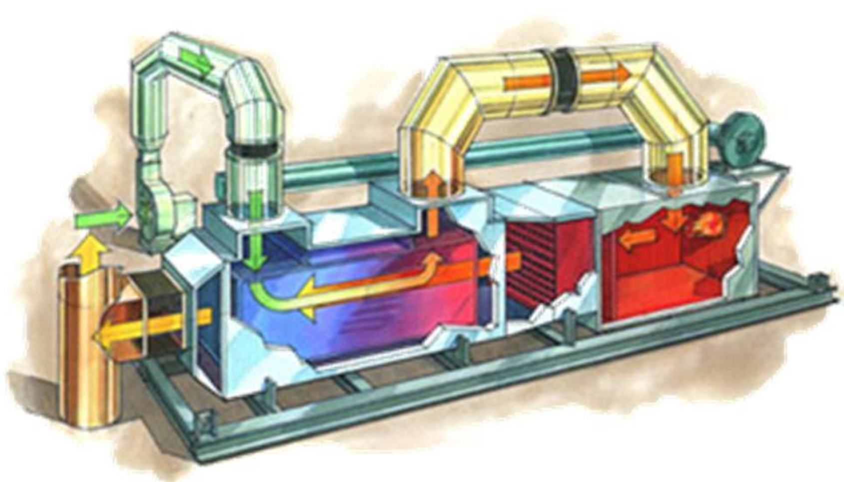
PROCESS HEATERS AND BOILERS

- Boiler must operate at 40-100% of full load
- Contaminated gas stream flow rate should be small portion of total
- Nothing corrosive or that causes deposits

35

CATALYTIC OXIDIZER



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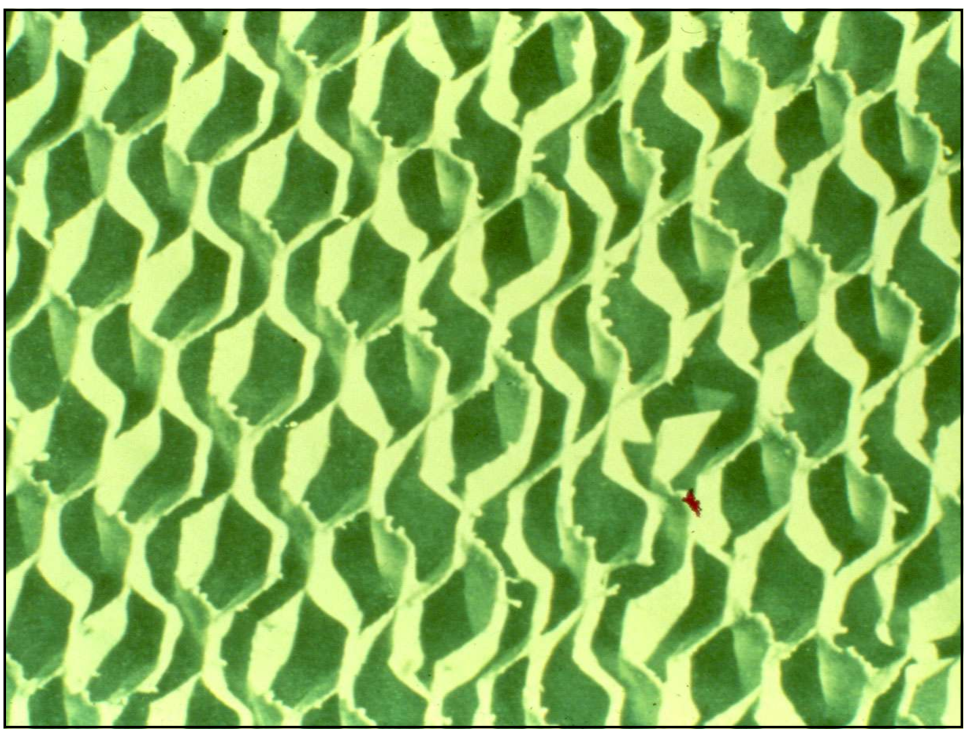
CATALYST MATERIALS

- Noble metal oxides
  - Platinum
  - Palladium
  - Rhodium
- Base metal oxides
  - Vanadium
  - Titanium
  - Manganese

37



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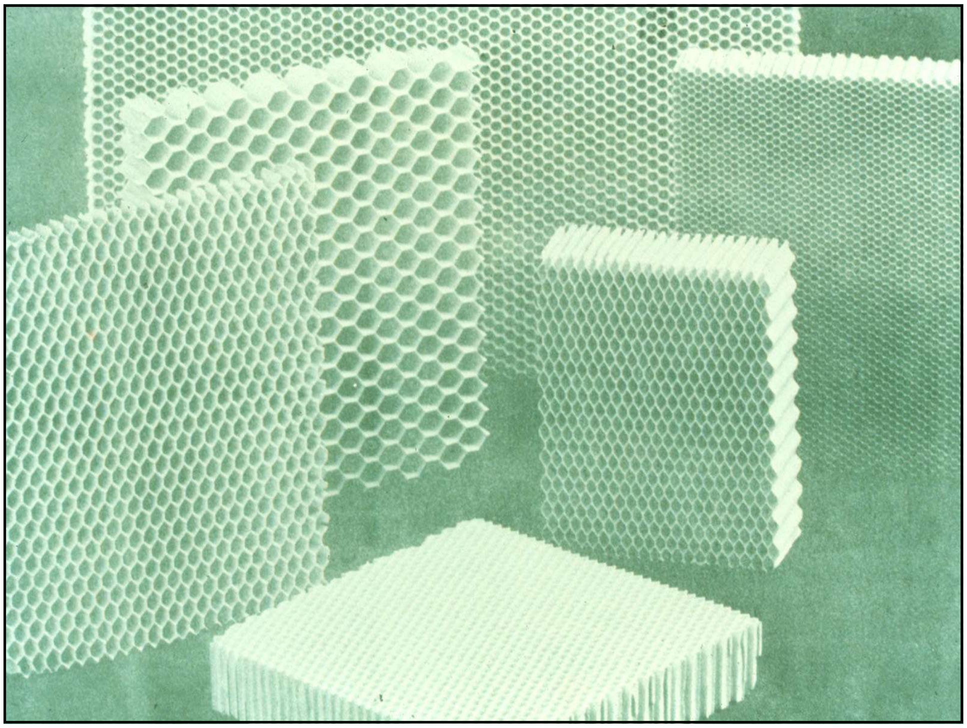

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TEMPERATURE

- ~100°F above catalyst light-off temperature
- Typical inlet temperature: 500-600°F
- Typical outlet temperature: 700-900°F
- Maximum outlet temperature: 1,100-1,200°F

40

SPACE VELOCITY

$$\text{Space Velocity} = \frac{Q}{BV}$$

Q = standard flow rate (60°F)

BV = catalyst bed volume

Typically, 30,000-40,000 hr^{-1} for noble metals

10,000-15,000 hr^{-1} for base metals

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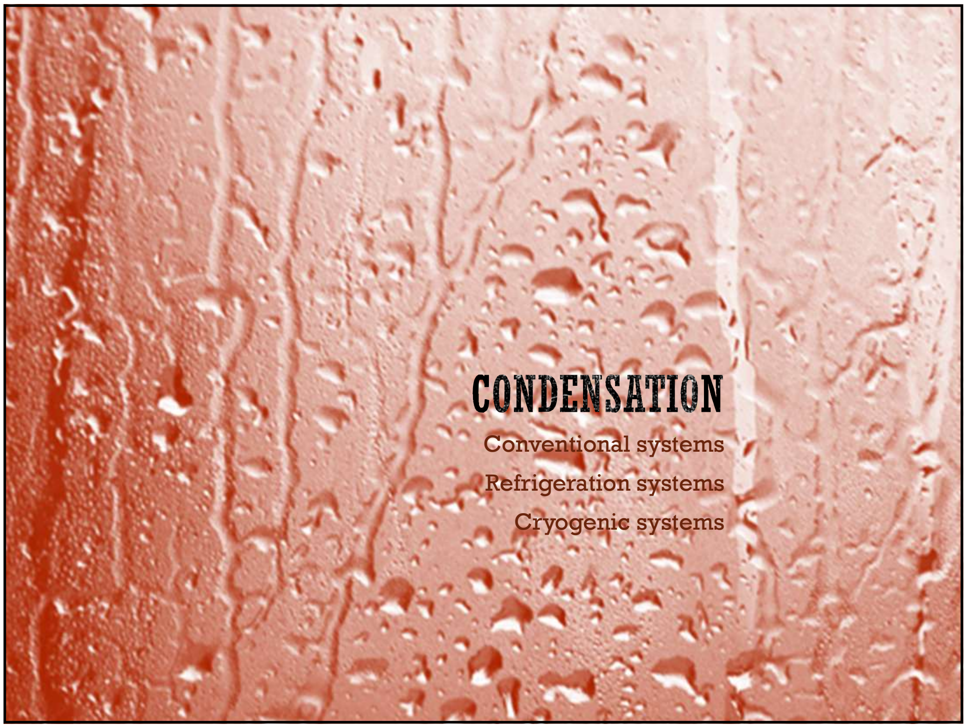
CATALYST PERFORMANCE PROBLEMS

- Fouling
- Poisoning
- Masking
- Thermal aging

42



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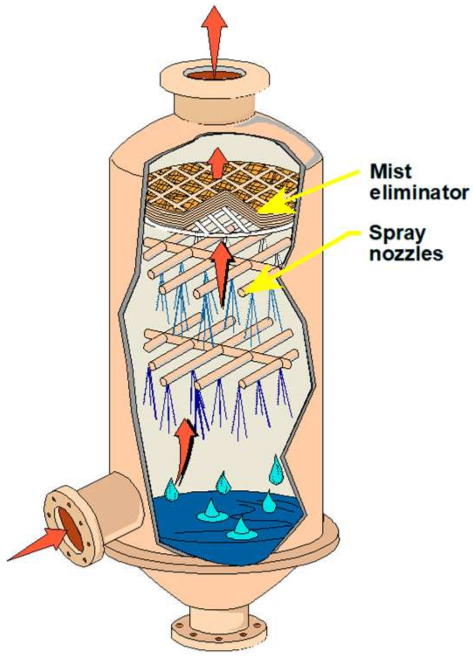
TYPES OF CONDENSERS

- Direct contact condensers
- Surface condensers

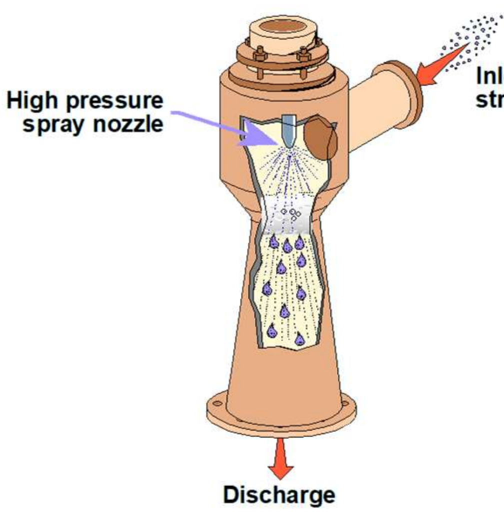
44



DIRECT CONTACT CONDENSER

45

EJECTOR CONDENSER



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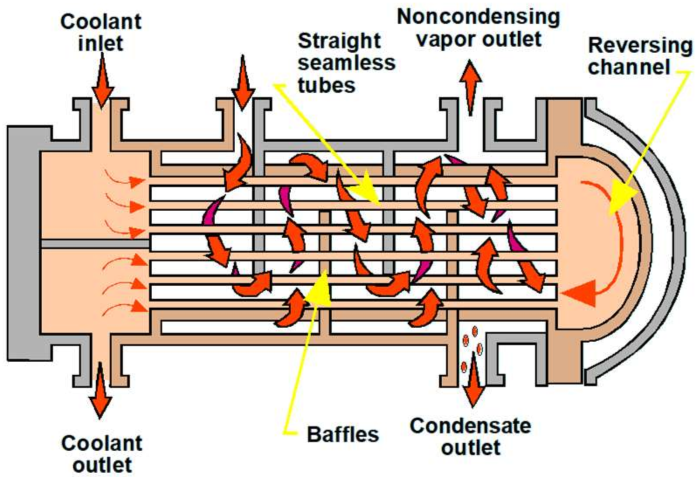
SHELL AND TUBE CONDENSER



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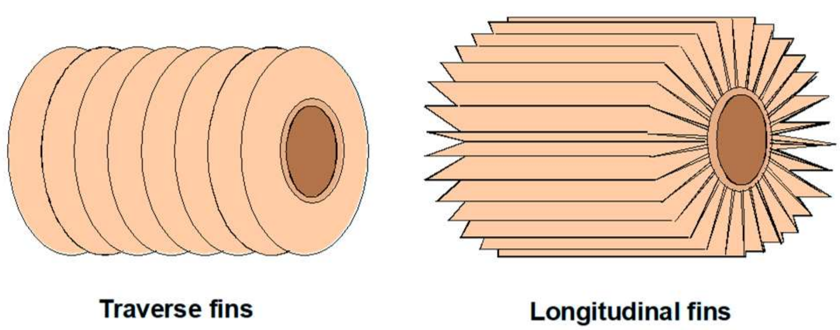
TUBE AND FIN CONDENSER



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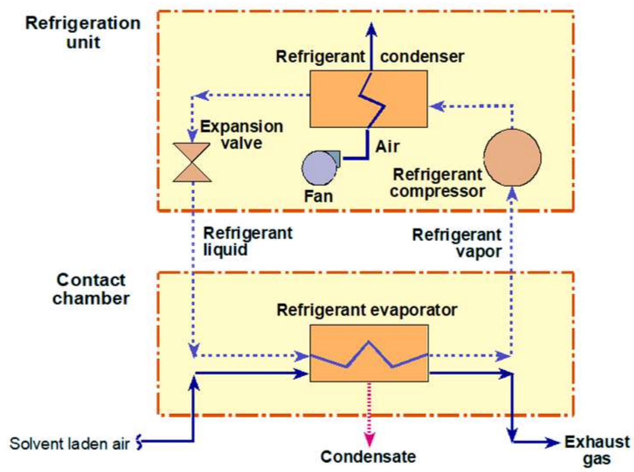
REFRIGERATION CYCLE



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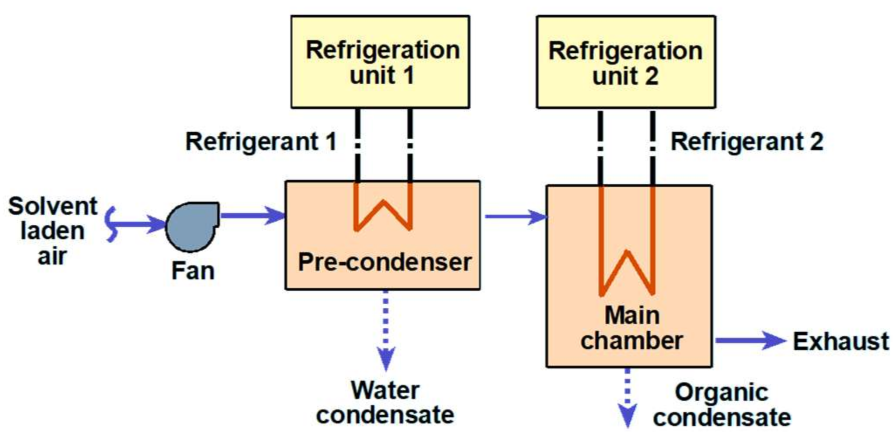
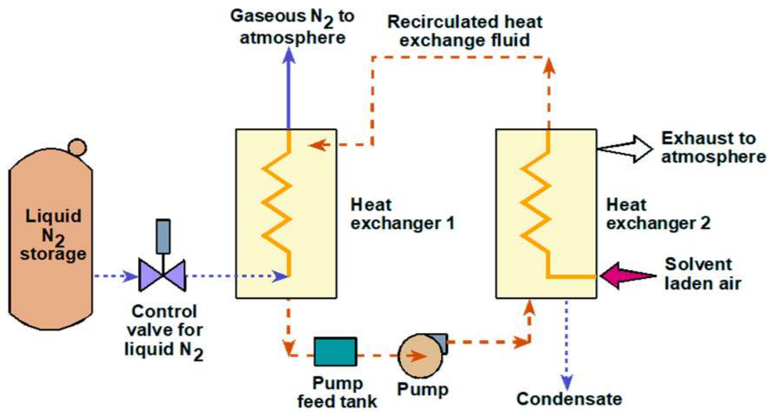
REFRIGERATION SYSTEM



50

DUAL HEAT EXCHANGER CRYOGENIC SYSTEM



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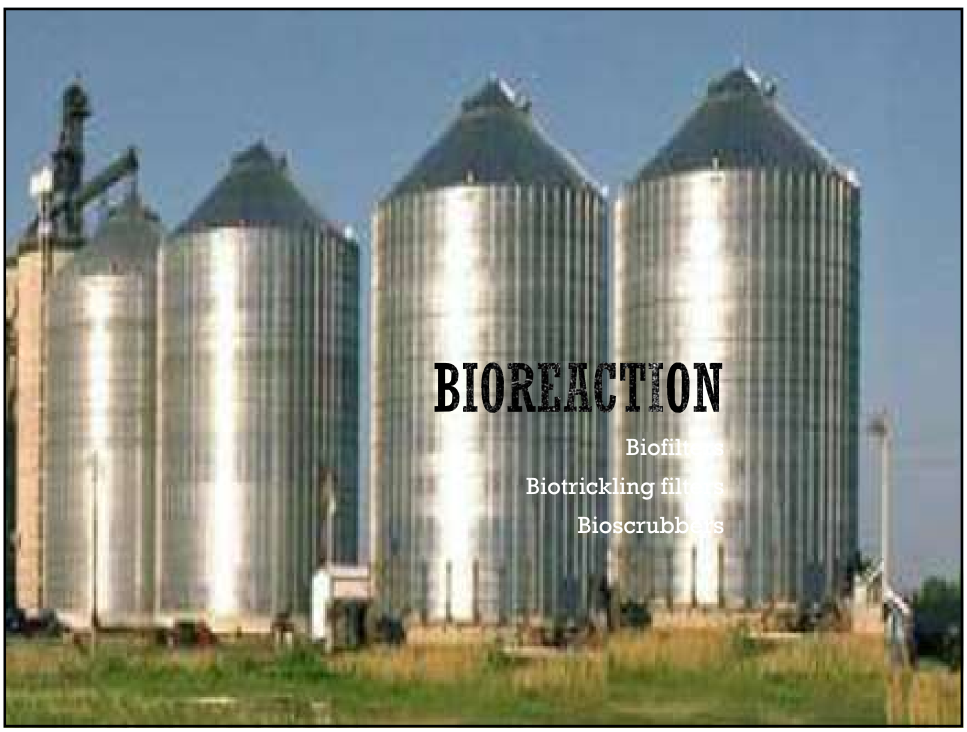

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MICROBIAL POPULATION REQUIREMENTS

- Sufficient moisture
- Sufficient nutrients
- Temperature of 60°F to 85°F
- pH of 6 to 8

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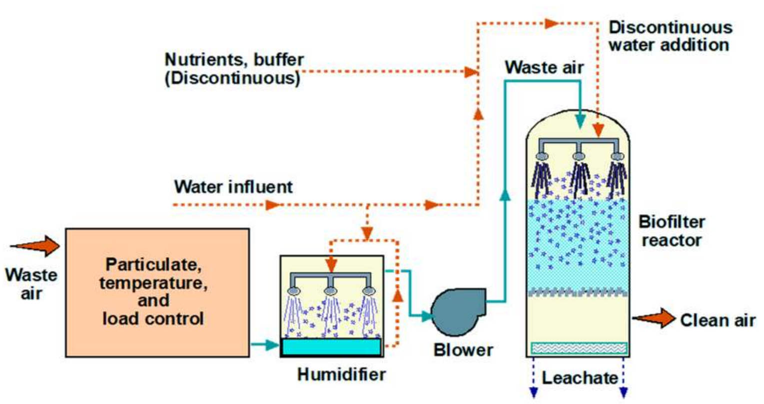
BIOFILTER SYSTEM



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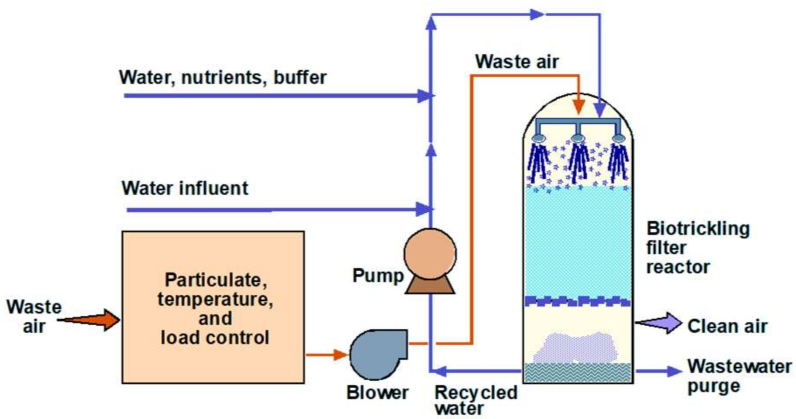
BIOTRICKLING FILTER SYSTEM



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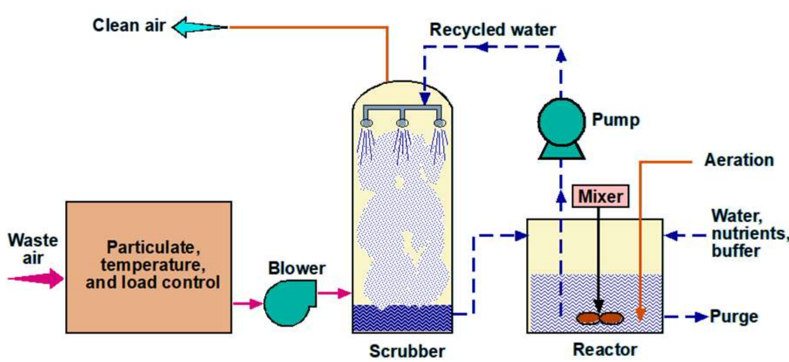
BIOSCRUBBER SYSTEM



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MAJOR VOC CONTROL TECHNOLOGIES: COMPARISON

Technology	Typical role	Strengths	Limitations	Key monitoring
Carbon adsorption	Recovery or polishing	High efficiency; solvent recovery possible	Humidity, PM, high temperature, breakthrough	Outlet VOC, bed temperature, pressure drop, regeneration
Thermal oxidizer	Destruction	Handles many VOC mixtures	Fuel use, NOx, acid gases if halogenated/sulfur VOCs	Combustion temperature, residence time, flow
RTO	Destruction with heat recovery	High heat recovery; good for high flow/low VOC	Valve leakage, bed fouling, maintenance	Chamber temperature, valve operation, pressure drop
Catalytic oxidizer	Lower-temperature destruction	Lower fuel use	Catalyst poisoning/fouling/thermal aging	Catalyst inlet/outlet temperature, ΔT, catalyst condition
Condenser	Recovery	Good for concentrated streams and valuable solvents	Low outlet temperature needed; moisture/ice issues	Outlet temperature, coolant condition, condensate recovery
Biofilter/biotrickling filter	Biological destruction	Low energy; useful for dilute biodegradable VOCs	Needs moisture, pH, nutrients, large footprint	pH, moisture, temperature, pressure drop, inlet/outlet VOC

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