

Guide for Safe Storage and Handling of Heated Petroleum-Derived Asphalt Products and Crude-Oil Residua

API RECOMMENDED PRACTICE 2023
THIRD EDITION, AUGUST 2001
REAFFIRMED, JUNE 2006



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Downstream Segment

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FOREWORD

The purpose of this recommended practice is to provide industry with guidelines and precautions for safe storage and handling of petroleum-derived asphalt products and crude-oil residua when being stored and handled while heated. The first edition of this publication was derived based on an early study conducted by a committee of the American Petroleum Institute dealing with safety and fire protection issues. Updates are based on industry experience and changes in scientific knowledge.

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Guide for Safe Storage and Handling of Heated Petroleum-Derived Asphalt Products and Crude-Oils Residua

1 Introduction

1.1 PURPOSE

This publication provides information to assist in the safe storage and handling of heated petroleum-derived asphalt products and crude-oil residua. The understanding of potential hazards, and application of this knowledge, can help reduce the probability and severity of incidents.

1.2 SCOPE

This publication describes phenomena which can occur and precautions to be taken in the storage and handling of asphalt products and residua derived from crude petroleum. It applies when these materials are stored in heated tanks at refineries and bulk storage facilities and transported in tank vehicles. Storage temperature may be either below or above the boiling point of water. The products to which these precautions apply include all petroleum materials for which similar storage and handling precautions are suitable, specifically those which need to be heated for storage and handling. This includes materials in the following categories:

- Performance grade asphalt cement used as a binder for paving (called bitumen in some areas).
- Road oils.
- Cutback asphalts and asphalts compounded with special diluents.
- Asphalt emulsions.
- Fillers and industrial asphalts, such as used for roofing and waterproofing.
- Blowing fluxes.
- Crude-oil residua.
- Heavy crude oils of low volatility that may be stored at temperatures above the boiling point of water.
- Asphalts containing polymers.

The scope of this document does not include “end-use” and application by customers. Information addressing end use applications can be obtained from a variety of organizations, including those listed in Appendix H. Some storage and handling practices for industrial and marine residual (bunker) fuels and low gravity heavy crude oils fall within the scope of this Recommended Practice (RP). The content may be applicable to those materials at the discretion of facility management.

1.3 RETROACTIVITY

Any provisions in this publication related to design are intended for reference when designing new facilities or when

considering major revisions or expansions. It is not intended that any recommendations in this publication be applied retroactively to existing facilities. This recommended practice should provide useful guidance when there is a desire or need to review programs or facilities.

1.4 CONCEPT OF HAZARD VS RISK

Hazards are properties of materials with the inherent ability to cause harm. Flammability, toxicity, corrosivity, stored chemical or mechanical energy all are hazards associated with various industrial materials. Risk requires exposure. A hot material can cause thermal skin burns or a corrosive acid can cause chemical skin burns, but only if there is contact exposure to skin. There is no risk when there is no potential for exposure.

Determining the level of risk involves estimating the probability and severity of exposure that could lead to harm. While the preceding examples relate hazards to the risk to people, the same principles are valid for evaluating property risk. For instance, hydrocarbon vapors in a flammable mixture with air can ignite if exposed to a source of ignition resulting in a fire which could damage property.

2 Referenced Publications

The most recent editions of each of the following standards, codes, and publications are referenced by this Publication as useful sources of information. Additional information also may be available from the cited Internet World Wide Web sites.

API¹

Std 650	<i>Welded Steel Tanks for Oil Storage</i>
Std 2000	<i>Venting Atmospheric and Low-Pressure Storage Tanks: Nonrefrigerated and Refrigerated</i>
RP 2001	<i>Fire Protection in Refineries</i>
RP 2003	<i>Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents</i>
Publ 2015	<i>Cleaning Petroleum Storage Tanks</i>
Publ 2021	<i>Management of Atmospheric Storage Tank Fires</i>
Publ 2021A	<i>Interim Study—Prevention and Suppression of Fires in Large Aboveground Atmospheric Storage Tanks</i>
Publ 2210	<i>Flame Arresters for Vents of Tanks Storing Petroleum Products</i>

¹www.api.org

Publ 2216	<i>Ignition Risk of Hydrocarbon Vapors by Hot Surfaces in the Open Air</i>
RP 2350	<i>Overflow Protection for Petroleum Storage Tanks</i>
Std 2610	<i>Design, Construction, Operation, Maintenance and Inspection of Terminal and Tank Facilities</i>

ACGIH²

2000 Edition of TLVs® and BEIs® Based on Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices

Asphalt Institute³

IS-180 *Safe Storage and Handling of Hot Asphalt*
MS-4 *The Asphalt Handbook*

ANSI⁴

B31.3 *Chemical Plant and Petroleum Refinery Piping*

EAPA⁵

ACGIH guideline TLVs for year 2000—change to measurement basis for asphalt (bitumen) fumes

NFPA⁶

Fire Protection Handbook
Flammable and Combustible Liquids Code Handbook
30 *Flammable and Combustible Liquids Code*
77 *Static Electricity*
325 *Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids*
385 *Tank Vehicles for Flammable and Combustible Liquids*

NIOSH⁷

NIOSH Pocket Guide to Chemical Hazards
Literature Review of Health Effects Caused by Occupational Exposure to Asphalt Fumes—Interim
Review Produced by NIOSH In Support of Nomination to the National Toxicology Program

²American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, Building D-5, Cincinnati, Ohio 45211. www.acgih.org

³Asphalt Institute, Research Park Drive, P.O. Box 14052, Lexington, Kentucky 40512-4052. www.asphaltinstitute.org

⁴American National Standards Institute, 25 West 43rd Street, New York, New York 10036. www.ansi.org

⁵European Asphalt Paving Association, P.O. Box 175, 3620 AD Breukelen, The Netherlands. www.eapa.org

⁶National Fire Protection Association, Batterymarch Park, Quincy, Massachusetts 02269. www.nfpa.org

⁷National Institute for Occupational Safety and Health (NIOSH)/Centers for Disease Control and Prevention (CDC), NIOSH/CDC, 4676 Columbia Parkway, Cincinnati, Ohio 45226. www.cdc.gov/niosh

OSHA⁸

1910.132 *Personal Protective Equipment*
1910.1200 *Hazard Communication*
1910.1000 *(and following) Subpart Z, “Toxic and Hazardous Substances”; see especially Section 1910.1002*

3 Definitions

3.1 acute hazard: Capable of causing effects occurring from exposure over a short time, usually a few minutes or hours. An acute exposure can result in short-term or long-term health effects.

3.2 API gravity: 141.5 divided by specific gravity at 60° F (15.56°C) minus 131.5 (lower numbers represent heavier, more dense materials; water has an API gravity of 10—anything with a numerically lower API gravity is “heavier than water”).

3.3 asphalt: Dark brown or black solid or semi-solid material obtained as residuals in refining petroleum (also called bitumen or petroleum asphalt).

3.4 asphalt cement: In Europe “asphalt” refers to “asphalt mix” and “bitumen” refers to the U.S. phrasing “asphalt cement”; in the United States, performance grade asphalt cement is the binder used for paving asphalt mix.

3.5 asphalt, cut-back: Asphalt which has been blended with a petroleum distillate to maintain a liquid consistency at lower temperatures; often used for coating road surfaces. Slow-, medium-, and rapid-curing cutback asphalts have progressively lower boiling point petroleum distillates.

3.6 asphalt compounded with special hydrocarbon diluents: May be used for roofing or adhesives; handling properties can be similar to cutbacks, depending on the hydrocarbon diluent used.

3.7 asphalt, emulsion: Low viscosity suspension or emulsion of asphalt in water; used for treating roadways, cement waterproofing and roofing compounds.

3.8 asphalt mix: A mixture of asphalt cement and aggregate for use in paving; in Europe the term “asphalt” refers to “asphalt mix”.

3.9 autoignition temperature: The minimum temperature at which a material will ignite with self-sustained combustion without an external source of ignition (such as a spark or flame). Autoignition temperature (also called autogenous or spontaneous ignition temperature) is dependent upon nature and duration of heating, specimen size, heat loss con-

⁸U.S. Department of Labor, Occupational Safety and Health Administration, 200 Constitution Avenue, N.W. Washington, D.C. 20210. www.osha.gov

ditions and other variables such as moisture content and contaminants. One widely used test is ASTM method E 659—Standard Test Method for Autoignition Temperature of Liquid Chemicals

3.10 bitumen: Petroleum asphalt; a synonymous term often used outside the USA for “asphalt cement”.

3.11 blowing fluxes: Asphaltic materials used as an intermediate to produce blown asphalt.

3.12 blown asphalt: Asphalt produced by blowing air through hot asphalt to produce material with special properties (especially raising the softening point).

3.13 boilover: The sudden overflow or ejection of the contents of a storage tank (containing a mixture of light and viscous hydrocarbons) during a full surface fire due to a heat wave (layer of hot, heavy oil) reaching water or water-oil emulsion at the bottom of the tank (see Appendix E.7 and API 2021 for more information).

3.14 bunker fuels: A name given to residual fuel oils derived from processing crude oil when used for marine applications (see Residual Fuels, and Fuel Oil, #5 & #6).

3.15 chronic health hazard: Capable of causing effects occurring from exposure over a long period of time (often at low-level concentrations).

3.16 coal tar pitch: A dark brown residue left after coal tar is redistilled; solid at ambient temperature. Not a petroleum process product.

3.17 cracking: Cleavage of molecules caused by high, localized temperatures; can lower flash point and cause flammable gas evolution.

3.18 crude-oil residua: Heavy hydrocarbon materials that are the “residue” after light hydrocarbons are separated by distilling; further processed to produce asphalt.

3.19 crude oils of low volatility: “Heavy” crude oils with gravity below 20 degrees API that may need to be transported and stored at elevated temperatures.

3.20 frothover: The overflowing of a tank when water (or volatile hydrocarbon) boils under (but near) the surface of a viscous hot oil.

3.21 fuel oil, #5 & #6: (See Residual Fuels, Bunker Fuels) #6 fuel oil is also called Bunker “C” Oil.

3.22 fume: Small diameter particulate matter formed by condensation from the gaseous state of vaporized high molecular weight materials. Although solids, fumes are small enough to behave like gases.

3.23 hazard: An inherent chemical or physical property with the potential to do harm (flammability, toxicity, corrosivity, stored chemical or mechanical energy).

3.24 heavy crude oil: Crude oil under 20 degrees API gravity is generally considered “heavy”.

3.25 IDLH: The NIOSH traditional definition is the maximum concentration of an air contaminant from which one could escape within 30 minutes without a respirator and without experiencing any escape-impairing or irreversible health effects.

3.26 natural asphalt: Naturally occurring petroleum materials which possess physical characteristics similar to asphalt derived by processing crude oil. Found in nature as lake (pit) or rock asphalt.

3.27 particulate: Inhalable materials considered by ACGIH to be hazardous when deposited anywhere in the respiratory tract (see Appendix J).

3.28 penetration: The penetration (hardness) test measures the distance in units of $\frac{1}{10}$ millimeter that a weighted standard blunt needle of a penetrometer will penetrate an asphalt cement sample at a prescribed temperature (usually 100 g at 77°F) in 5 seconds.

3.29 petroleum asphalt: Asphalt obtained by refining petroleum crude oil.

3.30 PCA: A polycyclic aromatic hydrocarbon (frequently used synonymously with PNA).

3.31 petroleum pitch: A product of petroleum processing (frequently used as a refinery intermediate).

3.32 PNA: A polynuclear aromatic hydrocarbon (frequently used synonymously with PCA).

3.33 pyrophoric: Iron sulfide or carbonaceous materials which, when exposed to air, can oxidize and heat, providing a source of ignition if a flammable vapor/air mixture is present.

3.34 residual fuels: Fuels based on residual components of crude oil, sometimes blended with lighter hydrocarbon to achieve an appropriate fuel viscosity. These fuels normally require special pre-heating burners and suitable handling and storage facilities (see bunker fuels).

3.35 risk: The probability of exposure to a hazard which results in harm.

3.36 risk assessment: The identification and analysis, either qualitative or quantitative, of the likelihood and outcome of specific events or scenarios with judgements of probability and consequences.

3.37 risk-based analysis: A review of potential needs based on a risk assessment.

3.38 road oils: Asphalt for treating road surfaces which has been diluted with a petroleum thinner to a liquid consistency at lower temperature (see cutback asphalts).

3.39 self-ignition temperature: See autoignition temperature.

3.40 slopover: The spilling of hydrocarbon material from a tank which can occur when a water stream is applied to the hot surface of a boiling oil, if the oil is viscous and its temperature exceeds the boiling point of water.

3.41 slurry oils: (Catalyst bottoms) are highly aromatic bottom fractions. Their high aromaticity gives them inherent solvency which makes them useful components to improve the stability of marine fuel blends.

3.42 tar: A dark-colored bituminous substance (not a petroleum process product), liquid or semi-liquid at ambient temperatures, obtained by the destructive distillation of coal, wood, peat, or other carbonaceous or vegetable materials.

3.43 vapor: The gaseous state of materials; vapor release requires elevated temperature for materials which are liquid or solid at ambient temperature. Materials can burn only when in their vapor state.

4 Hazards and Risk Reduction Associated With Heated Storage and Handling of Heavy Hydrocarbons

4.1 OVERVIEW

Heavy hydrocarbon hazards relate to the need to store and handle them at elevated temperature and from the basic composition of the materials.

Several inherent hazards relate to elevated temperature.

- a. Thermal burns.
- b. Increased release of hydrogen sulfide.
- c. Increased vapor release and fume formation.
- d. Increased release of flammable vapors.

Even at ambient temperature heavy hydrocarbons such as asphalt or residua may have inherent hazards related to their composition.

- a. Hydrogen sulfide (H_2S —see 4.3.1) is very toxic.
- b. Chronic exposure to heavy aromatic hydrocarbons containing PCA/PNA may cause skin cancer (see 4.4).
- c. Skin irritation can result from repeated hydrocarbon exposure.

Risk reduction involves recognizing these inherent hazards, controlling exposure and using good personal hygiene. The MSDS for the material should provide help in identifying composition and potential hazards.

Certain issues associated with management of tanks and storage at high temperatures are addressed separately in Sections 5 and 6.

In reviewing hazard information, it is important to recognize that terms frequently encountered in “common use” as

synonyms may actually refer to significantly different materials when “proper” names are used. While “asphalt” and “tar” are similar in appearance and historically have been used for some of the same applications—they are definitely not the same. As indicated in the definitions, asphalt is a petroleum product and tar typically is a residue from processing wood or coal to make charcoal, coke or “manufactured gas”. Handling either tar or asphalt (or other viscous materials) while hot involves similar concerns about potential burns from skin contact. However, chemical composition is significantly different (see App E.5). OSHA acknowledged this difference when it exempted asphalt (1910.1002) from the “coal tar pitch volatiles” standard, recognizing asphalt’s lower potential chronic hazards (see Appendix J).

4.2 THERMAL BURN HAZARDS TO PERSONNEL & RISK REDUCTION

Many asphalt, undiluted heavy crude oil and heavy residual fuel products are normally maintained at elevated temperatures to facilitate blending, transfer and transportation. Appendix E provides information on some typical storage and handling temperatures. High temperature contact exposure can cause serious burns. The hazard is increased with heavy hydrocarbons because they have high specific heat capacity, are good insulators and may stick to the skin.

Personnel who work with heated asphalt or heavy oil products should take precautions to avoid contact and exposure. Exposed skin should be protected by appropriate clothing, footwear, and gloves. Eyes should be protected by safety glasses, goggles, and/or a face shield. Precautions for avoidance of thermal burn should be familiar to personnel working in the refining industry.

Rapid cooling is the most important initial response to asphalt burns. The specific first aid (after immediate cooling) for burns from asphalt and similar materials includes special considerations, some of which are outlined in Appendix C. Removal of asphalt (or similar material) adhering to the skin usually requires special procedures and should be done with medical supervision. First aid guidance in Appendix C emphasizes the importance of obtaining professional medical treatment.

4.3 ACUTE HEALTH HAZARDS & RISK REDUCTION

Acute health hazards affect people during or shortly after exposure. The effects may be transient or longer lasting.

4.3.1 HYDROGEN SULFIDE HEALTH HAZARDS

Hydrogen sulfide (H_2S) is a highly toxic, colorless, flammable, heavier-than-air gas. H_2S can be present in asphalt, heavy crude or residual fuel storage vessels and transport vehicles. Because it is heavier than air it can accumulate in

the vapor space. Flammable limits are 4 to 44% volume in air. Although measurements taken a ft or more away from hatch openings or domes often show non-hazardous concentrations, dangerous exposures to high concentrations of H₂S can occur in the immediate vicinity of open tank vessels and tank truck, tank car or barge hatches or domes.

Very brief high (under 1000 ppm) H₂S exposures can cause severe respiratory difficulty, pulmonary edema, unconsciousness, and death. Relatively low concentration levels (under 100 ppm) can cause irritation of the eyes, nose, and throat. Moderate levels can cause headache, dizziness, nausea, and vomiting, as well as cough and breathing difficulty. The severity of effects depends on the concentration and duration of exposure. Personnel working around hydrogen sulfide should be aware that these symptoms can warn of potentially more dangerous exposure and trigger an investigation using appropriate protective gear. The original NIOSH IDLH level of 300 PPM was lowered to 100 PPM in the mid-1990s. The ACGIH TLV in 2000 was 10 ppm with an STEL/C of 15 ppm. ACGIH have published a “Notice of Intended Change” to lower their TLV to 5 ppm.

CAUTION: Although H₂S has a strong odor (often compared to rotten eggs), smell cannot be relied on to warn of danger. Brief exposure to high concentrations of H₂S can immediately paralyze the sense of smell and more extended exposure to lower concentrations has a similar olfactory nerve paralysis desensitizing effect. The strong odor of heated petroleum-derived asphalt products and crude oil residua can “mask” the odor of H₂S when present in these products and residua.

Personnel with the potential for exposure to hydrogen sulfide should be trained about H₂S hazards and where exposure to hydrogen sulfide could be possible. Respiratory protection should be required where appropriate. Candidate activities include tank gauging, maintenance and barge, tank truck or rail car filling. (e.g. open transfer).

The Agency for Toxic Substances and Disease Registry includes information on hydrogen sulfide in their publication “ATSDR Medical Management Guidelines for Acute Chemical Exposures: Chemical Protocols” posted on their web site at: www.atsdr.cdc.gov/mmg15.html.

4.3.2 INERT ATMOSPHERE HEALTH HAZARDS

Inert (oxygen deficient) atmospheres such as nitrogen or flue gas are sometimes used to blanket the liquid in a tank to reduce the probability of a fire (although an inert atmosphere encourages the build-up of pyrophoric material in tanks). The lack of oxygen in inert atmospheres represents an acute hazard to personnel under certain exposure conditions. In the unlikely case where a person manages to enter and stay in a totally enclosed space without any oxygen the person may collapse and death can occur. If the employee is briefly exposed or surrounded by a transient oxygen deficient atmosphere (such as

while gauging or venting an inert-blanketed tank) then dizziness might result. If this atmosphere is from the tank vapor space then there can be significant concentrations of hydrocarbon vapor which may compound the effects. These effects should pass when the person again is breathing normal air; however, during the period affected, there is risk of inadvertent action such as falling or contacting hot surfaces. See 6.2 & 6.3 for more information on pyrophorics.

4.3.3 FUMES AND VAPORS

Inhalation exposure to vapors and fumes from heated asphalt can have effects occurring from exposure over a short time, such as irritation of the eyes or respiratory system. “Cut-back” asphalt or residual fuel blended with lighter distillate hydrocarbons may release vapors from the distillate hydrocarbon component which can cause irritation, light-headedness or headaches. All of these short-term exposure effects are considered reversible when removed from exposure.

Threshold Limit Values and Permissible Exposure Limits are intended to address longer term repeated exposure. The 2000 edition of the ACGIH® publication *TLVs® and BEIs®—Threshold Limit Values For Chemical Substances and Physical Agents and Biological Exposure Indices*—lists “Asphalt (Petroleum; Bitumen) Fume” with a TLV of 0.5 mg/m³. This is a tenfold reduction from the previous TLV of 5.0 mg/m³. ACGIH indicate that this new limit is based on “irritation” (primarily of mucous membrane in eyes and respiratory tract).

There is no OSHA Permissible Exposure Limit (PEL) for asphalt fume. OSHA has stated specifically that limits for coal tar pitch volatiles (CFR 29 1910.1002) do not apply to asphalt from any source. Good industrial hygiene practice will educate employees in the importance of avoiding exposure to fumes and provide protective equipment where appropriate.

Appendix J discusses the TLV and PELs along with other health studies.

4.4 POTENTIAL CHRONIC HEALTH HAZARDS & RISK REDUCTION

Chronic health hazards require repeated or extended exposure and may not evidence effects for a long time after exposure. Hydrogen sulfide is not a chronic health hazard. Materials for which repeated or prolonged exposure are of interest when working around asphalt and heavy hydrocarbon residual materials are discussed in the following section.

The 2000 edition of the ACGIH TLVs® lists “Asphalt (Petroleum; Bitumen) Fume” with a carcinogenicity “Notation” of A4. This categorizes asphalt fume as “Not Classifiable as a Human Carcinogenic Agent” (see Appendix J). This conclusion, reached by the IARC in 1987, was also the conclusion of a 1997 NIOSH published review of scientific studies of asphalt fume.

Petroleum-derived asphalts and residua vary in composition. Source of crude oil, processing techniques, storage, and handling

dling temperatures, and added components (for example, clarified slurry oil or middle distillates added as diluents to produce cutback asphalts or lower viscosity residual fuels) all affect the potential hazards associated with a particular product.

There is some evidence of carcinogenic (cancer) and other health risks, such as skin and respiratory effects, associated with certain heavy petroleum materials or components. It is difficult to characterize this class of materials generically because of the wide variation in composition. Most studies of potential carcinogenicity of heavy hydrocarbons focus on polycyclic or polynuclear hydrocarbons. Some of these compounds have been identified as carcinogens (particularly of skin) while others clearly are not. The concentration of PCAs can increase with overall aromatic content of heavy hydrocarbons. This should increase emphasis on good hygiene, proper use of PPE and minimizing contact where higher aromatic materials are blended into products to improve performance. Appendix J.4 presents NIOSH's brief summary of their literature review of health effects and occupational exposure to asphalt fumes.

4.5 COMPATIBILITY OF MATERIALS AND AVOIDING FROTHOVERS

When a storage or transport vessel has a change of service to asphalt or residual product service, precautions should be taken to avoid combining potentially incompatible material which might result in a hazardous (or even violent) frothover. (See Appendix E.7 for a discussion of "Frothover", "Slop-over" and "Boilover".) If a tank has been out of service for an extended period, incompatible materials should be thoroughly purged. Both water and light hydrocarbons (such as distillate) are of concern. If hot product is discharged to the tank then water can boil and cause rapid expansion and potential overpressure of the tank. Light hydrocarbon will release vapor which can bring a tank vapor space into the flammable mixture range; large rates of vapor release can also overpressure a tank. Areas to consider when purging tanks include the internal tank structure and structural members, internal piping, inlet piping and chambers, and tank-bottom sumps. For transport trucks, rail cars or vessels the similar concept holds to purge the system wherever water or light hydrocarbon might be retained.

4.5.1 CONTAMINATION BY WATER OR LIGHT HYDROCARBONS

Accidental injection of water or light hydrocarbons into heated asphalt or crude-oil residua may produce a violent and rapid evolution of froth, steam, or vapor if the product temperature exceeds the boiling point of water or the light hydrocarbons. The resulting pressure buildup may cause the roof-to-shell seam to fail in tanks designed in accordance with API 650. The resulting potential frothover could affect a large area surrounding the tank.

4.5.2 POTENTIAL SOURCES OF CONTAMINATION

Water or light hydrocarbons may enter a heated tank with slop oil, from interconnecting lines, leaking coolers, or leaking hot-oil heater coils, or as a result of steam leaks or a unit start-up or upset. Water can also accumulate from condensate formed on the underside of the roof and the upper shell of the tank when the contents are below 212°F (100°C) or the tank is out of service. See 5.6 & 5.7. This condensate sometimes drains down the inside of the tank shell to the bottom of the tank.

4.5.3 PREVENTION OF COMPATIBILITY PROBLEMS

4.5.3.1 Removing Water (Bottoms) Prior to Input Of Heated Product

If streams entering a heated asphalt or residua product tank operating at temperatures above 212°F (100°C) are not free from water, significant problems can occur as described above. If interconnecting lines are necessary, either a roll-out spool or double block valves and a bleeder should be provided to prevent water or hydrocarbon from entering the tank. Water coolers in a line to such tanks should operate with product pressures higher than water pressure to prevent water from leaking into the tank. External heat tracing and insulation or external electrical heat tracing of lines is also recommended. Tanks that have been out of service for extended periods should be checked to ensure that water bottoms have not accumulated.

CAUTION: Steam-jacketed or steam-gutted hot-oil lines should not be used between process units and asphalt/residua storage and loading facilities. Leaks may develop and cause frothing of the product.

4.5.3.2 Monitoring Of Rundown Temperatures And Line Flushes

Monitoring and control of temperature of materials being "run down" into tanks can help reduce potential problems associated with inadvertent vaporization of light hydrocarbons. If the tank contains light material and the vapor space is lean, then hot rundown can bring the vapor space into (or through) the flammable range. If the vapor space is lean there shouldn't be any pyrophoric iron sulfide. However, increased temperature and flammable vapor may result in ignition by carbonaceous deposits. If hot rundown is introduced into a solvent-containing product there may be rapid vaporization of the solvent with potential to overpressure the tank. If the tank has been "empty", or out of service, there may be water or solvent concerns (see 5.7).

Related concerns are associated with line washes. If flushes are cool and contain water which is introduced into material stored above 212°F (100°C), boiling of the water can cause significant problems. If a light hydrocarbon flush is introduced into a hot tank there is the potential both for over-

pressure in the tank and for moving a lean tank vapor space into the flammable range.

4.6 FIRE PREVENTION

Before there is the possibility of a storage tank fire there must be a flammable mixture in the tank. Some actions to help prevent fires and explosions by controlling the vapor space in heated storage tanks are:

- Ventilating to remove vapors and keep vapor space in the "lean" range (for tanks with low volatility materials stored at least 50°F below their open cup flash point).
- Venting limited to a single vent that is properly sized [see API 2000].
- Preventing restriction caused by condensed, solidified deposits building up in the vent.
- Keeping gauge hatches closed during normal operation.
- Regulating the storage temperature to keep the evolved vapors outside the flammable range (either too lean or too rich—see Appendix D.3).
- Careful control if lines are blown with air (see 6.4).
- Careful control if using air for mixing (see 7.3).
- Inert blanketing the vapor space to reduce oxygen content.
- Temporarily inerting the vapor space with flue gas or another suitable medium when tanks are emptied at rates substantially above normal.

Ignition of hydrocarbon vapors is possible when the oxygen level is about 11% (by volume) or greater. To maintain a safety margin, SOLAS calls for a maximum of 8% (by volume) oxygen in inert blanketed tanks on board crude oil tankers. This is achieved using systems supplying inert gas with a maximum of 5% oxygen. Inert gas is lighter (lower molecular weight) than hydrocarbon/air mixtures. If blanketing is used, the potential "time effect" of the inerting technique should be recognized. If the inert gas is introduced near the top there can be stratification in the tank, with the heavier air/fuel mixture near the surface of the stored hydrocarbon. Diffusion and thermal currents will eventually provide dilution of the original atmosphere. If an empty tank is being inert blanketed this stratification effect can be used to advantage by venting the tank of HC vapors from the bottom with inert gas introduced near the top. This will tend to displace (instead of dilute) the heavier hydrocarbon/air mixture. Potential personnel exposure and environmental issues should be addressed. Tanks which have been inert blanketed may require special procedures when being removed from service (see 6.3.2) because inerting can cause a buildup of pyrophoric iron sulfide.

Precautions against exposure to sources of ignition should be emphasized and observed. If ignition occurs inside a tank there may be an internal explosion. The resulting overpressure may cause the tank's roof to fail and separate from the shell. The result will be a full surface (or partially impeded)

tank fire. Suppression is discussed briefly in 4.7 and Appendix K, and in more depth in API RP 2021. See Appendix A for some handling suggestions.

4.6.1 POTENTIAL FUEL SOURCES

Hydrocarbons must be in the vapor phase to burn and be in their flammable range. Temperature control and knowledge of material in tanks become very significant. This is especially true if a tank is being switched from one service to another, particularly where hot heavy product is being mixed with cool product containing a light fraction (e.g. cutbacks). As the temperature in the tank goes higher there will be more vapor generated. If the temperature goes very high (over approximately 450°F), or there is localized overheating, then light vapors may be generated as a result of cracking. In these cases, the light components released can increase the fire hazard.

Some situations in which tanks may have a flammable mixture include:

- Nearly empty tanks containing a product with an appreciable vapor pressure at the tank temperature. (Air will be drawn into vented atmospheric tanks as product is withdrawn).
- Tanks being filled from a relatively low level (with air in the headspace) with a product which has an appreciable vapor pressure at the rundown temperature.
- Tanks at a temperature higher than normal for low vapor pressure products.
- Tanks with a non-functioning inert gas blanket.
- While air-blowing asphalts.
- Mixing or contamination with a small amounts of light solvent
- Material heated above the flash point.
- Inadequate ventilation (normal vents do not draw off vapors)

From a practical standpoint it is useful to recognize that small quantities of absorbed gases and low molecular weight components can accumulate in the tank vapor space in concentrations higher than yielded by an intuitive judgement based on percentage. Since hydrogen sulfide is heavier than air and very flammable (4% to 44%) it can accumulate in the vapor space of tanks and represents fuel for a potential fire.

4.6.2 POTENTIAL IGNITION SOURCES

4.6.2.1 Electrostatic Ignition

Since asphalts are relatively good conductors of electricity, they do not accumulate electrostatic charges. Experience indicates that asphalts do not present a significant threat of electrostatic ignition. Handling distillates during the mixing of asphalt-solvent blends should be done with appropriate precautions, such as bonding and grounding (see API 2003). Activities such as flowing steam into the vapor space of

asphalt tanks can generate electrostatic charges which could ignite flammable vapors. Caution should be exercised to ensure the presence of thorough bonding and grounding if steam hoses are used as an approach to inert a tank with a known flammable atmosphere.

4.6.2.2 Pyrophoric Ignition

There are two distinctly different pyrophoric materials which can develop in petroleum storage tanks: iron sulfide and carbonaceous deposits. Pyrophoric iron sulfide forms in oxygen deprived (inert) conditions. When exposed to oxygen from normal air the deposits become a source of ignition. 6.2 and 6.3 discuss control of “low oxygen” inert blanket oxygen content (at approximately 5%) to prevent formation of these deposits. Pyrophoric carbonaceous deposits are common in asphalt tanks. They typically form from condensation of heavy vapors on the roof and walls of tanks. At high temperature [approximately 350°F (177°C) to 375°F (190°C)], and when oxygen is available, these deposits can glow and ignite flammable mixtures.

4.6.2.3 Hot Surface Ignition

Hot surface ignition is related to the autoignition temperature of the material being handled. Autoignition temperatures may be hard to find, considered variable, and where published are frequently identified as estimates. Where listed, most straight asphalts have autoignition temperatures estimated in a range of 700°F to 900°F. However, MSDSs for some cutbacks and specially compounded blends have autoignition temperatures listed as low as 400°F.

Hot surface ignition is possible whenever a glow of color is visible from a hot metal surface (minimum of approximately 750°F), such as from a torch used on the outside of a tank vapor space. Smoldering carbon deposits in insulation on the outside of the tank are a potential source of heating. API 2216 is dedicated to a discussion of hot surface ignition. Shown below are a few autoignition temperatures relevant to asphalt as listed on MSDSs:

Auto-ignition Temperatures

(source—various manufacturers’ MSDSs)

MC 30 Asphalt Cutback	> 400°F/204°C
Roofing Cements with solvent	> 500°F /260°C
Oxidized (Blown) Asphalt	> 700°F/370°C (approximate)
Roofing asphalt (flux)	> 700–900°F/370–480°C (approx.)

4.6.2.4 Open Flame Ignition

Welding or other “open flame” ignition sources should be subject to normal controls used for hot work (see API 2009). Special attention should be paid to the potential for the hot work itself to heat heavy material (such as waxy deposits inside a tank) and release vapors into a previously non-flammable area (see “Lessons Learned” Appendix D.1).

4.6.2.5 Lightning Ignition

Lightning as a source of ignition is essentially the same for all fixed-roof tanks. There cannot be ignition unless there is a flammable vapor mixture in the headspace of the tank (see 4.6.1). Pumping product out of a tank which does not have an inert blanket will normally draw in air. If the initial headspace was too rich to burn, then the addition of air may bring it into the flammable range. In these cases, it may be prudent to discontinue pumping from the tank during weather conditions conducive to lightning. API 2003 addresses electrostatic phenomena including lightning protection of tanks.

Flame arresters generally are not used on the vents of asphalt or other heavy hot-oil tanks and would not be effective in preventing lightning from being a source of ignition. Flame arresters are not recommended for use on any petroleum tanks equipped with P/V valves (see 5.2).

4.7 FIRE SUPPRESSION

Fire suppression for heavy oil products is a special case for the following reasons:

- The heat stored in hot product increases the challenge of fire suppression since a major mechanism is cooling the burning material to inhibit vapor release and thus extinguish the fire.
- The hot product makes it difficult to maintain a foam blanket to inhibit vapor release.
- Hot heavy-oil surfaces can experience “frothover” or “slopover” when water is applied.
- Heavy-oil materials with light fractions (crude oil, cutbacks, blended residual fuels) might be able to produce boilover conditions—IF water can accumulate at the bottom of the tank (the bulk storage temperature must be significantly below 212°F (100°C)).

The frothover, slopover and boilover phenomena are discussed in Appendix E.7 and API RP 2021. Although API 2021 explicitly omits coverage of heated tanks from its tank-fire suppression scope, the methodology used in emergency response planning and preparing to suppress tank fires are applicable, as is the discussion of heavy oil phenomena. Appendix K discusses fire suppression for heated heavy-oil tanks in more detail.

Note: Evacuate all non-involved personnel from potentially affected fire areas where attempted fire suppression involves burning materials with frothover, slopover or boilover potential. This is particularly important to do before suppression is started.

NFPA 11 cautions about applying portable foam streams to high viscosity materials heated above 200°F (93.3°C). They note “good judgement should be used in applying foam to tanks containing hot oils, burning asphalts, or burning liquids with a boiling point above the boiling point of water. Although the comparatively low water content of foams can

beneficially cool such fuels at a slow rate, it can also cause violent frothing and slopover of the tanks contents”.

Fire suppression specialists suggest gently cooling the burning surface using a variety of approaches prior to mounting a foam attack. This needs to be done judiciously to avoid excessive early water application (see "Lesson Learned" in Appendix D.3). Some facilities recommend blinding or removing any fixed or semi-fixed systems that can provide foam directly to the liquid in heated heavy-oil tanks. If foam is applied directly under a partially obstructed roof the resulting steam formation could blow the roof free of the vessel in an uncontrolled incident.

If the tank on fire is equipped with mixers it may be possible to “roll the tank”. This approach seeks to move cooler product to the burning surface at the top of the tank, reducing vapor release and thus interrupting burning. This can be done concurrently with “gentle water-cooling”.

If there is a fire inside a tank and the roof is still intact then routing inert gas into the tank head space has been successfully used for suppression.

Early in the fire suppression process any external heating of material in the tank should be stopped.

For spill fires, if the fire does not go out after cooling with water spray, a dry chemical (followed by foam) or dual agent attack may be successful.

5 Storage Tanks

5.1 TANK ROOFS

Asphalt tanks should have a watertight, free-draining roof. Tanks should receive regular internal inspections to detect accumulation of deposits on the underside of the roof. Deposit formation can be caused by condensation of vapors (especially near vents) or might be a result of over-filling. Heavy accumulation of deposits could overload the roof. If heavy roof deposits are the result of overfilling and accumulation underneath a cool roof surface, and the roof is supported by the overfull tank inventory, then failure might result when the supporting asphalt inventory is removed from the tank resulting in an air space beneath the roof.

Tank roofs should be provided with frangible seams in accordance with API 650. Maintenance and surveillance should recognize that accumulated carbonaceous deposits can be pyrophoric and may increase fire hazard (see 6.1 and 6.3).

5.2 TANK VENTS

Asphalt and other heavy hot-oil tanks are normally provided with an open, rainproof vent located at a high point near the middle of the roof (to avoid areas of low oxygen in the tank). Tanks should have only one vent to minimize the introduction of oxygen to the vapor space. Vents should be inspected frequently to remove accumulations of coke-like deposits. Consideration should be given to providing access to

vents for inspection (perhaps by providing walkways to avoid hazards of walking on roofs prone to corrosion) and to avoiding personnel exposure during inspection. Some facilities use an alternative vent placement just inboard of the roof/wall seam. They report that this appears to have eliminated buildup of condensation products on the roof and provides line-of-sight observation of tank venting from ground level.

Gauging hatches and roof manways should be kept closed. Unintended cross venting (where there is the potential for a natural draft rapidly changing the internal tank atmosphere flammability characteristics) should be avoided. For instance, use of manways for gauging can introduce flow significantly greater than provided by a gauge hatch.

Pressure-vacuum vents are not generally used in this service (see API 2000). Accumulation of condensed asphalt vapors may result in pallet sticking and subsequent tank collapse. Where inert blanketing is provided by carbon dioxide, nitrogen, or flue gas (approximately 3 to 5% oxygen desired), pressure-vacuum vents are necessary to maintain the inert blanket. Inert gas should be injected under the pressure-vacuum vent to keep the vent as clean as possible. Flame arresters are not generally used on asphalt or other heavy hot-oil tanks (or any tanks with P/V valves—see API 2210). Where these devices are installed on existing asphalt storage tanks a regular preventive maintenance program to inspect and clean these devices is needed to ensure they are functioning properly. The frequency of inspection varies with the service and application and should be determined using historical data and sound engineering judgement.

5.3 TANK TEMPERATURE MEASUREMENT

Temperature readings should be recorded routinely as a means of controlling the temperature of the product in the tank. The temperature-measuring device should be reliable and extend into the tank deep enough to obtain representative product temperatures. Readings should not be taken near the shell or bottom of the tank or near heating coils or fired tubes.

If the sensing element is exposed to vapor while the temperature control system is active, an erroneous low temperature signal might cause the tank's heat treating medium to circulate at maximum rate until product reaches the temperature sensor and a proper reading is sent to the control system. If stored product is in contact with overheated heating coils or fired tubes there may be cracking of the heavy hydrocarbons and/or generation of significant quantities of light hydrocarbon vapors.

Some facilities specify installation of temperature indicators on the product rundown line to the tank along with two additional temperature indicators in the tank located 60 degrees on either side of the fill line. This provides unit operators both backup instrumentation and diagnostic tools to evaluate abnormal conditions (such as when a "plume" of hot material is getting into the tank).

