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

API RECOMMENDED PRACTICE 2023
THIRD EDITION, AUGUST 2001

American
Petroleum
Institute

**Helping You
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Downstream Segment

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FOREWORD

The purpose of this recommended practice is to provide industry with guidelines and pre-cautions 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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INFORMATION CONCERNING SAFETY AND HEALTH HAZARDS AND PROPER PRECAUTIONS WITH RESPECT TO PARTICULAR MATERIALS AND CONDITIONS SHOULD BE OBTAINED FROM THE EMPLOYER, THE MANUFACTURER OR SUP-PLIER OF THAT MATERIAL, OR THE MATERIAL SAFETY DATA SHEET.

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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:

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

API[1]

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

[1]www.api.org

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Publ 2216   *Ignition Risk of Hydrocarbon Vapors by Hot Surfaces in the Open Air*

RP 2350   *Overfill Protection for Petroleum Storage Tanks*

Std 2610   *Design, Construction, Operation, Maintenance and Inspection of Terminal and Tank Facilities*

ACGIH[2]

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

Asphalt Institute[3]

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

ANSI[4]

B31.3   *Chemical Plant and Petroleum Refinery Piping*

EAPA[5]

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

NFPA[6]

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*

NIOSH[7]

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

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

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

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

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

[6]National Fire Protection Association, Batterymarch Park, Quincy, Massachussetts 02269. www.nfpa.org

[7]National 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

OSHA[8]

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-

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[8]U.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 posses 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 $1/10$ 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 H_2S 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) H_2S 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 H_2S has a strong odor (often compared to rotten eggs), smell cannot be relied on to warn of danger. Brief exposure to high concentrations of H_2S 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 H_2S when present in these products and residua.

Personnel with the potential for exposure to hydrogen sulfide should be trained about H_2S 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. "Cutback" 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 han-

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 carcinogicity 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", "Slopover" 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:

a. 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).
b. Venting limited to a single vent that is properly sized [see API 2000].
c. Preventing restriction caused by condensed, solidified deposits building up in the vent.
d. Keeping gauge hatches closed during normal operation.
e. Regulating the storage temperature to keep the evolved vapors outside the flammable range (either too lean or too rich—see Appendix D.3).
f. Careful control if lines are blown with air (see 6.4).
g. Careful control if using air for mixing (see 7.3).
h. Inert blanketing the vapor space to reduce oxygen content.
i. 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:

a. 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).
b. 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.
c. Tanks at a temperature higher than normal for low vapor pressure products.
d. Tanks with a non-functioning inert gas blanket.
e. While air-blowing asphalts.
f. Mixing or contamination with a small amounts of light solvent
g. Material heated above the flash point.
h. 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:

a. 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.

b. The hot product makes it difficult to maintain a foam blanket to inhibit vapor release.

c. Hot heavy-oil surfaces can experience "frothover" or "slopover" when water is applied.

d. 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).

5.4 LIQUID COVERAGE OF TANK HEATING SOURCES

It is important to ensure that the area close to an internal tank heat source is substantially covered with liquid. The tank's liquid level should never be drawn lower than several in. above fired tubes or other heat-exchange surfaces while heat is being applied. Without sufficient fluid coverage of the heating source there may be excessive localized heating. This could result in "cracking" of the product, generation of light ends and lead to creation of carbonaceous deposits above the liquid or on the roof. Under some conditions these deposits can become pyrophoric. New technology (such as radar, microwave or ultrasonic gauging) provides options for monitoring tank levels in service where conventional gauges require frequent maintenance.

5.5 TANK HEATING COIL CONSIDERATIONS

All-welded heating coils should be used for asphalt and residual product tanks. Heating coils should be tested when the tank is out of service to minimize the possibility of leaks. Locating the coils near the bottom of the tank improves heating and agitation of the bottom layers and reduces the possibility of pumping the product level below the coils.

Tanks equipped with steam coils or fired heaters should be checked frequently for steam leaks and hydraulic hammer phenomena which may damage coils. When the coils are inactive, an atmospheric bleed should be opened on the coil near the tank and should be checked frequently for condensate and product leaks. Isolation spools and car seals on double-block valves can provide positive separation and should be checked routinely.

5.6 EFFECTS OF TANK TEMPERATURE CYCLING

Many products, such as cutback asphalts, road oils, and emulsions, are stored at temperatures below 212°F (100°C) to prevent steam from evolving from associated or accumulated water. Tanks should not be operated in a range in which the temperature fluctuates above and below the boiling point of water. Fluctuations are conducive to the accumulation and rapid vaporization of water; these conditions often result in frothovers. Where tank contents are continuously above 212°F (100°C) and operate on a frequent cycle of filling and emptying, there is less opportunity for water accumulation by condensation. However, temperatures above the boiling point of water can cause milled emulsions to "break".

Temperature fluctuations in the range of 212°F – 265°F (100°C – 130°C) should be avoided as they could result in condensation, breaking of emulsions and frothing.

5.7 HAZARDS OF INACTIVE TANKS

Tanks which have been inactive may present hazards when being put into service (a "change" which should be recog-

nized and "managed"). The temperature of the product at the shell or bottom of an inactive tank may not represent the temperature of the tank's bulk contents. Even if the body of the product is maintained at a temperature above the boiling point of water, a long-inactive tank may develop cool layers at the bottom. Water or emulsion can accumulate within these layers. Mechanical agitation or other disturbances can mix the water with the heated asphalt and cause a rapid evolution of steam. The resulting increase in volume may exceed the capacity of the tank, rupture the tank's roof-to-shell seam, or cause violent frothovers.

To minimize the accumulation of water, the tank connection and draw-offs should be as near as possible to the tank sump or bottom. Movement of product into or out of a tank which has been inactive merits special precautions. Before product movement begins any accumulations of water or emulsion should be drained from the tank. Pumping should start at a low rate while the tank is monitored to note and respond to any abnormal conditions. This is particularly significant when material at a temperature above the boiling point of water is being pumped into the tank.

Similar concerns exist when there may be light hydrocarbon material remaining from prior storage. Hot incoming heavy material will vaporize the lighter hydrocarbon. This brings the potential for moving the tank vapor space into the flammable region creating a possible fire hazard (see 4.6.1). If large quantities of vapor are generated then the venting capacity of the tank may be exceeded with the potential to overpressure and rupture a tank seam.

Adding hot asphalt to a cool, inactive tank can result in rapid expansion of air/vapor in the vapor space inside the tank. Typical vent-sizing calculations are based only on air/vapor displacement caused by the incoming fluid. Rapidly expanding vapor/air can generate significantly greater quantities of air/vapor than displacement. Field experience shows that this can overpressure and damage a tank. This might be addressed procedurally by adding a small amount of hot product and allow the tank to heat up slowly prior to receiving the main delivery. An engineering solution could re-size vents to include a "worst case" condition when adding hot product to a cool tank.

5.8 STORING ASPHALT EMULSIONS

An asphalt emulsion is a nonflammable liquid mixture produced by combining asphalt and water (as much as 20 to 30%) with an emulsifying agent such as soap or colloidal clays (from 5 to 15%). Some asphalt emulsions may contain low-flash hydrocarbon components along with the water used to form the emulsion. Ideally, these products should be stored below the boiling point temperature of the hydrocarbon component. Most emulsions are blended to be liquid at temperatures near ambient. They should not be heated above the boiling point of water as there is a potential for the emulsion to break and the boiling

water to cause frothing. If asphalt emulsion experiences freezing conditions the emulsion will break releasing the water and allowing whatever phenomena occur in freezing weather (broken pipes, etc) to occur.

5.9 STORING & HANDLING POLYMER MODIFIED ASPHALT

Polymer modified asphalt (bitumen) is a generic name for physical blends or chemical cross-linked blends of asphalt (bitumen) and a variety of different types of polymers. In some cases the products also may contain non-polymeric additives or fluxes. For road construction, the typical polymer content is below 10%. For roofing application, blends with polymer content ranging from 10% to 40% may be used. Polymers are used to change the temperature characteristics of the blends.

Polymer modification may require asphalt to be handled at higher temperatures. Unmodified asphalt is relatively insensitive to heat when kept below its "cracking" temperatures. But, polymers used in modified asphalt can be susceptible to thermal degradation which is both time and temperature dependent. The higher the temperature and the longer the residence time, the more the polymer blend will degrade. Typical first generation polymer modified asphalts are stored with a maximum temperature below 380°F (although manufacturers literature indicates some specific polymers have higher temperature tolerance). The decomposition products may include vapors and fumes as well as causing product quality and operational problems.

Extended personnel exposure to decomposition products resulting from excessive temperatures may lead to respiratory irritation, dizziness, nausea and/or headaches. However, the European Asphalt Pavement Association (EAPA) cites comparative studies of emissions from standard paving grades and SBS-modified bitumen which confirm that under correct working conditions there was no increase or typical difference in fume formation. This conclusion was confirmed by studies done in Australia. [Exposure of this type is unlikely in closed systems, but provides an appropriate caveat for loading and unloading operations.]

The EAPA also notes that specific advice available from the suppliers (e.g. from MSDSs) on handling their products should be adopted. General "good working practice" for working with any asphalt include: work at the lowest operating temperature commensurate with good handling; minimize exposure to fumes by ensuring good temperature control and ventilation; and use personal protective equipment where appropriate.

6 Storage at High Temperatures

6.1 GENERAL HIGH TEMPERATURE OPERATING CONSIDERATIONS

A summary of temperatures useful in operational reviews appears below with explanatory paragraphs following.

Products stored in tanks without inert-gas blanketing should be maintained at temperatures at least 15°F below their minimum closed cup flash points (see Appendix B). This should normally maintain the vapor space fuel lean (below the flammable range), rendering the tank safe from ignition. For asphalt cutbacks, maintaining storage temperature below the flash point may not be possible. The flash point temperature is frequently below ambient temperature. Some companies deliberately maintain tank temperature high enough (greater than 15°F above the closed cup flash point) to ensure that the vapor space will be "fuel rich", and thus not flammable (see Appendix D.3).

Special consideration should be given to product storage at temperatures above 350°F (177°C). Deposits formed from condensation and subsequent oxidation of vapors can exist on the underside of the roof of heated asphalt storage tanks. Certain deposits may generate exothermic heat of oxidation at temperatures above 350°F (177°C) and may autoignite at temperatures above 375°F (190°C). This smoldering condition consumes oxygen, thereby significantly lowering the oxygen content of the air inside the storage tank and limiting the oxidation process. This balanced condition should be maintained in non-inerted tanks. The oxygen-depleted atmosphere is necessary to prevent autoignition of the carbonaceous deposits.

Inerting storage tanks that operate in the range from 350°F to 450°F (from 177°C to 232°C) is an alternative practiced by the industry, since inert-gas blanketing can prevent deposit oxidation. However, inerting provides an environment suitable for the formation of pyrophoric iron sulfides, which presents another potential hazard (see 6.3).

Product should not be stored above 450°F (232°C) without inert blanketing because thermal cracking and formation of light products may occur in heavy oils subjected to prolonged storage at temperatures approaching 500°F (260°C). Experience indicates that a safety margin of 50°F (28°C) below this temperature is a reasonable point at which inert blanketing of products should begin.

Table 1—Temperatures for Consideration During Heated Tank Operating Condition Review

Situation	Temperature	Action	Reason	Reference
Non-inerted Straight residual	Based on closed cup flash point	Maintain 15°F (9°C) below CC flash pt.	Seek to keep tank atmosphere fuel lean	Section 6.1 Appendix B
Non-inerted Straight residual	Based on open cup flash point	Maintain 50°F (28°C) below OC flash pt.	Seek to keep tank atmosphere fuel lean	Section 4.6
Non-inerted Cutback or solvent-containing	Flash at ambient or below	Raise temperature or volatility of solvent	Seek to keep tank atmosphere fuel rich	App. D.3
Non-inert bulk storage	350°F (177°C) or higher	Consider inert blanket	Carbon deposit exothermic activity begins	Section 6.1
Non-inert bulk storage Blowing lines with air	350°F (177°C) or higher	Minimize air flow	High temperature oxidation of deposits	Section 6.4
Non-inert bulk storage	> 375°F (190°C)	Consider inert blanket	Carbon deposits may autoignite and smolder	Section 6.1
Non-inert bulk storage	> 450°F (232°C)	Consider inert blanket	Prevent thermal cracking of stored material	Section 6.1
Inert blanketed storage	All temperatures	Keep O_2 at 5% to 8%	Inhibit pyrophoric iron sulfide formation	Section 6.2.,6.3
Maximum tank temperature	500°F (260°C)	Do not exceed— or use hi-temp tank	Tank thermal stress limit	Section 6.5 API 650

6.2 INERT-GAS BLANKETING

When the tank operating conditions (temperature, product movement or venting) or stored product composition (volatility and flash point) cannot be reliably maintained to prevent the tank vapor space from being in the flammable range, or when the product temperature exceeds 450°F (232°C), the vapor space of the tank should be inerted with flue gas, nitrogen or another suitable medium. For tanker ships, the SOLAS regulations require inert gas with 5% maximum oxygen which is used to maintain a tank vapor space concentration of no more than 8% oxygen. Steam has been used as an inerting medium but is a less desirable option since it can generate static charges (see 4.6.2.1) and is temperature sensitive. (Cooling, such as from rain, will condense steam and could draw in much more air than the same temperature change would if using a non-condensable inert gas.)

Inerting tanks storing sulfur-containing materials can encourage the formation of pyrophoric iron sulfide deposits, which are a potential source of ignition (see 6.3). Inerting with a material such as flue gas (when it contains approximately 5% oxygen) can minimize formation of pyrophoric iron sulfide deposits. Pressure-vacuum venting consistent with API 2000, coordinated with knowledgeable tank and venting specialists, is required to maintain the inert blanket without damage to the tank or unintended environmental releases.

The following potential concerns should be considered when an inert-gas blanket is used:

a. Use of inert gas introduces a personnel hazard (see 4.3.2).
b. There is potential for oxygen to enter the vapor space when a gauge hatch opens or if an abnormally rapid product withdrawal results in a P/V opening to equalize pressure using air.
c. Failure of the inerting system could allow oxygen (air) to enter the vapor space.

Additional concern arises when an inert blanketed tank is taken out of service, as discussed in 6.3.2.

6.3 PYROPHORIC DEPOSITS

6.3.1 Pyrophoric Phenomena

Two types of pyrophoric deposits may be found in storage tanks: iron sulfide and carbonaceous materials. Pyrophoric iron sulfide can be formed when hydrogen sulfide reacts with iron in the presence of moisture. This process is accelerated in an inert atmosphere. [Appendix E discusses this mechanism.] Carbonaceous materials are formed from condensation and subsequent oxidation of vapors in heated asphalt storage tanks. These solidified heavy hydrocarbons can form on the roofs and walls of tanks and inside piping. As noted in 6.2, experience has shown that maintaining approximately 5% oxygen in the inert-gas blanket inhibits formation of pyrophors. The exothermic heat of oxidation generated when

pyrophoric deposits are exposed to oxygen can cause the temperature of the deposits to rise enough for spontaneous combustion to occur. Combustion of the deposits can be a source of ignition if a flammable atmosphere is present. Efforts should be made to avoid allowing additional air supplies to enter the tank. [For instance, pumping product out of the tank normally draws in fresh air and opening manways or gauge hatches increases natural ventilation, and may trigger ignition if there are smoldering deposits.]

6.3.2 Taking Tanks Out of Service when Potentially Containing Pyrophoric Deposits

Special precautions should be followed when tanks potentially containing pyrophoric deposits are taken out of service (see ANSI/API RP 2016). This approach essentially involves keeping the pyrophoric deposits wet until the atmosphere is non-flammable and the deposits are either oxidized or removed. The similar concern arises onboard ships when the inert blanket in cargo tanks is replaced by atmospheric air. This situation arises frequently when unloading tank ships. To avoid potential pyrophoric ignition SOLAS recommends purging the tank until the hydrocarbon concentration in the vapor space is stabilized at less than 2%, before introducing air. This is intended to ensure that the atmosphere in the tank won't burn (fuel lean) even if iron sulfide reacts with air and could be a source of ignition.

6.4 BLOWING LINES WITH AIR

At temperatures above 350°F (177°C), the quantity of air used to blow lines such as oxidizer rundown lines should be kept to a minimum. Hot asphalt left on walls of tanks or lines is highly susceptible to rapid oxidation (burning) if it is exposed to large quantities of air. Procedures should be established to allow for a controlled release of product with a minimum amount of air displaced to the tank. Line temperatures should be monitored during the air-blowing process. An inert gas such as nitrogen can also be used. High-pressure compressed air should not be used to blow out obstructed lines.

6.5 TEMPERATURE STRESS LIMITATIONS OF TANKS

Storage tanks built in accordance with API 650 are not designed for temperatures above 500°F (260°C) because of stress limitations on the shell; however, some plants handle industrial grades with higher temperatures in tanks that are specifically designed for that purpose. If a change in service contemplates storage above 500°F (260°C) the suitability of the tank for that temperature should be reviewed.

6.6 RESPONDING TO ABNORMAL SITUATIONS

Appendix A addresses a number of abnormal situations which may occur when storing or handling heated heavy-oil products. Appendix D describes incidents which provide "lessons learned" for considering the impact of abnormal situations. Operating employee knowledge and awareness, coupled with appropriate operating procedures (start-up, shutdown, emergency) can assist in intervening and resolving these situations should these conditions arise. Appropriate management systems that address procedures, training and hypothetical drills relating to the operating environment are useful components of a preparedness program. Many elements of these programs can address significant issues of heat-management (heater control, use of mixers, external cooling or product movement), venting or inert-blanketing.

7 Mixing Procedures

7.1 MIXING—GENERAL

Part of the asphalt manufacturing process involves mixing components to provide a final product with the desired physical characteristics. During the mixing process certain inherent hazards can arise. Previously blended materials (such as cutbacks) may release light hydrocarbons during mixing. If air is available, the vapor space of the tank may pass through the flammable range. Potential sources of ignition (such as pyrophoric deposits) become of concern. If hydrogen sulfide is dissolved in the product, the agitation of mixing may increase the rate of H_2S release.

7.2 MECHANICAL MIXING

Facilities for adding diluents (especially hot stocks) to asphalts should include controls to prevent excessive vapor evolution. In-line blenders or a pump-around system that uses mechanical mixers can be efficient methods of mixing. In large tanks, adequate mixing may require multiple mixers.

7.3 AIR MIXING

Air mixing is efficient, but is a potentially hazardous method because it can generate a flammable vapor in the tank vapor space (and outside the tank if the tank is vented to the atmosphere). If air will be used for mixing, the asphalt temperature and the quantity of air being injected should be closely monitored. Rises in temperature of either the liquid or the gas phase are signs of potential problems (recognizing that oxidation is exothermic). The tank pressure should be monitored. Equipment that controls the quantity of air should be used to help protect the tank from overpressure. Precautions also are needed to ensure that water is not carried into the tank with air.

8 Hazards Associated with Tank Vehicles

8.1 VENTING AND WATER-FREEING

Vehicles that transport hot oils and asphalts should be properly vented (see NFPA 385). A frothover can occur when water (or volatile hydrocarbon) boils under the surface of viscous hot oil. This can occur if hot asphalt is loaded into a tank car that contains some water. The asphalt may cool initially from contact with the cold metal, and at first nothing may happen. When the water becomes hot enough to boil, expanding steam can cause the asphalt to overflow the tank truck or car. The application of froth suppressants can help minimize frothovers, particularly when tank cars or trucks are loaded with heated asphalt products; however, suppressants should be approved by the user or purchaser before being used. The use of suppressants does not eliminate the need to prevent water from contacting hot products. Loading should be interrupted when a popping or cracking sound is heard, indicating that moisture is present.

8.2 FIRED HEATERS ON TANK VEHICLES

Fired heaters on tank trucks or rail cars should not be operating while at a loading rack.

8.3 CLEANING TANK TRUCKS AND RAIL CARS

Cleaning tank trucks and rail cars involves the same concerns for personal hygiene discussed in 4.4. These tanks are normally permit-required confined spaces as regulated by OSHA, and appropriate preparation and permitting is required. Any cleaning of tanks involving the use of hydrocarbon solvents should ensure that:

1. Personal protective equipment needs have been evaluated and implemented.
2. That sources of ignition (such as truck heaters) are shut off.

3. That proper static ignition control is in place.

Incidents have occurred where spraying solvents without using appropriate work practices has resulted in explosion and serious injury. API 2003 provides information on grounding and bonding. Use of alternate cleaning methods not requiring hydrocarbon solvents should be considered.

8.4 INSPECTING TANK TRUCKS AND RAIL CARS

Entry into tank truck or rail car compartments for inspection requires consideration of permit required confined space entry requirements as indicated in the prior section. Specific attention should be directed to the potential hazards associated with properties of the prior cargo and whether the tank has an inert atmosphere.

8.5 LOADING AND UNLOADING TANK TRUCKS AND RAIL CARS

Loading of trucks or rail cars can provide increased opportunity for personnel exposure to hot asphalt products. The risk of thermal burns (see 4.2) increases. Hot asphalt may more readily release hydrogen sulfide (see 4.3.1) so awareness is needed to implement appropriate precautions when approaching or working around openings to the tank, such as loading hatches. Handling loading equipment such as hoses increases the potential for skin contact; maintaining good personal hygiene is important (see 4.4). Wearing of contaminated clothing such as gloves should be avoided.

9 Conclusions

Heated petroleum-derived asphalt products and crude-oil residua can be handled safely if proper procedures are followed. The information in this document (and in the references) can help develop safe work procedures which can be used to control exposure to inherent hazards and thus reduce risk.

APPENDIX A—GUIDE FOR ASPHALT/RESIDUA HANDLING

Table A-1—Guide for Asphalt/Residua Handling

Potential Hazard	Causes	Potential Remedies or Precautions
Tank overtemperature	Control malfunction Operator error	Consider redundant instrumentation. Plan operator response action to reduce temperature.
Frothing	Water or volatile hydrocarbons in (or entering) a hot tank, truck, or tank car	Keep water out: hatches closed, roofs intact, steam coils, steam heaters, and coolers leak free; conduct tightness tests Avoid cycling tank temperatures (near the boiling point of water). Keep blending components free from water and/or volatile hydrocarbons when blending with hot residuals. Minimize, accurately measure and control temperatures. Thoroughly mix components as they are added to a tank; do not add and then mix. Allow entrained water to boil off gradually to avoid rapid steam generation.
Vapor flashing (ignition)	Presence of hydrocarbon vapors and air and ignition source; vapors evolve as a result of heating mixes or cracking	Minimize storage temperatures (preferably below 350°F). Avoid using air for blowing lines to tank if possible (consider inert gas instead). If air is used, minimize tank temperatures. Avoid flammable concentration. Recognize and control ignition sources.
Pyrophoric iron sulfide formation	Oxygen-deficient atmosphere in the presence of H_2S and iron	Blanket the tank with an inert gas. Keep gauge hatches closed. Wet interior tank surfaces when tank is opened for repair or inspection. Maintain 3 to 5% oxygen in tank head space.
Pyrophoric carbon	Buildup of carbonaceous deposits	Maintain 3 to 5% oxygen in tank head space if inert gas blanketed. Minimize storage temperature (target below 350°F). Avoid deposit buildup in insulation on outside of tank near vents.
Autoignition	Inherent property of hydrocarbons	Inert blanket tanks (preferably w 5% oxygen). Minimize temperatures. Eliminate or minimize uncontrolled ingress of air. Avoid accumulation of carbonaceous tank deposits.
Damage to skin and eyes	Burns and splashes	Prevent spills, leaks & overfilling. Wear proper personal protective equipment.
Hydrogen sulfide exposure (acute hazard; vapors can cause death)	Vapor accumulation during loading operations	Provide training in materials hazards. Avoid breathing vapors (stand upwind of open hatches and use appropriate respiratory protection as required). Do not put face near tank openings or vents or put head inside enclosed spaces.
Asphalt and residual product vapor or fume exposure	Vapor accumulation during loading operations	Wear respiratory protection if appropriate. Do not put face near tank openings or vents or put head inside enclosed spaces (e.g. when gauging).
Roof collapse	Accumulation of asphalt, residua or carbon deposits on underside of roof	Inspect and clean periodically.
Heat stress failure	Tank overtemperature	Include maximum temperature in procedures. Keep tank temperature within heat-stress limits.
Overpressure	Internal ignition Low vent capacity	Avoid blowing air into tanks if possible. Size vent properly; inspect and clean vent periodically. Use open vent with hat design.
Bottom failure	Steam from water under a hot tank	Provide drainage for water.

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APPENDIX B—FLASH POINT TEMPERATURES, SPECIFICATIONS AND TESTS FOR ASPHALT & RESIDUAL PRODUCTS

Type and Grade	Reference Specification	Minimum Open Cup Flash Point Temperature* (degrees)	
		Fahrenheit	Celsius
PG asphalt binder (all grades)	AASHTO MP1	446 min.	230 min.
Asphalt cement (AC)			
2.5	AASHTO M226	325	163
5	ASTM D 3381	350	177
10		425	219
20		450	232
40		450	232
Rolling thin-film oven test			
1,000	AASHTO M226	400	205
2,000	ASTM D 3381	425	219
4,000		440	227
8,000		450	232
16,000		460	238
Penetration			
40 - 50	AASHTO M20	450	232
60 - 70	ASTM D 946	450	232
85 - 100		450	232
120 - 150		425	219
200 - 300		350	177
Medium cure (MC)			
30	AASHTO M82	100	38
70	ASTM D 2027	100	38
250		150	66
800		150	66
3,000		150	66
Rapid cure (RC)			
70	AASHTO M81	—	—
250	ASTM D 2028	80	27
800		80	27
3,000		80	27
Slow cure (SC)			
70		150	66
250	ASTM D 2026	175	79
800		200	93
3,000		225	107
Dampproofing and waterproofing			
A	AASHTO M115	350	175
B	ASTM D 449	400	205
C		400	205
Underseal	AASHTO M238	425	218
	ASTM D 3141		

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Type and Grade	Reference Specification	Minimum Open Cup Flash Point Temperature* (degrees)	
		Fahrenheit	Celsius
Membrane	AASHTO M239 ASTM D 2521	425	218
Built-up roofing			
I	ASTM D 312	437	225
II		437	225
III		437	225
IV		437	225
Residual fluxes	Industry sources	500	260
Residual Fuels			
#4	MSDSs	> 140	> 60
#5	MSDSs	> 140	>60
#6	MSDSs	> 140	>60

Note:

*Flash points are normally determined using COC open cup procedures ASTM D 92 and AASHTO T48. Because of the diluent volatility of MC and RC cutback grades the TAG open cup apparatus is used with a glass cup. Some practitioners use a closed cup procedure for all cutback products containing volatile hydrocarbon diluents. The International Safety Guide for Oil Tankers & Terminals uses closed cup values for flash points, recognizing that the open cup value is higher by "about 6°C or 10° F" and that the closed cup results are more repeatable. The UN Dangerous Goods Regulations define flammable as having a flash point not more than 60.5°C (140.9°F), closed-cup test, or not more than 65.6°C (150°F), open-cup test. This regulation includes the following note: *Since the results of open-cup tests and of closed-cup tests are not strictly comparable and even individual results by the same test are often variable, regulations varying from the above figures to make allowance for such differences would be within the spirit of this definition.* http://www.unece.org/trans/main/dgdemo/mr-ch22.htm

B.1 Sources of Specifications and Procedures

AASHTO[9]

MP1	*Performance Graded Asphalt Binder*
M20	*Penetration Graded Asphalt Cement*
M81	*Cutback Asphalt (Rapid-Curing Type)*
M82	*Cutback Asphalt (Medium-Curing Type)*
M115	*Asphalt Used in Dampproofing and Waterproofing*
M226	*Viscosity Graded Asphalt Cement*
M238	*Asphalt for Undersealing Portland Cement Concrete Pavements*
M239	*Asphalt for Use in Waterproof Membrane Construction*
T48	*Flash and Fire Points by Cleveland Open Cup*

ASTM[10]

D 41	*Asphalt Primer Used in Roofing and Waterproofing*
D 92	*Cleveland Open Cup*
D 93	*Standard Method of Test for Flash point by Pensky-Martens Closed Tester*
D 312	*Asphalt Used in Roofing*
D 323	*Standard Method of Test for Vapor Pressure of Petroleum Products (Reid Method)*
D 449	*Asphalt Used in Dampproofing and Waterproofing*
D 946	*Penetration-Graded Asphalt Cement for Use in Pavement Construction*
D 977	*Emulsified Asphalt*
D 2026	*Cutback Asphalt (Slow-Curing Type)*
D 2027	*Cutback Asphalt (Medium-Curing Type)*
D 2028	*Cutback Asphalt (Rapid-Curing Type)*
D 2397	*Cationic Emulsified Asphalt*
D 2521	*Asphalt Used in Canal, Ditch, and Pond Lining*
D 3141	*Asphalt for Undersealing Portland Cement Concrete Pavement*
D 3381	*Viscosity-Graded Asphalt Cement for Use in Pavement Construction*

[9]American Association of State Highway and Transportation Officials, 444 North Capitol Street, N.W., Washington, D.C. 20001. www.aashto.org

[10]American Society for Testing and Materials, 100 Bar Harbor Drive, West Conshohocken, PA 19428. www.astm.org

APPENDIX C—FIRST AID FOR HOT ASPHALT-TYPE BURNS

C.1 General First Aid for Burns

Severe burns can lead to shock and serious infection if not treated properly. Patients with serious burn injuries should be referred to a burn center. The American Burn Association has established referral criteria for burn centers.

> American Burn Association (ABA) Central Office—Chicago www.ameriburn.org
> 625 N. Michigan Ave., Ste 1530
> Chicago, Illinois 60611
> Telephone: 312.642.9260
> [Member Toll-free: 800.548.2876]
> Fax: 312.642.9130
> email: info@ameriburn.org

Most MSDS and other first aid advice stress:

1. Immediate cooling (noting that heavy hydrocarbons have high specific heat capacity and are good insulators so extended time may be needed).

2. Getting professional medical attention for significant burns.

3. Not trying to wipe off or remove hot asphalt (so skin doesn't come with it). Allow solidified material to remain in place until cooled. Natural separation should occur in 48 to 72 hours.

4. If removal of cooled asphalt is attempted, mineral oil may be effective if worked into the skin around the asphalt while allowing the asphalt to "float off".

C.2 First Aid for Asphalt (Bitumen) Burns

The following first aid summary was extracted from www.concawe.be/Html/REPORT1-97/B/B43.htm:

Report no. 1/97 petroleum products—first aid emergency and medical advice © CONCAWE, Brussels, March 1997

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Prepared for CONCAWE's Health and Petroleum Products Management Groups by:

G.P. Ebbon, U. Fornari, J.-P. Gennart, A.J. Riley and B.J. Simpson.

Skin contact: In the event of accidental skin contact with heated bitumen, no attempt should be made to remove the bitumen from the skin, the injured part of the body should immediately be plunged under cold running water. In the case of a burn with adhesion of the bitumen completely around a limb or finger, the adhering bitumen should be split to prevent a tourniquet effect as the bitumen cools. Medical advice should be obtained without delay.

Eye contact: If hot bitumen is splashed into the eye it should be cooled immediately with copious amounts of cold running water. Medical attention must be obtained. In the event of eye contact with cold bitumen, immediately irrigate with copious amounts of water. If irritation occurs and persists obtain medical advice. If there is bitumen in the eye refer the patient to an eye unit/hospital.

Information for doctors: No attempt should be made to remove firmly adhering bitumen from the skin. However, where the cooled bitumen has formed a tourniquet, the adhering bitumen should be split to prevent restriction of blood flow. Once the bitumen has cooled, it will do no further harm and in fact provides a sterile covering over a burnt area. As healing takes place, the bitumen plaque will detach itself, usually after a few days. If it is considered necessary to remove adhering bitumen from the skin, because of the site of contact, liberal amounts of warm medicinal paraffin can be used. If such treatment is used, it should be followed by washing with soap and water, then the application of a proprietary refatting agent or skin cleansing cream.

Reference: CONCAWE (1992) Bitumens and bitumen derivatives. Product Dossier No. 92/104. Brussels: CONCAWE

APPENDIX D—LESSONS LEARNED RELATIVE TO SAFE STORAGE AND HANDLING OF HEATED ASPHALT AND RESIDUAL PRODUCTS

D.1 Fire and Explosion in an Empty Residual Fuel Tank

From Safety Digest of Lessons Learned, Section 6, Safe Operation of Storage Facilities (Page 24)

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Incident

Ignition occurred shortly after work started on top of an "empty" 140 ft diameter, 120,000 barrel bunker fuel tank. Workers were cutting an access hole with a torch. An internal fire quickly spread under the roof. About 5 to 7 minutes later, vapor flashed inside the tank splitting the roof's frangible weld seam in three places. There were no injuries.

Lesson(s) Learned

a. A torch can heat deposits (such as residual wax and heavy oil) on the roof and walls inside a tank sufficiently to liberate vapors and form a flammable mixture.

b. Traditional "gas testing" only evaluates conditions during the testing; added heat (such as from a torch) represents a "change" in conditions subject to review and "management".

c. Physical inspection of both sides of a surface may be necessary before permitting use of a torch.

d. Cold cutting may be the preferred approach for surfaces subject to deposits.

A fire and explosion in an "empty" 140-ft diameter, 120,000 barrel bunker fuel tank damaged the roof and walls. The fire started as a torch was cutting an access hole in the roof. Several days earlier the tank had been purged, permits issued for entry, and abrasive-blast cleaning started. Prior to the fire, sections of the floor had been removed using torches without incident.

Investigators concluded that the torch ignited a coating of residual wax and heavy oil on the underside of the roof. Vapor emitted by the heat of the fire subsequently flashed, resulting in extensive damage. The fire was brought under control in approximately 10 minutes.

Discussion

A month before the explosion, the tank was taken out of service to repair a floor leak. Furnace oil was pumped into the tank, heated and mixed to dissolve heavy waxy hydrocarbon on the tank bottom. The tank was emptied of furnace oil flushings, blinded, and turned over for maintenance and gas-freed. Several days before the incident the tank had been purged, permits issued for entry, and abrasive-blast cleaning started. Prior to the fire, sections of the floor had been removed using torches without incident.

It was decided to replace the entire floor. After the weekend, a hot-work permit was issued to cut a hole in the roof with a torch to provide access so that new floor plates could be lowered into the tank. This procedure had been used 3 months earlier on another bunker tank.

Shortly after cutting work started on top of the tank, ignition occurred under the roof where they were cutting with the torch. The fire spread quickly, and the two boilermakers scampered off the tank. About 5 to 7 minutes after the fire started, vapor flashed inside the tank. The internal overpressure split the roof's frangible weld seam in three places and damaged the walls; flames and heavy black smoke emitted from the open seams and manways. The fire was extinguished by directing fire hoses into the bottom of the tank to create steam and by monitors directed at open roof-to-shell seams. The fire was brought under control 10 minutes after ignition.

Conclusion

The fire apparently started when the torch being used to cut the hole in the roof ignited a coating of residual heavy oil and wax on the underside of the roof. The fire was not preceded by any explosion, indicating the absence of an explosive atmosphere in the top part of the tank. Considering the intensity and duration of the fire, a considerable amount of hydrocarbon was probably in the tank. This may have been residual heavy oil and wax adhering to the upper courses of the tank shell, the rafters, the roof supports, and the underside of the roof. A gas test (which was not done at the roof) might not have detected any combustible material.

In retrospect the decision to use a torch to cut the hole in the roof was a poor one. The hole should have been made by cold cutting the metal plate. It was not possible to determine whether proper gas testing to detect an explosive mixture would have avoided the fire or whether the cause was simply ignition of residual heavy hydrocarbon on the underside of the tank roof.

D.2 An Oversight Causes an Explosion

From Safety Digest of Lessons Learned, Section 6, Safe Operation of Storage Facilities (Page 16)

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Incident

An explosion and fire ripped open approximately 30 ft of the frangible roof-to-shell seam of an insulated cone-roof asphalt tank 90 ft in diameter and 30 ft high. Some roof insulation was torn off, and members of the internal roof support were dislodged. Investigators concluded that the explosion resulted from the admission of asphalt at a temperature of 500°F or above into a tank containing a large amount of air.

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Lessons Learned

a. Asphalt above 500°F can autoignite.

b. Low-gauged tanks can provide special hazards when initiating run-down since the tank has excess air and there is no "cool" inventory in the tank to absorb excess heat.

c. Visible vent gases may provide early warning of overheated inventory in the tank.

Background

The tank containing 60/70-penetration asphalt had been pumped down to the 6-in. level. At the time of the incident, a 6-in. suction/filling line that extended 1 ft inside the tank and elled down to within 4 in. of the tank bottom was being used to fill the tank. [Using either of two other lines would have resulted in residuum being sprayed into the vapor space of the tank.]

The No. 4 pipestill was rerunning mixed gas oil. This operation produced 2,000 barrels per day of vacuum bottoms which was sent through a shell-and--tube cooler to standard fuel tankage. The cooler could reduce the bottoms temperature to below 450°F at the 2,000-barrel-per-day rate. Near the end of the day shift, an emergency shutdown of the unit was necessitated by water in the feed.

The pipestill was returned to service on the next shift to process crude for production of 60/70-penetration asphalt about 6,000 barrels per day. At this rate, the shell-and-tube cooler was not of sufficient capacity to reduce the temperature to below 450°F. Under these conditions, normal procedure was to route the bottoms through an additional box cooler at an adjacent pipestill for further cooling.

Operators had been experiencing difficulties in bringing the unit on stream, and through an oversight, these vacuum tower bottoms had not been routed through the box cooler; they were cut to the asphalt tank at 3:00 a.m. The tank was still essentially empty, so the vapor space of the tank contained excess air. The temperature of the bottoms leaving the unit was 557°F at 3:00 a.m. and 525°F at 7:00 a.m. The explosion and fire occurred at 8:45 a.m.

Description of the Explosion

Several persons in the vicinity of the tank when the explosion occurred. They reported a rumble accompanied by a belch of flame extending into the air from the tank. This flame appeared to be as much as 300 ft high but lasted only a few seconds. The fire smoldered around the rip in the roof-to-shell seam for about 8 hours and was eventually extinguished by injecting steam into the vapor space.

The operators at a nearby unit, downwind from the tank, had noticed a considerable amount of blue haze in the area for several hours before the explosion, but had not notified the asphalt operator of this condition.

Cause of the Explosion

Investigators concluded that the explosion resulted from the admission of asphalt at a temperature of 500°F or above

into a tank containing a large amount of air. A review of industry experience indicated that ignitions and explosions in asphalt tanks under conditions similar to this case had occurred previously.

The committee made recommendations related to this incident:

a. Asphalt above 450°F should not be pumped to tankage, particularly if this causes the contents of the tank to exceed a temperature of 450°F.

b. The asphalt pipestills should be provided with adequate cooling for residuum going to asphalt and other tankage.

c. A high-temperature alarm set at 450°F should be installed on each of the asphalt rundown lines from the pipestills. The alarms should sound in the pipestill control house.

d. Continuing efforts should be made to inform operating personnel of the serious consequences of sending asphalt to tankage at temperatures above 450°F.

e. Asphalt operating personnel should be alert for excessive vaporization from tank vents and should take corrective action when indicated.

Other Asphalt Storage Operation Safety Recommendations were:

a. Plugged vents can be a problem and should be inspected periodically to avoid pulling a vacuum when a tank is pumped out.

b. The practice of prohibiting the free fall of asphalt into a tank from elevated connections, or from entrance lines that do not turn down within the tank, should be emphasized continually.

c. The pressure on the residuum side of water coolers at the pipestills should be maintained above the waterside pressure.

d. Gas oil or light catalytic cycle effluent from washing residuum coolers should be diverted to mixed gas oil tankage or standard fuel tankage.

e. Check valves should be installed in slop lines connected to asphalt systems to help prevent the backup of light material into these systems, but check valves should not be relied on for positive protection.

f. They also noted that another refiner emphasizes that cold residual rundown tankage should have very specific detailed procedures for slow heating through the range from 200°F to 220°F.

D.3 Cutback Asphalt Tank Fire

From Safety Digest of Lessons Learned, Section 6, Safe Operation of Storage Facilities (Pages 12 – 14)

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Incident

A refiner reported that a lightning strike caused an explosion and fire in an 80,000-barrel (117 ft in diameter and 42 ft high) cone-roof, rapid-cure cutback asphalt tank. The tank was steam heated with a normal bulk storage temperature of 135°F – 140°F. At the time of the fire, the tank was in active

rundown service and held about 62,000 barrels of product ($^3/_4$ full), leaving a vapor space above the liquid. The frangible seam allowed the roof to rip away from the shell most of the way around the circumference; it fell back into the tank.

Lessons Learned

a. Tanks can be in the flammable range (e.g. not fuel rich) at a storage temperature of 135°F for rapid-cure cutback with that specific specification/composition.

b. Rapid application of foam to a viscous oil fire can cause dramatic frothover/slopover, especially after an extensive pre-burn.

c. The cooling effect of rain on a vapor space of a tank can condense hydrocarbon vapors, thus reducing pressure and causing the tank to draw in air with the potential for bringing a rich atmosphere into the flammable range.

d. Operational changes within specifications can be used to maintain a head-space too rich to ignite.

e. Operational changes made without consideration of the impact on storage might have negative impact.

Response and Suppression

The rapid-cure cutback asphalt rundown stream was diverted to another tank shortly after the fire started, and transfer of mate-rial already in the burning tank to another was begun.

Cooling water was sprayed on the shell of the burning tank 5 to 10 minutes after the explosion. However, the intensity of the fire prevented the application of foam to the interior of the tank until about 2 hours after the fire started. It was raining very hard, there were several in. of water within the firewall, and the fire fighters were concerned that an adjacent tank could ignite. For these reasons, a 100-ton crane was used to erect foam towers so that personnel would not have to enter the dike area. This took time. Immediately after injecting foam into the tank, the flame intensity increased sharply, sending flames 150 ft above the tank. After a few minutes, the fire began to subside. A second foam system was put in service one-half hour later, and the fire was out about 3 hours after it started. The fire was contained within the tank. The roof fell in and most of it sank; the top three courses of the shell buckled.

Investigation

The refiner's subsequent study of this problem covered experiences from other refineries and marketing people, the cause or causes of fires, and methods of eliminating hazards. The vapor spaces of a rapid-cure asphalt tank were analyzed at the normal tank temperature of 135°F. The result showed 2.3% hydrocarbon content—well above the 1.5% lower flammable limit. A limited survey found some refiners eliminated concerns caused by flammable vapor space in tanks by direct in-line blending to transport vehicles, thus eliminating cutback storage; however, this refiner continued to use cutback storage tanks. To eliminate future asphalt tank fires, the refiner made the vapor space too rich to ignite, since it was impractical to keep the composition below the lower explosive limit. The refiner suggested that three things need to be done to make the storage of rapid-cure cutback asphalt safe:

a. Cutback naphtha should be produced with increased light ends content as near the specified maximum percentage distilled at 200°F as is possible. This had no effect on meeting the final product specifications.

b. The temperature of the rapid-cure cutback asphalt storage tank should be increased from 135°F to 150°F to raise the vapor space above the upper explosive limit of 8%.

c. The tank should be insulated to prevent the vapor space from becoming explosive as a result of the cooling effects of a rainstorm. (The refiner also evaluated natural gas blanketing versus insulation. The investment cost is about the same. Insulation is preferred because its total cost should be lower and it saves energy).

Long-term "MOC" Considerations

The refiner found that during the past few years he had slowly decreased the light ends in the cutback naphtha to the lower end of the naphtha specification. This was economically desirable and satisfactory to the ultimate user; since it reduced foaming in the field. The safety aspects of storage were overlooked. Tank temperatures were maintained at the level necessary to assure satisfactory loading conditions and conserve utilities. The need to insulate tanks to prevent cold rains from creating explosive mixtures in the vapor space was not recognized.

Conclusions and Recommendations

The explosive hazard of rapid-cure cutback asphalt in storage tanks can be eliminated by the following measures:

a. Maximizing the light ends in cutback naphtha, as limited by naphtha specifications.

b. Storing the cutback asphalt in insulated tanks at higher temperatures.

c. Reexamining operating practices and product specifications periodically to ensure that time has not permitted the gradual establishment of unsafe practices.

The cost of these measures is significant, but the measures were considered necessary to eliminate the hazard.

Note: Some companies deliberately maintain cutback asphalt storage tank temperature high enough (greater than 15°F above the closed cup flash point) to ensure that the vapor space will be "fuel rich".

D.4   Fires in Refinery Pitch Storage Tanks

From Safety Digest of Lessons Learned Section 6, Safe Operation of Storage Facilities (Page 6)

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Incidents

During a 12-month period, four explosions and fires occurred in a company operation shortly after vacuum pipestill pitch production was turned into unfluxed pitch tankage. The pitch tanks involved were in utility plant fuel service. They ranged in size from 42 $^1/_2$ ft in diameter and 40 ft high to 23 ft in diameter and 24 ft high. Three of the explosions and fires occurred in the larger tanks. All four tanks were intermittently filled with pitch at a temperature above 500°F. In each instance the gas oils used for pitch fluxing and line flushing had autoignition temperatures below 500°F.

Lessons Learned

a. Rundown temperatures above 500°F can lead to autoignition.

b. Procedures should be in place to identify contamination by low autoignition temperature product.

c. Review of procedures can identify satisfactory, safer (e.g. lower temperature) operating conditions.

Specific Recommendations of the Refiner

a. Fluxing oil should be kept out of pitch tankage, and unfluxed pitch should be kept out of bunker fuel oil tankage. Line washing involves either contaminating pitch storage with gas oil or running hot unfluxed pitch into fuel oil storage. Thus, lines used for the delivery of pitch from vacuum pipestills to storage should be steam traced and insulated to alleviate the need for line washing.

b. The pitch produced at these refineries can be satisfactorily used as utility fuel at a temperature of 350°F to 400°F. To prevent accidents in the event of low-autoignition components reaching pitch storage due to unforeseen circumstances, the temperature of pitch to tankage should not exceed 400°F.

c. Tanks should always be gauged before, during, and after oil movement to detect contamination.

d. Measures should be taken to prevent the leakage of lighter oils into pitch tankage. One refinery installed Hamer blanks in series with the valves through which fluxing oil leakage might be expected.

D.5   Tank Explosions When Backflushing Hot Oil Pumps

From Safety Digest of Lessons Learned, Section 6, Safe Operation of Storage Facilities (Pages 22 – 24)

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Incident

Minor explosions related to backwashing bottoms pumps occurred in two cone-roof tanks within a 6-day period in one refinery. The tank damage was limited to the failure of the roof-to-shell seam at several points and minor buckling of the top tank ring. In both cases, the cause of the explosion was attributed to inadvertent entry of a 715°F short residue stream from a vacuum tower at a temperature above the autoignition point.

Lessons Learned

a. Rundown temperatures above 500°F can lead to autoignition.

b. Configurations that allow hot oil to spray into the vapor space can lead to rapid ignition; both tanks were equipped with an "overshot" filling line.

Incident 1

Early on the day shift, problems were encountered in maintaining a stable vacuum on the lube department's high-viscosity index column. A short residue stream off the bottom of this tower, at a temperature of 715°F, was normally cooled to about 250°F and then routed to an atmospheric storage tank. After 2 hours of unstable column operations, this cooled short residue stream was rerouted to the thermal cracking department, and the line to storage was blown with inert gas. Operating personnel backwashed a partially plugged pump suction screen with the hot short residue stream to resolve continuing operational problems.

The hot oil backwash stream, at 715°F, normally combined with the cooled residue stream (250°F +) to storage. On this occasion, the cooled residue was lined up to thermal cracking, and thus the 715°F short residue slipstream was the only product routed to the storage tank.

Shortly after the backwashing operation started, an explosion occurred in the 22,000-barrel tank (60 ft in diameter and 40 ft high), which contained 15 ft of oil. The fire burned out quickly.

Incident 2

Six days later erratic flow indicated that the suction screen on the same bottoms pump was starting to plug. The pump was shut down and prepared for backwashing. The valve positions in the short residue piping were checked to ensure that the portion of the column bottoms stream passing through the cooler was routed to storage along with the hot backwash stream. The pump screen was then back-washed for 4 or 5 minutes, and the backwash system blocked off before returning the pump to service. Considerable difficulty was encountered in getting good suction on the pump and two more backwashings followed.

During the last backwash, the flow routed to storage via the coolers was observed to be below normal, and the column bottoms low-level alarm light appeared briefly. This prompted an inspection of the column bottoms level to determine whether the level controller was causing the low flow rate through the cooler. Both level instruments indicated normal levels, and both appeared to move freely. While the third backwashing was still in progress, an explosion occurred in a 9,400-barrel tank (40 ft in diameter and 40 ft high), which contained about 6 ft of product. The explosion ripped the roof loose at the frangible seam for about 50% of the circumference, and the fire persisted somewhat longer than in the first incident. Upon hearing the explosion, operators blocked off the backwash piping, and the short residue stream was diverted from storage.

Approximately 10 minutes later, the short residue flow returned to the normal rate.

Conclusions

Although the circumstances were different in each case, both fires occurred in conjunction with backwashing of the bottoms pumps. The first fire resulted from an improper lineup, which routed the hot residue backwash stream to storage while the balance of cooled residue was going to thermal cracking. In the second incident, the hot and cooled residue streams were combined en route to storage, but the flow of the stream through the coolers became greatly restricted. The recorder indicated that the flow through the cooler had been erratic and marginally higher than normal for 6 hours before the bottoms pumps were backwashed. During the backwashing, the short residue flow through the cooler was drastically reduced for 45 minutes. Efforts to correlate the three 4-to-5-minute backwash periods with the 45 minutes of varying low flow rates were not successful. The appearance of the low-level alarm light indicates that the column bottoms level fell below the control point so that the level control valve upstream from the cooler closed. With this valve closed, the 715°F short residue stream being used for backflushing would not be cooled, and as in the first incident, oil above its autoignition temperature could enter the storage tank.

That the explosions followed so quickly after the back-flushing was started can probably be accounted for by the fact that both tanks were equipped with an overshot filling line. This fact forms a basis for an explanation of the ignition and nature of the fire. In both cases, the hot flushing oil entered the tank vapor space at a temperature above its autoignition point, ignited, and self-extinguished in a relatively short time because of the amount of hot fuel combined with a limited availability of oxygen.

Recommendations

The refiner proposed several possible solutions to problems of this type. The simplest approach being to eliminate the backflushing operation by:

a. Opening the strainer and cleaning manually.

b. Installing a coke-crushing impeller on the pump. (The use of such an impeller was the preferred solution, providing the pump could be so modified.)

In situations where eliminating backwashing was not feasible, the refiner felt that under carefully controlled conditions, backflushing could be performed safely by relocating the backwash connections to a point in the exchanger train where the oil was at a temperature of 400°F, well below the autoignition temperature. This would probably require some throttling at the outlet of the final coolers to establish the pressure differential necessary for backflushing.

D.6 Asphalt Tank Foundation Failure

From Safety Digest of Lessons Learned, Section 6, Safe Operation of Storage Facilities (Page 8 & 9)
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Incident

An asphalt tank foundation failed because of a buildup of steam pressure within the foundation substructure, which burst outward with a violent explosive force. The tank supporting pad settled and the tank ruptured, dumping heated asphalt over a 17-acre area. Equipment and piping in the vicinity were badly damaged by the force of the explosion and the violent action of the hot asphalt when it came in contact with water in a nearby oil-water separator.

Lessons Learned

c. Construction safety reviews for hot tanks should consider subsurface conditions and foundation design.

d. Water confined under heated tanks can generate steam with explosive BLEVE (Boiling Liquid Expanding Vapor Explosion) potential.

e. Environmental clean-up costs can exceed the costs of property damage.

Background

A tank constructed in 1922 was dismantled in 1956. All design and construction records of the original tank foundations had been lost in a fire. After the tank was demolished, its sand pad was removed. The foundation was visually examined and found to be in good condition. The sand pad was replaced, and a new 62,500-barrel cone-roof tank was erected. This new tank, 100 ft in diameter and 48 ft high, was smaller than the original tank. Four steam coils were installed to keep the tank contents hot. After the new tank was completed, it was used to store asphalt at temperatures of 250 – 275°F. Six years later, after installing 2-in.-thick fiberglass insulation, the tank operating temperature rose to 300 – 350°F.

The tank was filled to capacity with road asphalt before the start of the summer shipping season. Seven months later, the foundation failed because of a buildup of steam pressure within the foundation substructure causing tank failure and a massive product spill.

Investigation

A detailed inspection after the damaged tank was removed indicated that the foundation was of double concrete slab construction. The lower slab was supported by piles and the upper slab was supported by 7-ft pile stubs embedded in the lower slab. The tank rested on a 12-in.-thick sand pad.

Incident analysis concluded that stagnant groundwater was a primary contributing factor. Before the tank collapsed, the groundwater level was nearly stagnant because of a long period of low rainfall but still remained in contact with the bottom of the pad. The ground surrounding the tank was found to be tightly packed, except in the area of the blowout,

where muck or river mud existed just below the tightly packed surface.

With a tank bottom temperature of 350°F the heat could transfer to, and through, the upper slab. The conditions—the stagnancy of the water, the container formed by the double slab construction, and the tightness of the soil around the tank—allowed elevating the temperature of the groundwater to make steam of sufficient explosive force to blow the pile stubs and fill material out from under the slab at the point of least resistance. The slab then dropped, with subsequent rupture of the tank. The violence of the force generated was evidenced by the distance the concrete, pile stubs, and fill material were blown outward from the blowout point. The evidence suggests a BLEVE caused by superheated steam suddenly losing containment.

Cleanup

The asphalt, a 90/100-penetration paving-grade material, spilled over a 17-acre area, presenting a difficult cleanup problem. The material, contaminated with water, sticks, and stones, was not salvageable and therefore became a disposal problem. After experimenting with various types of equipment, front-end loaders and drag-line cranes proved to be the most satisfactory means of removal. The asphalt was dumped in trucks whose beds were first lined with sand and was then covered with more sand. Local authorities insisted on this procedure to avoid spills on the highways during transportation. Areas suitable for dumping this quantity of contaminated asphalt are difficult to find. It was necessary to mix the asphalt with sand and bury it to avoid pollution of watercourses and to prevent a safety hazard. Cleanup proved to be the most costly single item connected with the accident.

D.7   Asphalt Tank Rupture

Incident

"Empty" asphalt tank #1 contained asphalt plus a relatively small quantity of MC-70 cutback from relieving line pressure. The 13-in. liquid level in the tank was below the heating coils. Flow of heat medium to the coils began Friday afternoon in preparation for putting the tank back into normal service. The scheduled product transfer was not made. On Saturday at 8:15 a.m. an operator noted white puffs coming from the tank vent. The second operator went to the tank and closed the heat medium valve to the heating coils to "one-third thread". Five minutes later, they heard a "swooosh" as a sudden increase in internal pressure ruptured the tank's roof and bottom. No flames were visible as white smoke came from the tank vent and ruptures at the edges of the roof. Approx. 400 gallons of asphalt spilled into the containment area. Nearby tanks and a building were sprayed with asphalt. There were no injuries.

Lessons Learned:

a. Understanding and following procedures can avoid incidents.

b. Heating coils above the liquid level in the tank can be a source of ignition.

c. Line wash into an in-service, partially full tank may be OK, but can introduce a hazard for an "empty" tank.

d. Use of MOC (Management of Change) concepts are appropriate when new procedures are needed or abnormal conditions arise.

e. Unit operators may put themselves at unnecessary risk working to resolve problems.

Investigation

The practice of washing an MC line (potentially 20 to 30 gallons per wash) into tank #1 began months before the incident while the tank was in service. The practice continued after the tank was "emptied", drawing the tank level down far enough to expose the heating coils. The last recorded line wash was 2 1/2 months before the incident. On the day before the incident, the schedule called for putting tank #1 back into normal service and transferring asphalt to it.

Preparing the tank heating system for service was part of preparation for the transfer. Significant work was ongoing to resolve contamination and plugging problems which were affecting the hot oil system. The afternoon before the incident the poppet in the hot oil temperature-controller solenoid valve for tank #1 was discovered stuck in the closed position; the poppet was removed [also disabling automatic control of heat medium to that tank]. Twelve hours before the incident full flow through this hot oil valve was restored; a valve was "pinched back" to restrict flow.

A frozen transfer line kept the product transfer to tank #1 planned for Friday from being done. The temperature in the air/vapor space of tank #1 reached about 350°F by 8:00 a.m. Saturday. Shortly thereafter the overpressure incident occurred. The white smoke turned dark for a short period after the overpressure and then returned to white. Vapor from the tank could be seen for 4 hours after the incident during which period the tank air/vapor temperature remained elevated (approximately 350°F). About 5 hours after the incident the air/vapor temperature dropped to approximately 200°F.

The facility concluded the following:

Postulated Root Cause

Failure to follow procedure for Hot Oil coils; heat applied to tank with product below the coils caused autoignition of vapors.

Cause Analysis

Line washing MC-70 line into empty tank #1 over a period of three months, and then heating tank prior to covering the coils, producing the vapors and the hot surface for ignition.

Contributing Factors

a. Standing procedure of line washing cutback to asphalt tank not considered a good practice.

b. No MOC conducted during turnaround of hot oil unit.

Recommendations/corrective actions

a. Follow procedures—do not apply heat to hot oils coils when coils are exposed.

b. Prepare MOC if procedures are altered.

c. Conduct MOC if new procedures are needed (changing oil in hot oil system to resolve plugging).

d. Revise line wash handling practice.

e. Establish process for checking tank vents.

Near Miss

An employee put himself at risk of serious injury when he proceeded to close the hot oil valve located on the side of tank #1 after he noticed smoke from the vent on tank #1. Approximately 5 minutes later the tank bottom ruptured just below the hot oil valve. The facility judged that a safer procedure would be to proceed to the hot oil unit, located away from the tank area, and shut down the entire hot oil system.

Management of Change (MOC)

The facility emphasized the benefits of using MOC concepts to recognize potential hazards and reduce the risk of incidents. Several "changes" identified prior to the incident were:

a. Beginning practice of washing MC-70 line into asphalt tank #1.

b. Line wash continuing when low-gauged tank was "empty".

c. Removing the poppet in the heat-medium solenoid temperature control valve when it was discovered stuck in a closed position [which disabled the automatic temperature control].

d. Delaying the planned product transfer from tank # 6 to tank #1 [which would have covered the heat medium coils].

APPENDIX E—QUESTIONS & ANSWERS RELATIVE TO SAFE STORAGE AND HANDLING OF HEATED ASPHALT AND RESIDUAL PRODUCTS

E.1 What are Some Typical Storage and Handling Temperatures?

The following table shows some typical storage and handling temperatures.

Some Typical Storage Temperatures		
Material	Temperature, °F	Temperature, °C

Asphalt
  USA (typical)
  Europe (typical)
	450 max
	300 – 350
	300 – 390
		230 max
		150 – 175
		150 – 200

Asphalt, cutback	Can be above flash point	Can be above flash point
Asphalt emulsion	Below 180	Below 82
Polymer modified asphalt—SBS	380 max	193 max
Fuel Oil, #5 & #6— (residual fuels, bunker fuels, bunker "C" oil)	approximately 120 – 150	approximately 50 – 65
Residual fluxes	approximately 350 – 375	approximately 175 – 90
Heavy crude oil	160	70
Note: Information gathered from industry publications, guides, specifications and MSDSs; for illustrative purposes only.		

Some Representative Handling Temperatures*		
Material and Situation	Temperature, °F	Temperature, °C

Asphalt tank truck delivery
  USA
  Europe & UK
	300 – 350
	300 – 390
		150 – 75
		150 – 200

Marine bunker & distillate fuels storage	18°F above pour point No more than 18°F below closed cup flash point	10°C above pour point No more than 10°C below closed cup flash point
Heavy crude oil tank train	160	70

Proprietary hitemp polymer asphalt
  Blending
  Storage
	385°F minimum
	325°F
		196°C minimum
		163°C

Note: Information gathered from industry publications, guides, specifications and MSDSs; for illustative purposes only.		

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E.2 What are Some Reported Sulfur Level and Physical Properties of Various Products?

The values in the following table show the wide range of properties which may be encountered in various asphalt and heavy oil residual products. These have been gathered from a variety of sources and generally represent one manufacturer's product at some point in time. It is important for each facility to obtain proper information on the specific material that they will be processing, storing or handling.

Reported Sulfur Content and Physical Properties					
Material	Sulfur Content,%w	Flash Point F°/C°	Density (g/ml) @ 15°C	API Gravity	Pour Point F°/C°
Belridge heavy crude	1	> 194°F / > 90°C	0.9746	13.6	36°F/ 2°C
Bitumen (athabasca)	4.4 – 5.4		1.006 – 016	7.7 – 9.0	
Paving asphalt		> 500°F/ > 260°C PMCC	0.99		
AC asphalt (P)		> 425°F / > 218°C D92 COC	1.01 – 1.02		
MC 30 asphalt (Kerosene cutback) (Autoignition > 400°F/204°C) ASTM E 659		> 100°F / > 37.8°C Tag open cup	0.98		
Paving asphalt spec (WhRy)		> 450°F /230°C COC > 400°F /204°C PMCC			
Roofing flux (WhRy)		>570°F /299°C COC > 400°F/204°C PMCC			
Roofing flux (ASF) Auto-Ignition Temperature 370 – 480°C (approx.)		265°C (approx.) COC			
Asphalt flux (WhRy)	3 – 3.6	> 385°F / > 196°C COC	0.95 – 1.05		
Fuel Oil #2	0.2		0.8641	32.1	
Fuel Oil #4 (Autoignition > 505°F / > 263°C)		78°C > 60°C	0.9285 0.89 varies		–3°C
Fuel Oil #5 (bunker B)	1.5	> 54°C > 140°F / > 60°C > 109°C (closed cup)	0.9349 0.91 varies 0.90		–18°C –15°C
Fuel Oil #6 (AH) (Autoignition > 765°F / > 405°C	2.6	> 150°F/ > 65.5°C >407°C) > 100°C (closed cup)	0.97 varies 0.95		
Bunker C fuel (CoS)	2.4	/ > 62°C	0.969 – 0.983	12.3 – 14.1	15°C
Bunker C (Alaska)	0.5	/ 83°C	0.9891	11.4	–2°C
Bunker C (I/W)	1.9	115°C	0.9879	11.6	6°C
Marine diesel oil specification	1 – 2 max	> 60°C (closed cup)	0.89 – 0.92 Max		0 max
Bunker fuel specification	5 max	> 60°C min (closed cup)	0.991 max		30°C max
Road oil		149 – 288	1.0999		

E.3   How are Heavy Crudes Handled for Storage and Shipping, and at What Temperatures?

The following discussion gives examples of three different methods for moving heavy crude oil used in California, Canada and Venezuela. Note that two approaches avoid the need to transport while heated and store in heated tanks at the receiving end.

California:

In California, some heavy crude oil (approximately 13 degrees API) is produced using thermal recovery. It has been shipped both by insulated pipelines and on unit trains. When shipped by unit train the crude is transported at approximately 160°F and transferred into 80,000 barrel receiving tanks. It is inline blended with lighter crude and cooled to 130°F to meet both the viscosity and temperature requirements of subsequent pipeline shipment

Canada:

In one Canadian system "heavy crude" of approximately 11° API gravity is blended with a solvent diluent (natural gas condensate) to meet the minimum pipeline gravity specification of 21.2° API. The diluted crude can be shipped at ambient temperature. The condensate is removed at the refinery and recycled. Heated storage is needed only at the initial production end.

Venezuela:

In Venezuela a solvent extraction process is used to remove extra heavy crude (a natural bitumen with gravity as low as 9° API) from the ground. The diluent solvent is removed and recycled for more production. In a proprietary process the heavy crude oil is "cleaned up" to remove salt water and any other contaminants (such as sand) then mixed with a surfactant emulsifying agent and fresh water. Processing through high shear mixers forms a stable emulsion. Once processed, the emulsion can be handled in conventional installations, providing that bulk temperatures are kept within a range of 10 – 40°C. Under normal conditions, these would not be stored in heated tanks. The emulsion is sold into the market as a competitor to industrial residual fuel.

E.4   What Is the Mechanism of Pyrophoric Iron Sulfide Ignition?

The most familiar pyrophoric material encountered in the petroleum industry is pyrophoric iron sulfide. A reduction reaction can convert iron oxide to iron sulfide in an atmosphere where hydrogen sulfide gas concentration exceeds that of oxygen. When the iron sulfide is subsequently exposed to air, it is oxidized back to iron oxide. If this exothermic oxidation process is rapid it can be accompanied by the generation of enough heat for particles to glow and become ignition sources for flammable hydrocarbon mixtures. [If the oxida-

tion of iron sulfide is controlled by using low levels < 5% of oxygen then industry experience suggests that ignition conditions can be avoided.]

Formation of pyrophoric iron sulfide requires three conditions and is influenced by several others. Required constituents are: the presence of iron oxide (rust); the presence of hydrogen sulfide gas (such as from sour crude or sulfur bearing heavy products); and a low oxygen environment (as in an inert atmosphere). Influencing factors are: the concentration of hydrogen sulfide gas relative to oxygen; the porosity of the iron oxide (which influences surface area available to react); temperature (most chemical reactions double in speed for each 18°F/10°C increase in temperature); the rate of flow of hydrogen sulfide over the iron oxide surface; and time (which allows even low levels of hydrogen sulfide to reduce iron oxide to iron sulfide if the other factors are favorable). The presence of oxygen (approximately 5%) will inhibit the conversion of iron oxide to iron sulfide.

Pyrophoric iron sulfide deposits can accumulate in storage tanks holding a variety of products: sour crude; process intermediate streams containing sulfur; bunker fuel; and asphalt. When taking sour tanks or equipment out of service the equipment should be purged of flammable mixtures before oxygen is allowed to enter. It is recommended practice to keep all internal surfaces thoroughly wet during ventilation to inhibit pyrophoric reaction. Deposits and sludge should be kept wet until removed to a safe area where they can oxidize and subsequent ignition will cause no damage. Experience shows that fires can occur when deposits dry out prematurely.

E.5   What is the Difference Between Asphalt and Coal Tar?

Asphalt and coal tar are two totally different materials, despite their similar appearance. Although both are dark brown or black and solid or semi-solid at ambient temperatures, they differ in source, processing, chemistry and hazards.

Asphalt (also called bitumen or petroleum asphalt) is obtained as a residual product in refining crude oil. Early sources of "natural" asphalt were used by the Romans and before. These naturally occurring petroleum materials possess physical characteristics similar to asphalt derived by processing crude oil. Natural asphalt is still found as lake (pit) or rock asphalt. Most asphalt used today is derived from processing crude oil.

Tar is obtained by the high-temperature destructive distillation of coal, wood, peat, or other carbonaceous or vegetable materials. Further distillation of tar forms pitch. Coal-gas tar is a by-product of coke production, and water-gas tar is distilled from tar vapors. Originally, they were byproducts of "manufactured gas" production. Water-gas tar may be used with coal-gas tar as a flux.

Research studies comparing the chemical composition of coal tar and asphalt cement found that coal tar's high process-

ing temperatures (> 1000°C) produce primarily unsubstituted polynuclear aromatic hydrocarbons (PAHs). A number of these compounds have been identified as both animal and human carcinogens. Asphalt, unlike coal tar, contains only low levels of unsubstituted PAHs, primarily because the crude oil from which it is produced has only low levels of these compounds, and it is processed at a much lower temperature. Also distinct from coal tar, asphalt contains significant amounts of aliphatic (straight chain) compounds. Finally, asphalt has much lower levels (ppm) of phenols than does coal tar (> 1000 ppm). This difference in chemical make-up is believed to be the basis for the more restrictive exposure limits on coal tar (as discussed in Appendix J).

Physically coal tar is about 10% to 20% more dense than asphalt (s.g. of 1.1 to 1.25 vs approximately 1.0).

Although the high poly-aromatic content of coal tar makes it heavier, it is reported to have a lower flash point than asphalt. One source quotes a flash point for coal tar pitch of 248°F (120°C) compared to a minimum of 425°F (218°C) for paving grade asphalt. The source notes that "care must be taken on construction sites, therefore, as the material is always heated above the flash point temperature".

E.6 Does NFPA 30 Apply to Asphalt, Residual Products or Heavy Crude Oil Which are Solid at 100°F?

NFPA 30 "Flammable and Combustible Liquids Code" defines a liquid as "anything with fluidity greater than an ASTM D5 penetration of 300", and in A-1-1.2(a) states that "liquids that are solid at 100°F or above, but are handled, used or stored at temperatures above their flashpoints should be reviewed against pertinent portions of this code."

E.7 What is the Difference Between "Frothover", "Slopover" and "Boilover?"

All three of these phenomena involve hot, heavy hydrocarbons and water. In each, water boils beneath the surface of a heavy oil product or residuum. As the terms are used, a *frothover* is the overflowing of a tank that is *not on fire* when water (or volatile hydrocarbon) boils under the surface of viscous hot oil. *Slopover* and *boilover* refer to situations where a tank is *on fire*. In terms of amount of hydrocarbon expelled and surrounding area impacted, the slopover is generally the least severe and the boilover the most severe. Slopovers occur near the surface while frothover and boilover are deeper under the surface or at the bottom of the tank. (The appendices of API 2021 provide more information.)

A *slopover* is relatively minor frothing that occurs when water is sprayed on the hot surface of burning oil. The oil must be viscous and its fluid temperature must exceed the boiling point of water. Since only the surface oil is involved, a slopover is a relatively mild occurrence which can be controlled by slowing or stopping application of water.

One example of a *frothover* is when hot asphalt is loaded into a tank car that contains some water. The asphalt is cooled initially by contact with the cold metal, and at first nothing may happen. When the water becomes hot enough to boil, the expanding steam generated can cause the asphalt to overflow the tank car.

Another *frothover* situation arises when a tank used to store emulsions at temperatures below 200°F (93°C) receive a substantial addition of hot residuum at a temperature well above 212°F (100°C). When the hot oil reaches the product in the tank the emulsion will break, progressively releasing water. As the water is heated a prolonged boiling action can occur. Pressure from the steam generated can rupture the tank roof and spread hot-oil froth over a wide area.

In these frothover cases there is a hazard created by the hot oil, but it is not on fire.

Boilovers are serious, potentially life-threatening events typically associated with open surface crude-oil tank fires. After a long period of quiet burning, residues from surface burning become more dense than the unburned oil. The dense oil will sink below the surface to form a hot layer, which progresses down faster than the liquid surface is burning away. When this hot layer, called a "heat wave", reaches water (or water-in-oil emulsion) in the bottom of the tank, the water is first superheated and then boils, almost explosively, overflowing the tank.

This sudden eruption can eject great volumes of burning oil above the rim of the tank. A burning froth wave may travel rapidly over the ground around the tank. In extreme cases this can create a serious hazard for hundreds of ft surrounding the tank. The height of the burning column of expelled material may be as much as ten times the diameter of the tank.

Experience suggests that boilovers occur only when the material burning in the tank has a wide range of components, including both light ends and viscous residues. These characteristics are present in most crude oils but could be produced in blended mixtures such as asphalt cutbacks or residual fuels diluted with lighter hydrocarbons to reduce the oil's viscosity. Residual products are mostly made up of dense, low API gravity components. This makes them much less susceptible to formation of the "heat wave" required for a boilover, which moves down through the tank by gravity because it is more dense that the material below.

APPENDIX F—DEFINITIONS OF PETROLEUM INDUSTRY TERMS

Note: Terms defined in Section 3 are not repeated here.

F.1 boiling point: The temperature at which the vapor pressure of a liquid equals the surrounding atmospheric pressure. For purposes of defining the boiling point, atmospheric pressure shall be considered to be 14.7 psia (760 mm Hg). For mixtures that do not have a constant boiling point, the 20% evaporated point of a distillation performed in accordance with ASTM D86 shall be considered to be the boiling point.

F.2 classes of fire: NFPA 10 classifies fires based on the fuel involved—either type A, B, C, or D. Fire extinguishing agents are often identified by this system based on the type of fire for which they are effective (i.e., a dry chemical fire extinguisher may carry a Class ABC rating where a pressurized water extinguisher carries only a Class A rating).

a. *Class A* fires are those involving ordinary combustible solid materials such as wood, coal, paper, rubber, and many plastics.

b. *Class B* fires are those involving flammable and combustible liquids and gases such as gasoline, crude oil, asphalt, alcohols, LPG, and hydrogen.

c. *Class C* fires are those involving energized electrical equipment. While electricity is not a fuel, it represents a significant hazard to firefighters if improper (electrically conductive) extinguishing agents or methods are used. Once the electrical circuit is de-energized, the fire is then treated as a Class A or B, depending upon the fuel involved.

d. *Class D* fires are those involving combustible metals such as sodium, potassium, aluminum, magnesium, lithium or zirconium.

F.3 fire point: The temperature (usually a few degrees above the flash point) at which a liquid produces enough vapors to sustain combustion.

F.4 flammable range: A range of vapor-to-air ratios within which ignition can occur. The lower flammable limit (LFL) is the minimum vapor-to-air concentration below which ignition cannot occur. Atmospheres below the LFL are referred to as too lean to burn. The upper flammable limit (UFL) is the maximum vapor-to-air concentration above which ignition cannot occur. Atmospheres above the UFL are referred to as too rich to burn. Flammable ranges can vary widely, as illustrated by flammable vapor-to-air ranges for gasoline (1.4 – 7.6%) and acetylene (2.5 – 100%).

F.5 flash point: The lowest temperature at which a liquid gives off enough vapor to produce a flammable mixture with air immediately above the surface. A source of ignition is needed for flash to occur. When this temperature is above ambient, vapors will ignite but will not continue to burn until heated to the "fire point". The flash point temperature can be very low for volatile petroleum products; for instance, the flash point for gasoline is typically quoted as about –45°F (–43°C). Different laboratory flash point determination methods can yield different values (for instance "closed cup" test procedures such as ASTM D93 will give lower flash points than "open cup" ASTM D92). For direct comparison of results, the same test procedure should be used. Open cup tests are most often used for asphalts (however, closed cup tests may better characterize products in storage, especially those with light components such as asphalt cutbacks).

F.6 Flammable liquids have closed cup flash points below 100°F (37.8°C) and vapor pressures not exceeding 40 psia (2068 mm Hg) at 100°F (37.8°C). Liquids with vapor pressures above 40 psia (276 kPa) at 100°F (37.8°C) are considered gases by NFPA.

1. Class IA—Flash point below 73°F (22.8°C) and boiling point below 100°F (37.8°C).
2. Class IB—Flash point below 73°F (22.8°C) and boiling point at or above 100°F (37.8°C).
3. Class IC—Flash point at or above 73°F (22.8°C) and below 100°F (37.8°C).

F.7 Combustible liquids have closed cup flash points at or above 100°F (37.8°C).

1. Class II—Flash point at or above 100°F (37.8°C) and below 140°F (60°C).
2. Class IIIA—Flash point at or above 140°F (60°C) and below 200°F (93.4°C).
3. Class IIIB —Flash point at or above 200°F (93.4°C).

In the General Industry standards OSHA generally uses NFPA definitions for flammable and combustible. Alternate systems using 140°F (60°C) as the dividing point between flammable and combustible appear in ANSI/CMA Z129.1-1994 and the regulations of the U.S. Department of Transportation and the United Nations. The NFPA classification system is used in this document and is widely used for facility-based fire protection purposes in the USA. For regulatory compliance purposes (such as labeling for off-site transportation) reference should be made to the specific regulations or codes governing the activity of concern.

APPENDIX G—UNITS OF MEASUREMENT

Values for measurements used in this document are generally provided in both "Customary" and SI (metric) units. To avoid implying a greater level of precision than intended, the second cited value may be rounded off to a more appropriate number. Where specific Code or test criteria are involved an exact mathematical conversion is used. The unit "gallon" refers to US gallons.

Table G-1—English to Metric (SI) Units of Measure

Customary Unit	Metric Unit	Conversion Factor
Fluid Volume		
US gallon, USG	liter, L cubic decimeter, dm^3 (e.g. 1 liter) cubic meters, m^3	1 USG = 3.785 L 1 USG = 3.785 dm^3 1 m^3 = 264.2 USG
Barrel (42 USG)	Liter	1 barrel = 158.988 liters
Weight		
Short ton Long ton Pound	kilograms, kg kilogram, kg metric ton	2000 lb = 907.18 kg 2240 lb = 1016.05 kg 1 lb = .45359 kg 1 kg = 2.20462 lb 1000 kg = 2204.62 lb
Density of Foam Application		
Gallons/ minute/square ft, gpm/ft^2	liters per minute per square meter, $L/min\text{-}m^2$	1 gpm/ft^2 = 40.746 $L/min\text{-}m^2$ 4.1 $L/min\text{-}m^2$ = 0.1 gpm/ft^2
Volumetric Flow Rate		
Gallons per minute	cubic meters per hour Liters/minute = Lpm	1000 gpm = 227 m^3/hr 1000 gpm = 3785 Lpm
Pressure		
pounds per square inch, psi	mm Hg	1 psi = 51.7 mm Hg
pounds per square inch, psi	pascal, Pa	1 psi = 6894.757 Pa
pounds per square inch, psi	bar	1 psi = 0.0689 bar
	bar	1 bar = 10^5 Pa
pounds per square inch, psi	kilopascal, kPa	1 psi = 6.895 kPa
Length		
Foot, ft	Meter, m	1 ft = 0.3048 m
Inch, in.	Meter, m	39.37 in = 1 m
Area		
Square feet, ft^2	Square meters, m^2	1 ft^2 = .0929 m^2 1 m^2 = 10.76 ft^2
Temperature		
Degrees Fahrenheit, °F	Degrees Celsius, °C (e.g., Centigrade)	(°F – 32)/1.8 = °C
Heat		
BTU/hr	Watts, W	1 BTU/hr = 0.293 W
$BTU/hr/ft^2$	kW/m^2	1 $BTU/hr/ft^2$ = 3.155 W/m^2 1.00 kW/m^2 = 317 $BTU/hr/ft^2$

APPENDIX H—SOURCES OF REFERENCE INFORMATION FOR END-USERS

The following organizations provide a variety of health, safety, environmental and application information relevant to use of asphalt and residual materials by customers:

American Association of State Highway and Transportation Officials
www.aashto.org
444 North Capitol Street, NW, Suite 249
Washington, DC 20001

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

Australian Asphalt Pavement Association
www.aapa.asn.au
Level 2, 5 Wellington Street, KEW Victoria 3101 Australia
AAPA Risk Assessment Management Guide
Summary of SBS Bitumen Fume Monitoring

CONCAWE
www.concawe.be
Madouplein 1,
B-1210 Brussels, Belgium

Eurobitume Central Secretariat
www.eurobitume.org
European Bitumen Association
Madou Plaza (25th Floor), Place Madou 1
B-1210 Brussels, Belgium

European Asphalt Pavement Association
www.eapa.org
P.O. Box 175, 3620 AD
Breukelen, The Netherlands
Health and Safety in the Asphalt Pavement Industry Management Guidelines

Institute of Petroleum
www.petroleum.co.uk
61 New Cavendish Street
London, W1M 8AR, United Kingdom

National Asphalt Pavement Association
www.hotmix.org
NAPA Building
5100 Forbes Boulevard
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IS-86 Safety Procedures for the Prevention of Fires and Explosions in Hot Mix Asphalt Facilities

APPENDIX I

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APPENDIX J—EXPOSURE LIMITS AND HEALTH STUDIES RELATED TO ASPHALT FUME

J.1 Health Concerns Related to Asphalt

Information concerning safety and health hazards and proper precautions with respect to specific materials and conditions should be obtained from the employer, the manufacturer or supplier of that material, or the material safety data sheet.

A typical asphalt MSDS provides cautions regarding exposure to asphalt similar to cautions for many heavy hydrocarbons. Hydrogen sulfide (if present) is a significant acute hazard discussed in 4.3.1. The potential for burns has been addressed in 4.2 and Appendix C. Prolonged or repeated fume or liquid exposure could cause skin irritation or a phototoxicity reaction in sunlight similar to sunburn. Asphalt has low level of acute toxicity if orally ingested (swallowed). Vapor exposure (unlikely at ambient temperature) can cause irritation and potential mild to severe central nervous system effects.

Some MSDSs include information on potential carcinogenicity. Some specific molecules which may be found in asphalt are confirmed or suspect carcinogens. This especially applies to "polycyclic aromatics" (PCAs)—also called "polynuclear aromatics" (PNAs). Certain of these materials have been tested and shown to be carcinogenic to rats. Coal and coal derived products such as "coal tar pitch" contain relatively high levels of these compounds compared to most asphalt.

The key to risk reduction is avoiding exposure.

J.2 Asphalt Fume Threshold Limit Value (TLV®)

Starting with the 2000 edition of their TLVs, ACGIH lists "Asphalt (Petroleum; Bitumen) Fume" with a TLV of 0.5 mg/m³, a tenfold reduction from the previous TLV of 5.0 mg/m³. This limit is for the "inhalable fraction". ACGIH indicate that this new limit is based on "irritation" (primarily of mucous membrane in eyes and respiratory tract). The use of the designation "respirable" is a change from the former TLV based on total particulate. This change is reported to require new sampling and analytical techniques for which standardized methods may need development.

Appendix D, of the ACGIH 2001 TLV book defines the categories of particulates as:

Particulate-inhalable materials considered by ACGIH to be be hazardous when deposited anywhere in the respiratory tract.

Particulate-thoracic materials considered by ACGIH to be hazardous when deposited anywhere in the lung airways and gas-exchange regions.

Particulate-respirable materials considered by ACGIH to be be hazardous when deposited anywhere in the gas-exchange region.

Particulate-total—Airborne material sampled with a 37mm closed face cassette

At least one industry reviewer states that ACGIH documentation shows that for most situations total particulate and inhalable particulate are broadly the same. Therefore, if prior studies based on total particulate show acceptable exposure levels the exposure levels based on respirable fraction should be comparable.

The 2001 edition of the ACGIH TLVs also lists "Asphalt (Petroleum; Bitumen) Fume" with a "designation" of A4 in respect to possible carcinogenicity. The ACGIH Chemical Substances TLV Committee has established five categories to classify materials for which there may be concern regarding carcinogenicity.

The five ACGIH categories are:

A1—Confirmed Human Carcinogen

A2—Suspected Human Carcinogen

A3—Confirmed Animal Carcinogen with Unknown Relevance to Humans

A4—Not Classifiable as a Human Carcinogen

A5—Not Suspected as a Human Carcinogen

ACGIH states that the A4 category is for "agents which cause concern that they could be carcinogenic for humans but which cannot be assessed conclusively because of a lack of data. In vitro or animal studies do not provide indications of carcinogenicity which are sufficient to classify the agent into one of the other categories". The ACGIH Committee assigns asphalt fume to this category. Substances for which no human or experimental animal carcinogenic data have been reported are assigned no carcinogenicity designation.

J.3 No OSHA Permissible Exposure Limit for Asphalt Fume

In the 1970 enabling legislation the US Federal government adopted the then-current ACGIH TLVs into OSHA regulations as legally enforceable Permissible Exposure Limits (PELs). There was no limit for asphalt then, and there never has been a specific US (PEL) for asphalt fume. At this time (2001) there is no OSHA PEL for asphalt fume nor rulemaking proposed (although there have been periodic proposals typically suggesting the prior TLV of 5mg/m³). The limits for "nuisance dust" [total = 15mg/m³ and respirable = 5 mg/m³] do apply.

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There has been periodic confusion regarding whether the "coal tar pitch" PEL in Subpart Z includes asphalt. OSHA in interpretations specifically stated that limits for coal tar pitch volatiles do not apply to petroleum asphalt or natural or mined asphalts. This interpretation now appears in the regulation at 29 *CFR* 1910.1002 stating:

As used in 1910.1000 (Table Z-1), coal tar pitch volatiles include the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum (excluding asphalt), wood, and other organic matter. Asphalt (CAS 8052-42-4, and CAS 64742-93-4) is not covered under the "coal tar pitch volatiles" standard. [48 FR 2768, Jan. 21, 1983]

J.4 NIOSH Literature Review of Health Effects and Occupational Exposure to Asphalt Fumes

In 1997, NIOSH published the "results to-date" of their review of the health effects of asphalt fume. It concludes in agreement with an earlier IARC study which said "the carcinogenicity of bitumens (which include asphalt) is unclassifiable in humans". This is consistent with the ACGIH rating of A4 discussed in the preceding section.

Summary paragraphs from NIOSH state:

This interim review was produced by niosh in support of nomination to the national toxicology program 6/23/97

Chemical name—Asphalt; CAS number—8052-42-4

Partanen and Boffetta [1994] conducted a review and meta-analysis of the epidemiologic studies regarding cancer risk in asphalt workers and roofers. They concluded that existing data are insufficient to make a judgment with regard to asphalt. Most epidemiologic studies for lung carcinogenicity (as well as other cancer sites) are either too non-specific for exposure (e.g., highway maintenance workers, census occupational data), or confounded by coal tar exposure.

In 1987, the International Agency for Research on Cancer (IARC) evaluated the available studies involving asphalt fumes [IARC 1987] and concluded that the carcinogenicity of bitumens (which include asphalt) is unclassifiable in humans.

NIOSH investigators (Kyle Steenland) agree with the review of Partanen and Bofetta [1994]. In addition to the studies' deficiencies already enumerated, insufficient latency for workers exposed to asphalt is also noted. Deficiencies of the Hansen [1989, 1991] studies include the unresolved controversy concerning possible exposure to coal tar, possible selection biases, and the appropriate beginning of person-time at risk.

From NIOSH Web site at http://ntp-server.niehs.nih.gov/htdocs/Chem_Background/ExecSumm/AsphaltFumes.html

J.5 Asphalt End-Use Worker Risk Reduction Emphasis

The construction paving industry is a major end-user of asphalt products. Associations serving that sector have been actively involved in health and safety studies and initiatives. One primary effort conducted in cooperation with NIOSH focused on equipment design to help reduce worker exposure during paving operations. This study is reviewed in DHHS (NIOSH) Publication No. 97-105 "New Highway-Class Pavers".

The document states "although the health risks from asphalt exposure are not yet fully defined, all partners agreed that prudent action was needed to reduce worker exposures". The work involved collaborative efforts of industry, labor, and government to protect workers exposed to asphalt fumes during paving operations. Guidelines were developed for implementing engineering controls that reduce highway asphalt fumes at the source and thus reduce the opportunity for exposure.

Appendix H provides reference and contact information for several organizations that produce or provide reference information for end users of asphalt or crude oil residual products.

APPENDIX K—FIRE SUPPRESSION TECHNIQUES FOR HEATED HEAVY-OIL PRODUCT TANKS

K.1 General

As discussed in 4.7, fire suppression for heavy oil products in heated tanks is a special case. The stored material (the "fuel") is already hot, making vapor suppression by cooling very difficult. The hot fuel surface tends to destroy foam as it is applied. And, heavy oils can exhibit unusual phenomena when water is applied (Appendix E.7). One key goal is to put out the fire without "unnecessarily" precipitating any of those unusual phenomena. This keeps the safety of personnel as a first priority while it is also conservative of property.

K.2 Prudence in Heated Oil Tank Fire Suppression

The precaution noted earlier in 4.7 emphasizes the priority on personnel safety:

*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.*

On any tank which has the potential for boilover, emergency responders should have the capability of evaluating whether a heat wave is forming, and monitoring heat wave movement, if present. Thermal energy (such as infrared) cameras may be helpful. In the unlikely event that size-up determines that there is a heat wave and boilover potential, then full precautions as outlined in API 2021 should be instituted. These emphasize personnel safety followed by protection of surrounding exposures.

K.3 Stop All External Tank Heating

Since fires require heat, a preplanned Operations response to a fire should be to cut external heat to the tank on fire. This includes shutting down heaters and stopping rundown of hot product to the tank.

K.4 Suppression When Roof Still on Tank

There may be a fire inside a tank with the roof still intact. In this situation routing inert gas into the tank head space has successfully achieved suppression. Applying cooling water on the sides of the tank at (and above) the liquid surface level may be beneficial in reducing temperature and inhibiting vapor formation.

K.5 Suppression When Roof Partially or Completely Off the Tank

Where a burning heavy fuel surface is exposed to the atmosphere, it will be necessary to cool the surface of the burning fuel. This will be necessary first to allow a foam blanket application and finally to suppress vapor release and extinguish the fire. A variety of approaches are discussed in the following sections.

K.5.1 "ROLLING THE TANK"

If the temperature in the tank was the same throughout before the fire, then the material below the surface should be cooler than the burning surface. If the tank on fire is equipped with mixers it may be possible to "roll the tank" to move cooler liquid from the bottom to the top. This approach seeks to cool the burning surface to reduce vapor release and thus inhibit burning. This can be done concurrently with "gentle water-cooling". This approach is only appropriate if the tank contains low volatility material (e.g. not where the stored product on fire is a distillate-containing "cutback"). Mechanical or air mixing should stop before major fire suppression activities begin.

Use of air injection at the base of the tank has been proposed as an approach for "rolling a tank" which does not have mixers, but is "tricky" since air encourages combustion.

K.5.2 USE OF WATER AND FOAM ON ANY TANK

A fire where the bulk temperature of the burning hydrocarbon fuel is above the boiling point of water is a significant challenge. 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."

Some tank firefighting specialists recommend that any fixed or semi-fixed systems attached to the tank that can provide foam directly to the liquid in heated heavy-oil tanks should be removed or blinded to prevent inappropriate foam application. If foam is applied under a roof still partially attached to the tank the steam formation could blow the roof free of the vessel in an uncontrolled incident.

When the frothover reaction from initial cooling water application subsides, the application of foam can be attempted. There needs to be sufficient outage for the foam once application is begun. One or more "slopovers" should be expected and increased space in the tank will help minimize the amount of material ejected. If water is applied incrementally in a pulsed or "batched" sequence then there is some measure of control over the amount of slopover by judging the reaction and adjusting water flow accordingly. (Indeed, if

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control of the fire is being achieved with judicious water application then foam may not be needed.)

Extreme caution should be exercised when considering pumping material from the tank on fire to another storage tank. Careful monitoring of temperature is required to ensure that products are not transferred to a tank at a temperature which will create a potential boilover, slopover, or frothover problem in another vessel. Volatility and the potential presence of water in the receiving tank are essential considerations.

K.5.3 USE OF WATER AND FOAM ON SMALL TANKS

Basically, fire suppression specialists suggest trying a variety of approaches to get firewater applied gently to the surface for cooling to be followed by a foam attack. This needs to be done judiciously to avoid excessive early application (see "Lesson Learned" in Appendix D.3 where use of foam towers after an extensive preburn had a dramatic undesirable effect).

One potential approach is to apply water spray at an initial low rate (comparable to a gentle rain) with the intent of cooling the top surface; large capacity monitors can be used to build this "water curtain". The smaller droplet size and lower application rates of water should mean lower rates of surface boiling and less potential slopover. This might be achieved with wider-angle spray patterns yielding smaller drops. In the past some success has been realized on smaller tanks by slowly passing water streams from side to side (beginning from off the tank surface, progressing across the width of the tank again clear of the surface) allowing the water in the form of droplets to cool the surface, then repeating enough times until it appears to have cooled the surface enough to initiate foam application.

When the frothing or slopover from the gentle water application seems relatively calm then foam application at the normal rates can be initiated. A relatively low expansion ratio will probably be required to reach the surface through thermal updrafts, while higher expansion rates may provide the necessary cooling with less slopover.

This general approach has "proven successful" on small tanks (up to 80 ft in diameter).

K.5.4 USE OF WATER AND FOAM ON LARGE TANKS

Fortunately, there have been very few reported fires in large asphalt tanks. Based on other fires, for tanks larger than 80 ft it will be difficult to position a monitor close enough to achieve a gentle flow of droplets. From a distance, the stream may provide a more dense water application than desired and precipitate slopovers. Thermal updrafts will be strong making the task of gentle application more challenging. None-the-less, the same principles hold, and the fire suppression leadership will be faced with choosing a course of action based on the fire-ground situation and the nature of the product involved.

K.5.6 SPILL FIRES

If the product burning does not contain much light material it will probably be possible to extinguish asphalt or residual product spill fires using only water spray. As with tank fires, caution should be exercised to avoid water-hot oil phenomena. (There is low potential for these unless the bulk temperature was very high and the spill has significant depth.) A brief application of a light water spray should provide a visual indication of the situation. For spill fires where significant quantities of light hydrocarbons are involved, 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.

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