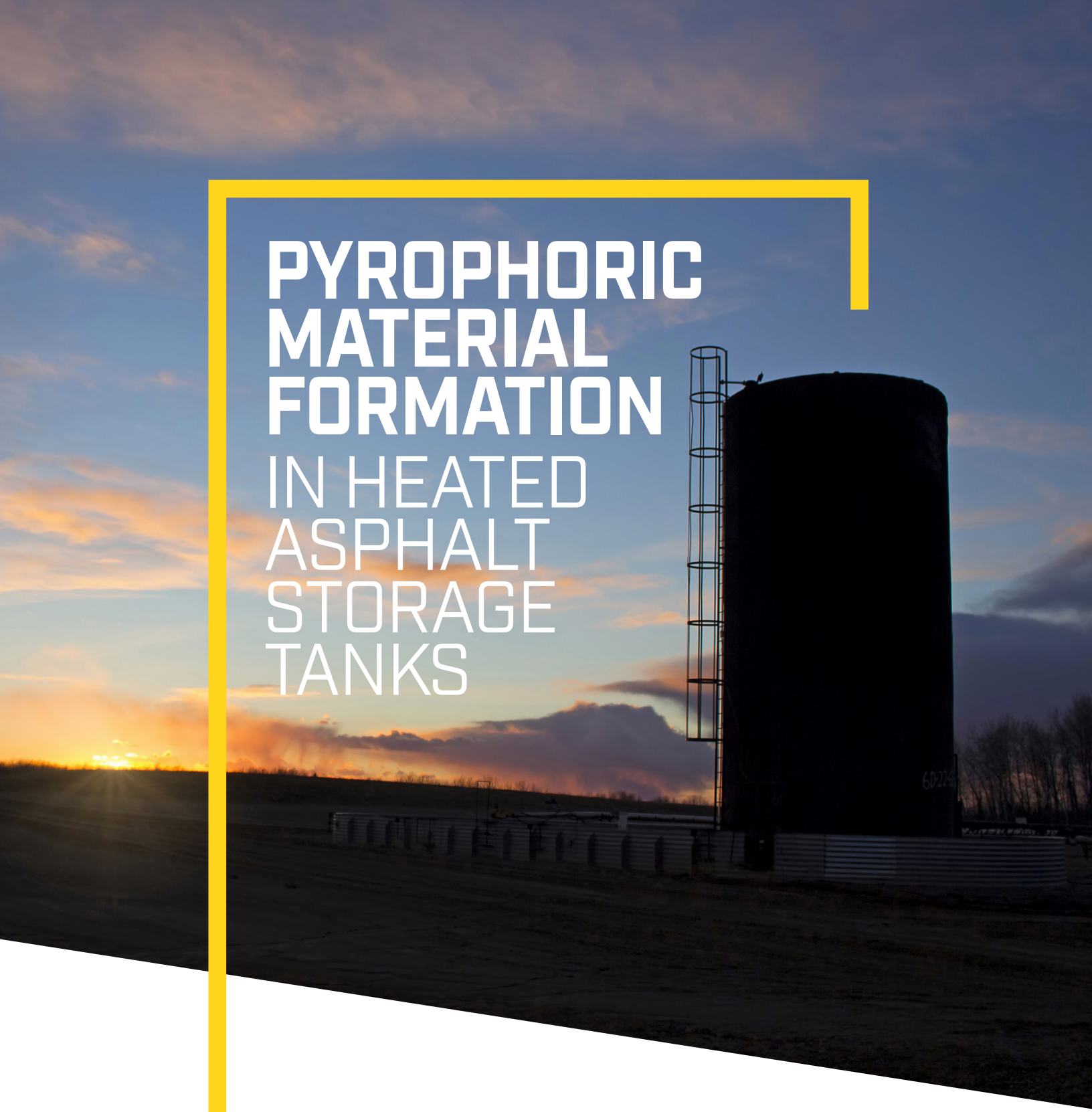

PYROPHORIC MATERIAL FORMATION IN HEATED ASPHALT STORAGE TANKS

asphalt institute

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in Heated Asphalt Storage Tanks

Introduction

The purpose of this document is to provide information on pyrophoric material formation in storage tanks for both oxidized and non-oxidized asphalts. The information provided in this document should not be considered exhaustive or complete but rather as an initial information source to allow the heated asphalt storage tank owner/operator to evaluate potential pyrophoric material formation and prevention. Citations are included in this document so that the owner/operator can perform a more detailed evaluation if necessary.

In addition, the Asphalt Institute does not intend for this document to make any requirements or set any standards, nor is it intended to imply standards of any kind. You should always know and comply with all applicable governmental rules, regulations and standards and abide by all applicable company policies and procedures.

Information in the literature varies and can be confusing. Any references to "should" or "must" were made by the original author(s) of the referenced publication and are presented as such. They are not requirements or standards defined by or advocated by the Asphalt Institute.

The following are two unforeseen pyrophoric accidents. They are based on unspecified events involving a heated asphalt storage tank.

The first event takes place in a terminal that was processing polymer-modified asphalt cement (PMAC). A single tank was used for mixing polymer with asphalt and reacting it with sulfur, resulting in a residence time long enough for H_2S to build up to a high level. The terminal also operated the tank at high levels which further contributed to high concentrations of H_2S in a small head space. The H_2S reacted with the carbon steel roof to create an iron crust with pyrophoric iron stalactite deposits. While the terminal was processing PMAC, an explosion separated the roof from the tank. Metal guards prevented the roof from relocating. It was later determined that pyrophoric iron reacted with oxygen to cause the explosion.

In the second event, a radar level probe was removed from the top of a heated asphalt storage tank for maintenance. The removal of the probe allowed entry of air into the tank through the opening. Shortly thereafter, the storage tank started to "rumble" with a resulting explosion causing the tank roof to separate from the tank with fire and damage to the facility.

In the second event, an analysis ruled out hot work, human error, equipment malfunction, static electricity, and lightning. This evaluation concluded that auto-ignition of pyrophoric material in asphalt deposits on the inner surfaces of the heated asphalt storage tank was the cause. Atmospheric air containing oxygen entered the heated asphalt storage tank after removal of the probe reacting with pyrophoric materials such as iron sulfide that then ignited combustible vapors in the headspace.

What Is Pyrophoric Material?

Pyrophoric is derived from the Greek for "fire-bearing." According to Webster's dictionary, "pyrophoric material" means "any material igniting spontaneously or burning spontaneously in air when rubbed, scratched, or struck." Pyrophoric materials in heated asphalt storage tanks are compounds that form on the inner surfaces of the tank that can ignite spontaneously upon exposure to atmospheric oxygen. In this industry, these pyrophoric materials are predominantly iron/sulfur compounds or pyrophoric carbonaceous deposits.

What Is the Source of Pyrophoric Material in Heated Asphalt Storage Tanks?

Heated asphalt storage tank pyrophoric materials are most often deposited in the "coke" that forms on the sides and top of the asphalt storage tank. Coke forms when asphalt fumes/vapors solidify on the top and side of the heated asphalt storage tank. Pyrophoric materials are caused by the chemical reaction between corrosive sulfur compounds such as hydrogen sulfide (H_2S) that can occur with asphalt and the oxidized iron (rust) on the interior tank surfaces. This formation can occur when the headspace oxygen concentration is less than 3% [1].

Note also that the American Petroleum Institute states in API RP 2023 that formation of pyrophoric materials increases in heated asphalt storage tank headspace when oxygen content is less than 5% [2]. However, other papers cite slightly different oxygen levels that would be conducive to pyrophoric material formation in the tank. The owner/operator of a heated asphalt storage tank should be cautious in selecting a maximum and minimum oxygen concentration in the heated asphalt storage tank headspace. The Asphalt Institute is not advocating which oxygen level the owner or operators should use, and throughout this document, we will provide references and highlight recommendations from known sources such as API which recommends using the 5% level.

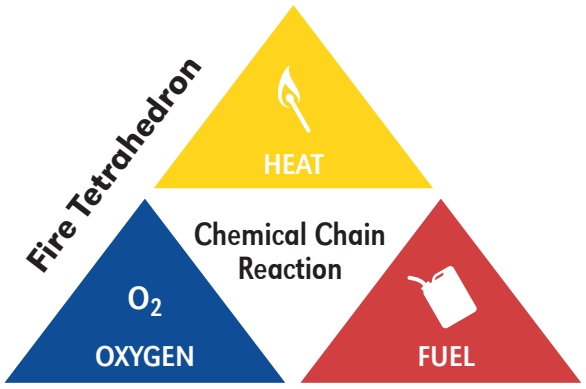
Dimpfl proposed that coke formation was due to factors beyond those of the asphalt stored [3]. He referenced incidental thermal cracking and residual light hydrocarbons generated during oxidation. He proposed that vapors and/or fumes from the heated asphalt can condense and "harden" on the underside of the tank roof. Dimpfl also proposed that "smoldering" coke deposits in heated asphalt storage tanks reduce oxygen concentrations below levels at which combustion would occur which implies these deposits are not uncommon [3].

Davie reached the same conclusion based on electron microscopy and elemental analysis showing the presence of pyrophoric iron sulfide in heated asphalt storage tank coke deposits [4].

There are multiple publications presenting recommendations related to oxygen content in heated asphalt storage tank headspace. The publications reference a range of target oxygen concentrations. The Asphalt Institute presented this range of target oxygen concentrations and the publication citation to allow the owner/operator to make their own decision about target oxygen concentration. The Asphalt Institute is not recommending a target oxygen concentration for heated asphalt storage tanks.

Why Are Pyrophoric Materials of Concern in Heated Asphalt Storage Tanks?

A heated asphalt storage tank fire requires four elements: oxygen to sustain combustion, fuel that is usually some combination of fume/vapors, a source of ignition, and an ongoing exothermic reaction that continues the combustion process. Pyrophoric materials can serve as the source of ignition for heated asphalt storage tank fires.



[5]

Dimpfl [3] showed headspace readings of a heated asphalt storage tank to have vapor concentrations above the lower explosive limit (LEL). Dimpfl [3] also confirmed the exothermic nature of heated asphalt storage tank pyrophoric materials and detected "high levels of sulfur in areas rich in iron". Davie et.al [6] used thermal analytical techniques to demonstrate that exothermic pyrophoric materials were contained in coke deposits found in a heated asphalt storage tank. They also determined that "oxidation/smoldering reactions" occur in the pyrophoric materials at temperatures found on the interior surfaces of a heated asphalt storage tank.

Thus, when air containing oxygen is introduced into a heated asphalt storage tank and the other three factors of the Fire Tetrahedron are present, the pyrophoric materials reactions referenced by Dimpfl [3] and Davie et. al. [4, 6] can serve as a source of ignition causing a heated asphalt storage tank fire.

Pyrophoric materials can serve as the source of ignition for heated asphalt storage tank fires.

What Role Does Pyrophoric Material have in Heated Asphalt Storage Tank Fires?

When the pyrophoric materials, in the coke formed on asphalt storage tanks, are exposed to the oxygen in atmospheric air, iron sulfides in the pyrophoric materials are oxidized back to iron oxide and other sulfur-containing compounds. This reaction is exothermic, generating heat energy that can ignite organic vapors in the heated asphalt storage tank headspace. For spontaneous ignition to occur, the rate of heat generated through chemical reaction must exceed the rate of heat removal by conduction or thermal radiation [6].

What Is the Source of Oxygen in Asphalt Storage Tanks?

Atmospheric air containing oxygen is drawn into a tank during product transfers. Opening a heated asphalt storage tank during repair, maintenance, etc. can also allow entry of atmospheric air containing oxygen into the tank [7].

What Are the Effects, if Any, of Asphalt Processing Additives on Pyrophoric Materials Formation?

To date, the Asphalt Institute is not aware of any research or other efforts to identify and/or quantify the effect of asphalt additives on the formation of heated asphalt storage tank coke and related pyrophoric materials. However, asphalt additives affect the rate and type of chemical reactions during asphalt processing and storage. Thus, the potential of asphalt additives to influence the formation of pyrophoric materials in an asphalt storage tank cannot be ruled out. For example, a metal-based H_2S scavenger added to asphalt may react with polyphosphoric acid (PPA) to form excess H_2S.

Some asphalt additives have been shown to contain H_2S, iron, and/or sulfur that theoretically if the headspace of the heated asphalt storage tank has the required conditions, could increase the rate of pyrophoric material formation. They also contain "light hydrocarbons" that could also influence the type and rate of deposition on the interior surfaces.

Asphalt Institute is not aware of data that demonstrate asphalt additives reduce the probability of pyrophoric material formation in heated asphalt storage tanks. Additives are not expected to reduce the level of asphalt fume/vapors in the heated asphalt storage tank headspace. Any fire management plan for an asphalt facility that uses additives should consider the potential risk of formation of pyrophoric materials.

How Can Heated Asphalt Storage Tank Fires Due to Pyrophoric Materials Be Prevented?

Lack of or removal of any one of the fire tetrahedron's four essential elements will prevent a heated asphalt storage tank fire. Control of the conditions that produce pyrophoric materials on heated asphalt storage tank surfaces is the best method for fire prevention. This can be accomplished by:

Air Sweep

Continuous circulation of air through the headspace of the heated asphalt storage tank can reduce the formation of pyrophoric materials. Air Sweep maintains oxygen concentrations at levels above those promoting pyrophoric material formation. It also removes asphalt fume/vapors that could add to heated asphalt storage tank surface deposits. This method typically incorporates an emissions control device to reduce the emissions and meet regulatory requirements. When using an Air Sweep the heated asphalt storage tank headspace oxygen content should be continuously monitored.

Headspace Blanketing

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, but inert atmospheres can also encourage the buildup of pyrophoric materials in the tank. API recommends oxygen content should be targeted between 5% and 8% because oxygen content above 8% can cause the heated asphalt storage tank headspace to be above the Lower Explosion Limit (LEL). And, heated asphalt storage tank headspace oxygen content below 5% can increase the formation of pyrophoric materials [2].

Any time mechanical methods are used to clean heated asphalt storage tank precautions should be taken to prevent the air containing oxygen to react with the coke.

Another researcher, Davie [8], recommends maintaining oxygen content between 4% to 10.5%.

If the tank headspace vapor is not flammable, then an inert or lean headspace may not be needed, and the higher concentration of oxygen in these tanks prevents the formation of pyrophoric iron sulfide. These systems can be vented to the atmosphere with vapor recovery units to capture hydrogen sulfide [9]. This is applicable to head spaces above 5% oxygen.

Asphalt Storage at Lower Temperatures

Generation of asphalt fume/vapors is temperature-dependent; the higher the asphalt temperature the more asphalt fume/vapors are generated. The heated asphalt storage tank operating temperature should be maintained as low as possible to reduce energy usage and the probability of pyrophoric materials formation and generation of asphalt fume/vapors. If not present, adding instrumentation to automatically monitor and adjust the heated asphalt storage tank operating temperature will be the most effective way to assure proper control. This will also help prevent fires due to heated asphalt storage tank overheating events. The heated asphalt storage tank operating temperature as well as tank shape may make one type of measurement device preferable over another. Check with the manufacturers of these devices to determine which device is best for your situation.

Adequate Asphalt Level in a Heated Asphalt Storage Tank

Liquid asphalt should always be maintained at least one foot above the heating coils or fire tubes. If not, the asphalt can be over-heated causing "cracking "of the asphalt resulting in asphalt fume/vapors, causing higher concentrations in the heated asphalt storage tank headspace, and increased coke formation. However, there may be tank heating designs that cannot be operated this way. If so, the owner/operator can include appropriate alternative methods to prevent pyrophoric materials formation.

Heated Asphalt Storage Tank Filling

Fill pipes in asphalt storage tanks should be low enough to assure that asphalt flows into the tank below the liquid surface. This prevents asphalt splashing due to cascading asphalt and reduces asphalt fume/vapors formation. Some sort of level control technology should be used to control tank filling and reduce the probability of overfilling. Radar, microwave, ultrasonic, pressure or volume-based devices such as differential pressure transducers can be used to measure the tank levels.

Routine Inspections and Cleaning

Heated asphalt storage tanks should be monitored for asphalt coke buildup on inside walls. Regular cleaning of the heated asphalt storage tank buildup should be performed based on the amount of materials accumulated on the inner surfaces, historical data, engineering judgment, and operator knowledge.

Davie quantified a heated asphalt storage tank coke depositional rate of 0.31 g/m^2 hour at 63.8°C – 132.8°C (temperature of the underside roof shell) [4]. Subsequent numerical modeling showed that the critical thickness for pyrophoric materials generation and deposition was 5.5mm. Davie also recommended a 22-month interval between heated asphalt storage tank cleanings to prevent pyrophoric materials deposition [4]. However, the Asphalt Institute is not aware of data verifying that this interval is universally applicable. The interval used for each heated asphalt storage tank should be based on the specific use conditions of that heated asphalt storage tank and the asphalt and/or other materials stored in it.

If tank usage changes, the tank should be emptied, cleaned, and monitored until the required cleaning cycle is determined and proven effective.

Reduction of Reactive Surface Area Inside the Heated Asphalt Storage Tank

The surface area inside an asphalt storage tank can be reduced by using stainless steel or application of a barrier coating to the level at and above the safe fill capacity of the tank. High-temperature coatings such as phenolic epoxy can be used to prevent rust formation. Application of a coating forms a barrier on the surface of the steel. This hinders the chemical reaction of the sulfur and oxidized iron (rust) to prevent the formation of pyrophoric material.

Minimize Air Introduction by Mechanical Means

Single vents are usually used on the top of the heated asphalt storage tank. The vent can be located in the middle of the roof to minimize asphalt clogging during filling or mixing operations. Any roof vent should be regularly inspected, and if necessary, maintenance activities performed to assure that the vent is not clogged. An alternative location is to have the vent located near the heated asphalt storage tank wall and roof interface.

Gangway hatches and roof manways should be closed and latched to prevent leakage of air containing oxygen into the heated asphalt storage tank headspace. The manways and hatches should be regularly inspected, and if necessary, maintenance activities performed to assure that they are not clogged. Note that using the manways and hatches to gauge tanks can allow the introduction of air containing oxygen which can ignite causing heated asphalt storage tank fires.

Walkways should be used to safely inspect and perform maintenance on vents, hatches, and manways, thereby avoiding walking on the roof of the heated asphalt storage tank.

How Can I Remove Pyrophoric Materials?

Often, heated asphalt storage tank coke deposits are removed using hand tools, jackhammers, and other mechanical means. However, this approach allows potential contact of pyrophoric materials with atmospheric air containing oxygen. This can result in the ignition of the coke materials in the tank. Thus, any time mechanical methods are used to clean heated asphalt storage tank precautions should be taken to prevent the air containing oxygen to react with the coke. This can be accomplished by keeping the deposits wet during vapor and gas freeing, degassing, and ventilation operations. Hoses used to apply water to the tank surfaces should be electrically bonded. High-pressure water jetting is also used and may reduce and/or prevent pyrophoric materials from reacting with atmospheric oxygen.

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