

## EXPLOSION HAZARDS IN TANKS OF HIGH FLASH POINT LIQUIDS

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### ABSTRACT

Reports of explosions in cargo and storage tanks of high flash point liquids such as residual fuel oil, asphalt, and oily waste water have shown that these explosions have occurred even when the liquid temperatures are well below the liquid nominal flash point. The reasons for these seemingly paradoxical explosions are reviewed and results of recent laboratory tests are presented to better define the conditions leading to flammable vapor atmospheres in these tanks. The potential effectiveness of various prevention measures are discussed including inerting, monitoring tank vapor concentrations, and periodic cleaning of condensation and deposits on the tank walls and roof.

### INTRODUCTION

The flash point of a combustible liquid is defined in NFPA 30 [1] as "the minimum temperature at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid within the vessel as specified by appropriate test procedure and apparatus." Liquids having a flash point of 93 °C or higher are tested in the Pensky Martens Closed Cup Tester [2]. Fire and explosion protection guidelines in NFPA 30 and other standards depend greatly on whether or not the combustible liquid is being stored below or above its measured flash point.

The preceding definition of flash point notwithstanding, there are several types of high flash point liquids that can have a flammable vapor atmosphere in their storage tanks even when the bulk liquid temperature is well below its measured flash point. The objectives of this paper are:

- 1) to provide a brief overview of fire and explosion incidents involving combustible liquids being stored or transported at temperatures below their measured flash points;
- 2) to provide an explanation of the phenomena that are responsible for these paradoxical fires and explosions; and
- 3) to present results of recent research into the effectiveness of various explosion prevention measures for storage tanks containing these liquids.

### OVERVIEW OF STORAGE TANK AND TANKER FIRE AND EXPLOSION INCIDENTS

The U.S. Coast Guard, which is the U.S. government agency responsible for regulating and inspecting commercial shipping in U.S. waters, contracted with Worcester Polytechnic Institute (WPI) to conduct a review of explosion incidents involving high flash point liquids, specifically liquids with open cup flash point greater than 66 °C (Grade E cargo in Coast Guard terminology). After reviewing incident reports written by the Coast Guard and the National Transportation Safety Board, WPI identified the eight explosion incidents listed in Table 1 as being tanker and barge explosions in which the liquid was probably at a temperature below its nominal flash point. The term nominal flash point is used here to denote measurements of the liquid flash point before it was loaded into the tank. In some cases the liquid flash point was not actually measured but tests with similar liquids have shown the flash point to be significantly higher than the liquid bulk temperature.

Four of the incidents listed in Table 1 involved residual fuel oils, two involved oily waste water, one involved asphalt, and one involved sewage sludge. Two of the incidents involved hot work (metal cutting) or torch heating of the tank or attached piping such that there was undoubtedly localized heating of the liquids to temperatures that could well have exceeded their flash points. In at least two other incidents (one involving hot work above an open tank), contamination with lower flash point liquids was reported to have been a significant factor. The causes of the flammable vapor atmosphere in the tank were not reported for the other four incidents. There were a total of eight fatalities and eight injuries in the eight incidents.

**Table 1**  
**Tanker/Barge Explosions Involving High Flash Point Type Cargo\***

Date	Vessel Name	Vessel Type	Cargo	Cargo Flash Point (°C)	Cargo Bulk Temperature (°C)	Operation at Time of Incident
11/3/77	INTERSTATE 71	Tank Barge	Asphalt	332	128	Torch Heating of Drain Line
8/23/81	D-204	Tank Barge	Sewage Sludge	?	20 – 30 (Ambient Air)	Off-loading
8/12/82	EXXON NEW ORLEANS	Tanker	Bunker C Oil	?	23 (Ambient Air)	Hot Work (cutting) on Tank Wall
11/18/83	RECOVERY I	Tank Barge	Oily Waste Water	> 100	4 – 10 (Ambient Air)	Cargo Loading
12/6/84	BRAZOS SEAHORSE	Offshore Supply	Oily Waste Water	?	20 – 30 (Ambient Air)	Cargo Loading and Inerting
10/28/86	OMI YUKON	Tanker	No. 6 Fuel Oil (bunker fuel)	67 - 91	49 – 54	Hot Work (cutting) Above Main Deck
8/31/88	FIONA	Tanker	No. 6 Fuel Oil	100	58	Product Sampling Prior to Off-loading
3/6/90	CIBRO SAVANNAH	Tank Barge	No. 2 Fuel Oil	63 - 64	6	Just Completed Cargo Loading and departed dock

\*Data from Zalosh and Finnegan (1994)

Davie et al [4] recently reviewed reports of 73 fire and explosion incidents involving asphalt storage tanks in the U.K. Table 2 is a listing of the various types of incidents they identified. The largest number of incidents (30%) listed in Table 2 involved external fires due to tank overflow or to the combustion of tank insulation. The second largest category (16%) involved spontaneous combustion smoldering of either the vapor or condensate on the tank roof, which is usually at a substantially lower temperature than both the asphalt and the tank walls. Only four of the 73 incidents (5.5 %) involved accidentally heating the bulk liquid to a temperature approaching or exceeding its flash point, and only 12% involved hot work or torch heating of the tank or its appurtenances.

Although the author is not aware of any other recent surveys of high flash point liquid storage incidents, there have been numerous accounts of explosions involving fuel oil at a bulk temperature well below its nominal flash point. In many cases, there was hot work or torch heating on or near the tanks. However, in many other cases the causes were either not identified or not publicly released because of restrictions imposed during litigation.

Phenomena that seem to have been involved in several of these incidents include the development of flammable vapor concentrations in the tank, spontaneous ignition and smoldering, and the reduction in flash point by contamination with lower flash point liquids. Brief reviews of these phenomena follow.

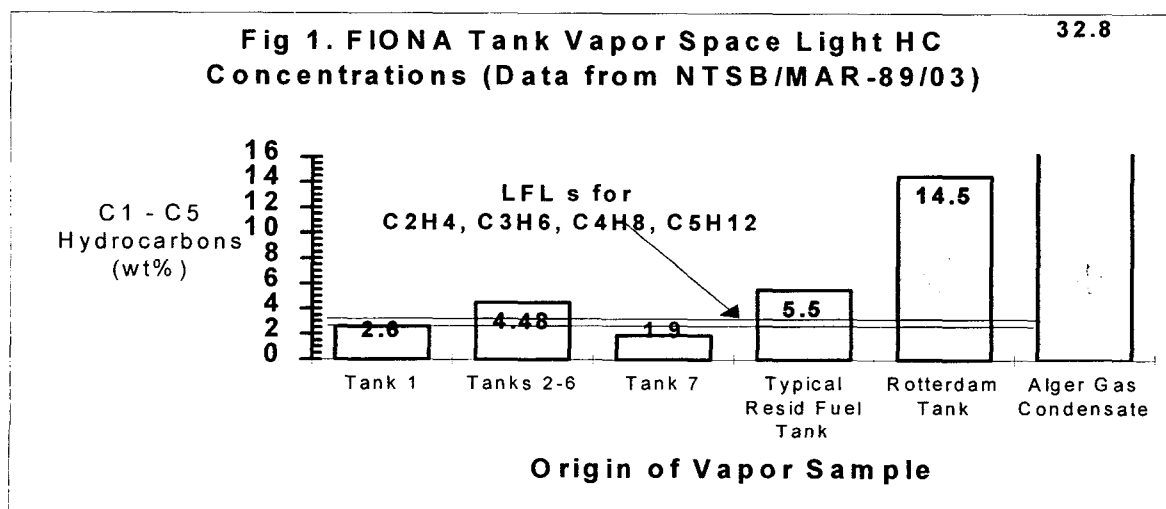
**Table 2**  
**Asphalt Storage Tank Fires and Explosions in the U.K. During 1971-1992\***

Type Of Incident	Number Of Incidents	Percent
External Fires Due to Tank Overflow or Tank Insulation	22	30.1 %
Spontaneous Combustion/Smoldering	16	16.4
Hot Work or Torch Heating	9	12.3
Open Manhole Cover	7	9.6
Exposure of Heating Tubes or Thermostat	7	9.6
External Hot Surface Ignition of Vapor	6	8.2
Miscellaneous (e.g. entry of aqueous emulsion)	6	8.2
Overheating Due to Thermostat or Flame Tube Failure	4	5.5
<b>TOTAL</b>	<b>73</b>	<b>100 %</b>

\*Based on data from Davie, Nolan, and Hoban, 1994

#### FLAMMABLE VAPOR ATMOSPHERE IN STORAGE AND CARGO TANKS

During the tanker FIONA incident investigation [5], the National Transportation Safety Board (NTSB) conducted an extensive analysis of the flammability of the vapor space in the FIONA's cargo tanks. They obtained samples of the vapor in all the tanks, including the tank in which the explosion occurred (Tank 1), and had the samples analyzed to determine the hydrocarbon concentrations. The C1 to C5 hydrocarbon average concentrations reported by the NTSB are shown here in Figure 1. The other concentrations shown in Figure 1 are the NTSB

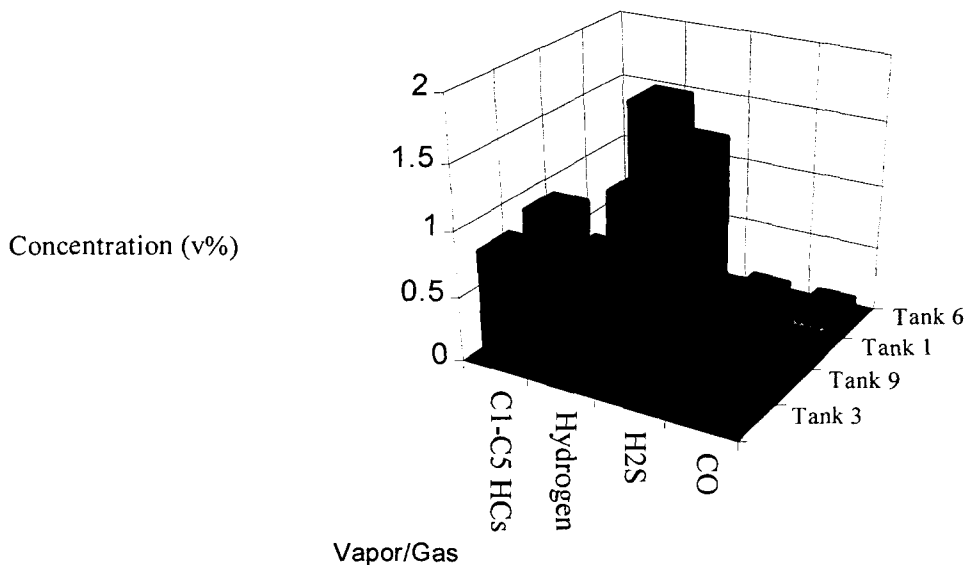


results for the vapor space in the Rotterdam tank from which the FIONA cargo originated, from the tank of Algerian gas condensate that was the cargo on the preceding voyage of the FIONA, and from typical tanks of Number 6 residual fuel oil. Horizontal lines representing the range of lower flammable limit concentrations for ethane, propane, butane, and pentane are also indicated in Figure 1.

The data in Figure 1 indicate that hydrocarbon concentrations in most of the FIONA's tanks and in typical tanks of Number 6 fuel oil are well above the lower flammable limits of light hydrocarbons. These flammable vapor concentrations, which are consistent with the combustible gas detector readings taken in the FIONA's tanks, existed even though the oils were at temperatures well below their flash points. The NTSB report concluded that one reason for the anomalously high hydrocarbon concentrations was contamination by the previous cargo. The report also recommended additional research to investigate the causes and extent of high hydrocarbon concentrations in other tanks of Grade E cargo.

High concentrations of hydrocarbons and other flammable gases have also been measured in asphalt storage tanks. Dimpfl [6] sampled several tanks containing asphalt at temperatures far below their flash points (typically 250 °C to 350 °C), and measured concentrations of C1 to C5 hydrocarbons, hydrogen, hydrogen sulfide, and carbon monoxide. Results for four of the tanks are shown in Figure 2. Although the concentrations of the individual gases/vapors are below their lower flammable limits in normal air, the mixtures may well be flammable, particularly since the oxygen concentrations in the tanks ranged from 14 volume % to 18 v%.

Fig. 2 Flammable Vapor Concentrations in Asphalt Storage Tanks; Data from Dimpfl (1980)



Dimpfl attributed the high concentrations of flammable gases and vapors to smoldering of coke like deposits on the underside of the tank roofs. This smoldering is responsible for the reduced oxygen concentrations in the tanks. According to Dimpfl, the smoldering is caused by reactions of the steel roof with hydrogen sulfide to form pyrophoric iron sulfide. Additional research on smoldering and spontaneous ignition in storage tanks is described in the following section.

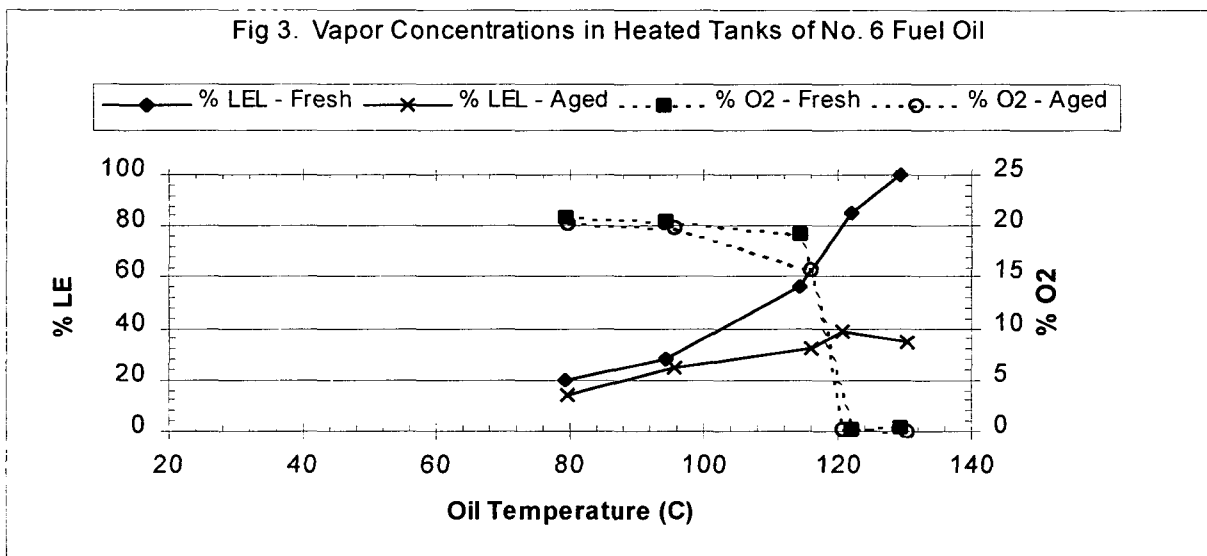
## SPONTANEOUS IGNITION AND SMOLDERING IN STORAGE TANKS

Dimpfl's study [6] of asphalt storage tank smoldering suggested that deposits on the underside of the tank roofs can auto-ignite at temperatures of about 190 °C or lower if pyrophoric iron sulfide is present in the deposits. Davie et al [7] recently conducted thermal stability tests of roof deposits and found that the self-heating onset temperature and the extent of self-heating are quite sensitive to the availability of oxygen. They observed exotherms beginning at temperatures in the range 64 °C to 133 °C. According to Davie et al, these temperatures are comparable to the usual tank roof underside temperatures of 60 °C to 160 °C.

The studies of both Dimpfl and Davie et al suggest that the smoldering of the tank roof deposits can lead to oxygen depletion, which in turn can promote the formation of pyrophoric iron sulfide. Sudden entry of air into the tank vapor space can then cause the iron sulfide to be rapidly oxidized and generate temperatures capable of igniting the flammable vapors in the tank. Davie et al analyzed the chemical composition of some of the coke deposits and found both iron and sulfur, in some cases in the form of iron sulfate. The latter is an oxidation product of FeS<sub>2</sub>.

Recent laboratory tests at WPI [9] have provided evidence of low temperature oxidation in tanks of residual (Number 6) fuel oil. The tests were conducted in a 65 liter carbon steel tank equipped with electrical strip heaters on the external walls. As the tank was heated, a multi-sensor combustible gas detector measured the percent of the Lower Explosive Limit (%LEL), the oxygen concentration, and the hydrogen sulfide and carbon monoxide concentrations. The %LEL sensor was a catalytic combustion sensor calibrated with a pentane-air mixture.

Figure 3 shows the %LEL and oxygen concentration data obtained in two of the WPI tests. One test was conducted with a fresh batch of oil (obtained from a delivery to the boiler plant), while the second test was conducted with oil that had been stored for three months in a room temperature container. The measured flash points were 95 °C for the fresh oil and 110 °C for the aged oil. The %LEL data in Figure 3 show the concentrations of flammable vapor increasing with increasing temperature, but not reaching 100%LEL until at least 30 °C beyond the flash point. The apparently low %LEL readings may be attributable to condensation of the vapor on the sintered metal filter in front of the sensor catalytic element.



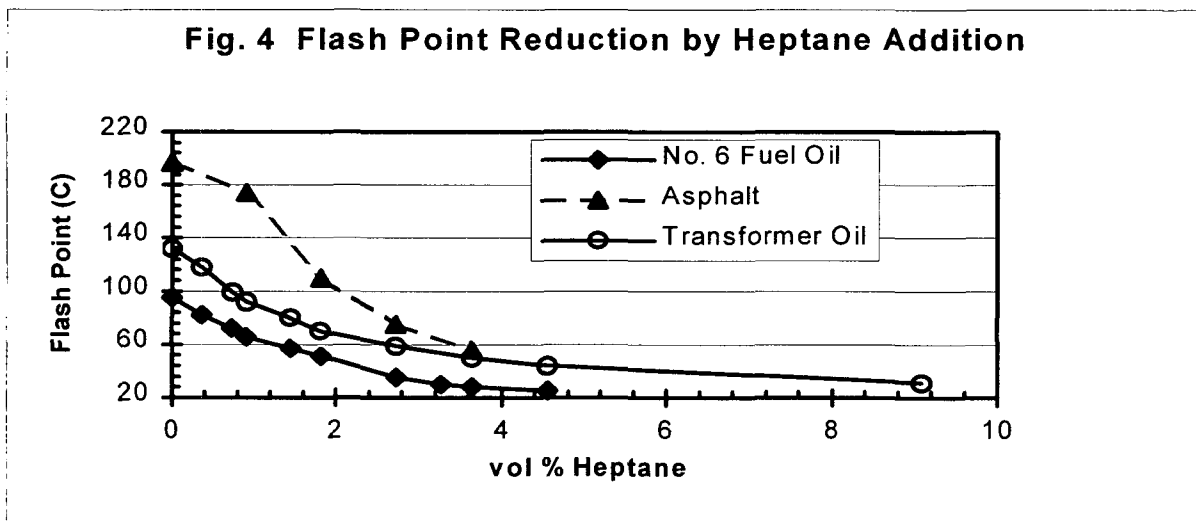
The most interesting aspect of the data in Figure 3 is the reduction in oxygen concentration at a temperature of about 116 °C. Virtually all of the oxygen in the tank vapor space has been

reacted at temperatures of 120 °C and higher. There were correspondingly large increases in the CO concentrations at these temperatures. This is clear evidence of an oxidation reaction. Since no flame was observed in these tests, the oxidation seems to be either smoldering or a cool flame. Thus the spontaneous ignition hypothesis reported by Dimpfl and by Davie et al for asphalt storage tanks seems also to be a significant factor in at least some residual fuel oil storage tanks.

### FLASH POINT REDUCTION BY CONTAMINATION

Contamination of cargo tanks with low flash point liquids seems to have been a factor in some of the tanker explosion incidents. Laboratory experiments were conducted at WPI to determine the extent of the flash point reduction that can result from the addition of small quantities of low flash point liquids. The experiments were conducted using a Pensky-Martens flash point tester with various combinations of liquids [3,10].

Flash point reductions measured with n-heptane (flash point = -4 °C) additions to Number 6 fuel oil, asphalt, and transformer oil are shown in Figure 4. The reductions are large as the heptane concentration increases from zero to about 3 volume percent, and then seem to gradually level off. The mixture flash point reductions at 3 vol % heptane addition are about 60 °C for Number 6 fuel oil, about 74 °C for transformer oil, and about 137 °C for asphalt. Details of the experiments and results for other pairs of liquids can be found in the M.S. thesis of Finnegan [10]. Comparisons of test data with theoretical predictions for ideal solutions of homogeneous liquids are also presented in the thesis.



### EXPLOSION PREVENTION MEASURES

Since flammable vapor atmospheres can exist in some combustible liquid storage and cargo tanks even at temperatures below the liquid nominal flash point, are there more reliable explosion prevention measures? It would be preferable to have some in-situ measure of the flammability of the tank vapor space. Combustible gas detector sampling of the vapor space would be particularly desirable, but results indicated by Figure 3, and other data obtained at WPI indicate that these detectors provide erroneously low measurements in heated tanks. For

example, in one test with Number 6 fuel oil, an electric match in the tank vapor space successfully ignited the vapor-air mixture at a liquid temperature of 108 °C even though two combustible gas detectors gave readings below 50%LEL. The low concentrations seem to be caused by vapor condensation prior to reaching the catalytic element.

Should combustible liquid tanks be inerted even when the liquid temperature is well below its flash point? There is some evidence that partial inerting may be preferable to complete elimination of oxygen in the vapor space. Complete inerting of tanks containing liquids with high sulfur contents could be counterproductive if the reductions in oxygen concentration lead to increased generation of pyrophoric iron sulfide. Subsequent entry of air into the vapor space can then lead to ignition. Davie et al [4] suggest that oxygen concentrations in the range 5% to 8% are effective in providing inerting of asphalt tanks without allowing iron sulfide formation.

Another prevention measure being practiced in many facilities with asphalt storage tanks is to periodically clean the tanks to remove condensate and other deposits that form on the tank walls and roof. The frequency of cleaning depends on the rate of deposit formation and growth since the thicker deposits are the ones that are more prone to self-heating and subsequent ignition of the vapor space.

The importance of avoiding even temporary or localized heating of the liquid to temperatures above its flash point cannot be overemphasized. One experiment at WPI involved heating Number 6 fuel oil above its flash point and then allowing the liquid to cool for a period of several hours in the 65 liter tank. An electric match ignition attempt when the liquid temperature had cooled to 60 °C (40 °C below its flash point) caused a mild deflagration with the cover of the tank lifting to relieve the pressure generated.

## CONCLUSIONS

A review of fire and explosions involving high flash point liquids in storage and cargo tanks has shown that many of the incidents occurred while the liquid was at a temperature well below its nominal flash point. The causes of these seemingly paradoxical incidents have included: 1) hot work or torch application to the tank or attached piping causing localized heating of the liquid above its flash point; 2) contamination with lower flash point liquids; and 3) spontaneous combustion and smoldering of vapor condensate and pyrophoric iron sulfide on the underside of the tank roof. Flammable vapor concentrations measured in storage tanks of residual fuel oil and of asphalt have shown the presence of flammable concentrations even when the liquid is well below its flash point.

With regard to localized or temporary heating of the liquid above its flash point, laboratory tests have shown that flammable vapor concentrations can remain in the tank long after the liquid has cooled to temperatures well below its flash point. With regard to contamination with lower flash point liquids, laboratory tests have shown that addition of only three volume percent heptane to Number 6 fuel oil, transformer oil, and asphalt, causes flash point reductions of between 60 °C and 137 °C. With regard to spontaneous combustion and smoldering, recent laboratory tests have shown that exothermal reactions can begin at temperatures in the range 64 °C to 133 °C with deposits from asphalt storage tanks, and that oxidation in the vapor space of residual fuel oil tanks can dramatically reduce the oxygen concentration to near zero at oil temperatures of about 120 °C.

The monitoring of the tank vapor space with commercially available combustible gas detectors has shown that these detectors significantly underestimate the vapor concentration in heated tanks. More effective explosion prevention measures for these storage/cargo tanks include: inerting to reduce the oxygen concentration to the range 5 vol% to 8 vol%, and frequent cleaning of condensate and coke deposits from tank walls and roof. Additional research would

be helpful in developing improved detectors for heated tanks, and in further delineating the conditions leading to the generation of flammable vapor concentrations at temperatures below the liquid flash points.

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