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Fire and Explosion Hazards of Grade E Cargo

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Interim Report
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16. Abstract

This study was motivated by a cargo tank explosion incident involving No. 6 fuel oil at a temperature well below its flash point. The overall objective of the study has been to evaluate the general fire and explosion hazards of high flash point liquid cargo, i.e., Grade E cargo.

A review of Coast Guard and National Transportation Safety Board incident reports identified several other explosion incidents involving high flash point liquids at temperatures below their flash points. Three other incidents involved residual oil, two involved oily waste water, and one involved asphalt. The flammable atmosphere in the cargo tank in these incidents (and in other reported cases where there was no explosion) is due in some cases to cargo contamination by more volatile liquids, and in other cases to vapor evolution from the Grade E cargo itself, particularly when it is heated and/or transferred to other tanks.

Laboratory tests have been conducted to determine the effect of small concentrations of contaminants on the closed cup flash point of representative Grade E cargo. Results show the addition of only 0.7% heptane by liquid volume to a sample of No. 6 fuel oil reduces its flash point from 95^{o} C to 72^{o} C, which is a typical temperature during No. 6 fuel oil transfer operations. Data for other Grade E cargo show similar qualitative effects, with the magnitude depending on both the cargo and contaminant flash points.

These results, as well as a review of previous studies and current practices in the shipboard use of combustible gas detectors, are combined to provide an overall assessment of Grade E cargo hazards and possible protection measures.

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METRIC CONVERSION FACTORS

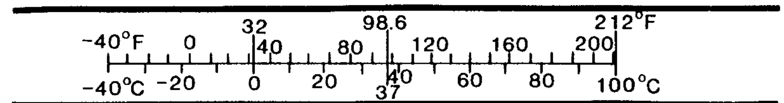
Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (WEIGHT)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (EXACT)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly).

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (WEIGHT)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	0.125	cups	c
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (EXACT)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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SECTION 1.0 INTRODUCTION

1.1 Definition of Grade E cargo

Coast Guard regulations for tank vessels (Reference 1) define a Grade E cargo as any combustible liquid having an open cup flash point of 150°F (65.5°C) or above. Common Grade E cargoes, including No. 6 Fuel Oil, are described in Section 2.1. Grade E cargo tanks need not be inerted according to current Coast Guard regulations.

1.2 Motivation for Study

On August 31, 1988, a combustion explosion in a No. 6 Fuel Oil cargo tank on the Maltese Tank Vessel FIONA killed one person and blew the top off the cargo tank. The fuel oil had a measured flash point over 200°F (93°C) and was at a temperature of 136°F (58°C) at the time of the explosion. This is an apparent paradox in that combustible liquids should not be ignitable at temperatures well below their flash points.

The National Transportation Safety Board (NTSB) investigated the FIONA explosion and concluded (Reference 2) that contamination of the Number 6 fuel oil by more volatile cargo (carried by the FIONA on its previous voyage) was the primary source of explosive vapors in the cargo tank that exploded. The NTSB also concluded that explosive concentrations of vapor obtained from several other cargo tanks on the FIONA were generated by No. 6 Fuel Oil releasing light hydrocarbons during the 11-day voyage culminating in the explosion. Furthermore, the NTSB made several recommendations (Reference 2) to the Coast Guard regarding the monitoring of Grade E cargo tanks for flammable vapors and for inerting the tanks unless they are shown to be gas free. Similar recommendations were propounded to the American Petroleum Institute and to the International Chamber of Shipping.

The study described in this report was conducted to assist the Coast Guard in responding to the NTSB recommendations regarding Grade E cargo tanks. The specific study objective has been to determine the potential of Grade E cargoes to produce flammable/explosive atmospheres at temperatures below their flash points.

1.3 Previous Studies

The potential for marine fuel oil to generate flammable vapor concentrations in tanks was well known in the 1950s, and led the Navy to develop a Federal Test Method for "Explosive Vapors in Boiler Fuel Oil," (Reference 3). The test entails heating a sample of fuel oil to a temperature of 125°F (52°C) and measuring the vapor concentration to determine if it exceeds one half of the lower flammable limit.

In 1972, Affens and McLaren (Reference 4) demonstrated that only a small amount of a highly volatile contaminant in a relatively nonflammable fuel can significantly lower the fuel's flash point. In the case of simple multicomponent hydrocarbon solutions with known composition, Affens and McLaren (Reference 4) showed that the laboratory data could be predicted theoretically from the vapor pressures and flammability limits of the individual components.

Members of the Oil Companies International Maritime Forum (OCIMF) have submitted data on combustible gas measurements in the vapor space of residual fuel oil tanks. A 1992 OCIMF report (Reference 5) on this data indicates that measured vapor concentrations exceeded 50% of the lower flammable limit in about 2% of the 1246 measurements. These alarmingly high concentrations occurred even in the absence of any contamination of the fuel oil. They are due in many cases to the trace amounts of light hydrocarbons normally present in residual fuel oils. According to the OCIMF report, these C_1 to C_8 hydrocarbons are generated by fuel cracking at local hot spots in the tank (e.g at heating coils) and by vapor bubbles being released from occlusions in the oil. Usually, the vapor release occurs during oil transfer, stirring, or heating.

The 1992 OCIMF report further points out that flash point data often do not reveal the presence of these light hydrocarbons. One reason the flash point data may not be reliable is that small concentrations (below the lower flammable limit) of these vapors may be consumed each time the pilot flame is inserted into the sample cup. Another reason is that the light hydrocarbons (particularly the C_1 to C_4 range) may be lost by leakage from the test apparatus. Dimpfl, in a paper (Reference 6) on asphalt tank flammability, suggested that these vapors are often lost during tank sampling and in pouring sample into the flash point apparatus. Comparing sample flash point data to vapor composition measurements via gas chromatography, Dimpfl concludes that "There is no relationship between the flash point of an asphalt sample and how much explosive gas is in the tank outage."

Taken as an aggregate, these previous studies strongly suggest that the FIONA tanker explosion was not an isolated incident, but was a manifestation of well documented flammability phenomena associated with the storage and transport of residual fuel oil and asphalt.

1.4 Scope of this Study

The approach to Grade E cargo flammability analysis adopted in this study has been:

(1) to compile available shipping data on commonly carried Grade E cargo;

(2) to review Coast Guard casualty records pertaining to Grade E cargo fires and explosions; and

(3) to generate flash point data for samples of common Grade E cargo with small additions of more volatile hydrocarbons.

Results of these tasks are then combined with the results from the previous studies cited above to provide an overall assessment of the ability of open cup and closed cup flash point tests to predict the fire risk of Grade E cargo.

SECTION 2.0 GRADE E CARGO: COMPOSITION, SHIPMENTS AND REGULATIONS

2.1 Composition

Typical Grade E combustible liquids are heavy fuel oils, motor oil, lubricating oil, asphalt, coal tar and fish, animal, or vegetable oil. Petroleum base oils are the most common Grade E cargoes because they make up the majority of the bulk liquids carried (Reference 7).

Heavy fuel oils, such as No. 2, No. 4, and No. 6 Fuel Oil, and petroleum based asphalt are residues of the distillation of crude oil (Reference 8). (No. 4 Fuel Oil is commonly blended from No. 6 and No. 2). Asphalt and No. 6 Fuel Oil are of such high viscosity that they usually have to be heated in order to be transferred. These residual oils are comprised mostly of aromatic hydrocarbons with some paraffin and naphthene hydrocarbons. It is the lighter paraffin hydrocarbons, such as butane and pentane, that can be easily released during heating, handling and blending of fuel oils and asphalt. These light hydrocarbons comprise the explosive vapor that exists in ullage spaces above residual oils (Reference 9).

Lubricating oils have very high boiling ranges and are usually produced by a vacuum distillation step following two-stage distillation. They consist of alkanes, cycloalkanes and hydroaromatic compounds. Lube oils are engineered for high temperature stability and low temperature fluidity. They are not thermally decomposed by extreme temperatures and flow easily at low temperatures. Lube oils also undergo solvent extraction which removes the lighter hydrocarbons and leaves the more thermally stable alkanes (Reference 10).

Vegetable, fish and animal oils are compounds of carbon, hydrogen and oxygen which are found naturally in all plants, animals and fish. They are chemical combinations of glycerin and fatty acids. The resulting compounds are called triglycerides or neutral glycol ethers. There is a large number of different fatty acids each with different properties. Any one vegetable, fish, or animal oil generally has one kind of acid predominant in it along with a number of other acids in smaller amounts. No one vegetable, animal, or fish oil has any fixed combination of different fatty acids present in it, but the proportions of these will vary with the locality, soil, season, food and various other factors. Vegetable, animal and fish oils do not distill like petroleum and do not give off flammable vapors unless they are heated to about 200°C (400°F) or higher. Since they flow easily at low temperatures, they do not require to be heated for transfer (Reference 11).

In summary, the Grade E cargoes that possess the most potential for explosive atmospheres are the residual fuel oils, asphalt and any other liquids that contain light hydrocarbons in solution.

2.2 Handling and Shipment

Due to the higher cost of production and ease of handling, lubrication, animal, vegetable and fish oils are typically transported in modern chemical carriers or design class tankers. These ships are maintained under strict cleanliness and safety codes with inerting and venting systems to protect their more dangerous cargoes. Residual fuel oils and asphalt are normally transported in older tankers, barges and many reconfigured vessels which can no longer carry original design cargo due to age or regulation changes. This is due to the difficulty in handling and cleaning tanks after residual oils and the misconception that there is little to no danger in handling combustible liquids with flash points above 65.5°C (150°F) (Reference 12).

Present regulations (Reference 13) do not require tanks with Grade E cargoes to be inerted or Gas Free Tested before pumping unless structural defects exist in ship tanks or delivery systems or if one of the last three cargoes had a flash point less than the Grade E minimum. Asphalt is typically heated to 149°C (300°F) prior to transfer, No. 6 Fuel Oil is heated to 71°C (160°F), No. 4 and No. 2 Fuel Oil flow easily at room temperature and are heated to 25°C (77°F) only if previously stored at very low temperatures. The release of light hydrocarbons during heating and blending, the age and lack of inerting systems in these vessels, and the lax attitude usually present with handling this cargo greatly contribute to the likelihood of mishaps and explosions.

Individual ports and respective port authorities track and record all shipping activities including those involving various Grade cargo. Port Authorities maintain very detailed records, but unfortunately, there is no standardized method for taking port cargo statistics and most ports do not identify specific cargo carried by each vessel. Access to these records also varies from port to port. Ports on the west coast use private companies to compile and publish yearly cargo statistics. These reports are available at a relatively high cost. Ports operating on the east coast still maintain public access to reports, but as previously mentioned, the methods differ and many do not directly identify Grade E cargoes. Despite the diversity of statistics, there is ample data that reveals a considerable flow of Grade E cargoes in U.S. waters. The following is a breakdown of port cargo statistics for the east coast available as of 01 December 1993.

PORT OF BOSTON Vessel Arrivals by Cargo

	1993	1992	1991	1990
No. 6 Fuel Oil	35	58	63	64
Asphalt	7	12	7	10
Bunkers	8	4	6	9
Palm Oil	11	14	15	13

PORTS OF PHILADELPHIA/DELAWARE RIVER PORTS Vessels Discharged & Loaded

	1992	1991	1990
No. 6 Fuel Oil	43	19	13
Asphalt	8	8	15
Lube Oil	25	2	13

PORT OF NEW ORLEANS Cargo by Short Tons

	1992	1991
Petroleum Products	10,841,076	2,518,912
Animal/Vegetable Oils	7,257	35,123

PORT OF HOUSTON Cargo by Short Tons

	1992	1991
Fuel Oils	6,141,515	5,807,452
Lubricating Oils	7,289,397	4,619,685
Mineral Tars	141,393	135,735
Animal & Vegetable Oils	9,096	18,068

PORTS OF NEW YORK/NEW JERSEY Cargo by Long Tons

	1992	1991	1990
Residual Fuel Oils	7,866,645	10,228,200	14,964,627
Pitch and Asphalt	179,389	476,468	380,185
Petroleum Lubricants	26,448	34,258	23,438
Vegetable Oils	180,665	132,170	158,742

PORTS OF NORFOLK VA Cargo by Vessel Type

	1993	1992	1991
Tankers	206	287	260
Bulk	272	265	301
Combo (Fuel & Bulk)	251	198	292

Despite the lack of a national standardized method for classifying and tracking cargo shipments, these statistics indicate that the majority of Grade E cargoes being transported to and from U.S. waters are residual fuel oils, lubricating oils, and asphalt.

2.3 Relevant Coast Guard Regulations

All vessels conducting business in U.S. waters must comply with the requirements of 33 CFR 151, 155, 156, 157, 164, (Reference 14) and/or 46 CFR 32.53 (Reference 13). These regulations stipulate that owners/operators of U.S. and foreign tank vessels must submit plans and operating manuals required by 33 CFR 157 to U.S. Coast Guard Headquarters in order to obtain Coast Guard acceptance documentation. Submitted plans include cargo type and flash points for flammable and combustible cargo.

All vessels designed to carry combustible liquids with flash points below 65.5°C (150°F) as determined by an open cup tester, or equivalent cup testing method, are required to have an inert gas system. An inert gas system (IGS) is a system that supplies to cargo tanks a gas mixture of gases which are so deficient in oxygen content that combustion cannot take place within the cargo tanks. The specific requirements for the design and operation of an IGS are contained in 46 CFR Part 32 (Reference 13). An IGS must be activated prior to cargo transfer for combustible liquids with flash points below 65.5°C (150°F). There are no requirements for a vessel carrying Grade E cargo to have an IGS unless the vessels also carry cargoes with flash points below 65.5°C (150°F) and there are no requirements for an IGS to be used for a Grade E cargo unless one of the last three cargoes had a flash point below 65.5°C (150°F), or because of contamination. The only other regulations which directly identify requirements for Grade E cargoes pertain to elevated temperature cargoes, and are summarized as follows.

Federal regulation 46 CFR 36.01 (Reference 13) contains the requirements for the transportation in bulk of materials considered to be Grade E liquids when shipped in molten form at elevated temperatures except for materials having a flash point of 149°C (300°F) or above. Inspection and testing is required when making alterations, repairs, or other such operations involving riveting, welding, burning, or like fire-producing actions.

In U.S. territorial waters, the inspection shall be made by a marine chemist certified by the National Fire Protection Association. If the services of such certified marine chemist are not reasonably available, the Officer in Charge of Marine Inspection, upon the recommendation of the vessel owner and his contractor or their representative, can select a person qualified to make such inspection. If the inspection indicates that such operations can be undertaken with safety, a certificate setting forth the fact in writing is issued by the certified marine chemist or the authorized person before the work is started.

For Grades A, B, and C cargoes, radio transmissions, boiler fires, galley fires, smoking and the use of non-safety matches are prohibited unless authorized by the senior deck officer. No tank hatches, ullage holes, or butterworth plates shall be opened or shall remain open without flame screens, except under the supervision of the senior members of the crew on duty, unless the tank opened is gas free.

All cargo tanks carrying liquids at elevated temperatures for the purpose of maintaining the material in the molten form are installed with the access openings located above the weather decks. Cargo pump relief valves and pressure gauges may be omitted, however, a suitable device must be fitted to stop the pumping before the designed pressure of the piping is exceeded. Flame screens may be omitted in the vent lines on cargo tanks. Where personnel are required to enter pump rooms located below the weather deck under normal circumstances of handling cargo, such pump rooms shall be equipped with power ventilation. There are no requirements for an IGS to be installed or used.

2.4 International Maritime Organization Regulations (IMO)

IMO Regulations (Reference 15) do not specifically identify Grade E cargoes. Tankers carrying petroleum products having a flash point exceeding 60°C (140°F) (closed cup test), as determined by an approved flash point apparatus, comply with fire safety regulations for cargo ships and are fitted with a fixed deck foam system. Only tankers carrying crude oil, petroleum products and liquid products having a similar fire hazard having a flash point not exceeding 60°C (closed cup test) are required to have and operate inert gas systems (IGS).

Despite the lack of regulations concerning Grade E cargoes, several ship Carriers and Charter Companies require an IGS for ships carrying Grade E cargo (Reference 12). Apparently, these companies appreciate that flash point alone is not a sufficient nor direct measure of the flammability of a Grade E cargo tank vapor space.

SECTION 3.0 GRADE E CARGO INCIDENT REPORTS

3.1 Coast Guard Incident Report Database

A search for Grade E cargo fire and explosion incident reports was carried out with the assistance of Coast Guard Headquarters. The CASMAIN database was queried by CG Headquarters personnel using data fields suggested by WPI personnel. The search was difficult because the cargo category designation is not identified in many of the incident report records. However, a listing of all the fire and explosion incidents involving ships certified to carry cargo of various grades was obtained, and full reports of candidate Grade E cargo incidents were requested and reviewed.

In addition to the Coast Guard database and reports, various National Transportation Safety Board marine accident reports were reviewed and relevant information from these reports is included in the compilation described here. Other sources either did not contain pertinent reports or could not be fully tapped in the time frame of this study.

Table 3-1 lists eight pertinent incidents in which there was an explosion involving either Grade E cargo or some similar high flash point liquid. The cargo/liquid flash point was not reported in three of these incidents (but is believed to be in the Grade E cargo range) and in the last incident the flash point is marginal between Grade D and Grade E. In six of the eight incidents, the explosion was followed by a fire.

Brief descriptions of each of the eight incidents listed in Table 3-1 are provided in Sections 3.2 to 3.9. Unless otherwise noted, the descriptions are based on documentation provided to WPI from the Coast Guard casualty report file for that incident.

Table 3-1

Explosion Incidents Involving Grade E Type Cargo

Date	CG Incident Number	Vessel Name	Vessel Type	Vessel Cargo Certification	Cargo	Cargo Flash Point (°F)	Fatalities	Injuries
11/3/77	?	INTERSTATE 71	Tank Barge	Grade E	Asphalt	630	1	0
8/23/81	3125-SLM81	D-204	Tank Barge	Grade B	Sewage Sludge	?	0	0
8/12/82	0174-POR82	EXXON NEW ORLEANS	Tanker	Grade B	Bunker C Oil	?	1	2
11/18/83	0314-MOB83	RECOVERY 1	Tank Barge	None	Oily Waste Water	> 212	1	0
12/6/84	MC84000149	BRAZOS SEAHORSE	Offshore Supply	Grade E	Oily Waste Water	?	0	1
10/28/86	MC86005373	OMI YUKON	Tanker	Grade B	No. 6 Fuel Oil*	152 - 212	4	4
8/31/88	MC88004916	FIONA	Tanker	Grade B	No. 6 Fuel Oil	> 200	1	0
3/6/90	?	CIBRO SAVANNAH	Tank Barge	Grade B	No. 2 Fuel Oil	146 - 148	0	1

* OMI YUKON Fuel Oil was bunker fuel for its own boiler, not cargo.

3.2 INTERSTATE 71 Barge Explosions and Fire: 11/3/77

The following information on this incident was obtained from the article by Halvorsen and Roussel in the Proceedings of the Marine Safety Council (16).

INTERSTATE 71 is 380-ft (116-m) long and has a cargo capacity of 81,759 barrels (12,999 m^3) in 10 cargo tanks. On November 3, 1977, the cargo consisted of about 68,000 barrels (11,000-m^3) of asphalt (open cup flash point of 630°F (332°C)) heated via cargo tank heating coils to a temperature of about 262°F (128°C). As the INTERSTATE 71 was approaching its destination in Providence, Rhode Island, one of the tankermen was using a propane torch to melt solidified asphalt in an uninsulated pump drain line.

Apparently, asphalt vapors in the drain line were ignited by the hot pipe wall. The auto-ignition temperature for asphalt is reported to be 900°F (482°C), which is readily produced by extended heating with the propane torch. Another, less likely, explanation is that the asphalt residue in the drain line was heated sufficiently to undergo "coking" in which it pyrolyses or oxidizes and glows red hot.

Flame initiated in the drain line must have propagated into the ullage space of one of the cargo port tanks. Flames were observed to rise 20-ft (6-m) into the air, and the tankerman who had been heating the drain line was killed when he was blown against the pumphouse. About 10 minutes after the port tank explosion and fire, there was a second explosion, this time at a starboard tank. The explosions cracked and bulged the main deck, and breached two bulkheads. The fire resulting from the second explosion burned for about an hour before being extinguished by responding Coast Guard personnel.

Two days after the incident, a marine chemist measured flammable vapor concentrations of 40% to 100% of the lower flammable limit in the undamaged INTERSTATE 71 cargo tanks while the asphalt liquid temperature was 200°F (93°C), i.e. about 430°F (220°C) below the asphalt nominal flash point. Furthermore, subsequent measurements in the land storage tank from which the cargo originated indicated vapor concentrations up to 50% of the lower flammable limit, with a liquid asphalt temperature of 335°F (168°C).

This incident demonstrates that asphalt flash point is not a reliable measure of the vapor space flammability. Asphalt tank vapor flammability has been studied extensively by Dimpfl (Reference 6), and his results are discussed in Section 7 of this report.

3.3 D-204 Tank Barge Explosion: 8/23/81

According to correspondence in the CG files for this incident, sewage sludge is an unregulated product, rather than a Grade E cargo. Nevertheless, flammable vapors in a cargo tank containing sewage sludge (classified by the CG as bulk liquid) were ignited as the tank discharge valves were being opened to initiate off-loading at Liverpool, Illinois on 23 August 1981. The resulting explosion damaged the barge deck sufficiently that the barge was sold for scrap. Ignition was attributed to somebody on the barge deck lighting a cigarette.

3.4 EXXON NEW ORLEANS Explosion: 8/12/82

The EXXON NEW ORLEANS is an 800-ft long (240-m), 32,000 gross tons tanker certified for Grade B in most cargo tanks and Grade E in its deep tanks. At the time of the explosion, the EXXON NEW ORLEANS was in a Portland, Oregon dry dock undergoing maintenance, including hot work (cutting). This hot work was intended for a certified gas free tank, but the cutting torch mistakenly penetrated the No. 6 port bunker tank, which contained

3,400 barrels (540-m^3) of bunker C. The cutting torch ignited flammable vapors in the 37-ft (11-m) ullage space above the fuel oil.

The resulting explosion killed one dry dock worker and burned two others. These was extensive smoke from the low volatility bunker C, but no fire. Structural damage entailed $450,000 in repairs.

This is a clear example of a situation in which flammable concentrations of vapors existed above the high flash point fuel oil. However, there is a possibility that at least some of the vapors may have been generated by the cutting torch heating oil residue on the tank walls before the torch actually penetrated the wall. In any event, the incident is an unfortunate demonstration of the hazard of doing hot work on a tank containing Grade E cargo.

3.5 RECOVERY 1 Explosion: 11/18/83

RECOVERY 1 was a 275-ft (87-m) long tank barge operating on the Mobile River. It had been certified to carry B and lower combustible liquids at one time, but the certification expired and the barge owners decided not to have it recertified. At the time of the incident, it was being used to store and transport wastewater from an oil/gas field. The wastewater was delivered to the barge by tank trucks.

On November 18, 1983, RECOVERY 1 was being loaded with wastewater that originated from an oil/gas well and water that had been used to hydro test oil field piping. The water had been treated in a separator but still contained volatile hydrocarbons. As the water was being discharged from a tank truck (pressurized with an air tank) via a hose to a barge cargo tank, an explosion occurred. The truck driver, who was apparently standing on the deck at the cargo tank open butterworth (tank hatch), was killed.

The steel deck over the cargo tank was ripped open, as was the tank bulkheads. A fire ensued, and the barge partially sank.

Samples of water from other cargo tanks on the barge showed hydrocarbon concentrations in the range 10 to 100 micrograms per milliliter. All samples had a Pensky Martens closed cup flash point over 100°C.

The ignition source in this incident is suspected to be either the truck driver lighting a cigarette, or non-intrinsically safe electrical wiring on the barge deck. Deck lights were on at the time of the explosion. Laying a discharge hose through an open butterworth, allowed tank vapors to be released on the barge deck and eventually reach one of these ignition sources.

3.6 BRAZOS SEAHORSE Explosion: 12/6/84

The BRAZOS SEAHORSE is an offshore platform supply vessel that was servicing the platforms offshore Santa Barbara, California, at the time of this incident. A large, portable tank on the BRAZOS SEAHORSE was being filled with platform contaminated brine water when a combustible gas meter measured a vapor concentration approaching or exceeding the lower flammable limit. Tank filling was suspended and carbon dioxide inerting procedures were initiated.

While flooding the tank with CO_2, an explosion occurred in the tank. A crew member in the tank was burned by the flames, but survived. Although the CG documentation did not specify the ignition source, CO_2 systems are known to generate electrostatic charges when not properly grounded.

3.7 OMI YUKON Explosions and Fires: 10/28/86

Information for this incident was obtained from the NTSB report (Reference 17).

The U.S. tanker OMI YUKON was 811-ft (247-m) long and had a cargo capacity of 610,000 barrels (97,000-m^3). It was Grade B cargo certified, and was being used to carry Alaskan crude oil to Hawaii and other U.S west coast ports.

On October 28, 1986, the OMI YUKON was underway without any cargo. Flame cutting operations were initiated to remove obsolete equipment above the main deck. Apparently, hot slag from the flame cutting fell into the plume of fuel oil vapors emitted from a fuel oil tank vent. Since the vent did not have a flame arrestor, flame propagated through the plume and the vent into the tank. This triggered the first of three explosions severely damaging the tank, the adjacent engine room, and the accommodations house above the engine room. Multiple fires ensued. Four people were killed, four others were seriously injured, and everyone had to abandon ship. After being towed to a shipyard and inspected, the OMI YUKON was sold for scrap.

Number 6 fuel oil for its boiler had been loaded onto the OMI YUKON from an Hawaiian refinery five days prior to the accident. The fuel was loaded through a 4,000-m (13,000-ft) long subsea pipeline from the refinery to an offshore mooring station. A sample of fuel oil obtained during fuel loading was tested after the accident, and had a flash point of 91°C (196°F). However, there is reason to suspect that the fuel was not homogeneous and at least some fuel had a much lower flash point.

Refinery personnel had used "flush oil" in the subsea pipeline to push the fuel oil and flush the pipeline between different loads of product. This flush oil is a mixture of almost every type of product in the refinery. On the day the OMI

YUKON was loaded, the pipeline contained about 10,000 barrels (1,600-m^3) of Number 6 Fuel Oil followed by about 4,000 barrels (60-m^3) of flush oil. There was no provision to prevent mixing of fuel oil and flush oil, which can have a much lower flash point. On at least one other occasion involving another tanker, flash point tests, with samples of what should have been No. 6 Fuel Oil loaded through the pipeline, revealed flash points of 85°F and 124°F (29°C and 51°C).

Samples of fuel oil were obtained by the NTSB from the intact tanks and manifolds 10 days to 72 days after the accident. Flash points of the tank samples were 152°F and 173°F (67°C to 78°C) while the manifold samples had flash points ranging from 22°F (-6°C) to 180°F (82°C). This wide range may be indicative of extreme inhomogeneities in the fuel oil aboard the OMI YUKON, or it may be indicative of some decomposition and volatilization of fuel oil during the fires.

The fuel oil in the OMI YUKON storage tanks was probably at a temperature of 120°F to 130°F (49°C to 54°C) at the time of the explosions. This temperature range is below the nominal flash points of the fuel samples obtained during fuel loading and post accident samples from non-involved tanks. The fact that fuel vapors were indeed ignited implies that either 1) flash point data was not indicative of vapor phase flammability, or 2) local regions of lower flash point fuel (due to fuel contamination during loading) existed in certain portions of the tanks. The latter possibility is consistent with the low flash point data from the oil manifold samples.

3.8 FIONA Explosion: 8/31/88

The following description of the FIONA explosion is based on the NTSB report (Reference 2).

The FIONA is a 711-ft (217-m) long tanker with nine cargo tanks providing a total cargo capacity of 265,000 barrels (55,100-m^3). It is used for transporting various grades of oil, and is equipped with an inert gas system.

On August 17, 1988, after cleaning its tanks to remove petroleum condensate residue from its previous voyage, the FIONA began loading No. 6 Fuel Oil from a refinery in Rotterdam, The Netherlands. Loading was completed on August 19th after additional No. 6 Fuel Oil was blended at the refinery. The flash point of the composite of two No. 6 Fuel Oil samples obtained from the refinery tank was 100°C (212°F). During its voyage to the United States, the cargo tanks were neither inerted nor tested for flammable vapors.

On August 31st, the FIONA arrived at its destination in Long Island Sound, near Northport, New York. In order to even its keel, about 3,500 cubic ft (99-m^3) of product from other tanks was transferred to cargo tank 1, the forward most tank. The heating system was actuated in cargo tank 1 to facilitate cargo discharge. Several surveyors boarded the FIONA to take samples and measure product temperature and volume. According to these measurements, which required opening the ullage hatch cover, the fuel oil temperature in cargo tank 1 was 136°F (58°C). A steam leak from the tank heating system was observed through the open hatch cover.

As the temperature probe was being withdrawn from the open hatch cover, a flame was ignited within cargo tank 1, and a large explosion ensued. The explosion blew off the 46-ft by 34-ft (14-m by 10-m) tank cover, and generated a large fireball. One of the surveyors was blown overboard and killed. The other members of the surveying team apparently had time to run for cover and were uninjured. The explosion produced a fire in tank 1 that was extinguished by the crew with the FIONA's foam suppression system.

The NTSB investigation team tested samples of liquid and vapor from the FIONA cargo tanks as shown in Table 3-2. The results show high concentrations of C1 to C5 hydrocarbons, particularly in the vapor space. The data are consistent with combustible gas meter measurements which showed vapor concentrations above the lower flammable limit in all cargo tanks sampled.

The last sample listed in Table 3-2 had a measured flash point of 212°F (100°C) despite the high concentration of flammable vapor. Similarly high concentrations of volatile hydrocarbons were measured with three other No. 6 Fuel Oil samples not associated with the FIONA. These data demonstrate that No. 6 Fuel Oil tanks can and often do have a flammable vapor space even though the flash point of their cargo is well above the cutoff for Grade E cargo.

Table 3-2

Light Hydrocarbon and Oxygen Concentrations in FIONA's Tanks (based on data in Reference 2)

Cargo Tank No	C1 to C5 (wt%) in Liquid before explosion	C1 to C5 (wt%) in vapor space before explosion	Oxygen (v%) in vapor space after explosion
1	0.14	2.6*	-
2	0.06	4.6	19.5
3	0.08	4.8	18
4	0.06	4.1	15
5	0.07	4.7	18
6	0.06	4.2	18
7	0.50	1.9	15
1 - 7 composite	0.08	7.4	-
Rotterdam Tank	0.07	14.5	-

* measured after explosion in cargo tank 1.

A sample of Algerian condensate transported by the FIONA on its voyage to Rotterdam was also tested by the NTSB and found to have significantly higher liquid and vapor phase C1 to C5 hydrocarbon concentrations than the No. 6 Fuel Oil samples. Since the light hydrocarbon concentrations shown in Table 3-2 for FIONA tanks 1 and 7 are much higher than the light hydrocarbon concentration of the No. 6 Fuel Oil source (Rotterdam Tank), the NTSB report concluded that FIONA tanks 1 and 7 were contaminated by the condensate from the previous FIONA cargo. The contamination is thought to have entered cargo tank 1 either through small (invisible) cracks in the bulkhead separating the tank from the adjacent void space, or from residual condensate in the cargo intertank ducting used to transfer fuel oil between cargo tanks.

The NTSB report concludes that the ignition source for the FIONA explosion was the accumulation of electrostatic charge generated by the steam leak in cargo tank 1, and the subsequent discharge of that charge as the temperature probe was withdrawn from the tank.

The NTSB FIONA report also documents one other incident of flammable vapor concentrations being measured in a tanker cargo tank carrying Grade E cargo. In December 1988, the tanker ALDERAMINE SECONDA was transporting a load of 230°F (110°C) flash point fuel oil. After smelling fuel vapor on deck, the crew made combustible gas meter measurements in the tank vapor space. These measurements showed readings above the lower flammable limit. These measurements were later confirmed by laboratory gas chromatography tests on liquid samples from the cargo tank. This anecdote provided additional motivation for the NTSB recommendations for regulatory authorities to strengthen their requirements for preventing explosions in Grade E cargo tanks.

3.9 CIBRO SAVANNAH Explosion: 3/6/90

The following summary of the CIBRO SAVANNAH explosion is based on the account in the NTSB Marine Report Brief (Reference 18).

The CIBRO SAVANNAH is a 401-ft (122-m) long tank barge with a full-load cargo capacity of 136,745 barrels (28,466-m^3). It had satisfactorily completed a mid-period reinspection three weeks prior to the accident. The cargo certification was not included in the NTSB report, but it is presumed to be Grade B in view of the fact that it carried various fuels including gasoline as well as fuel oils.

On March 5, 1990, 105,000 barrels of No. 2 Fuel Oil were loaded onto the CIBRO SAVANNAH from an oil terminal in Linden, New Jersey. The flash point of the oil was 146°F to 148°F (63°C to 64°C) as measured with samples from the oil terminal storage tank. Since the flash point test method (closed cup or open cup) was not specified in the NTSB report, it is not clear whether the oil was nominally a Grade D cargo or a Grade E cargo. The oil temperature measured in the CIBRO SAVANNAH tanks prior to the explosion averaged 43.5°F (6°C), and the ambient air temperature was 27°F (-3°C).

Before departure, the fuel oil loading among the CIBRO Savannah tanks was adjusted to produce an even keel. A tugboat deckhand boarded the barge to prepare for departure. He later testified that he smelled fuel vapors "like in a service station."

A few minutes after the tugboat maneuvered the CIBRO SAVANNAH away from the dock at the oil terminal, a flash flame about 1-ft (0.3 m) wide was observed to propagate from a light fixture atop a kingpost on the barge deck to a point on the deck in the vicinity of a starboard tank vent. The flame was followed immediately by an explosion in the number 4 starboard tank. A few seconds later a second explosion occurred at the number 3 port tank. These explosions started a barge fire that was extinguished about 3.5 hours later by a fireboat and several Coast Guard vessels.

The explosions caused severe damage to the deck plates over the two cargo tanks involved. Damages were estimated at $4 million. There was one injury due to a crew member slipping and falling on the deck while evacuating the barge after the explosions.

The NTSB/CG investigation determined that the pressure vacuum valve for the number 4 starboard tank vent was not installed at the time of the explosion. This allowed a large flow rate of vapors to be discharged from the tank vent. It apparently also allowed flame to enter the tank even though there was a flame screen in the vent outlet. Thus the flame screen in this incident is not effective without a pressure vacuum valve on the vent.

The NTSB report attributes the flammable vapor space in the number 3 port and number 4 starboard cargo tanks to their partial load condition. This is not consistent with the ~147°F (64°C) flash point of the Number 2 fuel oil. Before this incident, the CIBRO SAVANNAH had carried one cargo of another heating oil, and two cargoes of gasoline. All cargo tanks were reportedly vacuumed after the last cargo of gasoline, and the NTSB report maintains that it is doubtful that there would be sufficient residual gasoline to produce a flammable atmosphere in the tanks. Tests with cargo samples obtained after the accident "revealed that all samples met the specifications for No. 2 Fuel Oil." Thus there is no clear explanation of why tank vapor spaces were in the flammable concentration range in this particular incident.

The generic question of flash point reduction due to contamination with more volatile hydrocarbons is evaluated with new flash point data presented in Section 5. Flash point testing methodology is described in Section 4.

SECTION 4.0 FLASH POINT TESTING AND DATA TRANSMITTAL

4.1 Flash Point Test Methods

According to 46 CFR 30.10-27 (Reference 1), "the term flash point indicates the temperature in degrees Fahrenheit at which a liquid gives off a flammable vapor when heated in an open-cup tester." The implication, of course, is that the flash point is the minimum liquid temperature at which a flammable vapor-air mixture exists above the liquid surface. Open-cup testing allows the flammable vapor to diffuse into ambient air which results in higher flash points than closed cup tests. Closed-cup testing purportedly simulates the condition inside the ullage of a storage tank. Flash points determined from closed-cup testers are typically 3 to 9°C lower than open cup results for many simple hydrocarbon liquids. Comparison data for representative Grade E cargo are shown in Section 5.

There are at least four different closed cup flash point test methods and two different open cup flash point test methods described in ASTM Standards (Reference 19). ASTM E 502-84 summarizes the various methods and provides guidance on the selection of an appropriate closed cup method depending on liquid viscosity and expected flash point range. NFPA 30 (Reference 20) prescribes similar guidance for closed cup test methods. The basic difference between the methods is the rate of sample heating and whether or not the liquid is stirred during the test. The ignition source in all three NFPA 30 specified closed cup methods (the Tag method, the Pensky-Martens method, and the Setaflash method) is a small flame directed into the vapor space of the closed cup tester at specified intervals.

The closed cup test method employed for this report is the Pensky-Martens Closed Cup Flash Point ASTM D 93-IP 34 (Reference 22). This test method covers the determination of flash point by Pensky-Martens closed cup tester (Figure 4-1) of fuel oils, lube oils, suspensions of solids, liquids that tend to form a surface film under test conditions, and other liquids of similar viscosities. This test method provides the only closed cup flash point test procedures for temperatures to 370°C (698°F).

The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. Rate of heating must not exceed 5 to 6°C per minute for ordinary liquids and 1 to 1.5°C per minute for suspensions of solids and highly viscous materials. Stirring is from 90 to 120 rpm for ordinary liquids and 250 rpm for suspensions of solids. The test flame is applied when the temperature of the sample is from 17 to 28°C below the expected flash point and thereafter at a temperature reading that is a multiple of 1°C for samples with flash points below 110°C and a multiple of 2°C for expected flash points above 110°C. Suspensions of solids and highly viscous materials are tested at temperatures of 11 to 15°C lower than the estimated flash point.

The test flame is lowered into the vapor space of the cup in 0.5 s, left in its lowered position for 1 s, and quickly raised to its high position. The sample is deemed to have flashed when a large flame appears and instantaneously propagates itself over the surface of the sample. Tests are conducted in a draft free room and the ambient barometric pressure is recorded at the time of the test. The flash point is corrected when the pressure differs from 101.3 kPa (760 mm Hg).

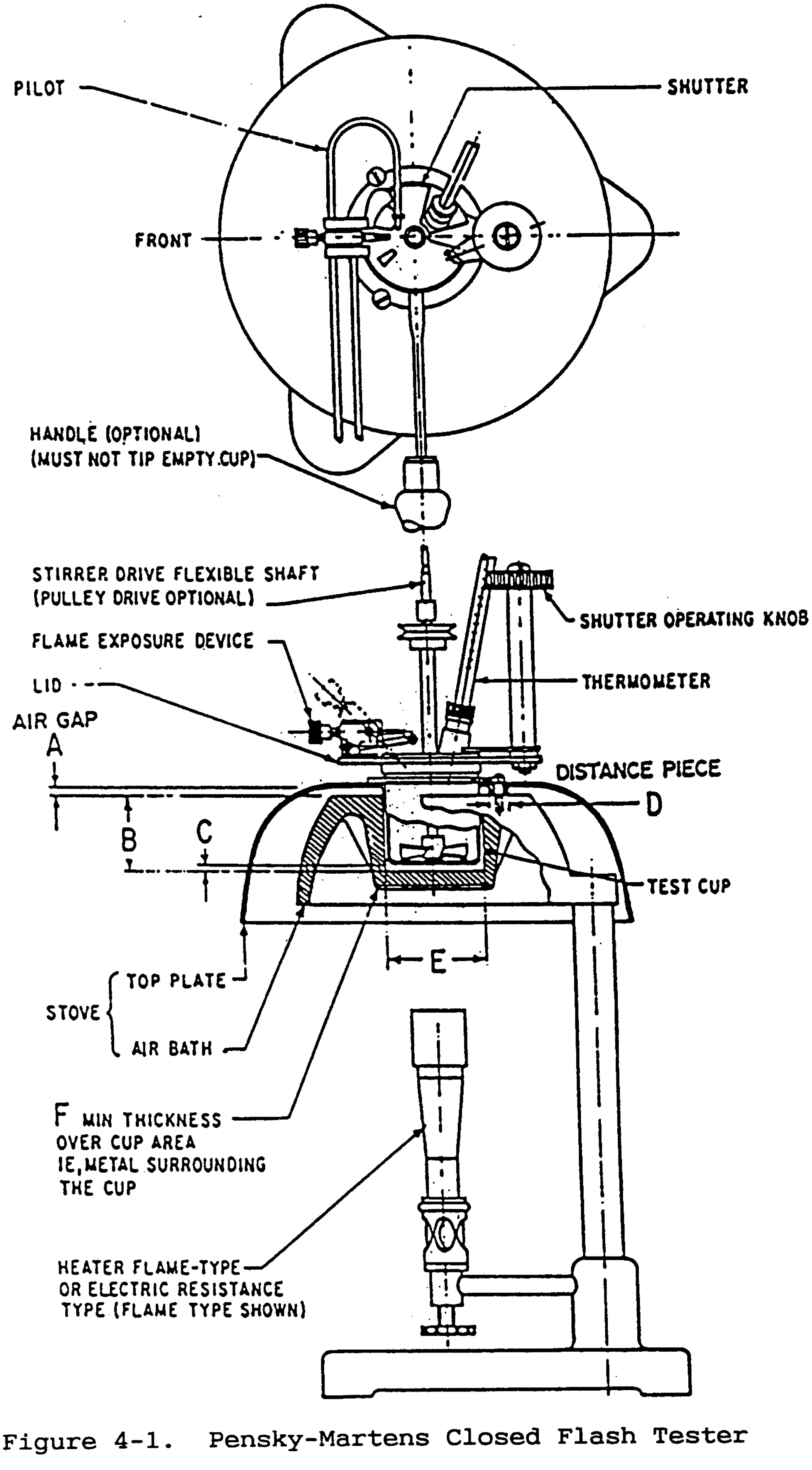

Figure 4-1. Pensky-Martens Closed Flash Tester

4.2 Data Transmittal

For ship flammable and combustible cargoes, flash point testing is conducted by a certified marine chemist prior to cargo shipment and on arrival. Arrangements are made by the ship's agent and buyer for required testing and verification of cargo type (Reference 21). Small samples are taken and tested when the ship is being loaded and again when off loading at the terminal. These samples and records are stored for an extended period of time for insurance purposes.

Flash point testing is not conducted while the ship is enroute and no detailed information of the cargo, except for the manifest, is usually available on board. Specific cargo information is handled by the shipping agent for owners and buyers and not made available for public records. During examinations, USCG Vessel Inspectors do not normally require flash point test results unless they believe there is a discrepancy between listed cargo and inspected cargo or for undesignated cargo (Reference 12). If such a case arises, shipping agents are required to hire a certified marine chemist to perform the testing.

Unless the captain of a vessel independently decides to monitor the cargo while underway, there is no indication of contamination or other problems until the cargo is being off loaded. This often too late to prevent a mishap.

SECTION 5.0 EFFECT OF CONTAMINANTS ON NOMINAL FLASH POINT

5.1 Test Methods

The objectives of the lab tests were to quantify the effect of light hydrocarbon contaminants on Grade E cargo flash points and to measure the disparity between open and closed cup flash points for representative Grade E cargoes. The Grade E cargoes chosen for testing were samples of No. 6 Fuel Oil, Asphalt and Lubricating Oil. These samples were chosen due to their high flash points and because they represent the majority of Grade E cargo shipped. The samples were obtained by independent suppliers operating in Massachusetts. Their open cup flash points were provided by independent testing laboratories.

The samples were tested at WPI in a Pensky-Martens Closed Cup Tester according to ASTM D 93-IP 34 (Reference 22) as summarized in Section 4-1. This testing procedure employs an air bath and a controlled heating rate. The test cup held a sample of 55 mL and the sample temperature was monitored by a thermocouple placed inside the cup at required depth. Each test was conducted twice for verification. Test results did not differ by more than 2.0°C. Contaminants were measured in a graduated cylinder and thoroughly mixed with the sample for 10 minutes before being heated.

The contaminants chosen were Heptane and a No. 2 Fuel Oil. These contaminants were chosen because they span a wide range of flash points from just below the Grade E cargo minimum flash point of 65.5°C (150°F) to an extremely low flash point of -4°C (25°F). Heptane (C_7H_{16}) is a light paraffin hydrocarbon that is present in many residual oils and can be released during cargo heating as well as by a contaminant. No. 2 Fuel Oil can be used as a tank cleaning agent and is normally transported in ships carrying No. 6 Fuel Oil.

5.2 Experimental Data

Table 5-1. Experimental Data on No. 6 Fuel Oil Sample

NO. 6 FUEL OIL	OPEN CUP FLASH POINT 101°C (214°F) CLOSED CUP FLASH POINT 95°C (202°F)		
CONTAMINANT	AMOUNT ADDED mL	VOLUME PERCENT %	MIXTURE CLOSED CUP FLASH POINT °C (°F)
HEPTANE	0.2	0.36	80 (176)
	0.4	0.73	72 (162)
	0.5	0.91	66 (150)
	1.0	1.82	51 (124)
NO. 2 FUEL OIL	2.0	3.6	92 (192)
	3.0	5.45	90 (194)
	15.0	27.3	67 (153)
	20.0	36.4	58 (136)

Table 5-2. Experimental Data on Asphalt Sample

ASPHALT	OPEN CUP FLASH POINT 238°C (460°F) CLOSED CUP FLASH POINT 197°C (387°F)		
CONTAMINANT	AMOUNT ADDED mL	VOLUME PERCENT %	MIXTURE CLOSED CUP FLASH POINT °C (°F)
HEPTANE	0.5	0.91	174 (345)
	1.0	1.82	110 (230)
	1.5	2.73	75 (167)
	2.0	3.64	56 (133)
NO. 2 FUEL OIL	1.0	1.82	151 (304)
	5.0	9.1	86 (187)
	10.0	18.2	75 (167)
	20.0	36.4	62 (144)

Table 5-3. Experimental Data on Lubricating Oil Sample

LUBRICATING OIL	OPEN CUP FLASH POINT 203°C (398°F) CLOSED CUP FLASH POINT 166°C (331°F)		
CONTAMINANT	AMOUNT ADDED mL	VOLUME PERCENT %	MIXTURE CLOSED CUP FLASH POINT °C (°F)
HEPTANE	0.5	0.91	91 (196)
	0.8	1.45	71 (160)
	1.0	1.82	61 (142)
	1.5	2.73	51 (124)
NO. 2 FUEL OIL	2.0	3.64	140 (284)
	10.0	18.2	95 (203)
	30.0	54.5	71 (160)
	40.0	72.7	65 (149)

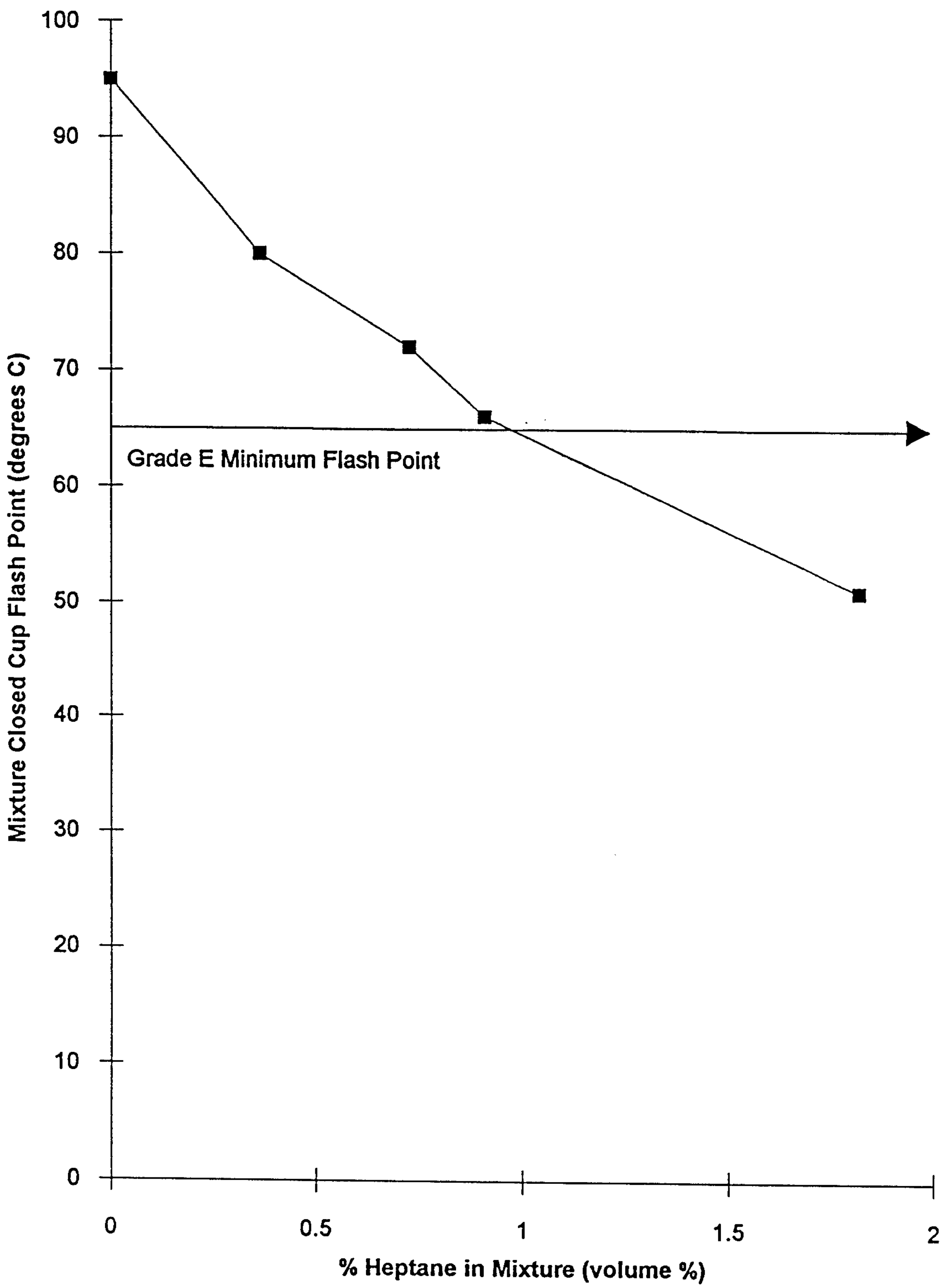

Figure 5-1. Effect of Heptane Contamination on No. 6 Fuel Oil

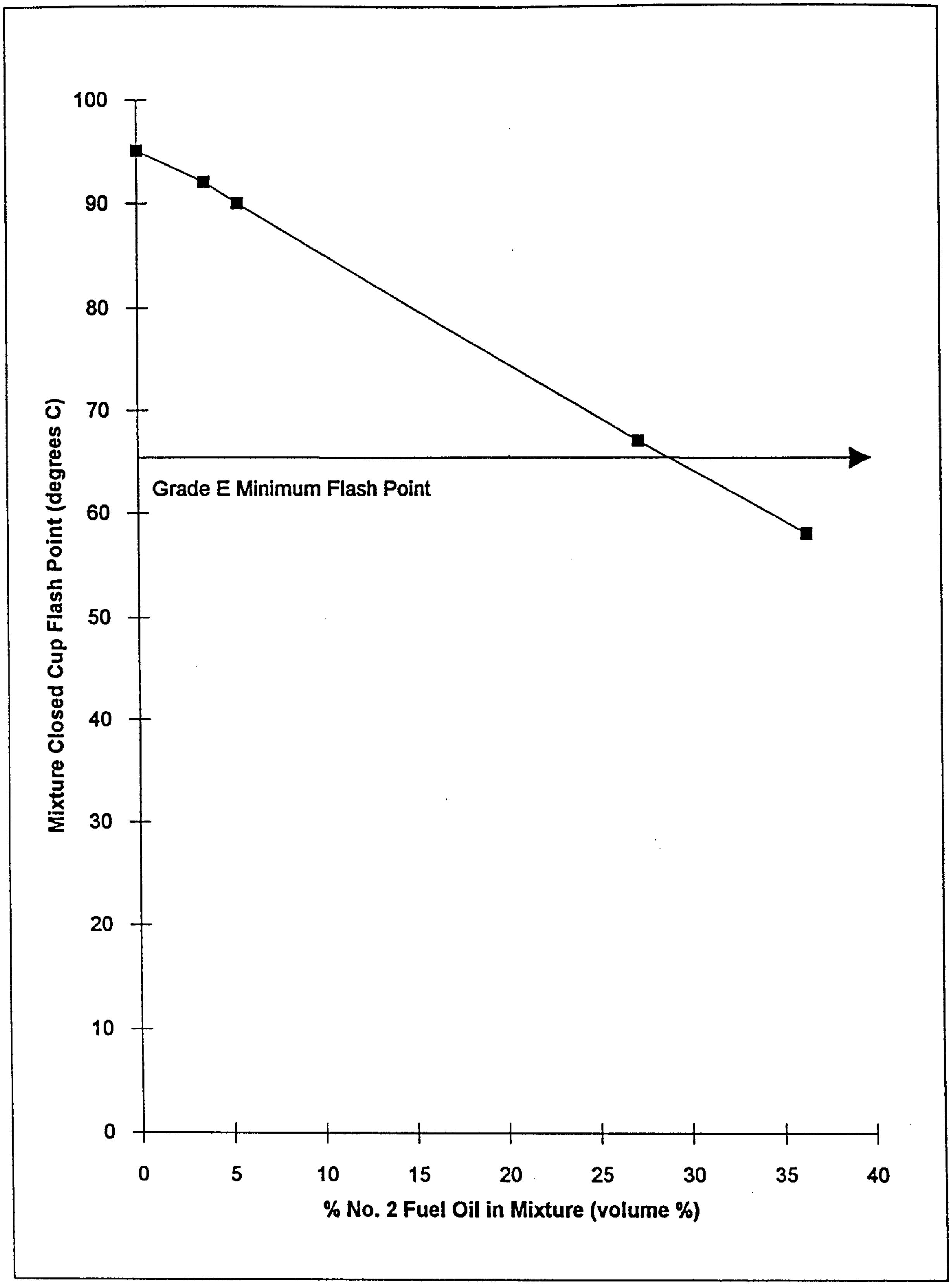

Figure 5-2. Effect of No. 2 Fuel Oil Contamination on No. 6 Fuel Oil

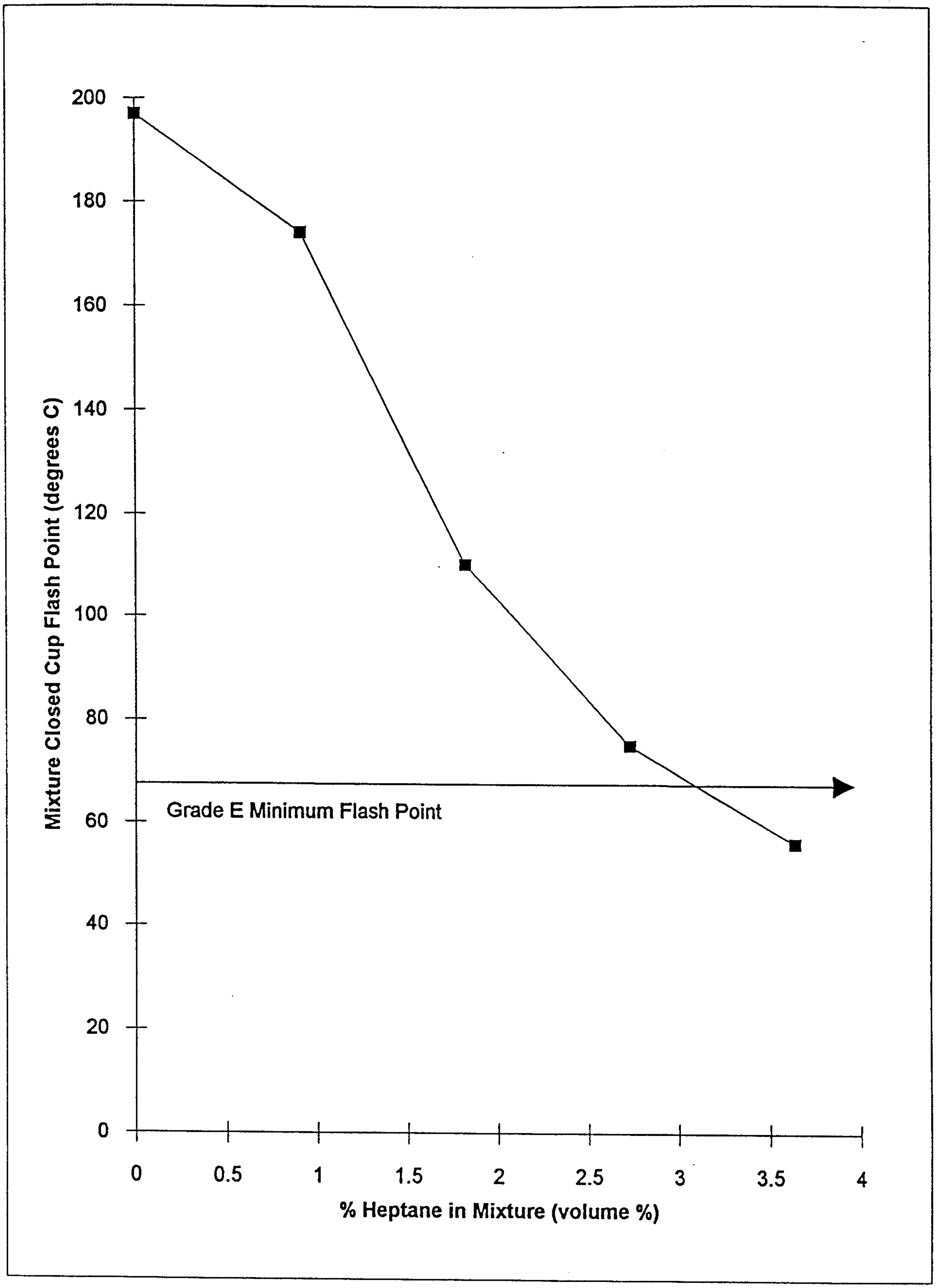

Figure 5-3. Effect of Heptane Contamination on Asphalt

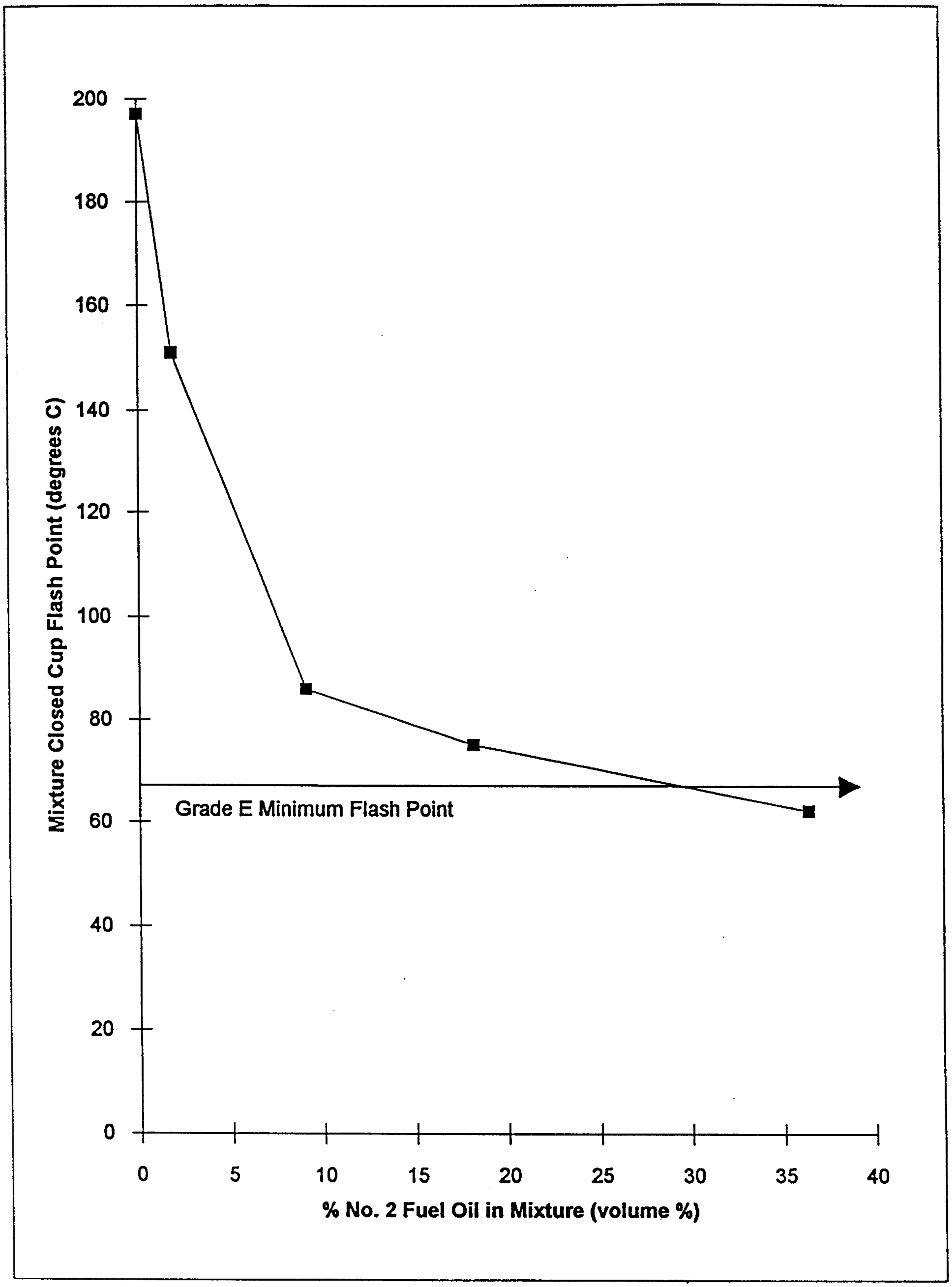

Figure 5-4. Effect of No. 2 Fuel Oil Contamination on Asphalt

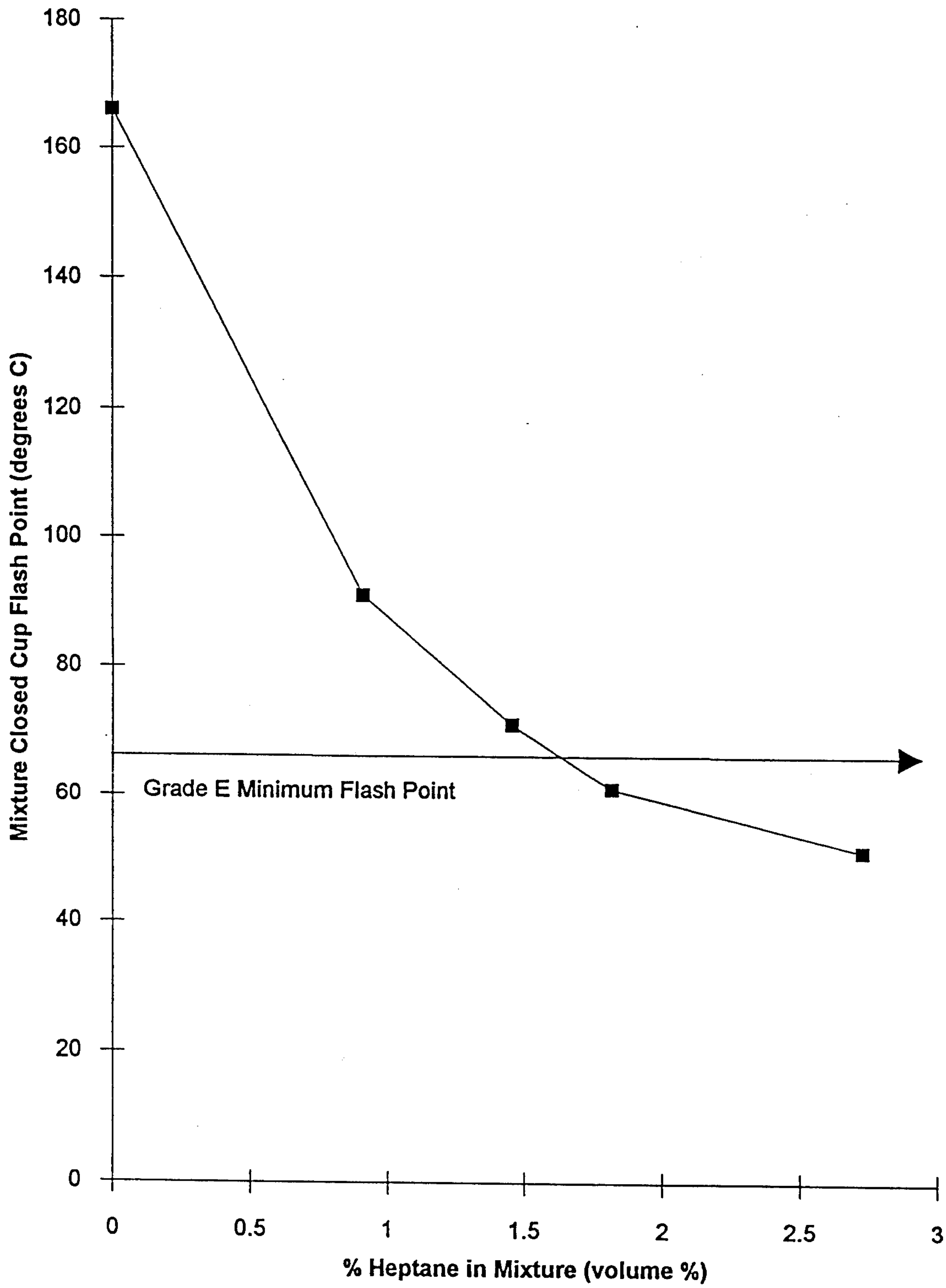

Figure 5-5. Effect of Heptane Contamination on Lubricating Oil

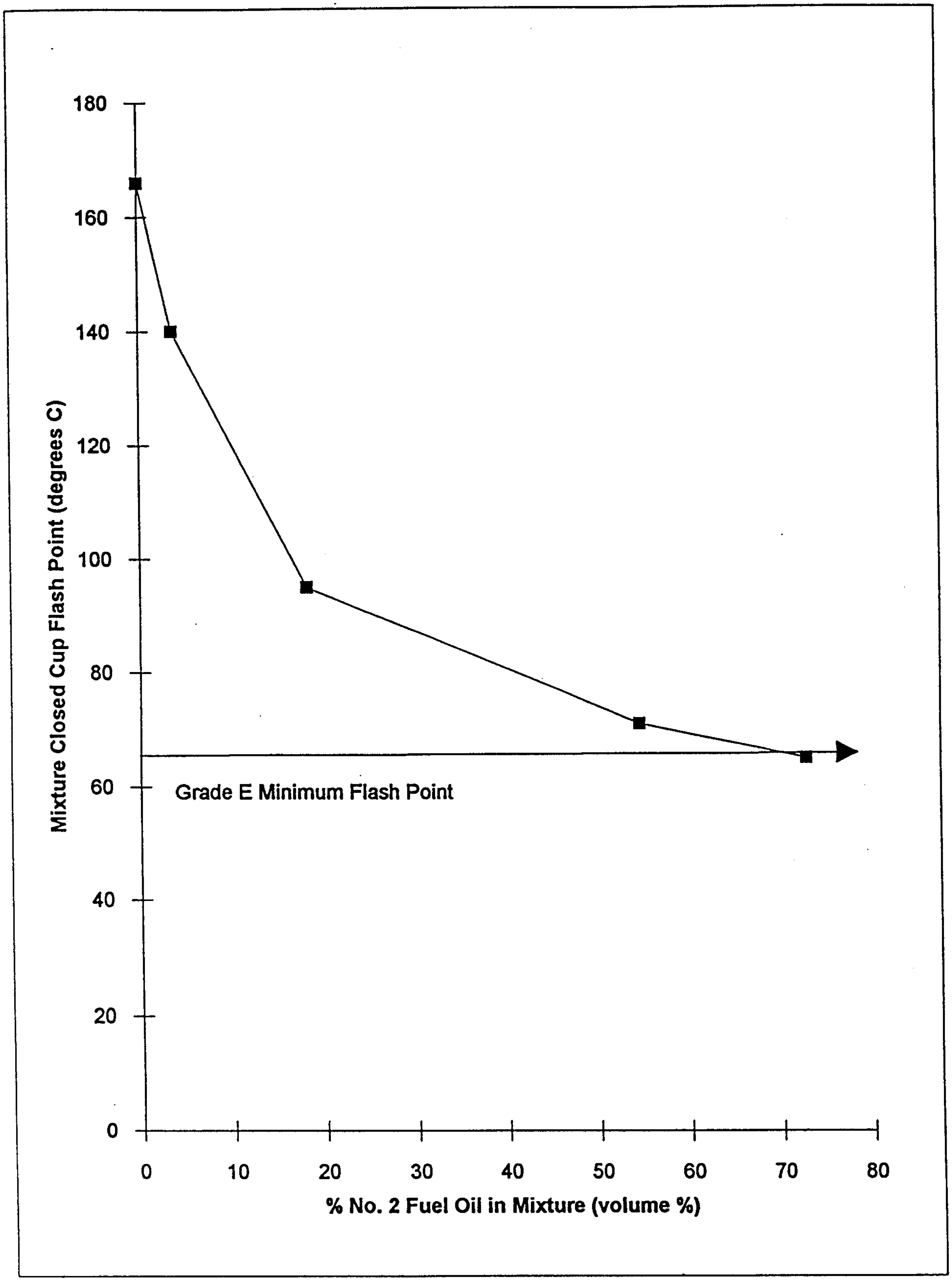

Figure 5-6. Effect of No. 2 Fuel Oil Contamination on Lubricating Oil

5.3 Test Results

Experimental results for the sample of No. 6 Fuel Oil revealed a 6°C difference between open and closed cup flash point testing. Only a 1% by volume contamination of heptane was necessary to lower the flash point of No. 6 Fuel Oil below the Grade E minimum flash point of 65.5°C (150°F). Contamination with No. 2 Fuel Oil was not as dramatic. A No. 2 Fuel Oil contamination of approximately 30% by volume was necessary to lower the flash point of No. 6 Fuel Oil below the Grade E minimum.

Experimental results for the sample of asphalt revealed a 37°C difference between open and closed cup flash point testing. Approximately 3.4% by volume contamination of heptane lowered the flash point below the Grade E minimum. A 33% contamination of No. 2 Fuel Oil was necessary to lower the asphalt flash point below the Grade E minimum.

Results for Lubricating Oil revealed a 37°C disparity between open and closed cup flash point testing. A 1.7% by volume contamination of heptane lowered the flash point below the Grade E minimum. A 73% by volume contamination of No. 2 Fuel Oil was necessary to lower the flash point of lubricating oil below the Grade E minimum of 65.5°C (150°F).

SECTION 6.0 COMBUSTIBLE GAS DETECTORS

6.1 Detector Design and Operation

By measuring flammable vapor concentrations, combustible gas detectors can provide an in-situ reading of vapor space flammability in a cargo tank. There are a variety of detector types, but only one type is used for cargo tank monitoring and inspection.

The combustible gas instruments in current use aboard tankers utilize the principle of catalytic combustion (Reference 23). Catalytic combustion occurs when a mixture of gases of suitable flammable concentration ignites on the surface of a heated platinum wire yielding heat in direct proportion to the gas or vapor concentration. The heat released increases the temperature of the platinum filament resulting in a change of electrical resistance. The change in resistance of the filament, which is one arm of a Wheatstone bridge, unbalances the bridge and causes a corresponding deflection of an electric meter. Similar devices may employ a porous catalytic mass instead of a wire and may sense the temperature by means other than the increase in electrical resistance.

Catalytic combustion instruments are specifically designed for measuring combustibles in air. The oxygen content of the atmosphere tested must be within 10 to 25% for an accurate reading unless the instrument has been specially modified. The meter is calibrated in percent Lower Flammable Limit (LFL) or Lower Explosive Limit (LEL). Both terms are synonymous. LFL is the lowest concentration of a combustible gas or vapor in air which, when ignited, will result in flame propagation or explosion.

Combustible gas detectors are often used to measure the level of hydrocarbons in the ullage of a tank or compartment atmosphere. The most prevalent and dangerous hydrocarbons that make-up cargo tank flammable atmospheres are the light hydrocarbons in the C1 to C8 range. These light hydrocarbons can be released under typical storage, handling, heating and transfer of hydrocarbon liquids.

Combustible gas detectors are factory calibrated to either pentane, hexane, or methane. Manufacturers provide scaling factors to account for the difference between calibration gases. The scaling factor is multiplied the percent LFL reading, but for an atmosphere containing unknown mixtures of light hydrocarbons, this procedure lacks accuracy. Alternatively, according to one manufacturer, certain detectors can be field recalibrated to pentane even though they have been factory calibrated to hexane or methane.

6.2 Limitations of Gas Detectors

The performance of catalytic combustion type explosimeters can be significantly degraded by filament poisoning. Filament poisoning is the desensitization of the catalyst when gaseous silicon compounds, sulfur compounds, halogen compounds, or the vapors of tetraethyl lead decompose and/or react with, or collect on, the catalytic filament. These substances can dramatically alter the electrical resistance of the filament and decrease its catalytic properties. In addition, dust particles and moisture can also collect on the filament and change its resistance. Some manufacturers supply an accessory chemical filter to prevent contamination and filament poisoning. The use of filters is recommended by the Oil Companies International Marine Forum (OCIMF), the International Chamber of Shipping (ICS), and the International Association of Ports and Harbors (IAPH) (Reference 28).

Application of explosimeters for the detection of low levels of hydrocarbons (below the LFL) at ambient temperatures is usually quite satisfactory, but high concentrations and elevated temperatures cause problems. Hydrocarbon concentrations greater than stoichiometric (which can occur either when there is a high hydrocarbon concentration or a low oxygen concentration) generate a false reading because the heat released by catalytic combustion is limited by the oxygen in the air. Furthermore, near-stoichiometric concentrations generate very high sensor temperatures that can damage the filament. Elevated gas temperatures cause a problem because the filament temperature is affected by the gas sample temperature as well as its concentration. Also, low readings may result when a sample is taken from heated areas and part of the vapors condense out before reaching the sensor. For this reason, unless otherwise indicated by the manufacturer, combustible gas detectors are not approved for use in temperatures in excess of 40°C (104°F) or below 0°C (32°F) (Reference 27). The 1986 OCIMF report concluded that efforts should be made to encourage the development of new instrumentation to provide accurate and consistently reliable measurements at elevated temperatures and compositions representative of hydrocarbon vapors present in bunker tanks.

The potential for erroneous readings at low oxygen concentrations does not appear to be a serious limitation for most Grade E cargo since they would not be expected to produce a fuel rich atmosphere in the tanks at normal handling temperatures. Even after the FIONA explosion (which consumed oxygen by combustion), oxygen concentrations in the tanks (from 15 vol% to 20 vol% as listed in Table 3-2) were well above the 10 vol% minimum suggested in the NFPA Handbook (Reference 23) as the lowest value for accurate measurements with catalytic combustion detectors. In the case of asphalt cargo, there is evidence (Reference 6) that smoldering in asphalt storage tanks typically reduces oxygen concentrations to values in the range

14-18 vol% on a dry basis. However, in one asphalt tank smoldering had proceeded to reduce the ullage oxygen concentration to 5.5 vol%. Therefore, it is prudent to use a combined oxygen and combustible gas analyzer to verify that low oxygen concentrations do not invalidate the combustible gas concentration reading.

6.3 Current Practices

Although combustible gas detectors are required on ships carrying Grade A-D cargo and on ships carrying heated Grade E cargo, there are no regulations (Reference 13) specifically requiring the testing of spaces containing Grade E combustible liquids prior to personnel/equipment entry or transfer. Testing is required for all other lighter hydrocarbon mixtures such as naphtha, gasoline and jet fuel (i.e., higher grade cargoes).

As a personnel safety measure during tanker inspections, Coast Guard Marine Safety Inspectors typically employ a detector (Scott Aviation, Scott 105) which uses a porous catalytic mass and is a combination combustible gas and oxygen detection instrument. This particular device is a microprocessor controlled, self-contained, portable instrument, designed to detect the presence of combustible gases and vapors in air and to provide a visual indication of the concentration. It also detects the presence or lack of oxygen in air and provides a digital indication of the oxygen concentration. The combustible concentration is displayed in percent (0-100%) of the Lower Flammable Limit (LFL).

The Coast Guard requires their detectors to be factory calibrated to pentane with an alarm setting of 5-percent LFL. The detector must be field recalibrated once a week by qualified instrument maintenance personnel. For the Coast Guard, qualified maintenance personnel must complete a 40-hour training course.

The sensitivity of the detector must also be adjusted on a daily basis.

These portable instruments are carried waist level by USCG Inspectors and are extremely reliable (Reference 26) except in very cold environments or atmospheres containing silicones, free halogens, halogenated hydrocarbons, metallic oxides and leaded gasoline vapors which tend to clog the porous catalytic mass.

Combustible gas detectors employed by Marine Chemists are primarily the platinum wire filament or pellister type (MSA Model 261). The combustible gas portion of the Model 261 utilizes the heat developed by a catalytic combustion of the sampled atmosphere's flammable elements on a pelletized filament, or pellement unit. The pellement unit has a much larger surface area than a normal filament type. Data presented in the 1986 OCIMF report (Reference 24) on combustible gas detectors indicates the response of the pellister type detector is more sensitive to the carbon number of the hydrocarbon vapor than is the response of a filament type detector. A battery-powered pump draws the sampled atmosphere into the instrument through a sampling line, where it diffuses into the sensing heads of the combustible gas and oxygen portions of the instrument.

In 1986, the Oil Companies International Marine Forum (OCIMF) submitted a report (Reference 24) to the International Maritime Organization concerning the application of explosimeters to the measurement of flammable head space vapors in ship's bunker tanks. The report was written in response to serious (but unspecified) explosions on board ships where low flash point cargo had been illegally or accidentally added to the fuel oil bunkers. According to the OCIMF report, explosimeters (combustible gas indicators) represented the only simple option for portable field measurement of hydrocarbon gas concentration in bunker fuel tanks. Measurements made by catalytic combustion type indicators were found to be very dependent on the gas used for calibration. Based upon laboratory testing of hydrocarbon vapors, it is preferable to calibrate the explosimeter against pentane standards rather than methane since pentane calibration would tend to slightly overestimate the hazard, whereas methane calibration would underestimate the actual concentration.

In 1992, the OCIMF issued a second report on combustible gas detectors. The 1992 OCIMF report (References 2 and 9) concludes that "the preferred and convenient use of commercial explosimeters can be justified if the instrument is calibrated on pentane," and "a measured level by explosimeter of headspace flammability over 50% LFL should indicate that precautionary action is required."

Federal regulation 46 CFR 35.30-5 (Reference 13) stipulates that "all U.S. manned tank barges and tank ships authorized to carry Grade A, B, C, or D liquids at any temperature, or Grade E liquids at elevated temperatures, shall be provided with a combustible gas indicator suitable for determining the presence of explosive concentrations of the cargo carried. An indicator which bears the label of Underwriters' Laboratories Inc., Factory Mutual Engineering Division, or other organizations acceptable to the Commandant will be accepted as meeting this requirement." Upon USCG vessel inspection, the designated operator must demonstrate the ability to accurately utilize the detector. Inspectors also recommend that detectors be calibrated to USCG alarm readings, but they cannot verify the particular gas calibration.

Combustible gas detector usage on U.S. flag vessels carrying Grade E cargo is very common despite the absence of regulations requiring its operation (Reference 12). Many U.S. Captains routinely check their cargoes during transport. This current usage bodes well for the eventual acceptance and use of combustible gas detectors on all vessels carrying Grade E cargo.

SECTION 7.0 OVERALL RISK ASSESSMENT

7.1 Fire/Explosion Hazard at Temperatures Below Cargo Flash Point

Numerous incidents described in Section 3 demonstrate that there is indeed a fire/explosion hazard due to flammable concentrations of vapor in many cargo tanks containing Grade E cargo (or similar high flash point liquids) at temperatures well below their nominal flash points. This apparent anomaly can occur due to one of the following situations:

1) very small quantities of low flash point components that may not have been included in the sample or may not have been contained in the sample tested;

2) vapor evolution (fuel devolatilization) due to local heating or to smoldering of pyrophoric deposits.

The first situation occurred in the explosions of the FIONA, the OMI YUKON, and the RECOVERY 1. It may also have occurred in several other explosion incidents and in many other vessels that never exploded because of the absence of an ignition source in the area of the flammable vapors.

Some, but not all, of these situation 1 incidents were associated with inadvertent contamination of the cargo during loading or during the voyage. Test data reported in Section 5 demonstrate that the addition of only 2.0% by volume of heptane (representative of gasoline in terms of flammability) to a typical No. 6 Fuel Oil sample lowers the fuel oil flash point by 43°C (78°F) to 51°C (124°F), which is a typical temperature of No. 6 Fuel Oil during cargo transfer.

Other situation 1 incidents (and other tanks in the vessels had some contaminated tanks) involved volatile components within the Grade E cargo itself. These volatile components are either dissolved in the residual oil cargo, are vapor bubbles trapped within semi-solid or highly viscous cargo, or are emulsified in water-based cargo. They can be released from the solution or emulsion during either cargo sloshing or during cargo transfer operations such as occurs during vessel trimming as well as in loading or unloading.

Once released from the cargo, the flammable vapors can accumulate in the tank ullage space and/or in the vent line. The potential for vapor accumulation is augmented by normally closed pressure/vacuum (P/V) valves, by goose neck vents (that allow heavier-than-air vapors to remain in the vent line), and by partially solidified condensation deposits in the relatively cool vent line of heated tanks. Eventually an increase in tank pressure or diffusion causes the flammable vapors to be vented from the tank and form a flammable plume in the vicinity of the vent or open hatch. If an ignition source is situated within the flammable plume, an effective flame screen or flame arrester or an approved high speed vent valve is needed to prevent flashback into the cargo tank.

The second type (i.e. local heating or smoldering) of situation seems to have been an important factor in the INTERSTATE 71 asphalt incident and in the EXXON NEW ORLEANS bunker C oil incident, both of which involved flame heating of a tank wall or transfer pipe. Situation 2 incidents can also occur without any external heating, particularly in asphalt cargoes.

Dimpfl (Reference 6) has demonstrated the occurrence of flammable vapor generation by smoldering in land based asphalt storage tanks. This smoldering was due to asphalt deposits on the underside of the tank roof creating the right conditions for the roof or hatch metal to react with hydrogen sulfide to form pyrophoric iron sulfide and eventually to auto-ignite upon exposure to air. According to the International Oil Tanker and Terminal Safety Guide (Ref 28, Chapter 22), iron sulfide should not form when there is a significant oxygen concentration in the tank because iron oxide (rust) will form instead. However, Dimpfl's study indicates that the roof deposits consisted of an outer (exposed) layer of iron oxide and an inner layer of iron sulfide beneath the exposed surface layer. When the exposed outer layer cracks or flakes off, the pyrophoric iron sulfide is exposed to the air and starts to smolder.

Gas samples analyzed by Dimpfl suggest that the smoldering deposits can produce flammable concentrations of C_1 to C_4 hydrocarbons in the tank ullage space. They also produce sufficiently large concentrations of CO_2 and H_2O to significantly reduce the oxygen concentration in the tank ullage space. This process is exacerbated when the asphalt is stored at temperatures approaching 190°C (375°F), and when there are significant concentrations of hydrogen sulfide in the tank.

In view of these vapor release and vapor generation phenomena, the flash point of a liquid sample of cargo is not a reliable measure of the tank fire/explosion hazard. Flash point data reliability can be increased somewhat by proper sampling techniques (Reference 25), but no matter how many different liquid samples are obtained, the liquid composition may not be indicative of the vapor composition in the tank.

Since Grade E cargoes are traditionally regarded as much less hazardous than lower flash point cargo, they are not subject to the same levels of ignition prevention. Besides not using inert gas systems for the tanks, there is often little or no concern about electrical equipment in the vicinity of the tank vent. There is also less care in avoiding electrostatic ignition sources such as those associated with ungrounded objects (instrumentation, nozzles, etc.) inserted into the tanks. This slackened attitude regarding potential ignition sources can significantly increase the inherent hazards of many Grade E cargoes.

7.2 Risk Quantification

An attempt has been made, without much success, to quantify the Grade E cargo fire/explosion risk probabilistically. The two risk quantification methods explored for this problem are: 1) historical incident frequency, and 2) tank flammability test data surveys.

In order to estimate the historical incident frequency of Grade E cargo fires/explosions, it is necessary to determine the approximate number of incidents in a given period, and the number of shipments of Grade E cargo during that period. Eight Grade E cargo type explosions over a period of 13 years were identified in Section 3. Many others may have occurred but the Coast Guard incident reporting and computer database makes it difficult to identify them. Furthermore, the lack of standardized categorizations and compilations of cargo shipments, as discussed in Section 2, has prevented any national estimate of Grade E cargo shipments per annum.

With regard to tank flammability data surveys, the only such survey known to the authors is the one reported in the 1992 submittal of the Oil Companies International Maritime Forum (OCIMF) (Reference 5). This survey involved 1,246 measurements of flammable vapor concentrations in the ullage space of bunker fuel tanks. Two percent of those readings revealed vapor concentrations over 50% of the Lower Flammable Limit (LFL), another 9% of the readings indicated vapor concentrations in the range 26-50% of the LFL.

Based on the OCIMF survey, it is tempting to say that about 2% of the tanks carrying No. 6 Fuel Oil are at risk of having a tank fire or explosion. However, this is not an accurate estimate because of the inherent inaccuracies of combustible gas explosimeters (as discussed in Section 6) as currently used in measurements of complex, elevated temperature, hydrocarbon mixtures such as No. 6 Fuel Oil. Furthermore, the fuel handling procedures (including fuel storage temperature) for those bunker fuel tanks may be different than those used for cargo storage. This could be important because flammable vapors are more likely to be released into the ullage space during fuel heating and transfer.

The two other Grade E cargoes that seem to be vulnerable to fires and explosions are asphalt and oily wastewater. There do not seem to be any reported tank flammability data surveys for these cargoes, so it would be virtually impossible to quantify their flammability risk probabilistically.

7.3 Possible Protection Measures

The most obvious protection measure to reduce or eliminate ullage space flammability is tank inerting. Is such a stringent measure warranted for all Grade E cargoes? Probably not, since cargoes such as vegetable oil and lubricating oil have not exhibited any propensity to generate flammable vapor concentrations in their tanks. If not required for all Grade E cargoes, which cargo should be inerted? Perhaps inerting can be limited to fuel oils, asphalts, and oily wastewaters, because these cargoes have experienced at least some tank explosions.

Another approach to deciding which cargo tanks should be inerted would be to employ tank/cargo specific combustible gas explosimeter readings. This approach may be feasible if reliable readings can be obtained with readily available instrumentation. This will require standardizing calibrations with representative vapor components such as butane or pentane. Another aspect to be resolved is the location of sampling in the tank. Are multiple locations needed or should one rely on a sample from the mid elevation or from just above the liquid surface? Finally, there is the question of whether reliable sampling can be accomplished with heated cargo; i.e. whether vapor condensation and gas sample temperature variations will preclude accurate concentration measurements.

Assuming that tank specific reliable flammability readings can be obtained, the cost and other impacts of inert gas system requirements for Grade E cargo need to be investigated. It should not be a cost or other burden for Grade B cargo certified tankers since these vessels already need such systems for Grade B cargo. On the other hand, there are several tankers that have been de-rated from Grade B to Grade E cargo certified because their owners wanted to avoid the cost of inert gas systems.

Attempts to inert tanks with carbon dioxide or steam have been known in some cases to actually ignite the vapor space. This has occurred because of electrostatic charges generated with steam injection and with carbon dioxide injection into the tanks. This is apparently not a problem with the flue gas inerting systems used on most tankers. Therefore, the possible use of inerting systems for certain Grade E cargo tanks should be limited to systems and operating conditions that avoid electrostatic charge generation.

Several other possible protection measures are possible for Grade E cargo tanks. These include:

1) use of tank ventilators (installed in the hatch covers) as an alternative to tank inerting for some cargoes;

2) classification of the area in the vicinity of the tank vent (spatial extent to be determined) as a hazardous area in which only intrinsically safe electrical equipment is allowed;

3) testing and certifying flame screens in tank vents to verify they are capable of preventing flashback into the tank; and

4) installing explosion vent panels on the tank roofs; i.e. on the deck plate above the tanks.

The last two measures may be applicable to other grade cargo tanks as well. The provision of explosion vent panels on the tanks is a last resort and may not be feasible if the panels need to be isolated to prevent crew from walking or standing on them. However, the number of injuries and fatalities caused by deck plates being blown away suggests that its feasibility should be carefully considered rather than dismissed out of hand.

SECTION 8.0 CONCLUSIONS

1. Reviews of accident reports and previously published reports and papers on the issue of flammability of high flash point liquids have led to the conclusion that flash point is not a reliable measure of the flammability of the vapor space in a Grade E cargo tank. Neither closed cup flash point tests nor open cup flash points are reliable in this regard. The tank vapor space can be flammable at liquid temperatures well below (more than 38°C (100°F) less than) the liquid flash point.

2. Laboratory tests have shown there is no simple relationship between closed cup and open cup flash points for representative Grade E cargo samples. In the case of the No. 6 Fuel Oil sample, the open cup flash point was only 6°C (12°F) higher than the closed cup flash point. However, in the case of an asphalt sample and a lubricating oil sample, the open cup flash points were 41°C (73°F) and 37°C (67°F), respectively, higher than the closed cup flash points.

3. Eight shipboard tank explosion incidents have been identified involving combustible liquids representative of Grade E cargoes. These incidents demonstrate that the Grade E cargoes most prone to fires and explosions are residual fuel oil (4 incidents), oily wastewater (2 incidents), and asphalt (1 maritime incident and many more land based incidents).

4. The apparent causes of flammable vapor concentrations in the tank explosion incidents reviewed here are: 1) small quantities of low flash point components that were not manifested in the flash point tests; and 2) vapor evolution during localized flame heating of the tank wall. Contamination of Grade E cargo with much lower flash point

liquid was a factor in some, but not all the explosion incidents.

5. Laboratory tests conducted in this project have demonstrated that small additions of low flash point contaminants can dramatically reduce the flash point of representative Grade E cargoes. For example, the addition of 2% by volume heptane to a No. 6 Fuel Oil sample lowered the closed cup flash point of the fuel oil from 95°C (202°F) to 51°C (124°F), which is a typical No. 6 Fuel Oil temperature during cargo transfer. The addition of 2% by volume heptane to an asphalt sample lowered the asphalt closed cup flash point from 197°C (387°F) to 110°C (230°F).

6. The historical frequency of Grade E cargo fires and explosions cannot be determined because of the lack of a national standardized method for classifying and compiling cargo shipments, and, to a lesser extent, because of difficulties in identifying all Grade E cargoes in marine accident databases.

7. According to an Oil Companies International Marine Forum survey of flammable vapor concentrations in bunker fuel tanks, vapor concentrations exceed 50% of the lower flammable limit in 2% of the tank readings.

8. Combustible gas detectors have been used successfully for monitoring the vapor space of cargo tanks containing Grade A, B, C, and D cargo. These gas detectors should also be useful for Grade E cargo tanks providing sampling guidelines are developed to facilitate representative vapor samples from the heated, nonhomogeneous tank vapor space.

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