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# Investigation of Grade E Cargo Flammability

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Final Report
March 1998

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# NOTICE

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16. Abstract

This research indicates that certain Grade E cargoes can ignite at temperatures below their flash point if they are first heated above their flash point, allowed to cool and then reheated. Ignition and chromatographic studies were performed on two No. 6 oils meeting Grade E cargo requirements to determine if they exhibit below flash point ignition behavior. Their flash points were obtained by the Pensky-Martens Closed Cup Method (ASTM Method D93). This was followed by tests to determine whether these oils could ignite at temperatures below their flash point. In addition, chromatographic analyses were performed on the bulk oils and their vapors to determine whether significant fractionation of light components was occurring. Chromatographic analyses comparing the bulk oils and their vapors(after heating, cooling, heating cycle) showed no evidence of preferential fractionation of the lighter components of the oil, a potential cause of the below flash point behavior. However, these analyses did indicate significant differences in the chemical composition of the two oils, which may affect differing ignition behavior. Significant mist formation in the vapor space was observed to occur just before ignition.

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# METRIC CONVERSION FACTORS

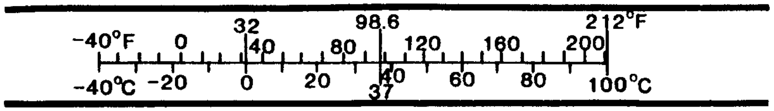
## Approximate Conversions to Metric Measures

| 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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# EXECUTIVE SUMMARY

Instances where Grade E cargo have ignited at temperatures apparently below their flash points have been documented by the U.S. Coast Guard. Most of the cases can be attributed to local heating to temperatures above the flash point. But, several instances have not been attributable to other causes.

The current study builds on earlier research indicating that certain Grade E cargos, e.g. some No. 6 oils, can ignite at temperatures below their flash point if they are first heated to temperatures above their flash point, allowed to cool and then reheated below their flash points. Ignition and chromatographic studies were performed on two No. 6 oils meeting Grade E cargo requirements to determine if they exhibit below flash point ignition behavior.

One of the test oils did ignite consistently below its measured flash point after a heating, cooling, heating progression. However, the difference between the ignition temperature and the measured flash point was within the reproducibility of the ASTM closed cup flash point procedure. The other test oil did not ignite below its flash point.

Chromatographic analyses comparing the bulk oils and their vapors (after a heating, cooling, heating cycle) showed no evidence of preferential fractionation of the lighter components of the oil, one possible cause of below flash point behavior. However, these analyses did show significant compositional differences between the two test oils, which may be related to their differing ignition behavior.

Significant mist formation in the vapor space was observed to occur just before ignition. This may also be related to the below flash point ignition behavior.

Refinements to the experimental equipment are recommended to better isolate and discriminate among potential causes of below flash point ignition behavior. Tests with a wider range of Grade E cargos are also needed to determine the extent of this behavior as well as its mechanism.

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## 1.0 BACKGROUND

Grade E cargo is defined in the Code of Federal Regulations (CFR) as a combustible liquid having an open cup flash point of 150°F (65.5°C) or higher.[1] Common Grade E cargoes include No. 6 fuel oil, asphalt, lubricating oil, animal and vegetable oils, and oily waste water.

Inerting the atmosphere over Grade E cargos carried in bulk on vessels is not required by the Code of Federal Regulations. This is apparently based on the belief that the heating of these cargos (which is necessary for handling) will not raise the temperature of the cargos above their flash point.

Reference 2 searched the U.S. Coast Guard (USCG) CASMAIN database for fires resulting from ignition of Grade E cargo at temperatures below the cargo's flash point. A total of eight incidents from November 1977 to March 1990 were found. The USCG and National Transportation Safety Board (NTSB) reports of these incidents were reviewed. Four of these incidents involved residual fuel oils, two involved oily wastewater, and one each involved asphalt and sewage sludge. Most of these fires could be explained by either (a) small quantities of low flash point contaminants mixed in with the Grade E cargo, or (b) localized heating above the flash point by open flames. Contamination with low flash point materials could result in a mixture of low flash point vapors that could ignite at temperatures below the flash point of the bulk cargo. Heating with an open flame, e.g., welding, could result in localized regions where the flash point of the cargo is exceeded. However, several of the incidents investigated do not have a clear explanation and may be the result of below flash point ignition.

The U.S. Coast Guard conducted earlier research[2-4] in an effort to quantify the problem and to identify potential monitoring devices that could be useful in alerting vessel crews of a potentially hazardous situation. This research identified that the Grade E cargos that possess the most potential for explosive atmospheres are petroleum derivatives such as residual fuel oils and asphalts.[3] Research to date indicated that standard combustible gas indicators were unsatisfactory in detecting the hazards posed by Grade E cargo.

However, research with a 2.25 cubic foot rectangular test tank did show evidence of below flash point Grade E oil ignition.[3] The oil studied did not ignite as it was heated to its flash point even though a spark ignition source was periodically applied. The oil did explode above its flash point, as expected. But, a spark applied after the oil had cooled to well below its flash point resulted in a second explosion. Normally, combustible materials do not ignite or explode below their flash point.

This behavior indicates an ignition mechanism different than occurs with an open or closed cup flash point tester. In flash point measurements, ignition theoretically occurs when the concentration of combustibles in the vapor, in equilibrium with the heated liquid, reaches a critical level. Below this temperature, combustion is not supported. However, the experiment described above does not appear to conform to this expected behavior.

Below flash point ignition behavior may be due to a variety of reasons, including:

- Not attaining equilibrium conditions during the open/closed cup flash point measurements
- Separation of the fuel into components with higher and lower flash points
- Preferential vaporization of organic components with different flash points
- Some other mechanism for ignition

This behavior is not a concern with cargos other than Grade E materials because the atmosphere over lighter cargos is inerted. But Grade E cargos are not considered sufficiently ignitable to warrant this safety protection at this time.

## 2.0 APPROACH

The current study was designed to extend the research conducted earlier.[3] Three Grade E oils were obtained from industrial sources for this study. Their flash points were obtained by the Pensky-Martens Closed Cup Method (ASTM Method D93).[5] This was followed by tests in the 2.25 cubic foot test chamber, mentioned earlier, to determine whether these oils would ignite at temperatures below their flash point. In addition, chromatographic analyses were performed on the bulk oils and their vapors to determine whether significant fractionation of light components was occurring.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Test Oils

Three No. 6 oils, all meeting Grade E cargo requirements, were obtained for this project from the following sources:

| | |
|---|---|
| Sample 1 - | Amerada Hess Corporation |
| Sample 2 - | The Somerset Refinery, Inc. |
| Sample 3 - | Colonial Oil Industries, Inc. |

The Material Safety Data Sheets (MSDS) for these oils are provided in Appendix A.

### 3.2 Flash Point Measurements

The closed cup flash points of these oils were obtained in accordance with the Pensky-Martens method. For this project, the flash point for each oil was determined twice in accordance with ASTM Method D93. The two flash points were then averaged.

The closed cup flash point of Sample 1 could not be determined due to its high water content. As an alternative, a Cleveland Open Cup Flash and Fire Point (ASTM Method D92) was conducted on this oil. The open cup flash point was 163°C (315°F). ASTM reports the reproducibility of this method to be ±17°C (30°F). The fire point was 202°C (396°F) with a reproducibility, reported by ASTM, of ±14°C (25°F). The high water content in this No. 6 oil (not an unusual occurrence) and the resultant inability to obtain a closed cup flash point made this oil unsuitable for the ensuing experiments.

The closed cup flash points for Samples 2 and 3 were as follows:

| | |
|---|---|
| Sample 2 - | 81.1°C (178°F) |
| Sample 3 - | 99.4°C (211°F) |

ASTM reports the reproducibility of the closed cup method to be ±10°C (18°F).

### 3.3 Ignition Tests

Samples 2 and 3 were then subjected to experimentation in the ignition test chamber utilized in the earlier studies and described in detail in Reference 3. Electrical resistance heaters controlled by a single thermostat were attached to the outside of the test chamber to heat the oil. Two thermocouples were placed in the bulk oil and two thermocouples were placed in the vapor space above the bulk oil. A temperature read-out was used to monitor the temperatures in the test chamber. Ignition sparks were provided by a spark plug inserted through the top of the chamber into the vapor space.

A general protocol was developed for these experiments. For each test, the chamber would be filled with the test oil to either 25% or 75% of capacity. When the test chamber was filled to 25% of capacity (about 3 inches deep), the two thermocouples in the bulk oil were placed approximately 1-1/2 inches from the bottom. The two vapor space thermocouples were placed approximately 6 inches from the top of the chamber. The spark plug was also placed at this level. When the test chamber was filled to 75% of capacity (9 inches depth) the bulk oil thermocouples were placed approximately 3 inches from the bottom. The vapor space thermocouples and the spark plug were placed approximately 2 inches from the top of the chamber.

The oil was heated by the electrical resistance heaters to approximately 11°C (20°F) above its measured flash point. The heaters were then shut off and the oil allowed to cool to approximately 11°C (20°F) below its measured flash point. At this point, the spark plug was discharged to see if ignition would result. If not, the temperature would be raised 3°C (5°F) and ignition was attempted (using the spark plug as the ignition source) again. The temperature was elevated in 3°C (5°F) increments until ignition did occur. Efforts were made to have the vapor space be at about the same temperature as the pool of oil in the bottom of the test chamber.

However, the very different heat capacities of the vapor compared to the liquid oil made this goal very difficult. During heating and cooling cycles, the vapor changed temperature much more rapidly than the liquid oil. The heaters were turned on periodically during the heating and cooling cycles in an attempt to keep temperatures as uniform as possible. This technique worked fairly well, especially after the operators became experienced at it.

The temperatures at which oil Sample 2 (flash point 81.1°C, 178°F) ignited are summarized in Table 1. The bulk oil and head space ignition temperatures are the average of the two thermocouple readings in the bulk oil and the two thermocouple readings in the vapor space. The results are listed in the order in which the experiments were conducted.

Table 1
Ignition Tests with No. 6 Oil - Sample 2

| Amt. Of Oil, % of Chamber Capacity | Ignition Temperature, °C (°F)<br>Bulk Oil | <br>Vapor Space | Comments |
|---|---|---|---|
| 25% | 75.2°C (167°F) | 75.6°C (168°F) | Orange-blue flame |
| 25% | 75.6°C (168°F) | 77.0°C (171°F) | Blue-orange flame |
| 25% | 75.9°C (169°F) | 74.7°C (166°F) | Orange-blue flame<br>(less intense than earlier) |
| 75% | 75.2°C (167°F) | 75.6°C (168°F) | Orange-blue flame |

The ignition measurements on Oil Sample 2 were remarkably consistent. In all four experiments, ignition occurred below the flash point by about 5.6°C (10°F). This tends to support the contention that this oil can ignite below its flash point after being heated above the flash point, allowed to cool, and then reheated slowly. However, the reproducibility of the closed flash point method, as stated by ASTM, is ±10°C (18°F). The test oil ignition temperature deviated from the closed cup flash point by less than the method's stated reproducibility. But, these data are certainly indicative of below flash point ignition.

A visual inspection of the vapor space was performed during the last two experiments before ignition (using the results of the first two experiments as a guide). The test chamber cover was lifted slightly in an attempt to observe whether significant mist formation was occurring. At temperatures below the point where ignition occurred, there was little or no mist formation in the vapor space. At the temperature where ignition occurred, mist formation was significant, essentially filling the vapor space with a smoky mist. This mist formation just prior to ignition was observed in the two experiments where it was checked. Mist formation may be an important factor in below flash point ignition by increasing the fuel-air interfacial surface area. This large surface area may allow for combustion with lower energy input, i.e. at lower temperatures.

The temperatures at which oil Sample 3 (flash point 99.4°C, 211°F) ignited are summarized in Table 2. The results are listed in the order in which the experiments were conducted.

Table 2
Ignition Tests with No. 6 Oil - Sample 3

| Amt. Of Oil, % of Chamber Capacity | Ignition Temperature, °C (°F) | | Comments |
|---|---|---|---|
| | Bulk Oil | Vapor Space | |
| 75% | 104°C (220°F) | 111°C (232°F) | Heavy smoke before ignition; orange flame |
| 75% | 110°C (231°F) | 116°C (240°F) | Blue-orange flame |
| 25% | 102°C (216°F) | 96.4°C (206°F) | Blue-orange flame; some surface burning |
| 25% | 98.3°C (209°F) | 113°C (235°F) | Orange-blue flame |

As with oil Sample 2, the results are rather consistent among the four experiments. But, with oil Sample 3, the ignitions occurred above the measured flash point in all cases. Thus, this oil did not exhibit any below flash point ignition behavior. Mist formation was not checked during these experiments, which were performed before the tests with Sample 2.

## 3.4 Chromatographic Analyses

Chromatographic analyses were performed to provide data on whether enhanced vaporization of the light ends of the test oils was occurring. If so, this could help explain the observed below flash point ignition of oil Sample 2. Chromatograms were obtained on both liquid test oils. Then the two oils were subjected to the same thermal progression as performed during the ignition experiments discussed above. The thermal treatment for the chromatographic analyses were performed in a small test chamber with a septum for withdrawal of a headspace sample. The test chamber was filled to 25% capacity with each test oil. Chromatograms of the headspace samples were obtained and compared with the chromatograms of the bulk oils to see if the lighter ends, especially for oil Sample 2, were vaporized preferentially.

The bulk oil samples were analyzed chromatographically by direct injection using a flame ionization detector. The chromatographic conditions were based on ASTM D2887 procedures. Standards of a reference No. 6 fuel oil and a calibration solution mixture were analyzed along with the samples. These standards provided a reference for the sample oils' peak patterns and provided some hydrocarbon peaks for comparison.

Figures 1 and 2 are the chromatograms of the bulk oil and vapor space for oil Sample 2. This is the oil that ignited below its measured flash point. These chromatograms are remarkably consistent in terms of both peak pattern and intensity. Thus, these chromatograms show no evidence of preferential vaporization of the lighter fractions of the oil.

Figures 3 and 4 are the chromatograms of the bulk oil and vapor space for oil Sample 3. This is the oil that did not ignite below its measured flash point. The peak pattern of the vapor space is quite similar to that of the bulk oil. However, the intensity of the peaks in the vapor space chromatogram changed significantly compared to the bulk oil chromatogram. The peak pattern and intensity of the two chromatograms were very similar up to the range of undecane (C11). Following this, the concentrations of the peaks in the vapor space sample chromatogram were increasingly intense through the eicosane (C20) range. If anything, the concentration of heavier ends increased in the vapor space sample, compared to the bulk oil.

The peak pattern and peak areas for oil Sample 3 corresponded with the peak pattern of the No. 6 fuel oil reference standard. However, the peak pattern and peak areas for oil Sample 2 did not correspond with the reference. This sample had a consistent peak "spiking" pattern of hydrocarbons, but was lacking the peak components in the main region of the No. 6 reference fuel oil pattern. Sample 2's peak pattern was similar to the reference up to the tetradecane (C14) range and after octacosane (C28). Between C24 and C28, the reference oil's pattern was not evident.

The chromatography results indicate significant compositional differences between oil Samples 2 and 3. These compositional differences may be relevant in the differing ignition of the two oil samples.

## 3.5 Discussion

The ignition tests provide strong, but not conclusive, evidence of below flash point ignition behavior with oil Sample 2. Such behavior was not observed with oil Sample 3. Clearly, Sample 2 consistently ignited about 5.6°C (10°F) below its measured flash point after being heated above its flash point, allowed to cool, and then reheated with periodic ignition attempts. However, ASTM reports the reproducibility of its closed cup flash point method to be ±10°C (18°F). Thus, the ignition behavior of Sample 2 is within its ASTM reproducibility.

The comparative chromatographic analyses of the oil samples and their vapors showed no indication of preferential fractionation of the light ends of either of the oils. But, the chromatographic analyses did indicate significant compositional differences between the two test oils which may be relevant to their differing ignition behavior.

Significant mist formation was observed in the vapor of Sample 2 just before ignition. This may be related to the observed below flash point ignition but more investigation is required.

The test apparatus worked well but a number of improvements are needed to provide data to better determine whether below flash point ignition is a real phenomenon under certain conditions and, if so, its mechanism. Recommended improvements include:

- Separate heating controls for the vapor space and the bulk oil heaters to provide more consistent temperature control in the two regions
- Controllers capable of finer temperature control in both the vapor space and the bulk oil
- Quantitative mist detector in the vapor space
- Oxygen concentration monitor in the vapor space
- Additional thermocouples to better characterize thermal gradients in the vapor space and the bulk oil
- Chromatographic analyses be expanded to include Hydrogen Sulfide ($H_2S$)

Finally, it must be recognized that the behavior of two oil samples can not be extrapolated reliably to characterize the behavior of the many Grade E oil cargos carried in commercial ships. Ignition tests and chromatographic analyses are needed on a much wider range of Grade E products to characterize the extent of below flash point ignition and the conditions under which it may occur.

Millenium Results Report: REPORT_FUELOIL
SampleName Fuel Oil #2 Headspace Date Processed 02/03/98 05:01:30 PM
Channel Descr. FID Vial 1 Inj 1 Channel SATIN Channel ID 5750

U N D E R W R I T E R S   L A B O R A T O R I E S

Project Name: PEGCFID
Sample Name: Fuel Oil #2 Headspace
Vial: 1
Injection: 1
Channel: SATIN
Date Acquired: 12/29/97 03:12:23 PM
Scale Factor: 1.00
Acq Meth Set: PE_GCFID
Processing Method: FUELOIL

System PE_GCFID
Sample Type: Unknown
Volume, uL 1.00
Run Time: 40.0 min
Date Processed: 02/03/98 05:01:30 PM
Dilution: 1.00000

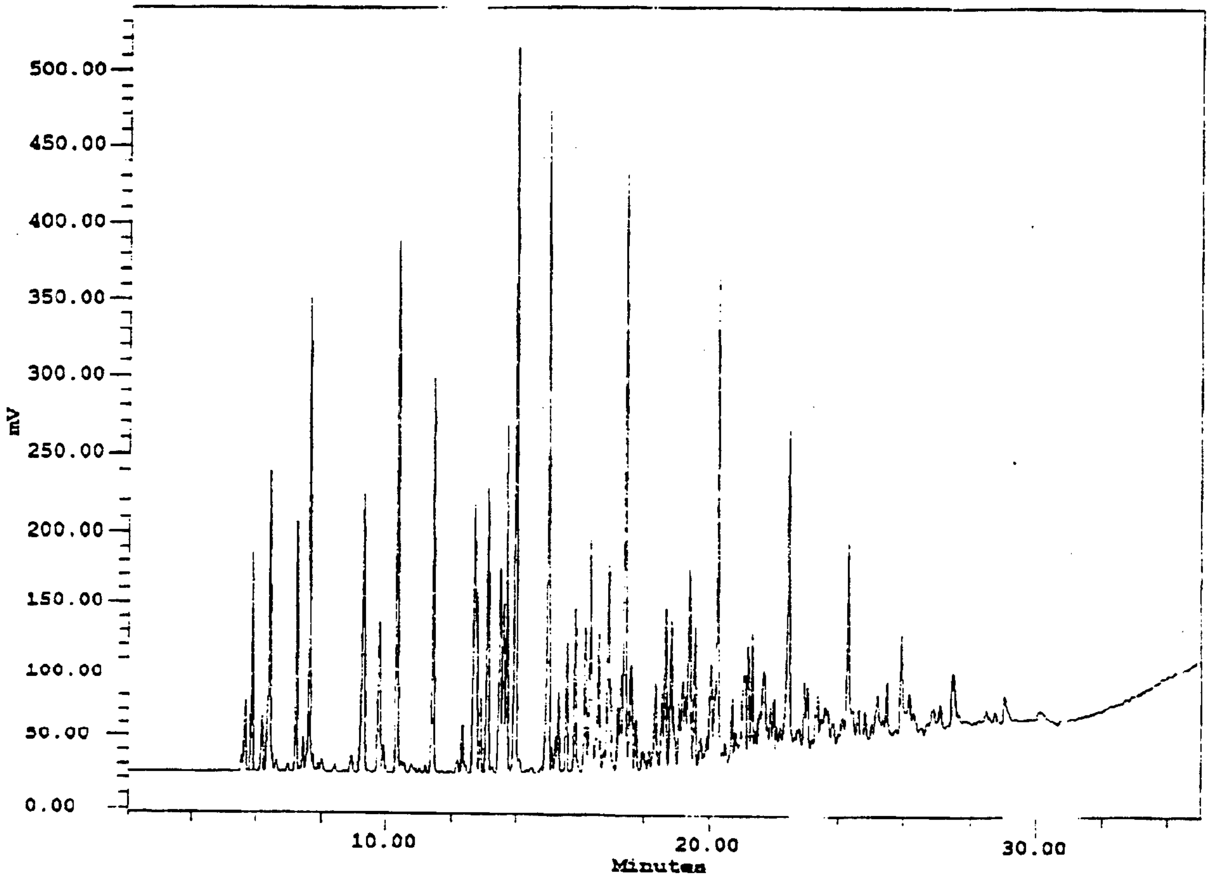

Figure 1
Chromatogram of Bulk Oil Sample 2

Millenium Results Report: REPORT_FUELOIL
SampleName #2 Headspaced w/heat&cool Date Processed 02/03/98 05:01:50 PM
Channel Descr. FID Vial 1 Inj 1 Channel SATIN Channel ID 5758

UNDERWRITERS LABORATORIES

Project Name: FEGCFID
Sample Name: #2 Headspaced w/heat&cool
Vial: 1
Injection: 1
Channel: SATIN
Date Acquired: 12/30/97 01:24:05 PM
Scale Factor: 1.00
Acq Meth Set: PE_GCFID
Processing Method: FUELOIL

System PE_GCFID
Sample Type: Unknown
Volume,uL 1.00
Run Time: 40.0 min
Date Processed: 02/03/98 05:01:50 PM
Dilution: 1.00000

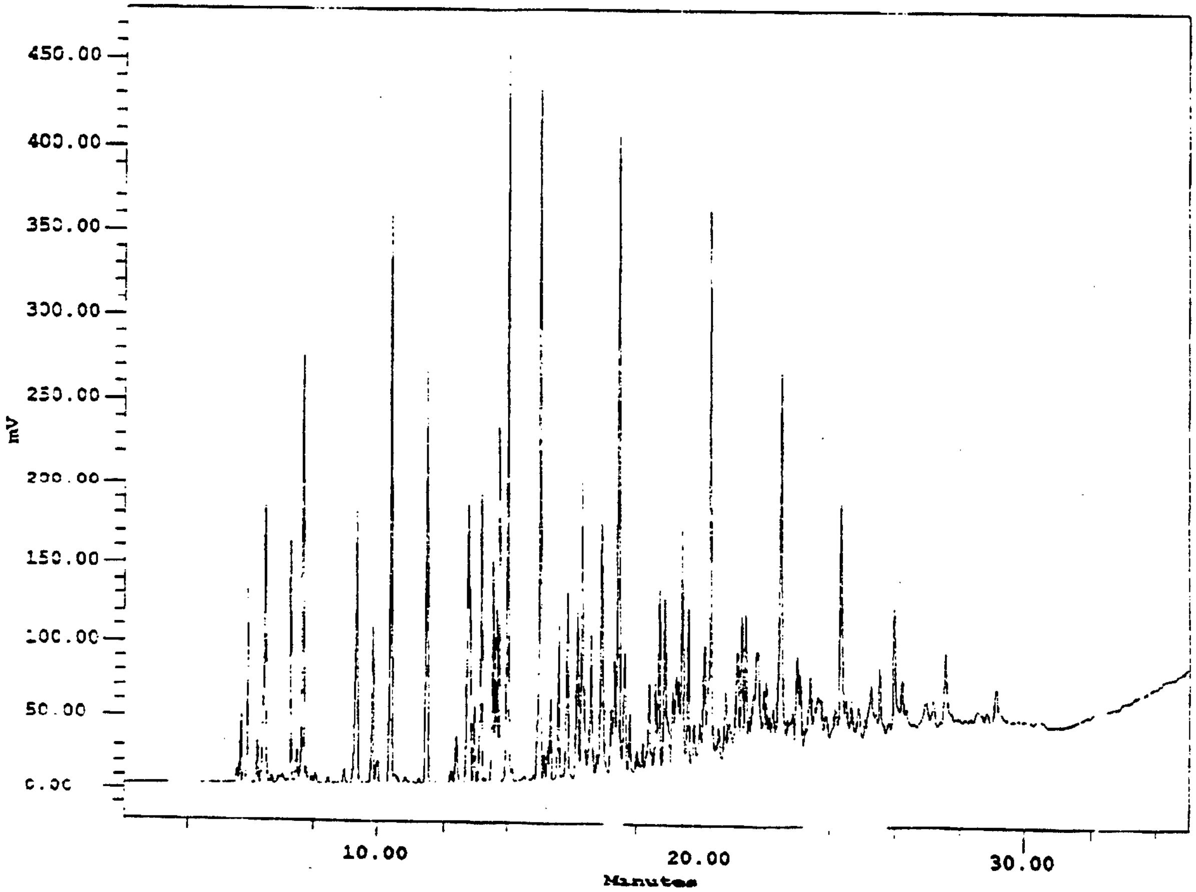

Figure 2
Chromatogram of Oil Sample 2 Vapor Source

Millenium Results Report: REPORT_FUELOIL
SampleName Fuel Oil #3 Headspace Date Processed 02/03/98 05:01:43 PM
Channel Descr. FID Vial 2 Inj 1 Channel SATIN Channel ID 5752

UNDERWRITERS LABORATORIES

Project Name: PEGCFID
Sample Name: Fuel Oil #3 Headspace
Vial: 2
Injection: 1
Channel: SATIN
Date Acquired: 12/29/97 04:11:40 PM
Scale Factor: 1.00
Acq Meth Set: PE_GCFID
Processing Method: FUELOIL

System PE_GCFID
Sample Type: Unknown
Volume,uL 1.00
Run Time: 40.0 min
Date Processed: 02/03/98 05:01:43 PM
Dilution: 1.00000

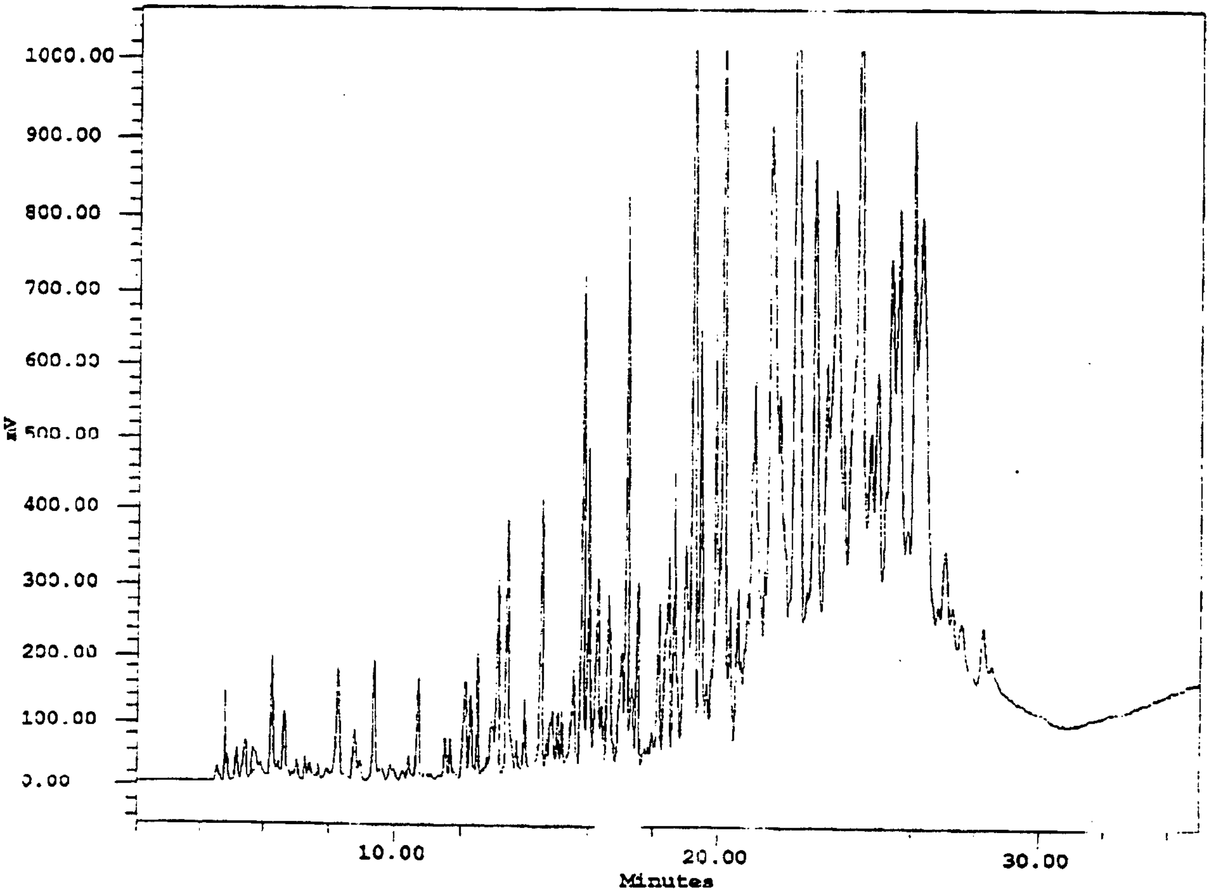

Figure 3
Chromatogram of Bulk Oil Sample 3

Millenium Results Report: REPORT_FUELOIL
SampleName #3 Headspace w/heat&cool Date Processed 02/03/98 05:01:57 PM
Channel Descr. FID Vial 1 Inj 1 Channel SATIN Channel ID 5764

UNDERWRITERS LABORATORIES

Project Name: PEGCFID
Sample Name: #3 Headspace w/heat&cool
Vial: 1
Injection: 1
Channel: SATIN
Date Acquired: 01/05/98 11:18:47 AM
Scale Factor: 1.00
Acq Meth Set: PE_GCFID
Processing Method: FUELOIL

System PE_GCFID
Sample Type: Unknown
Volume, uL 1.00
Run Time: 40.0 min
Date Processed: 02/03/98 05:01:57 PM
Dilution: 1.00000

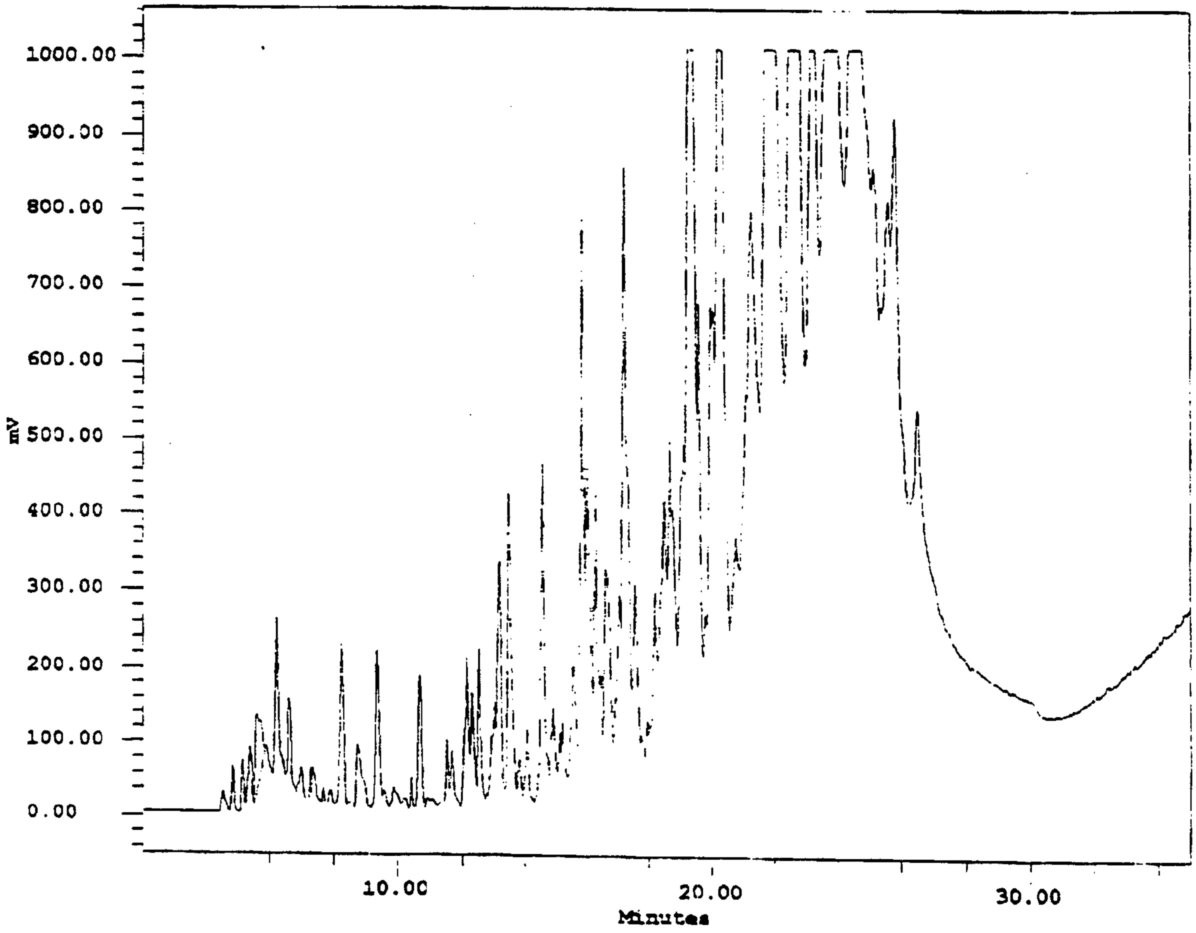

Figure 4
Chromatogram of Oil Sample 3 Vapor Source

## 4.0 CONCLUSIONS AND RECOMMENDATIONS

Ignition and chromatographic studies were performed on two No. 6 Oils meeting Grade E cargo requirements to determine if they exhibit below flash point ignition behavior. One oil did ignite consistently below its measured flash point, but the difference was within the reproducibility of the ASTM closed cup flash point procedure. The other test oil did not ignite below its flash point.

Chromatographic analyses did not indicate preferential fractionation of the lighter components of the oil, a potential cause of the below flash point behavior. However, these analyses did indicate significant differences in the chemical composition of the two oils, which may affect their differing ignition behavior.

Significant mist formation in the vapor space was observed to occur just before ignition. This may also be related to the below flash point ignition behavior.

Refinements to the experimental equipment are recommended to better isolate and discriminate among potential causes of below flash point ignition behavior. Tests with a wider range of Grade E cargos are also needed to determine the extent of this behavior as well as its mechanism.

## 5.0 REFERENCES

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# MATERIAL SAFETY DATA SHEETS FOR THE TEST OILS

# THE SOMERSET REFINERY, INC

600 MONTICELLO ST.
P.O BOX 1547
SOMERSET, KY 42502

## MATERIAL SAFETY DATA SHEET

MSDS NO. 11

| | |
|---|---|
| EMERGENCY PHONE NUMBER 606-678-8194 | CHEMTREC 800-424-9300 |

### I. PRODUCT IDENTIFICATION

| | | |
|---|---|---|
| PRODUCT: **#6 Fuel Oil** | CHEMICAL NAME: Petroleum Residual | |
| CHEMICAL FAMILY: Petroleum | FORMULA: C20-C80 | CAS NO. : MIXTURE |

| | |
|---|---|
| NATIONAL FIRE PROTECTION ASSOC. RATING CODE<br>LEAST (0),SLIGHT (1),MODERATE (2),HIGH (3)<br>EXTREME (4) | HEALTH CODE: 0<br>FIRE CODE: 2<br>REACTIVITY CODE: 0 |

### II. HAZARDOUS COMPONENTS

| INGREDIENT | % | OSHA LIMIT | TLV |
|---|---|---|---|
| Mixture-Petroleum Hydrocarbons | 100 | NA | 5MG/M3<br>(8 Hr. TWA) |

### III. PHYSICAL AND CHEMICAL PROPERTIES

| | | |
|---|---|---|
| BOILING POINT<br>300-760 F | VAPOR PRESS.<br><2 MMHG | EVAPORATION BUTYL ACETATE=1<br><1 |
| VOLATILE BY VOLUME %<br>NA | MOLECULAR WT<br>ND | APPEARANCE<br>Black Liquid |

### IV. FIRE PROTECTION INFORMATION

| FLASH POINT / METHOD | AUTOIGNITION TEMP | FLAMMABLE LIMITS % VOL IN AIR | |
|---|---|---|---|
| | | LOWER | UPPER |
| >200 | NA | 3.9 | 20.1 |

EXTINGUISHING MEDIA

Carbon dioxide, dry chemical, or foam. Water stream may spread fire, use water spray only to cool containers exposed to fire. If leak or spill has not ignited, use water spray to disperse the vapors.

HAZARDOUS DECMPOSITION PRODUCTS

Incomplete combustion can yield carbon monoxide and various hydrocarbons etc.

FIRE AND EXPLOSION HAZARDS

Never weld or use torch on containers, even empty.Can ignite explosively. Explosion hazard in fire situation. Vapor heavier than air and may travel considerable distance to a source of ignition and flash back.

| HAZARDOUS POLYMERIZATION | | STABILITY | |
|---|---|---|---|
| ☒ WILL NOT OCCUR | ☐ WILL OCCUR | ☐ STABLE | ☐ UNSTABLE |

## V. HEALTH INFORMATION

INHALATION

Inhalation of vapors can cause nasal and respiratory irritation, dizziness, weakness, fatigue,stupor.

EYE CONTACT

Acute: Irritation

SKIN CONTACT

Chronic: Irritation, dermatitis.

INGESTION

Can cause gastrointestinal irritation,nausea,vomiting and diarrhea. Aspiration of materials into the lungs can cause chemical pneumonitis which can be fatal.

REPORTED AS POTENTIAL CARCINOGEN OR CARCINOGEN

☒ NOT APPLICABLE
☐ INTER. AGENCY FOR RESEARCH ON CANCER
☐ NATIONAL TOXICOLOGY PROGRAM
☐ OSHA

OSHA REQUIRED LABEL: NOT AVAILABLE

## VI. FIRST AID PROCEDURES

INHALATION

Move exposed person to fresh air. If breathing has stopped, perform artificial respiration. Get medical attention as soon as possible.

EYE CONTACT

Immediately flush eyes with water for a minimum of 15 minutes, occasionally lifting the lower and upper lids.
Get medical attention promptly.

SKIN CONTACT

If clothing soaked, immediately remove clothing and wash skin with soap and water. Launder clothing before wearing. Get medical attention promptly.

INGESTION

Do NOT induce vomiting. Get medical attention as soon as possible. Aspiration of materials into lungs do to vomiting can cause chemical pneumonitis which can be fatal.

## VII. EMPLOYEE PROTECTION

RESPIRATORY PROTECTION

Approved organic respirator above the TLVs

PROTECTIVE CLOTHING

EYES- Chemical goggles, face shield.

SKIN- Gloves: Nitrile, neoprene or other material resistant to oil.

VENTILATION

Use in well ventilated area. In confined spaces mechanical ventilation may be required for TLV compliance. Responsible individuals should evaluate air concentrations of specific regulated

## VIII. TRANSPORTATION AND STORAGE INFORMATION

| | |
|---|---|
| DOT HAZARDOUS MATERIAL ☒ YES ☐ NO | DOT HAZARD CLASS<br>Combustible Liquid |

DOT SHIPPING NAME AND I: UN 1993

STORAGE

Do not handle or store near flame, heat. sparks, or strong oxidants.
Storage area should be well ventilated. Store as NFPA Class III Liquid.

## IX. ENVIRONMENTAL PROTECTION

SPILLS: Notify emergency response personnel. Evacuate area and remove ignition sources. Build dike to contain flow. Remove free liquid do not flush to sewer or open water: Pick up with inert absorbent and place in closed container for disposal

| | |
|---|---|
| EPA Hazardous Waste ☐ Yes ☒ No | Waste Characteristic : NA |

WASTE DISPOSAL:

User must determine if material is hazardous waste . Disposal should be in compliance with all local state and federal laws.

DISCLAIMER:

The information and recommendations contained in this publication have been complied from sources believed reliable and to represent the best current opinion on the subject at the time of publication. Since we cannot anticipate or control the may different conditions under which this information or our produce may be used, we make no guarantee that the recommendations will be adequate for all individuals or situations. Each user of the product described herein should determine the suitability of the described product for his or her particular purpose and should comply with all federal and state rules and regulations concerning the described product.

MANAGER'S SIGNATURE

DATE 2/7/97

# MATERIAL SAFETY DATA SHEET

MSDS NUMBER

## SECTION I MATERIAL IDENTIFICATION

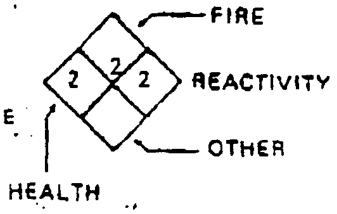
| | |
|---|---|
| PRODUCT/ CHEMICAL NAME ▸ | No. 6 fuel oil |
| PRODUCT/ CHEMICAL SYNONYMS ▸ | Bunker fuel, coker charge |
| CHEMICAL FAMILY/ FORMULA ▸ | Aromatic petroleum oil |
| OTHER IDENTIFICATION ▸ | |
| MATERIAL USE OR OCCURENCE ▸ | Industrial fuel oil |

## 24 HOUR EMERGENCY INFORMATION

| | |
|---|---|
| CLARK/APEX | 314 · 889-9600 |
| CHEMTREC | 800 · 424-9300 |

HAZARDS:

4 = EXTREME
3 = HIGH
2 = MODERATE
1 = SLIGHT
0 = LEAST



## SECTION II INGREDIENTS

| COMPONENT | % | TLV (Units) | COMPONENT | % | TLV (Units) |
|---|---|---|---|---|---|
| Petroleum<br>Heavy fraction consisting of a complex mixture of high molecular weight hydrocarbons.<br>May contain polynuclear aromatic hydrocarbons. | | Not established (recommended to maintain vapor concentrations below 0.2 mg/m$^3$ as benzene solubles.) | | | |

## SECTION III PHYSICAL DATA

| | | |
|---|---|---|
| BOILING POINT ▸ 400-1200 °F 204-649 °C | MELTING POINT ▸ Varies °F °C | VAPOR PRESSURE ▸ unknown mm Hg. @ °F °C |
| SPECIFIC GRAVITY ▸ ($H_2O$ = 1) 0.9402-1.000 | VOLATILE BY VOLUME ▸ Not established % | VAPOR DENSITY ▸ (AIR = 1) N/A |
| SOLUBILITY IN ▸ WATER Insoluble | EVAPORATION RATE ▸ Not established | |

APPEARANCE AND ODOR ▸ Amber to bronze color, heavy aromatic odor.

## SECTION IV FIRE AND EXPLOSION DATA

| FLASH POINT AND METHOD | IGNITION TEMPERATURE | FLAMMABLE LIMITS (%) | LEL | UEL |
|---|---|---|---|---|
| ▸ 150° TOC | ▸ Auto ignition = 765° | ▸ Not established | | |

EXTINGUISHING MEDIA

Foam, carbon dioxide, dry chemical.

SPECIAL FIREFIGHTING PROCEDURES AND PRECAUTIONS ▸

Do not use Foam at storage temperatures above 200°F. Firemen fighting fuel oil fires should use necessary protective equipment and breathing apparatus as would normally be used when fighting fires where there may be danger of breathing hazardous products of combustion.

UNUSUAL FIRE AND EXPLOSION INFORMATION ▸

None.

[illegible]

fuel Oil

| OSHA PEL ▸ | ACGIH TLV ▸ | ACTION LEVEL ▸ |
|---|---|---|
| Not established | Not established | Not established |

HEALTH EFFECTS

| | ACUTE | CHRONIC |
|---|---|---|
| INHALATION | Irration of respiratory tract mucous membranes, nausea, CNS depression, pulmonary edema. | Irration of respiratory tract muce membranes, possible mild chemical pneumonitis with high concentration |
| INGESTION | Large quantities can result in nausea, CNS depression. | No known effects. |
| SKIN CONTACT | Irritaion, particulary of mucous membranes. | Repeated and prolonged skin contact result in skin disorders and potenti. sensitization. |
| EYE CONTACT | Irritation of the cornea and/or conjunctiva. | Irritation of the cornea and/or conjunctiva. |

FIRST AID PROCEDURES ▸

INHALATION-remove from vapor to fresh air, if unconscious seek medical aid. INGESTION-DO NOT INDUCE VOMITING, seek medical aid. SKIN CONTACT-promptly remove oil soaked clothing, wash skin with soap and water, if irritation develops, seek medical aid. EYE CONTACT-flush with copious amounts of water, if irritation develops, seek medical aid.

## SECTION VI REACTIVITY DATA

STABILITY ▸ ☐ UNSTABLE ☒ STABLE

HAZARDOUS POLYMERIZATION ▸ ☐ MAY OCCUR ☒ WILL NOT OCCU

CONDITIONS TO AVOID ▸ Source of ignition, heat, etc.

INCOMPATABLES ▸ Strong oxidants, e.g., chlorine and concentrated oxygen.

TYPICAL DECOMPOSITION PRODUCTS ▸ Incomplete combustion will produce carbon monoxide, organic acids, aldehydes.

## SECTION VII SPILL OR LEAK PROCEDURES

Avoid excessive inhalation or skin contact. Absorb, scrape up, or incinerate under proper conditions or secure in a chemical land fill. Observe Federal, state and local governmental spill and water quality regulations. Contain spills by diking or impoundir to prevent entrance into water courses and ground water.

## SECTION IX OTHER INFORMATION

| | | | |
|---|---|---|---|
| VENTILATION | LOCAL EXHAUST ▸ Recommended where airborne concentrations exceed 0.2 mg/m³ as benzene solubles. | | |
| | GENERAL EXHAUST ▸ Recommended for use in enclosed or semi-enclosed work areas. | | |
| PERSONAL PROTECTIVE EQUIPMENT | RESPIRATORY PROTECTION ▸ Combination particulate and vapor air purifying or self-contained breathing apparatus recommended at or above 0.2mg/m³ as benzene soluble | | |
| | GLOVES ▸ Butyl rubber, neoprene, polyethylene PVC | EYE PROTECTION ▸ Splash goggles or shields with safety glasses. | OTHER ▸ Full body protective clothing. |

## SECTION VIII SPECIAL PROTECTION AND CONTROL INFORMATION

The information contained herein is based on data available at this time and is believec to be accurate. However, no warranty is expressed or implied regarding the accuracy of these data or the results to be obtained form the use therof. Since information contained herein may be applied under conditions beyond our control and with shich we may be unfamiliar, no responsibility is assumed for the results of its use. The person receiving this information shall make his own determination of the suitability of the material for his particular purpose.

Occupational Safety and Health Administration

# MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

## SECTION I

|  |  |
|---|---|
| MANUFACTURER'S NAME<br>Colonial Oil Industries, Inc. | EMERGENCY TELEPHONE NO.<br>(912) 236-1331 (24 hrs/day) |
| ADDRESS (Number, Street, City, State, and ZIP Code)<br>North Lathrop Avenue, P. O. Box 576, Savannah, Georgia 31402 | |
| CHEMICAL NAME AND SYNONYMS<br>Petroleum Heavy Fuel Oil | TRADE NAME AND SYNONYMS<br>NO. 6 FUEL OIL |
| CHEMICAL FAMILY<br>Petroleum Hydrocarbon | FORMULA<br>Complex mixture of petroleum hydrocarbons |

## SECTION II - HAZARDOUS INGREDIENTS

| PAINTS, PRESERVATIVES, & SOLVENTS | % | TLV (Units) | ALLOYS AND METALLIC COATINGS | % | TLV (Units) |
|---|---|---|---|---|---|
| PIGMENTS | | n.a. | BASE METAL | | n.a. |
| CATALYST | | n.a. | ALLOYS | | n.a. |
| VEHICLE | | n.a. | METALLIC COATINGS | | n.a. |
| SOLVENTS | | n.a. | FILLER METAL PLUS COATING OR CORE FLUX | | n.a. |
| ADDITIVES | | n.a. | OTHERS | | n.a. |
| OTHERS | | n.a. | | | |

| HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES | % | TLV (Units) |
|---|---|---|
| | | |
| | | |
| | | |
| | | |

## SECTION III - PHYSICAL DATA

|  |  |  |  |
|---|---|---|---|
| BOILING POINT (°F.) IBP-90% | 450-1100 | SPECIFIC GRAVITY ($H_2O$=1) | 0.969 |
| VAPOR PRESSURE (mm Hg.) @ 20°C | <0.01mm | PERCENT, VOLATILE BY VOLUME (%) | Negligible |
| VAPOR DENSITY (AIR=1) | >6 | EVAPORATION RATE (n-Butyl Acetate = 1) | <0.01 |
| SOLUBILITY IN WATER | Negligible | | |
| APPEARANCE AND ODOR Dark liquid. Strong asphalt-like odor. | | | |

## SECTION IV - FIRE AND EXPLOSION HAZARD DATA

| FLASH POINT (Method used) | FLAMMABLE LIMITS | Lel | Uel |
|---|---|---|---|
| PM Closed Cup 180°F. | | 0.9% | 6.0% |

EXTINGUISHING MEDIA
Foam, dry chemical, $CO_2$, water spray, or fog.

SPECIAL FIRE FIGHTING PROCEDURES
Use air-supplied rescue equipment for enclosed areas.

Cool exposed containers with water.

UNUSUAL FIRE AND EXPLOSION HAZARDS
Do not store or mix with strong oxidants.

n.a. - not applicable

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(Continued on reverse side)

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## SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
5 mg/m for oil mist.

EFFECTS OF OVEREXPOSURE
Prolonged or repeated skin contact may cause mild skin irritation.

EMERGENCY AND FIRST AID PROCEDURES
In case of skin contact, wash with soap and water. If splashed into eyes, flush with clear water until irritation subsides.

## SECTION VI - REACTIVITY DATA

| | | | |
|---|---|---|---|
| STABILITY | UNSTABLE | | CONDITIONS TO AVOID |
| | STABLE | X | |

INCOMPATABILITY *(Materials to avoid)*

HAZARDOUS DECOMPOSITION PRODUCTS

| | | | |
|---|---|---|---|
| HAZARDOUS POLYMERIZATION | MAY OCCUR | | CONDITIONS TO AVOID |
| | WILL NOT OCCUR | X | |

## SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Recover free liquid. Add absorbent to spill area.
Keep petroleum products out of streams and waterways.

WASTE DISPOSAL METHOD
Incinerate absorbed material.

## SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION *(Specify type)*
Normally not needed.

| | | |
|---|---|---|
| VENTILATION | LOCAL EXHAUST<br>Needed only to capture hot fumes. | SPECIAL |
| | MECHANICAL *(General)* | OTHER |

| | |
|---|---|
| PROTECTIVE GLOVES<br>Normally not needed | EYE PROTECTION<br>Normally not needed. |

OTHER PROTECTIVE EQUIPMENT
Oil-impervious apron if needed.

## SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Keep containers closed. Keep away from heat and open flame.

OTHER PRECAUTIONS
Avoid breathing of oil mist. Remove oil-impregnated clothing. Wash thoroughly after exposure.