

## MATERIAL SAFETY DATA SHEET FOR MARINE DIESEL, 3rd VERSION, JULY 2006

1. PRODUCT AND COMPANY DATA

1.1 PRODUCT DATA:

CAS Number: 68334-30-5

EINECS Number: 269-822-7

**USE**: As internal combustion fuel of special specifications, for ship supply.

1.2 COMPANY DATA :

HELLENIC PETROLEUM S.A., 17th km National Road Athens - Korinthos, 193 00 ASPROPYRGOS, GREECE EMERGENCY TELEPHONE NUMBERS: + 30 - 210 - 5533000, + 30 - 210 - 5539000 PERSON RESPONSIBLE FOR MARKETING THE PRODUCT: Director of Supply, International Sales and Risk Management, tel.: + 30 - 210 - 5539090.

2. COMPOSITION / INFORMATION ON INGREDIENTS

Complex combination of paraffins, olefins, naphthenes and aromatic hydrocarbons, having carbon numbers predominantly in the range of  $C_{10}$  -  $C_{28}$ . These hydrocarbons are petroleum distillates (typical composition : 70-80%) aliphatic, 20-30% aromatic and less than 5% olefins) or products of pyrolysis (typical composition : up to 75% aromatic, up to 25% aliphatic, up to 10% olefins) or mixtures of them.

Hazardous components : Polycyclic Aromatic Hydrocarbons, (mainly of 2-3 rings and relatively minor concentrations of 4-6 rings in petroleum distillates, but increased concentrations of 4-6 rings in products of

pyrolysis).

#### CLASSIFICATION OF THE MOST HAZARDOUS COMPONENTS \*

naphthalene

Carcinogenic Category 3, Harmful Xn, Dangerous for the Environment N Risk phrases: R40, R22, R50/53

trimethyl-benzene-1,2,4

Harmful Xn, Irritant Xi,

Dangerous for the Environment N

Risk phrases: R10, R20, R36/37/38, R51/53

trimethyl-benzene-1,3,5

Irritant Xi, Dangerous for the Environment N

Risk phrases: R10, R37, R51/53

n-propyl-benzene

Harmful Xn, Irritant Xi

Dangerous for the Environment N

Risk phrases: R10, R37, R65, R51/53

# 3. HAZARDS IDENTIFICATION

#### SAFETY

Risk of fire if product is heated to temperature higher than the flash point.

Marine diesel burns fiercely when ignited.

The low vapor pressure (relatively to more volatile petroleum products), reduces the risk of formation of an explosive atmosphere.

Risk of accumulation of electrostatic charge in liquid which can cause incendiary electrical discharge.

Under normal conditions of use and practice, marine diesel will not present a hazard to health, providing excessive skin contact is avoided.

There is no significant risk of exposure to marine diesel vapors under ambient temperature, due to the relatively low volatility.

The presence of polycyclic aromatic hydrocarbons in marine diesel is considered harmful, especially if they are obtained from cracking / hydrocracking processes.

Risks to health are minimized when the necessary precautions are taken, as storage and product handling take place in closed systems.



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#### ENVIRONMENT

Pollution of water resources with marine diesel can cause mortality to aquatic life.

Pollution of soil with large quantities of marine diesel can cause penetration of the product into the groundwater

#### CLASSIFICATION AND LABELLING OF PRODUCT ACCORDING TO DECISION 41/2002 OF THE SUPREME CHEMICAL COUNCIL

Harmful,

Xn\* Carcinogenic Category 2,

Carcinogenic Category 3,

Xn° Dangerous for the Environment, N







Risk phrases: R38<sup>D</sup>, R40<sup>+</sup>, R45<sup>S</sup>, R51/53, R65, R66<sup>++</sup>

### 4. FIRST AID

#### **GENERAL INSTRUCTIONS**

It is necessary to isolate the area from all potential sources of ignition.

The area to which the casualty will be transferred must be well ventilated.

All clothing must be drenched with water before taken off, in order to prevent static electricity hazard.

#### SKIN

Remove casualty from the incident area.

Take off clothing.

Wash carefully with cold water and neutral soap body parts which come into contact with the product.

If skin looks dry, carefully anoint with lanolin cream.

If skin has blisters and looks inflamed, continue washing with plenty of sterilized water and seek medical advice immediately.

#### EYES

Remove casualty from the incident area.

Wash eyes carefully with plenty of running water for 15', keeping eyelids open.

Seek medical advice - refer to oculist if pain or inflammation persists after washing.

DO NOT administer collyrium or other liquid without medical approval.

Remove casualty to a quiet, cool and well ventilated place.

DO NOT induce vomiting (risk of pulmonary complications).

Place casualty in supine position, with feet slightly elevated.

Loosen belt and collar, cover with blanket.

Seek medical advice.

### **RECOMMENDATION:**

As antidote, administer a spoonful of medicinal paraffin oil, to be followed by a glass of water containing a spoonful of magnesium or sodium sulfate, in order to slow down absorption through the gastroinstestinal tract. Gastric lavage should only be performed after endotrocheal intubation in view of the risk of aspiration which can cause inflammation of the lungs.

#### INHALATION

Remove patient to a quiet, cool and well ventilated place.

#### If patient remains conscious

Place patient in supine position, with feet slightly elevated.

Loosen belt and collar, cover with blanket.

Seek medical advice.



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#### B. If patient is unconscious or is conscious but breathes with difficulty

- Seek medical advice immediately.
- Place patient in supine position, with feet slightly elevated.
- Loosen belt and collar, cover with blanket.
- Provide oxygen, check respiration and pulse.
- If necessary, provide external cardiac massage.

#### C. If patient is not breathing

- Apply artificial respiration.
- Seek medical advice immediately.
- Place casualty in supine position, with feet slightly elevated.
- Loosen belt and collar, cover with blanket.
- Provide oxygen if respiration is restored.
- If necessary, provide external cardiac massage.

#### 5. FIRE FIGHTING MEASURES

- The most effective extinguishing agents are dry powder, foam and carbon dioxide.
- Sand may also be used in smothering small fires.
- Water must be used ONLY for cooling tanks and containers exposed to fire.
- Escape routes must always be open.
- Large fires are faced by properly trained personnel.

#### 6. ACCIDENTAL RELEASE MEASURES

#### **GROUND SPILLS**

- Isolate spill.
- Evacuate area of people not involved in dealing with the incident.
- Ensure absorption of leaking diesel with sand or other neutral material, wash area with water.
   ATTENTION! Leaks make surfaces slippery.
- Avoid washing into drainage systems.
- In case of leak or spill without fire, use water in spray form to order to disperse possible vapors and protect staff dealing with the incident.
- In case of large spills, inform inhabitants of surrounding area who are considered to be at greatest risk.
- Alert local authorities in case product pollutes soil, water or vegetation.

#### SEA SPILLS

- Spills from ships are faced according to Appendix of Protocol 1978 of the International Treaty 1973 and its amendments (MARPOL 73/78).
- Leaking quantities of marine diesel are blocked though the use of floating barriers.
- Alert coast guard, nearest port, local authorities and shipowning Company involved in incident.

# 7. HANDLING AND STORAGE

- Loading / unloading / storage temperature : Ambient
- Store diesel in specially designed containers, according to relevant regulations, in a well ventilated area, away from sources of heat or any other ignition source.
- It is important to label containers properly and keep them closed, away from children.
- It is important to earth storage tanks and transportation systems and take preventive control measures for possible leaks.
- When emission of high concentrations of vapors is possible (due to high temperatures), appropriate measures must be taken (ventilation, use of respiratory protection) in order to minimize exposure.
- When high concentrations of vapors or mists occur and it is not possible to make alterations, it is necessary to install general / local ventilation systems in order to keep concentrations at acceptable levels.
- Areas where large quantities of marine diesel are stored must have special fire-fighting systems and Emergency Plans according to relevant legislation.



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#### 8. EXPOSURE CONTROLS / PERSONAL PROTECTION

#### 8.1. EXPOSURE LIMITS

American Conference of Governmental Industrial Hygienists

ACGIH, 2002 TLV – TWA (8 hours) "total hydrocarbons, vapor-aerosol": 100 mg/m<sup>3</sup>

: 10 ppm

for naphthalene (Government Gazette 94A/99) : TWA for 8 hours exposure for trimethyl-benzene isomers (Government Gazette 94A/99) : TWA for 8 hours exposure

25 ppm

for hydrogen sulfide (H<sub>2</sub>S): TWA for 8 hours exposure

10 ppm 15 ppm

# Short term exposure

8.2. EXPOSURE CONTROLS

 Under normal conditions of use, dangerous exposure to marine diesel vapors/mist is unlikely due to the relatively low volatility. High concentrations may be formed under high temperatures.

Cleaning, inspection and maintenance of diesel storage tanks require the implementation of strict procedures
and precautions, such as issuing of relevant work permits, gas freeing, use of safety belts and air-supplied
breathing apparatuses.

When opening confined storage spaces use individual air-supplied breathing apparatuses and detectors of  $H_2S$  at the risk of  $H_2S$  accumulation.

■ Do not enter confined spaces where oxygen concentration is <20% v/v and H<sub>2</sub>S concentration is >10ppm.

It is necessary to keep rules of personal hygiene.

Avoid ingestion, contact with eyes and skin, as well as exposure to marine diesel vapors/mist.

Avoid using the product as a cleaning agent or solvent.

Exposure to product can arise from both industrial activities (due to mishandling) and extensive use (e.g. spilling of small quantities during filling of vehicle tanks) or indirectly as a consequence of leakages or spills.

#### PERSONAL PROTECTIVE EQUIPMENT

 When skin contact is possible, use impervious nitrile gloves (EN 374, 388, 407, 420), appropriate protective clothing (EN 340, 465, 466, 467) and safety shoes (EN 345, 346).

When contact with eyes is possible, use goggles or face shields (EN 166, CR 13464).

Use full face masks with filters for organic vapors/mist in case of minor spills (EN 136, 141).

 Use individual air-supplied breathing apparatuses (EN 137), impervious overalls, boots, gloves, during cleaning and inspection of equipment, as well as in major spill incidents.

In case of large scale fires, use fire resistant overalls (EN 469, 1486) and individual air-supplied breathing apparatuses (EN 137).
ATTENTION!

Protective clothing must be washed carefully after each use if it comes into contact with the product.

Footwear permeated with the product must be discarded.

# 9. PHYSICAL AND CHEMICAL PROPERTIES \*

Transparent liquid with characteristic odour which is dyed black, with the addition of appropriate color agent. It is thus made easily distinguishable from other liquid fuels.

Density at 15°C, kg/m³
 Flash point, °C
 Lower Explosion Limit (LEL), %v/v
 Upper Explosion Limit (UEL), % v/v
 Kinematic Viscosity at 40°C, mm²/s
 max 890
 min. 60
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## 10. STABILITY AND REACTIVITY

Thermal Stability: Stable.

Conditions to be avoided :

High temperatures, heat sources, naked flames and other sources of ignition.

Materials to be avoided: halogens, strong acids and oxidizers.

Hazardous decomposition products :

It does not decompose under normal temperatures.

Hazardous products of thermal cracking :

Carbon monoxide and dioxide, nitrogen oxides, sulphur dioxide, hydrogen sulfide, unburned hydrocarbons, polycyclic aromatic hydrocarbons, particulates.



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#### 11. TOXICOLOGICAL INFORMATION

Indicative values for the acute toxicity of marine diesel:

LD<sub>50</sub> (oral skin) LD<sub>50</sub> (inhalation, 4hr)

2.000 mg/kg

5 mg/l

There are indications that cracked streams have carcinogenic effects.

There are some indications that hydrocracked streams may have carcinogenic effects.

For streams obtained from atmospheric distillation there are no available data related to carcinogenic effects.

No mutagenic effects have been ascertained.

#### SKIN

Excessive or/and repeated contact with skin may cause dryness, irritation, dermatitis.

Under conditions of poor personnel hygiene excessive or/and repeated contact of diesel with skin may lead to acne and folliculitis that are likely to develop into malignant growths.

#### EYES

Contact of eyes with diesel droplets causes transient stinging and redness.

Exposure to high concentrations of diesel mist or vapors (in high temperatures) causes slight eye irritation.

#### INHALATION

Due to diesel's low volatility there is no risk of inhalation under ambient temperatures.

In high temperatures and under conditions of inadequate ventilation, inhalation of vapors gradually causes irritation to nose and throat, headache, nausea and mental confusion. Chance of hydrogen sulfide (H2S) emission which is particularly toxic. Concentration of  $(H_2S)$  above the exposure limits (8.1) also causes eye and upper respiratory tract irritation.

ATTENTION ! Prolonged exposure to H₂S paralyzes the sense of smell, raising the risk of poisoning in cases of increased concentrations.

Prolonged inhalation of high concentrations of diesel vapor may result in respiratory and nervous system depression, with eventual loss of consciousness.

Exposure to concentrations of diesel vapors exceeding 5 mg/m<sup>3</sup> causes irritation to the mucus membrane of the upper respiratory tract.

#### INGESTION

Accidental ingestion of significant quantities of diesel causes irritation of the gastrointestinal tract.

Vomiting is possible but this should not be induced.

Aspiration of liquid into the lungs (either directly or as a result of vomiting) causes damage to the lung tissue, with possible risk of chemical pneumonitis (possibility lethal in serious cases).

#### 12. ECOLOGICAL INFORMATION

Releases of marine diesel into water will result in films of hydrocarbons floating and spreading on the surface.

Volatilization is an important loss process for the lighter components. In the air, the hydrocarbon constituents of diesel react readily with hydroxyl radicals, and their half-life is less than one day.

The photoxidation on water surfaces is a significant loss process for polycyclic aromatic compounds.

The majority of diesel components is adsorbed on sediment.

Marine diesel does not contain hydrocarbons with a significant degree of solubility in water that would result in serious acute toxic hazard on aquatic life.

However, release of large quantities of the product in water causes mortality in marine life and has an adverse long-term impact on the aquatic environment. The rates of acute toxicity for aquatic organisms (fish, daphnia, algae) vary between 1 and 100 mg/l.

An acute toxic impact is also likely on sea life (birds and mammals) while quantities washed up ashore cause considerable pollution. Recolonisation takes several weeks.

The components of small molecular weight decompose relatively quickly under aerobic conditions, while the hydrocarbons of greater molecular weight (mainly polycyclic aromatics) biodegrade at slow rates.

Under anaerobic conditions, the biodegradability of diesel components is negligible.

The bioaccumulation tendency is practically limited due to the metabolic process. The log kow a values vary between 3.9 and >6 (Kow = Octanol /Water Partition Coefficient). The most commonly reported components found on clams are naphthalenes and methyl-naphthalenes.

In case small quantities of diesel come into contact with the soil, a significant part evaporates and the rest is absorbed by the upper aerobic layers of the soil.

In cases of soil pollution with significant quantities of diesel, a main part will penetrate the anaerobic layers, possibly reaching the groundwater level and polluting drinkable water. It is considered very unlikely that these components will remain for a period of time long enough to cause hazard for public health.

#### 13. DISPOSAL

Disposal of the product (usually through burning) must be according to relevant legislation.

The approval of local authorities is required

Do not dispose in sewers



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#### 14. TRANSPORT INFORMATION

Transportation through: tankers, tank - trucks, trains

Road / Rail transport: ADR/RID 2003:

Class: 3, Code: F1, Label: 3, Packing group: III, Hazard identification: Nr. 30





Symbol:

UN Number: 1202

Sea transport: IMDG - IMO Code 2002

Class: 3.3

# 15. REGULATORY INFORMATION

Safety phrases (According to Decision 41/2002 of the Supreme Chemical Council)

Keep out of the reach of children 52

S24\*°

Avoid contact with skin

S36/37®

Wear suitable protective clothing and gloves

S45\*

In case of accident or if you feel unwell, seek medical advice immediately

S53\*

Avoid exposure - obtain special instructions before use

S61

Avoid release to the environment. Refer to special instructions / MSDS

**S62** 

If swallowed, do not induce vomiting: seek medical advice immediately and show this container

or label

### 16. OTHER INFORMATION

### 16.1. Full text of relevant Risk phrases, referred in paragr. 2 and 3 of the present MSDS

Flammable (1,2,4-and 1,3,5-trimethyl-benzene, n-propylbenzene) R10

R20 Harmful by inhalation (1,2,4-trimethylbenzene)

R22 R37

Harmful if swallowed (naphthalene) Irritating to respiratory system (1,3,5-trimethyl-benzen, n-propyl-benzene)

R38

Irritating to skin (product \*)

R36/37/38

Irritating to eyes, respiratory system and skin (1,2,4-trimethyl-benzene)

R40

Limited evidence of carcinogenic effect (naphthalene, product May cause cancer (product )

R45

R50/53

Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic

environment (napththlene)

R51/53

Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

R65

(1,2,4- and 1,3,5-trimethyl-benzene, n-propyl-benzene, product)

**R66** 

Harmful: may cause drowsiness and dizziness (*n-propyl-benzene, product*) Repeated exposure may cause skin dryness or cracking (product \*\*)

## 16.2. Recommended restrictions on use

Use the product exclusively in ships' diesel engines.

# 16.3. Training advice

The information of the present document, may be used for training purposes

# 16.4. References

This MSDS is based on current legislation and on information from bibliography according to the latest scientific developments. Will be updated according to REACH R1907/2006 requirements.

Technical contact point: Chr.Kotsiki, tel.: +30-210-5539148.

The above information and recommendations concern only the specific material, as determined above, and may not apply for the same material if used in combination with any other material or in any process. They are accurate and reliable, according to data which HELLENIC PETROLEUM S.A. had available on the above date.

However, HELLENIC PETROLEUM S.A. cannot guarantee their accuracy and reliability and does not assume any responsibility for loss or damage which may arise from the use of the above materials.

The present SDS is supplied to consumers for them to consider and judge their adequacy concerning the particular use of the

material (the attention of consumers is particularly urged in case of changes in the packing of the above product).