A LITERATURE SURVEY OF DRILLING FLUIDS AND DENSIFIERS

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TABLE OF CONTENTS

INTRODUCTION

A literature search was conducted to investigate potential choices in drilling fluids and densifiers for use in deep ice core drilling programs. Previous practice has been to employ fuel (DF-A, kerosene or JP-4) and a heavy chlorinated solvent (PCE or TCE) to increase the density (specific gravity) from about 0.85 to 0.92.

Ethyl alcohol has been used by the Soviets. However, it does not satisfy hydrophobicity requirements and will attack ice grain boundaries as well as to affect oxygen isotope measurements.

Many other compounds are presently available which meet the general drilling requirements but fail to meet the criteria required to acquire a high quality ice core which will be sampled for chemical analysis. Also, many fluids are unacceptable because of their high toxicity.

This literature search of nearly 250,000 compounds and synthesis of data resulted in 15 compounds which may be considered for use as a drilling fluid or fluid densifier.

A Literature Survey of Drilling Fluids and Densifiers
(those in use, considered, and some alternatives)

This report centers on the hazards of the fluids in use and on several alternative fluids found by a computer search of the chemical literature.

Specified Drilling Fluid Requirements:

1. Non-toxic
2. Chemically clean:
   a) No salt ions: Na^+, K^+, Mg^{+2}, Ca^{+2}, Cl^-, NO_3^- (or HNO_3) and NH_4^+
   b) Not to interfere with analyses for:
      i) Al, Pb, Zn, Cu, Cd, Se, As, Sb
      ii) oxygen isotope ratios
      iii) CO_2
3. Hydrophobic (will not attack ice grain boundaries)
4. Density 0.92 g/cc from –50 to 0°C
5. Viscosity: less than 5 centistokes at 20°C
6. Will not attack stainless steel or viton
7. Dielectric desirable

The literature search for alternatives was accomplished by computer inquiry of the Heilbron and Merck data bases, using melting point (–200 to –20°C) and density (0.8 to 1.1 g/cc) as the two criteria. This search covered a quarter million of the compounds on the market (assuming density and melting point were listed). Visual inspection of the approximately one hundred matchess eliminated all but two dozen. Elimination was based on their obvious toxic, odor or other problems (e.g., pyridine, phenyl isocynate, etc.).

The upper limit of -20°C was based on the fact that the bore holes have a similar temperature zone. The upper density figure is based on the fact that only halogenated materials, or materials containing undesirable ligands (e.g., nitro, cyano and sulfate) occupy the higher density region.

Next, the remaining compounds were computer searched for potential problems utilizing the "Hazardline" data base. The following pages are extracts from that search. Final cuts from the list eliminated all: soluble compounds (item 3 above), and all compounds with toxicity or ignitability ratings above 2 (the same as the existing fuel use practice). All compounds are rated as "0" with respect to "reactivity," i.e., to explosion hazard.

Interpretation of CERCLA Hazard ratings:

Rating No.	Toxicity	Ignitability (°F)	Persistence
4-	Deadly	Below 73	
3-	Extreme Danger	Below 100	
2-	Dangerous	Below 200	
1-	Slight Hazard	Above 200	Low
0-	No Hazard	Will Not Burn	None

Descriptions of: Lethal Dose (LD), Toxic Dose (TD), regardless of route versus Lethal Concentration (LC), or Toxic Concentration (TC) in the air. The term "Lo" is used where the number of subjects studied was not a significant number.

Category	Exposure Time	Route of Exposure	TOXIC EFFECTS Human	Animal
TDLo	Acute or Chronic	All except Inhalation	Any Non-Lethal	Reproductive Tumerogenic
TCLo	Acute or Chronic	Inhalation	Any Non-Lethal	Reproductive Tumerogenic
LDLo	Acute or Chronic	All except Inhalation	Death	Death
LD50	Acute	All except Inhalation	Not Applicable	Death (Statistically Determined)
LCLo	Acute or Chronic	Inhalation	Death	Death
LC50	Acute	Inhalation	Not Applicable	Death (Statistically Determined)

Aquatic Toxicity: e.g., "TLm96" indicates the concentration that will kill 50% of the exposed organisms in 96 hours.

A rating of: 0 = >1000; 1 = 100-1000; 2 = 10-100 ppm.

Other abbreviations: IHL=inhalation; ORL=oral; HMN=human; GPG=guinea pig; UNK=Unreported; IPR=Intraperitoneal

Name of Compound:	**Fuel Oil No. 1**
Synonyms:	Kerosene, Coal Oil, JP-1, Diesel Fuel-Arctic (DF-A)
CAS Number:	8008-20-6
Reg. Toxic Number:	OA5500000
Chemical Formula:	Varies
General Description:	Colorless to light-brown liquid with mild petroleum odor
Solubility (water):	Insoluble
Freezing Point:	-50°C
Specific Gravity:	0.83

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	2
Persistence:	1

Toxicology: mg/kg

UNK-Man LDLo	1176 mg/kg
ORL-GPG	20 g/kg
Permissible Exposure:	None established
Dangerous Exposure:	None established

Aquatic Toxicity Rating:	0
TLm48:	Bluegill, 2820 ppm
Permissible Exposure:	None established

Remarks:

CURRENTLY IN USE

Jet fuels contain ca. 0.1 to 0.2 volume % cellosolve, a class of hydroxy ether compounds to prevent ice crystal formation.

A related literature entry is Diesel Fuel No. 1D. CAS No. 68334-30-5. Similar data to the above.

Name of Compound:	**Perchloroethylene**
Synonyms:	PCE
CAS Number:	127-18-4
Reg. Toxic Number:	KX3850000
Chemical Formula:	C_2Cl_4
General Description:	Colorless liquid, smells like ether/chloroform
Solubility (water):	1.5 (g/100 mL)
Freezing Point:	-19°C
Specific Gravity:	1.62

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	0
Persistence:	2

Toxicology: mg/kg

IHL-HMN TCLo	96 ppm/7 hrs; 280 ppm/2 hrs; 600 ppm/10 min
Permissible Exposure:	100-200 ppm; 300 ppm 5 min peak
Dangerous Exposure:	500 ppm

Aquatic Toxicity Rating: 2

Remarks:

CURRENTLY IN USE

Suspect animal carcinogen.

Protective clothing, etc., recommended in handling.

Name of Compound:	**Trichloroethylene**
Synonyms:	TCE
CAS Number:	79-01-6
Reg. Toxic Number:	KX4550000
Chemical Formula:	C_2HCl_3
General Description:	Colorless liquid, chloroform-like odor; photoreactive
Solubility (water):	0.1 (g/100 mL)
Freezing Point:	-73°C
Specific Gravity:	1.46

CERCLA Hazard Ratings:

Toxicity:	1
Ignitability:	1
Persistence:	2

Toxicology: mg/kg

IHL-HMN TCLo	6900 mg/m3 10 min; 160 ppm/83 min
IHL-HMN TDLo	812 mg/kg
IHL-Man TCLo	110 ppm/8 hrs
ORL-HMN LDLo	7 g/kg
Permissible Exposure:	100-200 ppm; 300 ppm 5 min peak
Dangerous Exposure:	1000 ppm

Aquatic Toxicity Rating:	1
TLm96 (sea water):	Plaice, 15 ppm

Remarks:

CURRENTLY IN USE but PCE preferred (?) - previous page.
Indefinite human carcinogen. Animal carcinogen.
Protective clothing, etc., recommended during handling.

Name of Compound:	**HyPerm/Bromoil**
Synonyms:	Numerous industrial acronyms, e.g., Bromkal, Polybrominated Phenyl Ether
CAS Number:	64741-85-1 (a mixture) and 32534-81-9
Reg. Toxic Number:	
Chemical Formula:	Varies. Nominally $C_{12}H_5Br_5O$
General Description:	Brominated aromatic ether diluted with mixed petroleum hydrocarbons. The ether is a clear, amber, dense liquid with a slight kerosene odor.
Solubility (water):	Insoluble
Freezing Point:	"-18°C" (solid in solution)
Specific Gravity:	Variable. 0.7 to 1.96 (the solid is closer to 3)

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	2 (indicates a high petroleum content)
Persistence:	

Toxicology: mg/kg

Eye irritant.

Permissible Exposure:	Not established
Dangerous Exposure:	

Aquatic Toxicity Rating:	Not established
Permissible Exposure:	Not established

Remarks:

CURRENTLY IN USE THIS YEAR

NOTE: This compound was developed for *high temperature* bore holes because of its heat transfer properties. (It is also used as a flame retardant.)

Depending on method of preparation, it contains between 4 and 9 bromine atoms. The compounds are *solids* which have to be ground to a powder, or dissolved in hydrocarbon solvent.

In order to prevent crystallization, it has to be diluted. *Presumably* the 0.7 density solution has the freezing point of -18°C.

Name of Compound: **Conoco LVT-200**
Synonyms: Mineral Oil
CAS Number:
Reg. Toxic Number:
Chemical Formula: A mixture. C_{10}-C_{19} Hydrocarbons.
General Description: Clear, colorless liquid, very mild non-offensive odor
Solubility (water): Insoluble
Freezing Point: -68°C
Specific Gravity: 0.81

CERCLA Hazard Ratings:
Toxicity:
Ignitability:
Persistence:

Toxicology: mg/kg
LD_{50} (rats): >5 g/kg
Permissible Exposure:
Dangerous Exposure:

Aquatic Toxicity Rating:

Remarks:
CURRENTLY IN USE

Name of Compound:	**Toluene**
Synonyms:	Methylbenzene
CAS Number:	108-88-3
Reg. Toxic Number:	XS5250000
Chemical Formula:	C_7H_8
General Description:	Colorless liquid, benzene-like odor
Solubility (water):	0.05 (g/100 mL)
Freezing Point:	-77°C
Specific Gravity:	0.87

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	3
Persistence:	1

Toxicology: mg/kg

IHL-HMN TCLo	200 ppm
IHL-MAN TCLo	100 ppm
Permissible Exposure:	200 ppm; 500 ppm 10 min peak
Dangerous Exposure:	2000 ppm

Aquatic Toxicity Rating:	2
TLm96:	Fathead, 34.3; Bluegill, 24; Goldfish 57.7; Guppy, 59.3; *Gambusia affinis*, 1180 ppm

Remarks:

PROPOSED USE by University of Tulsa.

Exceeds Ignitability 2.

Name of Compound:	**Ethyl Acetate**
Synonyms:	
CAS Number:	141-78-6
Reg. Toxic Number:	AH5425000
Chemical Formula:	$C_4H_8O_2$
General Description:	Colorless, clear volatile liquid, fruity odor
Solubility (water):	8.7 (g/100 mL)
Freezing Point:	-83°C
Specific Gravity:	0.89

CERCLA Hazard Ratings:

Toxicity:	1
Ignitability:	3
Persistence:	0

Toxicology: mg/kg

IHL-HMN TCLo	400 ppm
Permissible Exposure:	400 ppm
Dangerous Exposure:	

Aquatic Toxicity Rating: 1

Remarks:

Exceeds Ignitability 2, and has appreciable solubility.

Name of Compound:	**Propyl Propionate**
Synonyms:	
CAS Number:	106-36-5
Reg. Toxic Number:	UF7100000
Chemical Formula:	$C_6H_{12}O_2$
General Description:	Colorless liquid
Solubility (water):	Insoluble
Freezing Point:	-76°C
Specific Gravity:	0.88

CERCLA Hazard Ratings:

Toxicity:	1
Ignitability:	1
Persistence:	0

Toxicology: mg/kg

Permissible Exposure:	None established
Dangerous Exposure:	None established

Aquatic Toxicity Rating:

Remarks:

ALTERNATIVE

Name of Compound:	**1,2,4-Trimethylbenzene**
Synonyms:	Pseudocumene
CAS Number:	95-63-6
Reg. Toxic Number:	DC3325000
Chemical Formula:	C_9H_{12}
General Description:	Colorless liquid
Solubility (water):	Insoluble
Freezing Point:	-43°C
Specific Gravity:	0.88

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	2
Persistence:	1

Toxicology: mg/kg

IPR-GPG LDLo	1788 mg/kg
Permissible Exposure:	25 ppm
Dangerous Exposure:	

Aquatic Toxicity Rating:

Remarks:

A related compound, mesitylene, is 1,3,5-Trimethylbenzene.
ALTERNATIVE

Name of Compound:	**2-Octanol**
Synonyms:	sec-Octyl Alcohol
CAS Number:	123-96-6
Reg. Toxic Number:	NONE
Chemical Formula:	$C_8H_{18}O$
General Description:	Oily, colorless liquid with a pungent aromatic odor
Solubility (water):	Insoluble
Freezing Point:	-32°C
Specific Gravity:	0.82

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	1
Persistence:	0

Toxicology: mg/kg

Permissible Exposure:	None established
Dangerous Exposure:	None established

Aquatic Toxicity Rating:

Remarks:

ALTERNATIVE

Name of Compound:	**Anisole**
Synonyms:	Methoxybenzene
CAS Number:	100-66-3
Reg. Toxic Number:	BZ8050000
Chemical Formula:	C_7H_8O
General Description:	Yellow liquid with a sweet anise-like odor
Solubility (water):	Insoluble
Freezing Point:	-38°C
Specific Gravity:	0.996

CERCLA Hazard Ratings:

Toxicity:	1
Ignitability:	2
Persistence:	2

Toxicology: mg/kg

Permissible Exposure:	None established
Dangerous Exposure:	

Aquatic Toxicity Rating:

Remarks:

ALTERNATIVE

Name of Compound: **n-Hexanol**
Synonyms: Hexyl alcohol
CAS Number: 111-27-3
Reg. Toxic Number: MQ4025000
Chemical Formula: $C_6H_{14}O$
General Description: Colorless liquid
Solubility (water): Slight
Freezing Point: -47°C
Specific Gravity: 0.81

CERCLA Hazard Ratings:
Toxicity: 2
Ignitability: 2
Persistence: 0

Toxicology: mg/kg
Permissible Exposure: None established
Dangerous Exposure:

Aquatic Toxicity Rating:

Remarks:
ALTERNATIVE

Name of Compound: **Sec-Butylbenzene**
Synonyms: i-butylbenzene
CAS Number: 135-98-8
Reg. Toxic Number: CY9100000
Chemical Formula: $C_{10}H_{14}$
General Description:
Solubility (water): Insoluble
Freezing Point: -76°C
Specific Gravity: 0.86

CERCLA Hazard Ratings:
- *Toxicity:* 2
- *Ignitability:* 2
- *Persistence:* 2

Toxicology: mg/kg
- *Permissible Exposure:* None established
- *Dangerous Exposure:*

Aquatic Toxicity Rating:

Remarks:
ALTERNATIVE

Name of Compound:	**1-Heptanol**
Synonyms:	Heptyl alcohol
CAS Number:	111-70-6
Reg. Toxic Number:	MK0350000
Chemical Formula:	$C_7H_{16}O$
General Description:	Colorless liquid, fragrant odor
Solubility (water):	0.1 (g/100 mL)
Freezing Point:	-34°C
Specific Gravity:	0.82

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	1
Persistence:	0

Toxicology: mg/kg

Permissible Exposure:	None established
Dangerous Exposure:	

Aquatic Toxicity Rating:

Remarks:

ALTERNATIVE

Name of Compound:	**p-Cymene**
Synonyms:	p-isopropyltoluene
CAS Number:	99-87-6
Reg. Toxic Number:	GZ5950000
Chemical Formula:	$C_{10}H_{14}$
General Description:	Colorless liquid
Solubility (water):	Insoluble
Freezing Point:	-68°C
Specific Gravity:	0.86

CERCLA Hazard Ratings:

Toxicity:	2
Ignitability:	2
Persistence:	2

Toxicology: mg/kg

Permissible Exposure:	None established
Dangerous Exposure:	

Aquatic Toxicity Rating: 0

Remarks:

ALTERNATIVE

CONCLUSIONS

Past practice of employing fuel (DF-A, kerosene or JP-4) and a heavy chlorinated solvent to increase density (specific gravity) from about 0.85 to 0.92 seems to violate toxicity requirements, particularly the use of PCE and TCE. Also, PCE and TCE have slight water solubilities (ca. 1.5%).

The use of LVT-200 appears to be an acceptable fluid. However, Bromoil should be used with some caution because of its unknown low temperature properties (p. 8). Because of its unknown toxic factors and general structural resemblance, it may resemble the avochlors (PCB's) and brominated benzenes. The petroleum solvent appears to be a mix of number 1 and 2 fuel oils. Benzene content is unknown. LVT-200 is essentially free of these potentially offending components.

Ethyl acetate is a recommended alternative (p. 11), but its solubility and flammability are high. However, other esters such as propyl propionate (p. 12) have specific gravities at +20°C that are close to 0.9, are essentially insoluble, and their higher molecular weight may lower the ignition point. Other possibilities are amyl or butyl acetate, etc. These types of compounds at lower temperatures may have the required density without having to resort to halogenated additives. They are also biodegradable. It is recommended that further studies be made of the alcohol portion (not the acid) of the C_{3-5} esters.