

Hole fluids for deep ice core drilling

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Abstract: This paper is based on the data published in research report of P.G. Talalay and N.S. Gundestrup; Hole fluids for deep ice core drilling: A review. Copenhagen University, Copenhagen, 1999, 120 p. In the practice of deep ice core drilling only three types of bore-hole fluids have been used: 1) petroleum oil products (fuels or solvents) containing densifier, 2) aqueous ethylene glycol or ethanol solutions, 3) *n*-butyl acetate.

The main parameters of drilling fluids are 1) density and fluid top; 2) viscosity; 3) frost-resistance; 4) stability; 5) compatibility with polymers and metals; 6) volatility; 7) flammability; 8) ice and water solubility; 9) toxicological and environmental characteristics; 10) cost. The main properties of bore-hole fluids which have been used in practice for deep ice drilling as well as potential bore-hole fluids are described.

The analyzing of the property's data showed that there are no ideal drilling fluids. All types of used and potential drilling fluids have their own advantages and disadvantages.

Probably one of the most promising types of drilling fluid is low-temperature silicone oil. It is non-aggressive, inert, and non-toxic. The main problem of silicone oil use is the relatively high viscosity at negative temperatures that have influence on the travel time of the drill string and finally on the total time drilling.

The final choice of the drilling fluid depends on the possibilities and the ways of solving of indicating problems and depends on the rational correlation between the cost of drilling fluid and other properties of the fluid.

1. Introduction

The contemporary stage of ice core drilling began about 1950. The first experience of deep drilling showed significant hole closure in an open hole, and to prevent the hole closure, bore-hole are usually filled with a fluid. Fluids used in rock drilling have freezing points about 0°C and, therefore, they are not suitable for ice drilling.

For the first time drilling in ice with fluid was made by USA CRREL at Camp Century in 1966 and then at Byrd Station in 1967–1968 (Ueda and Garfield, 1969). The lower part of the bore-holes was filled with aqueous ethylene glycol solution and the upper part was filled by a mixture of diesel fuel of arctic blend DF-A with a densifier (trichloroethylene).

During more than thirty years after this event not many deep bore-holes in ice were drilled. The unfortunate choice of the type and of the parameters of fluid often caused

most of the accidents such as sticking of the drill. Therefore, the choice of the fluid appropriate for the drilling conditions is considered to be one of the most important parts of ice drilling technology.

In the practice of deep ice core drilling only three types of bore-hole fluids have been used: petroleum oil products (fuels or solvents) containing densifier, aqueous ethylene glycol or ethanol solutions, *n*-butyl acetate (Fig. 1). Probably, one of the most promising drilling fluids is silicone oil.

The main parameters of fluids used for deep ice core drilling as well as potential bore-hole fluids are collected in the report of the Copenhagen University (Talalay and Gundestrup, 1999) and generalized in the Table 1.

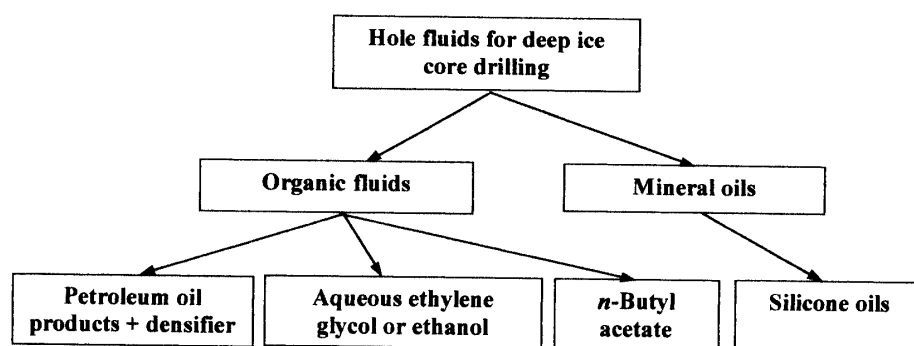


Fig. 1. Types of hole fluids for deep ice core drilling.

Table 1. Main parameters of fluids for deep ice core drilling.

Parameters	Cause and effect
Density and fluid level	Bore-hole closure \Rightarrow Drill sticking
Viscosity	Drill's lowering/hoisting rate \Rightarrow Total time of drilling \Rightarrow Cost of drilling project
Frost-resistance	Fluid freezing during storage and in the bore-hole
Stability	Changing of fluid properties during storage, transportation and use in bore-hole
Compatibility with polymers and metals	Destroying of cable and drill components
Volatility and flammability	1) Cleanness of the working place, clothes, ice core 2) Vapors problems with respect to human health and fire safety
Ice and water solubility	Ice dissolving from bore-hole walls \Rightarrow Forming of ice chips plugs in bore-hole
Toxicity	Health safety of drillers, scientists, technicians, and support personnel
Environmental characteristics	Environment contamination
Cost	Cost of drilling project

2. Density

For deep ice core drilling the petroleum oil products of the kerosene type are used mainly (Table 2). Kerosenes are composed chiefly of paraffins and naphthenes; naphthenes have very low freezing point and, therefore, impart good low-temperature properties to the kerosenes.

Table 2. *Petroleum oil products.*
(Diemand, 1991; Litvinenko et al., 1996; Talalay and Gundestrup, 1999; Producer's data)

Name	Application	Density at temperature, kg/m ³		
		Specification	Tests	
		15 °C	-30 °C	-50 °C
DF-A	Diesel fuel	770 - 840	837	850
Jet A-1	Turbine fuel	775 - 840	846	859
JP-8	Turbine fuel	775 - 830	841	856
TS-1	Aircraft fuel	776 - 786	833	848
Exxol D30	Solvent	758	788	803
Exxol D40	Solvent	771	800	812
Exxol D60	Solvent	758	822	836

Low-temperature fuels DF-A, Jet A1, JP-8, TS-1 are usually used for ice deep drilling and are all kerosenes and virtually indistinguishable. Other kinds of oil products suitable for deep ice drilling are petroleum solvents intended for cleaning. Solvents of Exxol family differ from fuels by the hydrocarbon composition. The concentration of aromatics in this kind of solvents is less than 0.5% (in fuels of kerosene type near 20%).

For the compensation of ice-overburden pressure the density of drilling fluid should be approximately equal or little higher than the density of ice. For most of organic liquids the density can be approximated with linear equation and may be defined by Mendeleeff's formula:

$$\rho_{fl}^t(z) = a_t(t - t_0) + \rho_0, \quad (1)$$

or

$$\rho_{fl}^t(z) = a_t t + b, \quad (2)$$

where ρ_0 is the density of the fluid at temperature t_0 ; a_t is the thermal coefficient, kg/(m³·°C); b is the density of fluid at 0°C.

Hydrocarbons of the kerosene type, mostly used as a drilling fluid, have a density of about 800–850 kg/m³ at –30°C compared to 920 kg/m³ for ice (Fig. 2).

Therefore, they are usually made denser by the addition of various densifiers of halogenated hydrocarbon or fluorocarbon types. The process here is illustrated by scheme presented in Fig. 3. Organic densifiers, which are used for blending with petroleum fuels and solvents, are listed in Table 3.

Density-temperature relations of densifiers HCFC 123 and HCFC 141b obtained as a result of experiments are linear (Fig. 4).

Density of mixture for compounds that are not in chemical or physical reaction may be calculated theoretically using densities of the compounds:

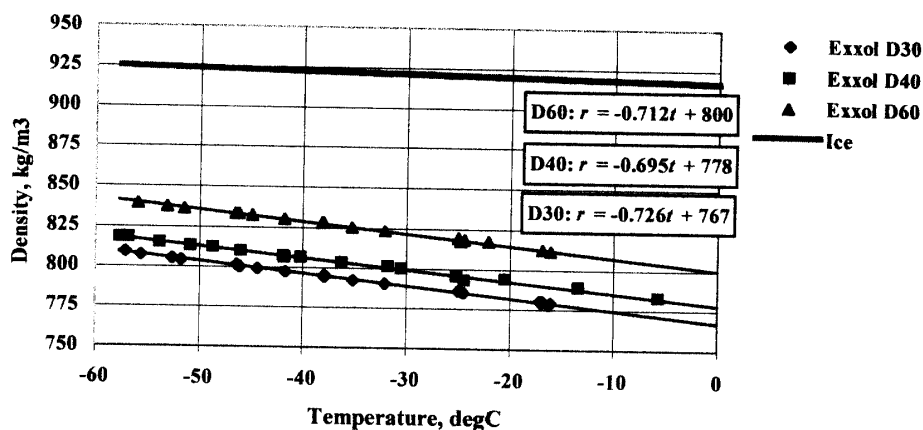


Fig. 2. Density of Solvents Exxol D30, D40, D60 versus temperature.

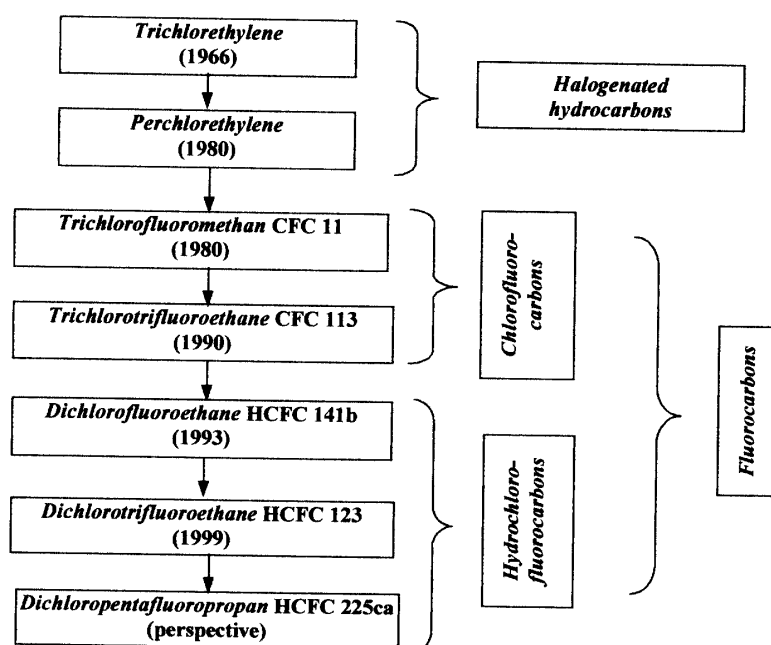


Fig. 3. Densifiers for deep ice core drilling (in brackets: the year of first use).

$$\rho_{fl} = (1 - 0.01 C_V) \rho_1 + 0.01 C_V \rho_2, \quad (3)$$

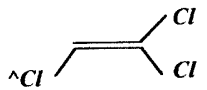
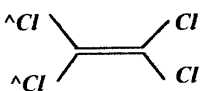
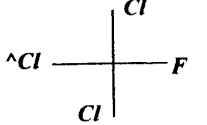
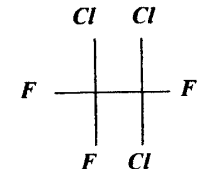
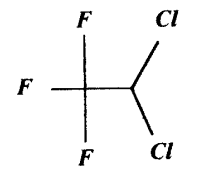
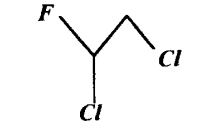
or

$$\rho_{fl} = \frac{\rho_1}{1 - \frac{C_M(\rho_2 - \rho_1)}{100\rho_2}}, \quad (4)$$

where ρ_1 and ρ_2 are the density of the base fluid and the densifier respectively, kg/m^3 ; C_V and C_M are the volume and mass concentration of densifier respectively, %.

For mixtures of Exxol solvents with densifiers HCFC 123 and HCFC 141b density was calculated using the theoretical method, and then the density of these mixtures was measured. Results were compared (Table 4). Experimental and theoretical equations are in good agreement: the difference between measured and calculated densities isn't more

Table 3. Organic compounds-densifiers.
(Handbook of Chemistry and Physics, 1976; Industrial Solvents Handbook, 1991;
Names, Synonyms, and Structures of Organic Compounds, 1995)

Name	Density, kg/m ³	Synonyms	Formula index	Structure	General description
Halogenated hydrocarbons					
Trichlorethylene	1464*	Trichlorethene; Chlorylen; Narcogen; Trieline	C_2HCl_3		Colorless, clear liquid with characteristic sweet odor of chloroform
Perchlorethylene	1625*	Tetrachloroethene; Didiakene; Perclene; Tetropil	C_2Cl_4		Clear, water-white liquid, ether chloroform odor
Fluorocarbons					
Trichloro-fluoromethane	1487*	CFC 11; FC11; FREON 11; F 11; FRIGEN 11; REFRIGERANT R11; GENESOLV A	CCl_3F		Clear, colorless liquid, faint ethereal odor
Trichloro-trifluoroethane	1570**	CFC 113; FC 113; FREON 113; F 113; FREON TF; FORANE 113; FLUGENE 113; ALKONE P; REFRIGERANT R113; GENESOLV D	$C_2Cl_3F_3$		Colorless liquid, ether odor
Dichloro-trifluoroethane	1480*	HCFC 123; FC 123; FREON 123; F123; SOLKANE 123; REFRIGERANT R123	$C_2HCl_2F_3$		Colorless liquid
Dichloro-fluoroethane	1240*	HCFC 141b, FC 141b; FREON F141b; SOLKANE 141b; FORANE 141b	$C_2H_3Cl_2F$		Colorless liquid, faintly ethereal odor
Dichloro-pentafluoro-propan	1543**	HCFC 225ca; R225	$C_3HCl_2F_5$	-	Clear liquid with a slight ethereal and alcoholic odor

*at temperature 20 °C, **at temperature 25 °C

than 0.3%.

Two types of aqueous alcohol solutions have been used in deep ice drilling (Table 5): ethylene glycol solution (Ueda and Garfield, 1969) and ethanol solution (Zagorodnov *et al.*, 1994). Density of aqueous ethylene glycol solutions increases with alcohol concentration growth from 1056 kg/m³ at mass concentration 40% to 1105 kg/m³ at 80% (temperature 10°C; Industrial Solvents Handbook, 1991). Density of aqueous ethanol solutions

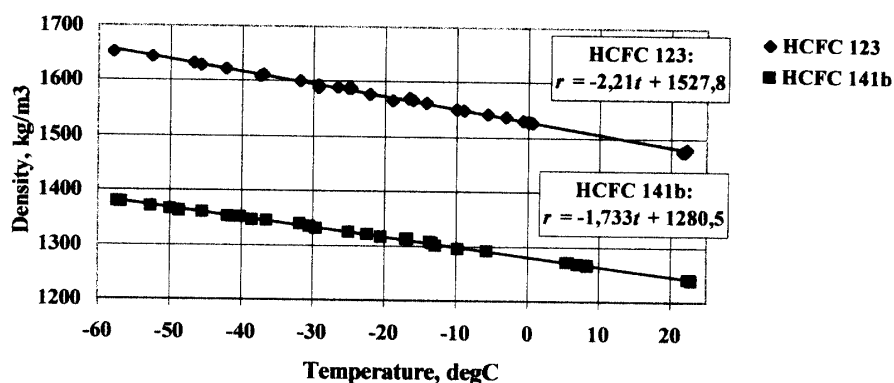


Fig. 4. Density of densifiers HCFC 123 and HCFC 141b versus temperature.

Table 4. Experimental and theoretical density-temperature equations for mixtures of solvents. Exxol D60 and D30 with densifiers HCFC 141b and HCFC 123.

Compounds		Tests		Theoretical method		Maximal difference, %
Base fluid	Densifier (mass concentration)	Experimental equations	Density, kg/m ³	Theoretical equations	Density, kg/m ³	
Exxol D60	HCFC 141b (C _M =31,7 %)	$\rho_T = -0,896t + 905,8$	932,7 ¹	$\rho_T = -0,899t + 908,0$	935,0 ¹	0,24*
Exxol D60	HCFC 123 (C _M =25,0 %)	$\rho_T = -0,878t + 906,1$	932,5 ¹	$\rho_T = -0,881t + 908,6$	935,0 ¹	0,27*
Exxol D30	HCFC 141b (C _M =34,2 %)	$\rho_T = -0,873t + 890,6$	934,3 ²	$\rho_T = -0,923t + 888,8$	935,0 ²	0,20**
Exxol D30	HCFC 123 (C _M =27,6 %)	$\rho_T = -0,921t + 888,3$	934,4 ²	$\rho_T = -0,911t + 899,4$	935,0 ²	0,12**

¹at temperature -30 °C; ²at temperature -50 °C

* in the temperature range from -30 to 0 °C; ** in the temperature range from -50 to 0 °C

Table 5. Alcohols and esters. (Industrial Solvents Handbook, 1991; Names, Synonyms, and Structures of Organic Compounds, 1995)

Name	Density*, kg/m ³	Synonyms	Formula index	Structure	General description
Ethylene glycol	1115	Glycol, Glycol alcohol, Ethanediol	C ₂ H ₄ (OH) ₂		Colorless liquid with mild odor
Ethanol	789	Alcohol, Ethyl alcohol, Spirit, Tescol	C ₂ H ₅ OH		Colorless liquid with strong fragrant odor
n-Butyl acetate	882	Butyl acetate, 1-Butyl acetate, Butyl ethanoate, Acetic acid, Butyl ester	C ₆ H ₁₂ O ₂		Water-white liquid with a characteristic fruity odor
Anisole	995	Anisol, Methoxybenzene, Phenyl methyl ether	C ₇ H ₈ O		Yellow liquid with a sweet anise-like odor

*at room temperature

decreases with alcohol concentration growth from 935 kg/m³ at mass concentration 40% to 844 kg/m³ at 80% (temperature 20°C; Handbook of Chemistry and Physics, 1976).

In 1989, specialists at PICO, University of Alaska, conducted a chemical literature survey in an effort to identify ice drilling fluid with necessary viscosity and density characteristics (Gosink *et al.*, 1989). Nearly 250 thousand compounds were electronically surveyed, and 11 potential drilling fluids were identified (anisole, hexanol, heptanol, octanol, p-cymene, s-butyl benzene, pseudocumene, propyl, *n*-butyl acetate, amyl acetate and propyl propionate). Specialists at PICO considered that of these eleven, only *n*-butyl acetate and anisole fully meet the requirements (see Table 5).

Experiments carried out at Copenhagen University showed that density of *n*-butyl acetate is equal to the ice density at -19°C (Fig. 5). As a result of these measurements a linear density-temperature relation of *n*-butyl acetate was obtained as opposed to the of parabolic relation used by PICO, University of Alaska (Gosink *et al.*, 1991).

Silicone oils (Table 6) are used in industry as hydraulic liquids and lubricants, and, at first, the suggestion to use silicone oil as drilling fluid was made by Japanese drillers, but they noticed that "it has a higher viscosity than the other candidates and it is expensive" (Fujita *et al.*, 1994). The density of silicone oil KF96-2.0 cs has a linear relationship with temperature and it is equal to the ice density at -27°C (see Fig. 5).

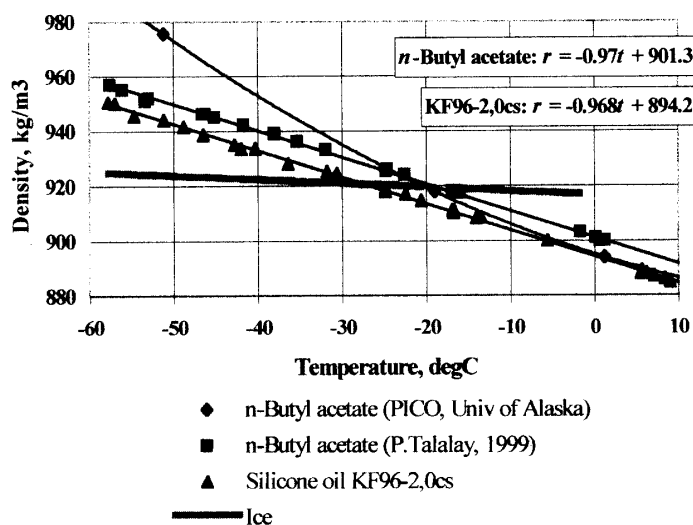


Fig. 5. Density of *n*-butyl acetate and silicon oil KF96-2.0 cs versus temperature.

Table 6. Silicone oils (dimethyl siloxane oils).

Name	Density*, kg/m ³	Synonyms	Formula index	General description
Decamethyl tetrasiloxane	850-855	KF96-1,5cs; PMS-1,5p	(CH ₃) ₁₀ Si ₄ O ₃	Clear water-white, tasteless, odorless and neutral liquid
Dodecamethyl pentasiloxane	870-875	KF96-2,0cs; PMS-2,0p	(CH ₃) ₁₂ Si ₅ O ₄	The same

*at room temperature

3. Viscosity

Ice core drilling technology includes the pulling up of the drill after each run for core and chips recovery. The time of lowering/hoisting operations takes from 50 to 90% of the total time of drilling (Vasiliev and Kudryashov, 1993). Therefore, increasing the drill's lowering/hoisting rate is very important for the ice production rate and to the overall cost of the drilling project.

The free drill's lowering rate depends on parameters of the drill (mass, length, diameter), bore-hole diameter and parameters of the fluid (viscosity and density). The main factors that determine the free drill's rate and finally the total time of drilling are the fluid viscosity and the clearance between drill and bore-hole walls (Onishin *et al.*, 1990).

There are two alternative ways for the achievement of the optimal drill's lowering rate. Either a low-viscosity fluid must be used, or bore-holes with larger clearance between drill and bore-hole walls must be drilled. Main disadvantages of larger diameter drilling are more expenditure time of penetration, increased cuttings or melted water and more energy consumption. Thus, low viscosity (less than 5–10 cSt; Talalay and Gundestrup, 1999) is one of the essential requirements for the drilling fluids.

The standard viscosity of fluids is presented in Table 7. The viscosity of fluids usually decreases with temperature and increases with pressure. The dynamic viscosity η (cP) and the cinematic viscosity ν (cSt) of most organic liquids versus temperature t_K (K) can be estimated according to (Dubovkin *et al.*, 1985):

$$\lg \lg(\eta + 1) = \frac{A}{t_K} - B, \quad (5)$$

and

$$\lg \lg(\nu + 1) = \frac{C}{t_K} - D, \quad (6)$$

where A , B , C and D are empirical coefficients.

Empirical coefficients shown in Table 7 are based on the experimental data and cover a wide temperature range to enable the determination of fluid viscosity at any desired temperatures in the bore-hole. For a few liquids the approximation with eqs. (5) or (6) gives a significant errors. In these cases viscosity-temperature equations of another type are used.

The estimation of the exact viscosity of drilling fluid under the high pressure in the bore-hole is very difficult because of the limited theoretical and experimental data available. The approximate calculations showed that the viscosity of Exxol type D solvents increases at near 25% under a pressure of 30 MPa (Talalay and Gundestrup, 1999).

The prediction of mixture viscosity due to viscosity of compounds is unreliable. Therefore, it is necessary to test viscosity of two-compound fluid at each discrete concentration of densifier (Table 8).

The viscosity of densifiers-chlorofluorocarbons and ethylene hydrocarbons-at negative temperatures is very low (less than 1–1.5 cSt). In mixtures with petroleum liquid densifiers decrease in the total viscosity is significant. This consideration was confirmed by experiments carried out in Copenhagen University (Figs. 6 and 7).

Table 7. Viscosity of drilling fluids under atmospheric pressure.
(Handbook of Chemistry and Physics, 1976; Bogdanov et al., 1976; Promyshlennyye hlororganicheskiye soedineniya, 1978; Dubovkin et al., 1985; Diemand, 1991; Talalay and Gundestrup, 1999; Producer's data)

Fluid	Standard viscosity		Empirical coefficients					
	Dynamic viscosity, cP	Kinematic viscosity, cSt	A	B	C	D	Temperature range, °C	
							min	max
Hydrocarbons								
Fuel DF-A	-	1,1-2,4 at 40 °C	-	-	403,2	1,74	-41	19
Fuel TS-1	-	1,27-1,48 at 20 °C	-	-	387,2	1,75	-60	20
Fuel Jet A-1	-	4,3 at -20 °C	-	-	408,6	1,75	-40	20
Exxol D60	1,29 at 25 °C	-	-	-	415,3	1,83	-55	25
Exxol D40	0,96 at 25 °C	-	-	-	379,6	1,80	-55	25
Exxol D30	0,75 at 25 °C	-	-	-	340,5	1,71	-55	25
Densifiers – ethylene hydrocarbons								
Trichlorethylene	0,58 at 20 °C	-	-	-	260,0	1,72	-60	20
Perchlorethylene	0,88 at 20 °C	-	-	-	266,3	1,63	-20	20
Densifiers - chlorofluorocarbons								
CFC 11	0,444 at 20 °C	-	312,6	1,87	-	-	-40	0
CFC 113	0,65 at 25 °C	-	-	-	-	-	-	-
HCFC 123	0,45 at 25 °C	-	$\lg \nu = \frac{316,1}{t_K} - 1,5$				-45	25
HCFC 141b	0,416 at 25 °C	-	216,6	1,54	-	-	-80	20
HCFC 225ca	0,59 at 25 °C	-	270,5	1,41	-	-	-65	-22
Alcohols and ethers								
Ethylene glycol	19,9 at 20 °C	-	-	-	516,2	1,65	-10	40
Ethanol	1,2 at 20 °C	-	$\lg(\eta + 1) = \frac{589,1}{t_K} - 1,75$				-98	0
n-Butyl acetate	0,732 at 20 °C	-	363,5	1,87	-	-	-47	20
Anisole	1,32 at 20 °C	-	287,2	1,47	-	-	0	40
Silicone oils								
KF96-1,5cs	-	1,53 at 25 °C	$\lg \nu = \frac{785,6}{t_K} - 2,51$				-58	-10
KF96-2,0cs	-	2,07 at 25 °C	$\lg \nu = \frac{582,2}{t_K} - 1,65$				-51	25

Table 8. Viscosity of mixtures under atmospheric pressure.

Base fluid	Densifier		Empirical coefficients			
	Name	Mass concentration, %	C	D	Temperature range, °C	
					min	max
Exxol D60	HCFC 141b	31,7	333,4	1,60	-44	25
Exxol D60	HCHC 123	25,0	331,7	1,56	-45	23
Exxol D30	HCFC 141b	34,2	284,2	1,53	-48	23
Exxol D30	HCFC 123	27,6	283,4	1,51	-47	24

Viscosity of *n*-butyl acetate is low: 1.41 cSt at -20°C and 2.88 cSt at -50°C (Gosink et al., 1991).

One of the main causes that kept back the use of aqueous solutions of ethylene glycol and ethanol is their very high viscosity at low temperatures. For example, at a temperature

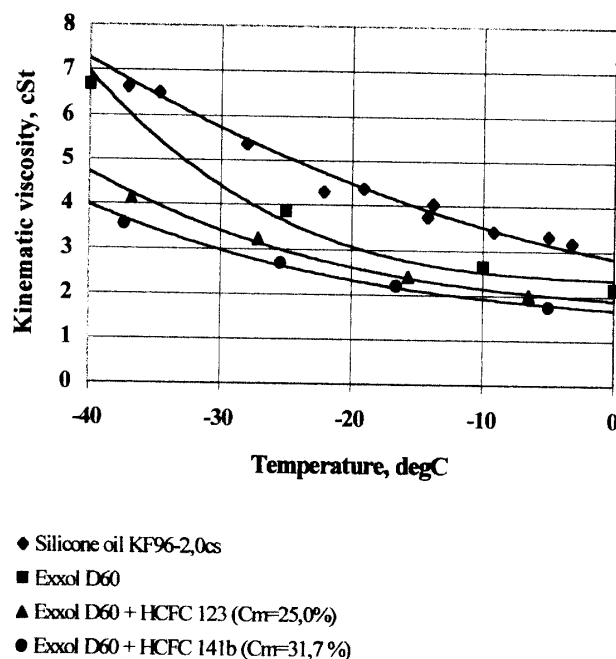


Fig. 6. Viscosity of potential drilling fluids for Central Greenland.

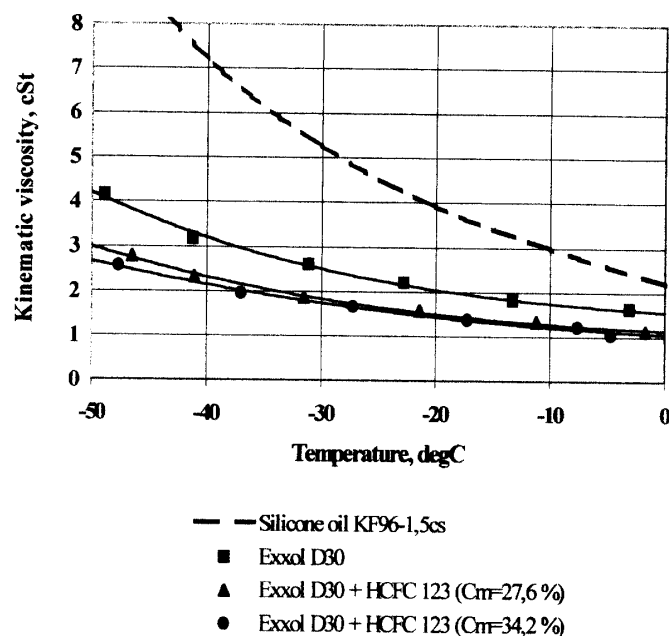


Fig. 7. Viscosity of potential drilling fluids for Central Antarctica.

of -30°C the dynamic viscosity of aqueous ethanol solutions rises to 18.1 cP at mass concentration of ethanol 70% and to 46 cP at concentration of 50% (Industrial Solvents Handbook, 1991). Therefore, Zagorodnov *et al.* (1994) suggest drilling bore-holes filled by aqueous ethanol solution with a larger clearance (10–12 mm) between drill and bore-hole walls.

The same problems were noted in deep ice drilling with aqueous ethylene glycol solution (Hansen, 1976). It is impossible to use aqueous ethylene glycol solution at low temperature (less than -30°C) because the fluid is too viscous.

Silicone oils of the KF96 series have the lowest variation in viscosity with temperature among all types of silicon oils, mineral oils and synthetic fluids. The viscosity of silicone oils KF96-1.5 cs and 2.0 cs is less than the viscosity of aqueous solutions of ethylene glycol and ethanol but it is rather high too (viscosity of KF96-1.5 cs is 10 cSt at -50°C , and viscosity of KF96-2.0 cs is 5.6 cSt at -30°C).

The mixtures of petroleum products of kerosene type with densifiers, as well as, *n*-butyl acetate have the most suitable viscosity for deep ice drilling.

4. Frost-resistance

Frost-resistance (Table 9) is one of the main technological characteristics of drilling fluid used at negative temperatures. The freezing point of the fluid should be higher not only than the minimal temperature in bore-hole but also the temperature of the air outside the drilling shelter (where the fluid is usually stored). This is important especially for drilling sites in Central Antarctica (for example, the average annual temperature at Vostok Station is -57°C and the absolute temperature minimum is -89.2°C).

Table 9. Frost-resistance of drilling fluids at standard atmospheric pressure. (Handbook of Chemistry and Physics, 1976; Dubovkin et al., 1985; Diemand, 1991; Industrial Solvents Handbook, 1991; Producer's data)

Fluid	Pour point, $^{\circ}\text{C}$	Freezing point, $^{\circ}\text{C}$
Hydrocarbons		
Fuel DF-A	-57	-51*
Fuel Jet A1	-51	-47
Fuel JP-8	-54	-46
Fuel TS-1	-	-60
Exxol D60	-	-57
Exxol D40	-	<-55
Exxol D30	-	<-55
Densifiers – halogenated hydrocarbons		
Trichlorethylene	-	-86,4
Perchlorethylene	-	-22,3
Densifiers - fluorocarbons		
CFC 11	-	-111
CFC 113	-	-35
HCFC 123	-	-107
HCFC 141b	-	-103,5
HCFC 225ca	-	-131
Other organic liquids		
Ethylene glycol	-	-12,6
Ethanol	-	-114,1
<i>n</i> -Butyl acetate	-	-78
Anisole	-	-37,4
Silicone oils		
KF96-1,5cs	-76	-
KF96-2,0cs	-84	-

*Cloud point

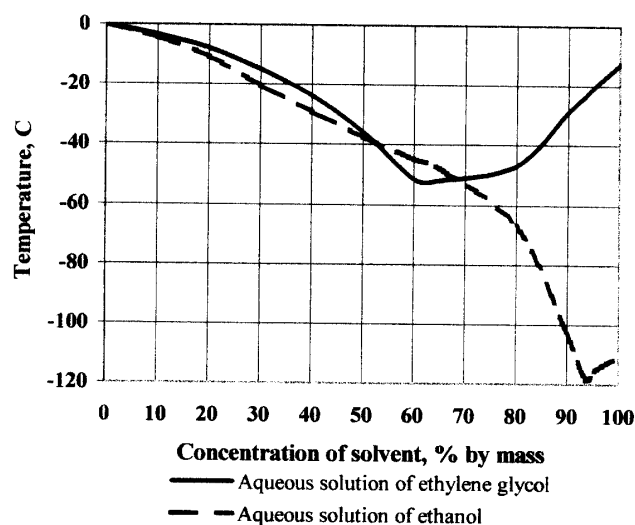


Fig. 8. Freezing point of alcohol aqueous solutions.

To estimate the freezing point of the mixture due to freezing points of the components is rather a difficult task. But, it is well known that the freezing point of a two-compound fluid usually is between freezing points of components. For example:

- freezing point of mixture of Jet A1 (freezing point -47°C) with 10.3% perchlorethylene (freezing point -22.3°C) is below -40°C (Gundestrup *et al.*, 1984);
- freezing point of mixture of *n*-butyl acetate (freezing point -78°C) with 10% of anisole (freezing point -37.4°C) is below -49°C (Gosink *et al.*, 1989).

The freezing point of aqueous solutions of ethylene glycol and ethanol depends on the concentration of the solvent (Fig. 8). At first, the freezing point of aqueous solutions of ethylene glycol and ethanol decreases with concentration of solvent and then has a minimum. Then the freezing point increases.

5. Stability

Stability is the property of a drilling fluid not to change properties during storage, transportation and use in bore-hole.

Some types of hydrocarbons containing petroleum products are able to react with air (oxygen) and metals to form resinous or solid sediments. This process is more active during abrupt changes in temperature. In general, stability of petroleum products depends on their composition. The turbine fuels that are produced by the direct distillation from crude oil are more stable than products containing cracking-compounds.

In the tanks with volume 25–30 m³ the resin content in fuel TS-1 achieves a standard maximal level after 5 years of storage. In tanks of smaller volume the products of oxidation are formed more quickly (Dubovkin *et al.*, 1985).

Stability of homogeneous liquids is very high under specified conditions. But the fluid stored in a opened or partially filled tanks causes water containing in air to dissolve and changes the fluid properties. Therefore, storage tanks should be kept full and hermetically sealed when not in use.

Stability of drilling fluids in the bore-hole has not been sufficiently tested. Most of

the drilling fluids for ice core drilling consist of two or more components. Stability of a two-compound mixture of petroleum product with fluorocarbon densifier can be estimated as an example of a two-compound mixture of fuel TS-1 with densifier CFC 11. Analyses of density measurements in the deep bore-hole 3 G at Vostok station (2202 m) shows that after long standing the densifier isn't precipitated to the bottom of the bore-hole (Menshikov and Talalay, 1993).

Hydrophilic liquids in a bore-hole are not stable because they are characterized by spontaneous dissolving of the ice bore-hole walls. This causes a decreasing of the solvent concentration and the formation of slush in the bore-hole. Bore-holes in Antarctica filled by aqueous solutions of ethylene glycol and ethanol were plugged by slush soon after the drilling.

6. Compatibility of drilling fluids with elastomers, plastics and other materials

Drilling fluid should be non-aggressive to the drill and cable components. One of the main problems is to choose material for gaskets and electrical insulation (lacquer on wire, plastic jacket of wire, insulation of electrical sockets, etc.) that won't swell, soften or become tacky in fluid.

Aromatics contained in petroleum products tend to cause swelling and degradation of certain rubber materials (NR, IR, SBR, BR, EPDM). However, there is a wide range of materials for seals and O-rings, which can operate in various petroleum fuels and other liquids of the kerosene type. O-ring and seals composed of nitriles, fluorocarbons and fluorosilicones (for example, NBR, ECO, MFQ, ACM) are commercially available for most of applications and are commonly designed for use down to at least -40°C (Diemand, 1991). Nitrile rubber (NBR) is probably the most common compound used in seals because of its good resistance to petroleum oils and its wide temperature range.

Densifiers—trichlorethylene and perchlorethylene are very aggressive solvents and they have various effects on the most elastomers and plastics. Fluororubber (FPM) is the only elastomer that can operate in these liquids for a long time.

Densifiers—fluorocarbons cause swelling or dissolving of most types of elastomers and plastics (Industrial Solvents Handbook, 1991). Problems can be experienced with natural rubber (NR), ethylene propylene rubber (EPDM), silicon rubber (Q), polystyrene (PS), polymethyl methacrylate (PMMA) and other polymers (Table 10).

Drilling fluids—alcohols (ethylene glycol and ethanol) have no effect on most elastomers. *n*-Butyl acetate is very aggressive solvent. There are no elastomers that are able to operate in *n*-butyl acetate for a long time. Even, butyl rubber (IIR) and ethylene propylene rubber (EPDM) are slightly destroyed in *n*-butyl acetate; and IIR cannot be used at low temperatures (Gundestrup *et al.*, 1994).

Gosink *et al.* (1991) considered that *n*-butyl acetate has no effect on the various materials employed in the PICO deep drill string. However, during drilling at Summit (GISP2 Project) it was necessary to abandon the cable after three seasons in the field because the proprietary lubricant on the Kevlar cable washed out and unlubricated cross-woven Kevlar fibers appear to cut each other after many trips over a sheave (Gosink *et al.*, 1994).

Silicone oils are compatible with the most plastics and elastomers. But the low-

Table 10. Changes (% of diameter enlarging) in O-ring gaskets after immersion in drilling fluids during 24 hrs at temperature of 25°C. (Gundestrup et al., 1994; Talalay and Gundestrup, 1999)

Fluid	EPDM	NBR
Exxol D80	34	1
CFC 113	17	3
HCFC 123	16	33
HCFC 141b	14	20
<i>n</i>-Butyl acetate	10	26
Silicone oil KF96-2,0cs*	0	0

*No visible changes during week

molecular silicone oils with viscosity less than 10 cSt can extract the plasticizers contained in some types of rubber and plastic, and cause weight and volume loss or smelling. Experiments carried out in Copenhagen University showed that there were no visible changes in O-rings gaskets (EPDM and NBR) after immersion in silicon oil KF96-2.0 cs during a week.

7. Volatility and flammability

The problem of volatility isn't simple. On the one hand, the high volatility of drilling fluid raises the human health and fire safety questions. For liquids with a high rate of vaporization it is necessary to organize careful control of air contamination and ensure the threshold limits in air and minimal inflammable concentration. From this point of view the use of fluid with a low rate of vaporization is preferably.

On the other hand, there are benefits of the high volatility. The work place and clothes became clean after a short time, and the ice core is easy to handle.

Usually the rate of vaporization of liquids is estimated in relative units in comparison with vaporization of diethyl ether, *n*-butyl acetate, acetone and other chemicals (Table 11).

Oil products consist of compounds with a wide range of boiling points. Therefore, the boiling point given for fuels has a wide range too. Petroleum producers often specify "distillation volume" that is the temperature at which the certain part (10%, 50%, or 90%) of the oil products will boil off (Table 12). End point (or "dry point") is the temperature at which no liquid remains.

The lighter, more volatile compounds will boil off at the lower temperatures of the 10–50% levels, while the heavier ones will not boil until a much higher temperature. Thus, a lower temperature at any of the levels implies a lighter, more volatile oil products, while the spread between the 10% level and the end point reflects incidentally the relative amount that can be obtained from the parent crude oil. The vaporization rate of oil products isn't linear. The lighter compounds are evaporated faster than heavier ones.

The boiling point of kerosene type liquids used for ice core drilling is about 200°C and the rate of vaporization is low (for example, the vaporization rate of solvent Exxol D60 is in 25 times lower than the rate of *n*-butyl acetate). Solvents of the Exxol D type have more homogeneous composition and the difference of distillation volumes (20–40°C) is narrower than fuels (80–150°C).

In order to compare the vaporization rate of drilling fluids, they were tested at room

Table 11. Volatility and flammable properties of drilling fluids.
(Handbook on Chemistry and Physics, 1994; Lewis, 1996; Producer's data)

Fluid	Vapor pressure at temperature, kPa	Specific density of vapors (air = 1)	Boiling point, °C	Flash point, °C	Relative rate of vaporization
Oil hydrocarbons					
Diesel fuel DF-A	0,6 @ 38 °C	-	-	38	-
Kerosene	-	4,5	175 - 325	65 - 85	-
Fuel Jet A1	1,4 @ 38 °C	-	205 - 290	38	-
Fuel JP-8	1,4 @ 38 °C	-	205 - 290	46	-
Fuel TS-1	-	-	-	28	-
Exxol D60	0,1 @ 20 °C 0,2 @ 38 °C 0,4 @ 50 °C	>1	190 - 221	62	4 (n-BuAc = 100)
Exxol D40	-	>1	145 - 200	40	14 (n-BuAc = 100)
Exxol D30	-	>1	130 - 166	28	44 (n-BuAc = 100)
Densifiers					
Trichlorethylene	0,6 @ -20 °C 1,2 @ -9 °C 2,3 @ 0 °C 7,5 @ 20 °C	4,53	86,7	Non-flammable	40 (ether = 100)
Perchlorethylene	0,6 @ 0 °C 1,9 @ 20 °C 2,5 @ 25 °C	5,83	121,2	Non-flammable	9 (ether = 100) 280 (n-BuAc = 100)
CFC 11	88,2 @ 20 °C 107 @ 25 °C	4,7	23,7	Non-flammable	160 (acetone = 100)
CFC 113	37,8 @ 20 °C 44 @ 25 °C	6,2	47,7	Non-flammable	123 (ether = 100)
HCFC 123	76,3 @ 20 °C 91,4 @ 25 °C	5,3	27,1	Non-flammable	-
HCFC 141b	64 @ 20 °C 81 @ 25 °C	-	32,1	Non-flammable	-
HCFC 225	21,6 @ -10 °C 26,7 @ 0 °C 33,5 @ 10 °C 43,0 @ 20 °C	-	54	Non-flammable	90 (ether = 100)
Other liquids					
Ethylene glycol	0,008 @ 20 °C 0,016 @ 25 °C	2,14	197,5	111	-
Ethanol	5,9 @ 20 °C 7,9 @ 25 °C	1,59	78,3	12	-
n-Butyl acetate	1,2 @ 20 °C 2,0 @ 25 °C	4,0	126,5	22	-
Anisole	0,4 @ 25 °C 1,3 @ 42 °C	-	153,8	52	-
Silicone oil KF96-1,5cs	-	-	194	50	-
Silicone oil KF96-2,0cs	-	-	229	75	-

temperature in University of Copenhagen (Fig. 9). Samples of liquids (10 ml) were poured out into cylindrical glass with inner diameter 56 mm and the mass-loss of the samples was periodically measured with accuracy 0.1 g. For comparison one of the tested liquid was water.

Densifiers—fluorocarbons (HCFC 123 and HCFC 141b) evaporate very fast. The vaporization rate of HCFC 123 is approximately in 1.5 time higher than the rate of HCFC

Table 12. Distillation volume of low-temperature fuels solvents of Exxol type.
(Deimand, 1991; Producer's data)

Fuel or solvent	Distillation volume, °C			End point, °C
	10 %	50 %	90 %	
DF-A	-	-	288	330,3
Jet A1	190,2	212	250	266,3
JP-8	190,2	212	250	266,3
Exxol D60	-	-	209	215
Exxol D40	-	169	-	188
Exxol D30	-	150	-	164

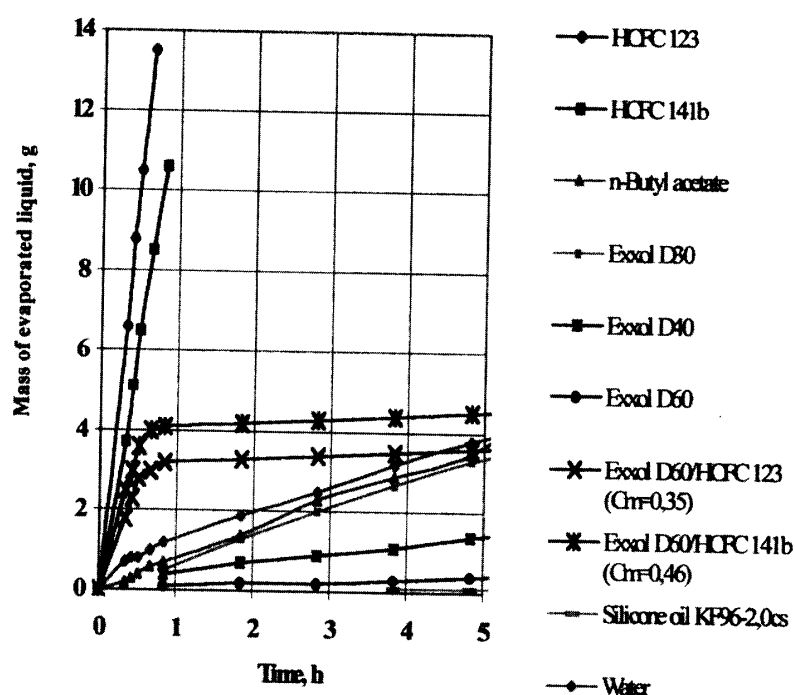


Fig. 9. Vaporization rate of potential drilling fluids and compounds.

141b.

Two tested mixtures of Exxol D60 with densifiers HCFC 123 and HCFC 141b have the same density (920 kg/m^3 at 22°C). At the beginning mixtures evaporate very fast but in both cases the vaporization rate is lower than the rate of pure densifiers. Mixture of Exxol D60/HCFC 141b evaporates faster than mixture of Exxol D60/HCFC 123 because the mass concentration of densifier in the first mixture (45%) is higher than second one (35%). The fast vaporization rises to the moment when the densifier completely evaporate from the mixture and then the vaporization rate is equal to the rate of pure Exxol D60.

The vaporization rates of *n*-butyl acetate and water at room temperature are very similar. At first, when the lighter compounds are evaporated from solvent Exxol D30, it has the same vaporization rate as *n*-butyl acetate, but the heavier compounds evaporated more slowly. Exxol D60 and silicon oil KF96-2.0 cs have the lowest rate of vaporization.

Most drilling fluids are dangerous with respect to fire hazard. The flash point of petroleum oil fluids depends on their chemical composition. The turbine fuel TS-1 and

solvent Exxol D30 contain more low-molecular-weight hydrocarbons and, therefore, have the low flash point (28°C).

The flash points of ethanol, ethanol-water solutions and *n*-butyl acetate are lower than flash points of petroleum drilling fluids and they should be used safely as a drilling fluid with respect to fire hazard.

8. Ice and water solubility

There are two polar opinions on the problem of ice and water solubility by drilling fluids. The first view is that drilling in ice is possible only with fluids that are inert to the ice (Litvinenko *et al.*, 1996), and the second view is that the drilling with active ice fluids is more advantageous (Zagorodnov *et al.*, 1994).

It is well known that active fluids dissolve ice or water formed after the destruction or melting of ice at the bottom of the bore-hole, as well, the ice from the bore-hole walls too. The process of dissolution rises to the equilibrium concentration of the aqueous solution. If the thermodynamic conditions in the bore-hole are changed the aqueous solution refreeze forming slush in the bore-hole.

Hydrophobic liquids (oil hydrocarbons, fluorocarbons—Table 13) are insoluble in water (maximal concentration is less than 1%) and completely inert to ice at negative temperatures: the ice samples don't lose weight during several days in contact with diesel fuel, fuel TS-1, solvents of Exxol D30 and D60, mixtures of petroleum liquids with densifiers—fluorocarbons (CFC 11, HCFC 123, HCFC 141b) (Pashkevich and Chistyakov, 1989; Gosink *et al.*, 1989; Talalay and Gundestrup, 1999).

The water content depends not only on chemical composition of the hydrophobic

Table 13. Water solubility of drilling fluids under atmospheric pressure.
(Handbook of Chemistry and Physics, 1976; Dubovkin *et al.*, 1985;
Industrial Solvents Handbook, 1991; Producer's data)

Fluid	Solubility of water in fluid, % by mass	Solubility of fluid in water, % by mass
Petroleum oil products		
Fuel TS-1	0,00865/at 20 °C	-
Exxol D60	-	<0,1/at 20 °C
Exxol D40	-	<0,1/at 20 °C
Exxol D30	-	<0,1/at 20 °C
Densifiers		
Trichlorethylene	0,02/at 25 °C	0,1/at 25 °C
Perchlorethylene	1,05/at 25 °C	1,5/at 25 °C
CFC 11	0,011/at 25 °C	0,011/at 25 °C
CFC 113	0,011/at 25 °C	0,017/at 25 °C
HCFC 123	-	0,39/at 25 °C
HCFC 141b	-	0,4/ at 20 °C
Other liquids		
Ethylene glycol		Miscible
Ethanol		Miscible
<i>n</i> -Butyl acetate	2,88/ at 25 °C	0,78/ at 25 °C
Anisole		Insoluble
Silicone oils of KF96 type		Insoluble

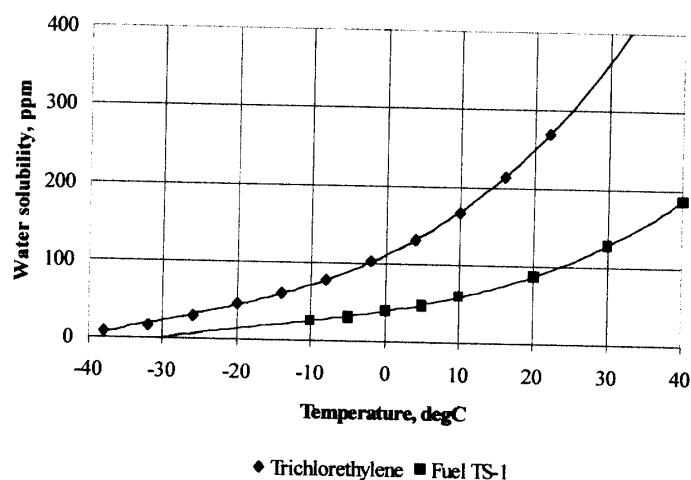


Fig. 10. Water solubility in hydrophobic liquids versus temperature at standard atmospheric pressure and relative humidity of 1.0.

liquid, but on the atmospheric conditions (temperature, pressure, and humidity). With temperature reduction water concentration decreases significantly (Fig. 10).

The maximal solubility in slightly soluble with water liquids (for example, perchlorethylene, *n*-butyl acetate) is 1–5%. These liquids slightly dissolve ice at negative temperatures: the process of dissolving is most intensive during the first few hours of contact, then the process is stabilized and finished, when the maximal water solubility is achieved at a given temperature (Gosink *et al.*, 1989).

Experiments carried out in Copenhagen University showed that a 30-g cube of ice lost 0.4 g of its weight in 110 g of cooling *n*-butyl acetate at temperature -15°C during 28 hours, and then the ice dissolving stopped. It means that water solubility of *n*-butyl acetate is about 0.35% at this temperature (Talalay and Gundestrup, 1999).

Hydrophilic liquids (ethanol and ethylene glycol) are mixed with water at any concentration and they are active to ice. These liquids dissolve ice up to the equilibrium concentration at given temperature. The equilibrium concentration of aqueous ethanol and ethylene glycol solutions is considered usually as the concentration of the solvent at the freezing point. Thus, the equilibrium concentration C_{eq} of ethanol solutions *versus* temperature t ($^{\circ}\text{C}$) is estimated in the limited range according to the linear relation (Zagorodnov *et al.*, 1994):

Table 14. The absolute rate of ice dissolving in hydrophilic liquids.
(Shamshev and Yokovlev, 1973; Gosink *et al.*, 1989; P.G. Talalay, unpublished)

Liquid	Concentration, % by mass	Temperature, $^{\circ}\text{C}$	Contact time, h	Rate of dissolving, g/h
Aqueous solution of ethylene glycol	11	-2,5	0,5	1,00
Aqueous solution of ethanol	8,5	-2,5	0,5	0,78
Ethanol	99,9	-19	2,0	7,60
Ethylene glycol	99	-11	1,75	12,5

$$C_{eq} = -0.01454t. \quad (7)$$

The rate of the ice weight loss in hydrophilic liquids and its aqueous solutions is very rapid and it depends on the temperature and on the concentration of the solution (Table 14).

9. Toxicological and environmental requirements

The choice of the non- or little toxic drilling fluid is one of the main requirements of toxicological and hazard control. Although the drilling sites may be outside of the national boundaries, employers should follow the standards and recommendations of the health safety for all types of workers employed as drillers, scientists, technicians, and support personnel.

There are many national regulations specified by different government agencies or recommendations by expert groups in USA, Germany, Denmark, Russia and other countries. Many countries and local administrative agencies throughout the world adopt the ACGIH TLVs (Threshold Limit Values of American Conference of Governmental Industrial Hygienists). As a result, these recommendations have a major effect on the control of workplace contaminant concentrations.

The recommended values of TLV are given in (ppm) or (mg/m³) usually. These units are connected with the following equation (Bespamyatnov and Krotov, 1985):

$$TLV(\text{ppm}) = \frac{22.4}{M} TLV(\text{mg/m}^3), \quad (8)$$

where M is the molecular weight of substance.

The workplace air contaminant TLVs listed at Table 15 shall be avoided, or protective equipment shall be provided and used. The permissible exposure is specified for a normal 8-hour workday, 40-hour workweek, to which nearly all workers may be exposed repeatedly without adverse effect. It is necessary to give some comments to toxic properties of *n*-butyl acetate and kerosenes.

Field-test results from the 1990 GISP-2 drilling season showed the following vapor concentration of *n*-butyl acetate in the drilling dome: sump under the drill vent 100–200

Table 15. *Threshold Limit Values (TLV) of vapor or gas in indoor air of working rooms at temperature 25°C and pressure 101325 Pa.*
(Patty's Industrial Hygiene and Toxicology, 1981;
Lewis, 1996; Producer's data)

Fluid	Workplace air levels, ppm (by vol.)
Solvents Exxol D30, D40, D60	100*
Trichlorethylene	50
Perchlorethylene	50
CFC 11	1000
CFC 113	1000
HCFC 141b	500
Ethylene Glycol	50
Ethanol	1000
<i>n</i> -Butyl acetate	150

* specification value of Exxon Chemical Denmark A/S (TLV for petroleum)

ppm; near carousel 40 ppm; rest of the dome < 10 ppm (Gosink *et al.*, 1991). We should mention that recommendations of *n*-butyl acetate exposure limit adopted in different countries are varied from 40 to 200 ppm (Nikitin and Ryabets, 1978):

- Russia, Hungary 40 ppm (200 mg/m³);
- Italy 120 ppm (600 mg/m³);
- USA, Finland, Sweden 150 ppm (710 mg/m³);
- Germany, Switzerland 200 ppm (950 mg/m³).

Personal communications of PICO drillers and Japanese drillers showed that after the workday in the drilling shelter workers felt damage of the central nervous system (dizziness, headaches).

The petroleum oil products are extremely complex mixtures of organic compounds (aromatics, naphthenes, olefins, and paraffins), contents of which are varied in a wide range. That is why TLV has not been established for these products.

NIOSH Recommended Exposure Level (REL) of kerosene is 14 ppm (100 mg/m³) and of refined petroleum solvents is 50 ppm (350 mg/m³) (Lewis, 1996). Maximum Permissible Concentration (PDK) of kerosene specified on the territory of Russia is 300 mg/m³ (Nikitin and Ryabets, 1978).

The content of aromatics (the most dangerous for human health hydrocarbons) in turbine fuels of kerosene type is 20–22% and in solvents of Exxol D type is less than 0.5%. That is why the use of the solvents is more preferable.

The value recommended by Exxon Corporation Medical Research for solvents of Exxol D type is 300 ppm (Industrial Solvents Handbook, 1991). The specification value of Exxon Chemical Denmark A/S is 100 ppm only (the same value as for petroleum) because “additional data are being obtained to help define a recommended occupational exposure limit more conclusively”.

There are no data concerning concentration of kerosene vapors in drilling shelter. But the low rate of vaporization of petroleum products (for example, the rate of vaporization of Exxol D60 is in 25 times lower than *n*-butyl acetate) helps to organize proper ventilation in drilling shelter.

Kerosene is a high environmental risk material since, in the event of a spill, it has a long residence time, particularly in a cold environment.

In 1974, M.J. Molina and F.S. Rowland (Roan, 1993) drew attention to a potential biologic hazard resulting from depletion of the ozone layer owing to release of fluorocarbons into atmosphere. Non-hydrogenated fluorocarbons (CFC 11, CFC 113, CFC 12 and others) are more stable in the atmosphere and are more dangerous for ozone layer than hydrogenated fluorocarbons (HCFC 123, HCFC 141b, HCFC 225 and others): the hydrogen-containing fluorocarbons have lifetimes about 5 to 100 times shorter than those for all non-hydrogenated.

Protocols signed by the most of the world countries in Montreal (1987) and in London (1990) ordered to reduce the production of the dangerous fluorocarbons up to 50% since 1995 and to stop the production of such fluorocarbons since 2000. The most dangerous non-hydrogenated fluorocarbons CFC 11 and CFC 113 are not allowed for use after 1995. The use of hydrogenated fluorocarbons is limited to a transition period, and they will be phased out in 2030 (Roan, 1993).

The widespread characteristics of environmental hazard of fluorocarbons are (Table 16):

Table 16. *Environmental properties of fluorocarbons.*
(Fully halogenated chlorofluorocarbons, 1990; Partially
halogenated chlorofluorocarbons, 1992; Producer's data)

Name	Atmospheric lifetime, years	ODP	GWP
CFC 11	100	1	1
CFC 113	100	1,07	1,4
HCFC 123	1,7	0,02	0,022
HCFC 141b	9,4	0,11	0,09
HCFC 225ca	2,7	0,025	0,04
HCFC 245fa	7,4	0	0,18
HCFC 365mfc	10,8	0	0,18

- a) for effect on stratospheric ozone—Ozone Depletion Potential (ODP) based on UNEP/WMO Scientific Assessment (1991) ($ODP_{CFC11}=1$);
b) for greenhouse effect—Global Warming Potential (GWP) calculated from UNEP Scientific Report (1991) ($GWP_{CFC11}=1$).

n-Butyl acetate has quite good biodegrading properties. The evaporation rate of *n*-butyl acetate is high, and therefore, if *n*-butyl acetate will be leaked out, most of it should rapidly evaporate.

Ethanol is easily biodegradable, natural, widely occurring product. It would be rapidly consumed by the microbiota in any water body into which it might be spilled, and its infinite solubility would assure its dispersion.

Silicone oils are absolutely safe to an environment. They are produced from the white silica rocks, otherwise known as sand. Silicon—the main component of silicone oils—is the second most common element in the Earth's crust, after No 1, oxygen. Silicone oils of KF96 type are harmless to microorganisms and animals.

10. Cost

The expenses for the purchase and for the delivery of drilling fluid are one of the main parts of the total cost of the drilling project. The cost of the majority of fluids is reduced in time because of the expansion and manufacturing improvements. It is concerned especially with densifiers—fluorocarbons. The cost of the mixture of Exxol D60 or D30 with densifier HCFC 141b is estimated in the range of 4–5 USD per *l*.

The cost of other fluids is decreased too. For example, the cost of silicone oil KF96-1.5 cs was near 40 USD per kg in 1993 and it is near 7 USD per kg now. One of the main considerations of the *n*-butyl acetate use by US specialists (Gosink *et al.*, 1989) and Japanese drillers was the low price of this fluid (0.8 USD per *l*).

The considerable cost for the use of drilling fluid comes not from the purchase, but from its transportation to the remote polar sites. The cost of transportation to Greenland or Antarctica is estimated about 3 to 4 USD per kg.

11. Conclusions

The short review of drilling fluid properties indicates that there are no ideal drilling fluids. All types of potential drilling fluids have their own advantages and disadvantages.

The following considerations emphasize the disadvantages of drilling fluids.

Solvents Exxol D30 and D60 are rather dangerous for the human health: they are severe skin irritants and permissible exposure of vapors in indoor air of working rooms is 100 ppm only. The use of Exxol D30 rises the fire-safety questions, and the use of Exxol D60 raises problems with respect to its relatively low volatility. From an environmental aspect, solvents Exxol D30 and D60 are difficult to biodegrade.

Although the ozone depletion potential of the hydrogenated fluorocarbons (HCFC 123, HCFC 141b, HCFC 225) is less than the potential of non-hydrogenated fluorocarbons (CFC 11, CFC 113), the hazard to the ozone layer of the atmosphere still remains. This type of the fluid is aggressive to the most types of elastomers, and, moreover, the presence of densifier HCFC 141b cause the inexplicable sedimentation of ice chips in bore-hole. Densifier HCFC 123 cause gluing of ice chips.

The main problem of *n*-butyl acetate use as drilling fluid is hazard to the physical and mental health of the people who work at the coring site. It is impossible to use *n*-butyl acetate without sufficient ventilation and some means of removing the *n*-butyl acetate vapors. *n*-Butyl acetate is very aggressive solvent: there are no elastomers that can able operate in *n*-butyl acetate during long time. Moreover, the fire hazard of *n*-butyl acetate is very high: flash point is 22°C only.

Probably one of the most promising types of drilling fluid is low-temperature silicone oil. It is non-aggressive, inert, and non-toxic. The main problem of silicone oil use is the relatively high viscosity at negative temperatures that have influence on the travel time of the drill string and finally on the total time drilling. Silicone oils have never been used in ice core drilling and, therefore, in situ use can bring some new "surprises".

The final choice of the drilling fluid depends on the possibilities and the ways of solving of foregoing problems and depends on the rational correlation between the cost of drilling fluid and other properties of the fluid (generally, density-viscosity properties and, as well as, toxicological and environmental properties).

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