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VEGETABLE OILS FOR OFFSHORE DRILLING OPERATIONS (VOODOO)

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VEGETABLE OILS FOR OFFSHORE DRILLING OPERATIONS (VOODOO)

by

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SUMMARY

The objective of this research project was to investigate the potential for using rapeseed oil as the base fluid in drilling muds of the type used to drill oil and gas wells offshore.

The research programme involved an extensive study of the stability of rapeseed oil under simulated downhole conditions, *ie* elevated temperature and pressure, and in the presence of typical drilling mud additives, *eg* calcium chloride brine, emulsifiers, oil-wetting agents and organophilic clays.

Crude rapeseed oil contains a variety of non-glyceride components, *eg* waxes, sterols and metal soaps, which are collectively known as gums (these are removed during the oil refining processes). The effect of these gums on the stability of rapeseed oil under simulated drilling conditions was assessed, and thus the physical specifications of a rapeseed oil meeting the requirements of the drilling industry were established.

During the course of the project an International Patent Application covering the development of a rapeseed oil based drilling mud was applied for.

After completion of the technical development of the drilling mud the oil industry partner identified an offshore well that could be drilled with the new mud formulation. An application was subsequently made to the Ministry of Agriculture, Fisheries and Food (MAFF) for a temporary Offshore Chemical Notification Scheme (OCNS) classification for the new mud plus permission to drill the offshore well. Following completion of a statutory toxicity testing programme specified by MAFF this was granted, but although the mud met the oil company's technical specification, the field trial did not proceed as agreement could not be reached between the industrial partners over how the additional costs of trialling a new mud system (ie, requirement for back-up system, disposal of used mud etc) would be shared. However, the project successfully completed its objective of producing a drilling fluid, based on rapeseed oil, which is ready for testing offshore and subsequent development/commercialisation by the industrial partners.

1 BACKGROUND

When drilling for oil or gas it is necessary to use a drilling fluid for several reasons, the most important of which are:

(i) it provides the means by which the drilled cuttings are removed from the hole;

(ii) it cools and cleans the drill bit;

(iii) when correctly 'weighted' it prevents blow-outs;

(iv) it provides lubrication between the drill pipe and the hole.

In order to achieve (i) and (ii) the drilling mud is pumped through the drill pipe, then through the nozzles in the drill bit, finally returning to the surface (along with the drilled cuttings) through the gap between the outer surface of the drill pipe and the surface of the hole. The mud and cuttings are then separated on the platform and the mud returned to the active mud pits from where it is again pumped to the drill pipe. The cuttings (which will still be contaminated with significant levels of drilling mud) are discharged into the sea.

To function correctly a drilling fluid must be able to withstand the temperatures and pressures experienced 'downhole'. Further, it should show no adverse reaction with the drilled cuttings and formation fluids. Rheology is also very important since a drilling mud should not be so viscous that it cannot be pumped easily, yet should be able to carry the cuttings to the surface and must be able to retain the weighting agent (barium sulphate) in suspension if drilling is temporarily halted.

An oil base mud might contain anything from 35 to 95% (vol/vol) oil, and in a typical North Sea operation 200 to 325 tonnes of this drilling fluid would be unreclaimable on completion of the hole. From an environmental viewpoint, it has been estimated that approximately 35-40% of this unreclaimable oil is discharged into the sea, principally in the form of mud-contaminated cuttings (the remainder being left 'downhole' or lost to the atmosphere).

Studies have demonstrated that the discharge of oil-contaminated cuttings has a major impact on the benthic communities over a 500 metre radius from a production platform[1]. Further, the response of the seabed fauna has been shown to follow an established pattern. In the immediate vicinity of the structure physical smothering results in a reduced number of individuals with few species present. On the periphery of the cuttings pile (slightly further from the platform) an organic enrichment effect is observed where large numbers of individuals of a few opportunistic species tend to dominate the fauna. Species richness and diversity only returns to pre-operational levels at a distance of 2,000 m from the installation.

In the seventies and early eighties diesel was predominantly used as the base oil for drilling muds in the North Sea. With a steady rise in the number of wells being drilled (325 in 1982 alone) and subsequent growth in the amount of oily cuttings lying on the seabed, concern was expressed over the environmental effect these discharges might have. Indeed, the amount of oil entering the marine environment by this route in the UK sector of the North Sea increased from 14,000 to 25,000 tonnes per annum between 1981 and 1983. However, a switch in 1984 from the use of diesel oil to lower aromatic content (and hence lower toxicity) mineral base oils has not resulted in an overall improvement in the situation as smothering and organic enrichment effects are still observed. A further problem concerns the slow rate of degradation of the mineral oil in the cuttings piles and hence the long estimated recovery times of twenty or more years before marine life re-establishes itself[2].

Drilling fluids based on vegetable oils will inevitably cause some of the effects shown by current oil base muds, *ie* smothering and organic enrichment. However, vegetable oils offer several potential advantages over mineral oils. These include:

(i) reduced toxicity both to benthic communities and to other organisms at higher trophic levels in the food chain;

(ii) reduction or elimination of tainting of commercially exploitable fish species which are present around production platforms;

(iii) enhanced recovery of the seabed, following cessation of drilling activity, resulting from the higher biodegradation and solubilisation rates predicted for vegetable base oils;

(iv) reduced treatment costs for cuttings transported ashore for disposal resulting from reduced toxicity of leachate and more rapid degradation.

The current alternative to (mineral) oil base muds, *ie* water base muds, is also in common use. However, oil base muds are generally preferred because holes can be drilled with fewer problems[3]. For example, the excellent lubricity of mineral oils reduces torque and drag problems when drilling long highly deviated (angled) wells.

Competition in the area of substitutes for mineral oils does exist. Henkel and Baroid, in joint cooperation, have published patents covering the use of synthetic esters and ethers in drilling fluids[4,5,6]. Environmentally, there are advantages in using esters and ethers, the main disadvantage, however, is that the cost of these mineral oil substitutes is currently substantial and is in the region of £1,000 - 1,300/tonne. Synthetic hydrocarbons *eg* poly (alpha-olefins) (PAOs) and linear alpha-olefins (LAOs) have also found use as mineral oil replacements in drilling muds[7,8,9], and these tend to be a lower cost than the esters and ethers.

1.1 RAPESEED OIL

Rapeseed oil is predominantly composed of esters of fatty acids and glycerol, *ie* glycerides. Glycerol has the ability to esterify three fatty acid molecules, and therefore the chemical description of a rapeseed oil molecule is a tri-acylglycerol or, more commonly, a triglyceride.

The fatty acids moieties found in rapeseed oil are predominantly unsaturated, and principally contain eighteen carbon atoms with either one, two or three double bonds per acid molecule.

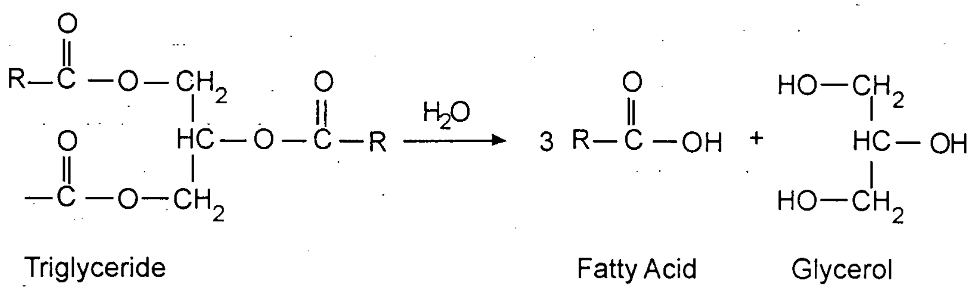
The high level of unsaturation found in rapeseed oil gives it its liquid nature at ambient temperatures and pressure. More saturated vegetable oils, *eg* coconut oil and palm kernel oil, are semi-solid at ambient temperature, while saturated fats, *eg* lard, are solid.

The presence of glyceride linkages and double bonds greatly influences the chemical stability of rapeseed oil. Reaction with water, *ie* hydrolysis, results in the formation of free fatty acids, di- and monoglycerides, and glycerol. The double bonds have the ability to polymerise and oxidise, but this is generally not observed below temperatures of ca 150°C.

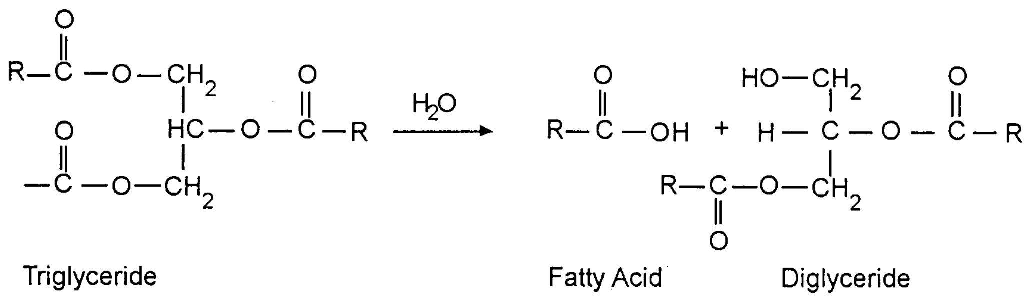
The general hydrolysis reactions of vegetable oil are shown in Figure 1.

FIGURE 1 Vegetable Oil Hydrolysis

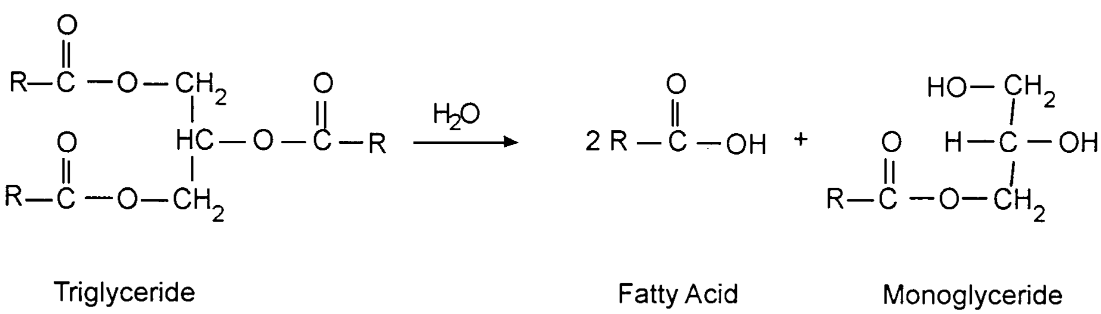
1 Complete Hydrolysis



2 Partial Hydrolysis to Diglyceride



3 Partial Hydrolysis to Monoglyceride



R represents the alkyl chain of the constituent fatty acids.

The fatty acid composition of the rapeseed oil used throughout the project can be found in the appendix.

2 OBJECTIVES

The objective of this research project was to investigate the potential for using rapeseed oil as the base fluid in drilling muds of the type used to drill oil and gas wells offshore.

3 EXPERIMENTAL PROCEDURES

3.1 PREPARATION OF DRILLING FLUIDS

The drilling muds were formulated as follows:

(i) the required quantity of base oil, *ie* rapeseed oil or a blend of rapeseed oil and an appropriate diluent, was placed into a beaker (2,000 ml);

(ii) the remaining oleophilic components were then added, *eg* emulsifiers, oil-wetting agents, fluid-loss additives and viscosifiers, and the resulting mixture stirred at 6,000 rpm in a Silverson laboratory mixer (model L4R) for approximately five minutes;

(iii) the aqueous phase of the drilling mud was prepared to the required activity/chloride ion concentration, by dissolving a pre-determined weight of calcium chloride in a known volume of fresh water;

(iv) the prepared brine was added to the stirred oil phase and stirring was continued for approximately five minutes;

(v) barite (barium sulphate), *ie* the weighting agent, was added to the stirred emulsion. Stirring was then continued for a total time of approximately fifty minutes. The maximum temperature of the drilling muds was limited to 65°C by the use of a cooling water jacket.

In general three laboratory barrels, *ie* 3 x 350 ml samples of drilling fluid were prepared simultaneously. The laboratory barrel is a convenient scaled down version of a field unit, *ie* 1 pound of any mud component per barrel (150 l) is equivalent to 1 gram of the component per laboratory barrel (350 ml).

3.2 MATERIALS

A large number of different products were used throughout the three year duration of the project. The following lists the mud components which were found to give the best performance in a rapeseed oil based system.

(i)	Rapeseed oil	a low erucic acid variety supplied by Peerless Products Ltd, Liverpool which was fully refined, *ie* so-called edible grade
(ii)	Ultidrill	a linear alpha-olefin, used as a diluent for the rapeseed oil
(iii)	Ultidrill Emul HT	an emulsifier designed for use in oil-based drilling muds, and which functions in the absence of lime

(iv)	Ultidrill OW	an oil-wetting agent which prevents solids from becoming water wet
(v)	Interdrill FL	an emulsion stabiliser and fluid-loss reducer
(vi)	Trudrill S	a fluid-loss reducer
(vii)	Truflo 100	a polymeric fluid-loss reducer
(viii)	Truvis	an organophilic clay used to provide viscosity control
(ix)	Vistone	an organophilic clay used to provide viscosity control
(x)	Calcium Chloride (83.5%)	a technical grade calcium chloride used to produce a brine of known salinity
(xi)	Barite	barium sulphate, *ie* the weighting agent used to produce muds to the required density

With the exception of the rapeseed oil, all materials were supplied by Schlumberger Dowell Ltd.

3.3 MUD TESTING

The prepared muds were subjected to a range of procedures designed to evaluate the performance of oil-based drilling muds.

The procedures used were taken from the relevant American Petroleum Institute standard, *ie* Recommended Practice Standard Procedure for Field Testing Oil-Based Drilling Fluids, API 13B-2.

Mud Ageing	Samples of prepared muds (generally 350 ml portions), were placed into stainless steel ageing cells and 'hot-rolled' in an oven, generally at 120°C (250°F), for a prescribed time, *ie* sixteen or seventy-two hours. Sixteen hours is an ageing time commonly used in the drilling industry. The use of seventy-two hours was to give information on the long term stability of the rapeseed oil system.
Mud Rheology	The rheological properties of the freshly prepared and aged fluids were determined using a Fann, six-speed rheometer, Model 35SA.
Electrical Stability	The breakdown voltage of the drilling mud emulsion; a measure of emulsion stability, was determined using an OFI Emulsion Stability Meter, Model ESM 30A.
Rapeseed Oil Hydrolysis	The extent of glyceride hydrolysis, occurring during the ageing process was determined by titrimetric analysis of the oil phase. A small portion of aged mud, ca 20 g, was centrifuged, 1 g of separated oil was withdrawn, dissolved in acetone (5 ml) and titrated using sodium hydroxide solution (0.1 Mol l^{-1}) and phenolpthalein indicator.

Contamination Testing — The response of the prepared muds to contamination by drill cuttings, cement and seawater was determined.

Elastomer Compatibility — The effect of vegetable oil on commonly used elastomer products which the oil may come into contact with during drilling was assessed using the method described in ASTM D471.

4 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 RAPESEED OIL VISCOSITY

One reason why rapeseed oil cannot be used as a direct replacement for mineral oils in drilling muds is because of its relatively high viscosity. A comparison of base oil viscosities is shown in Table 1.

TABLE 1 Comparison of Base Oil Viscosities

Base Oil	Kinematic Viscosity (40°C) (cSt)
Rapeseed Oil	27.4
Finagreen (ester)	4.9
Clairsol 350 m HF (hydrocarbon)	2.3
LTS (ether)	2.8
Emkarate (di-ester)	8.0
Ultidrill (linear alpha-olefin)	2.4

As the data in the above table shows, rapeseed oil is considerably more viscous than alternative base oils. The major drawback of this is that high viscosity base oils tend to produce high viscosity drilling fluids which are more difficult to manage, *eg* poorer pumpability, than low viscosity muds.

The rapeseed oil was, however, compatible with all of the above alternative base oils and it was found that these could be used as diluents to 'thin down' the rapeseed oil.

An example of viscosity reduction, using Ultidrill as the rapeseed oil diluent, is shown in Table 2.

TABLE 2 Effect of Ultidrill Content on Base Oil Viscosity

Percentage Content (v/v)		Kinematic Viscosity (40°C)
Rapeseed Oil	Ultidrill	(cSt)
100	0	27.4
90	10	27.3
75	25	17.1
65	35	13.3
50	50	7.1
25	75	4.9

As the above data indicates, the viscosity of the blends are less than the neat rapeseed oil. A relatively large proportion of the diluent is required however, *ie* ca 50% v/v, before the viscosity of the blend approaches the viscosity of the alternative base oils, see Table 1

As stated previously, a viscous base oil results in a viscous drilling mud. This assumes all other mud variables are constant, *ie* oil:water ratio, mud weight and solids content etc.

In order to overcome the base oil viscosity situation it was concluded that the water content of the rapeseed oil based drilling fluids would have to be kept to a minimum. During the course of the project a large amount of work was carried out at an oil:water ratio of 90:10 v/v, latterly however, formulations were produced with an oil:water ratio of 80:20 v/v.

4.2 RAPESEED OIL HYDROLYSIS

As described is Section 1.1, the glyceride bonds within the rapeseed oil molecule can undergo reaction with water (hydrolysis) to yield fatty acids, a mixture of di- and monoglycerides and glycerol, with non-hydrolysed triglyceride also being present.

Hydrolysis is enhanced at elevated temperature, particularly in excess of 100°C, and at extremes of pH.

A major experimental objective of the project was to minimise hydrolysis. This was considered the best scenario because of the following:

(i) a system undergoing change is less predictable and would be more difficult for a drilling crew to manage;

(ii) the di- and monoglycerides resulting from hydrolysis are themselves emulsifying agents, and might influence the stability characteristics of the drilling mud emulsions;

(iii) the fatty acids produced might, under appropriate pH conditions, react with divalent metal ions present, *eg* Ca^{2+} or Mg^{2+}, to produce greases which would tend to thicken the mud;

(iv) it has been established that fatty acids can remove the quaternary ammonium compounds from the surface of organophilic clays, thus reducing the viscosifying properties of the latter.

A study of the hydrolytic characteristics of the rapeseed oil formed a major part of the research programme.

4.2.1 Effect of Mud Additives on Hydrolysis

A series of rapeseed oil based fluids was prepared with differing quantities of individual additives. The muds were hot-rolled at 120°C for sixteen and seventy-two hours and the degree of hydrolysis determined. The hydrolytic effect of each additive was estimated and also the influence on hydrolysis of the chemical nature of the diluent *ie* ester, ether or hydrocarbon etc.

The composition ranges used are shown in Table 3.

TABLE 3 Composition Ranges of Fluids Used in Hydrolysis Study

Component	Quantity Æ (pounds per barrel, ppb)
Rapeseed oil*	184-252
Diluent	0-66
Interdrill OW	0-1.0
Emul HT	3.0-9.0
Vistone	7.8-10.0
Calcium chloride	4.7-12.2
Lime	1-6.0
Water	9.7-77.1
Barite	120.3-256.7
Specific Gravity	1.2-1.5
Oil:Water ratio	95:5-75:25

* When this study was undertaken a partially refined grade of rapeseed oil was used, *ie* so-called superdegummed oil. This contains approximately 2% of non-glyceride components.

Æ Equivalent to grams per 350 ml of finished mud.

The following general observations were made:

(i) varying the oil-wetting agent, emulsifier, clay and barite content had little effect on the extent of hydrolysis detected after ageing;

(ii) removing lime, *ie* calcium hydroxide, from the formulation had a significant effect on hydrolysis, *ie* reducing it from 55% triglyceride hydrolysis at 1 ppb lime, to 38% hydrolysis at zero lime, both measurements being taken after seventy-two hours ageing;

(iii) reducing the aqueous phase content from ca 10% to 5% v/v did give a slight reduction in the degree of hydrolysis detected after seventy-two hours, *ie* from 38% hydrolysis down to 32% hydrolysis;

(iv) increasing the aqueous phase content from ca 10% v/v to 25% v/v increased the extent of hydrolysis from 38% to 58% after seventy-two hours ageing;

(v) the addition of diluent to a lime-free formulation resulted in a slight increase in hydrolysis relative to the diluent-free fluid. There was one exception to this however, *ie* with the product LTS ether (di-n-octyl ether) supplied by Carless Refining and Marketing. The use of this diluent resulted in hydrolysis being reduced from 38% to 21% after seventy-two hours ageing.

Overall, the results from this work indicated that after seventy-two hours ageing at 120°C, by omitting lime from the formulation, selecting the appropriate diluent and minimising the water content of the formulation, the degree of triglyceride hydrolysis detected could be reduced from ca 55% to ca 21%.

4.2.2 Effect of Rapeseed Oil Refining on Hydrolysis

At the outset of the VOODOO project, it was decided to use a partially refined form of rapeseed oil, *ie* superdegummed. This grade of oil was selected because, in terms of its price, it fairly closely resembled mineral oil, *ie* £200-250 per tonne.

Superdegummed vegetable oils differ from edible grade oils in that they contain ca 1-2% of non-glyceride components (crude vegetable oils contain ca 5%). These non-glyceride components or gums, are multicomponent mixtures containing such things as phosphate esters, sterols (cholesterols), triterpane alcohols, fatty alcohols, waxes and minerals, *eg* sodium soaps etc. Many of these potentially have surface-active properties and could influence the chemistry of drilling fluid emulsions. In an attempt to determine the effects of these gums, two sets of formulations were prepared using edible grade rapeseed oil (Trex Rapeseed Oil, supplied by Princes Ltd of Liverpool). One set was formulated without the addition of a diluent, and one set with the addition of a diluent. Four replicate samples were made of each, which were hot-rolled for seventy-two hours at 120°C.

The compositions of these formulations, their average rheological properties and their degree of hydrolysis are shown in Table 4.

TABLE 4 Drilling Muds Comprising Edible Grade Rapeseed Oil

Component	Quantity (ppb)			
	Diluent-Free		Containing Diluent	
Rapeseed Oil	253.2		187.7	
Ultidrill^Æ	-		53.5	
Interdrill OW	1.0		1.0	
Emul HT	3.0		3.0	
Vistone	7.8		7.8	
Water	25.7		28.5	
$CaCl_2$ (83.5%)	12.2		9.7	
Barite	116.4		127.8	
Specific Gravity	1.2		1.2	
Oil:Water Ratio	90:10		90:10	
Rheological Property	***BHR**	***AHR**	***BHR**	***AHR**
Apparent Viscosity (cP)	65	69	39	39
Plastic Viscosity (cP)	58	62	31	31.5
Yield Point ($lb/100ft^2$)	15	18	15	14
6 rpm	8	10	7	6
10 sec gel	7.5	8	7.5	6.5
10 min gel	9.5	10	10.5	8
Electrical stability (volts)	1230	1540	1740	1770
Percentage Hydrolysis	nil	6	nil	6.6

* BHR - Before hot rolling.

* AHR - After hot rolling: 120°C, 72 hours.

Æ - At this stage of the project, the linear alpha-olefin, Ultidrill, supplied by Schlumberger Dowell Ltd, was identified as a suitable and readily available diluent.

As the above data indicate, the use of edible grade oil in place of superdegummed oil significantly reduced the degree of hydrolysis occurring, *ie* from ca 21% hydrolysis using superdegummed to ca 6% using edible oil.

The residual gums present in the partially refined oil were obviously capable of functioning as powerful hydrolysis catalysts. This phenomenon was further demonstrated by deliberately doping edible grade oil with gums. On the addition of 2% w/w and 4% w/w of gums to edible grade formulations, the extent of hydrolysis observed increased to 15% and 28% respectively.

It was concluded from this study that fully refined rapeseed oil was, from a technical standpoint, far more attractive than the superdegummed oil used initially. The current price (1997) for fully refined oil, *ie* edible grade, is £450/tonne.

4.2.3 The Effect of Temperature on Hydrolysis

The vast majority of the drilling mud ageing studies during the project were carried out at 120°C. This temperature limit represents the bottom hole temperature of the majority of oil wells drilled in the northern North Sea and, therefore, was used as the experimental norm.

In some applications, this bottom hole temperature is never reached whilst, in others, *eg* highly deviated and deep wells, bottom hole temperatures well in excess of 120°C are encountered. For these reasons, it was considered essential to determine the hydrolytic and rheological stability of the rapeseed oil based fluids over a temperature profile of 50°C to 150°C.

A formulation containing Ultidrill, similar to that shown in Table 4, was prepared. Replicate samples (six repeats) of the fluid were aged at 50°C, 80°C, 120°C and 150°C, for seventy-two hours and then characterised. The average results found at each temperature are shown in Table 5.

TABLE 5 Thermal Stability of Rapeseed Oil Muds

Rheological Property	Ageing Temperature (72 hour duration)				
	Freshly prepared	50°C	80°C	120°C	150°C
Apparent Viscosity (cP)	42	43.5	40	37.5	44
Plastic Viscosity (cP)	35	36.5	34	33	41.5
Yield Point ($lb/100ft^2$)	14	14.5	12	9	4.5
6 rpm	7.5	7.5	6.5	5.5	3
10 sec gel	7.5	7.5	6.5	6.5	2.5
10 min gel	10.5	10	9	8	3
Electrical stability (volts)	1265	1330	1186	1432	1722
Percentage Hydrolysis	0	0	0	8.6	73.5

The above data indicate that at relatively low temperatures, *ie* ca 80°C, zero hydrolysis is to be expected and the muds are stable. At 120°C, hydrolysis is observed but it is limited and the muds indicate good rheological stability. At higher temperatures, *ie* around 150°C, a large degree of hydrolysis would be expected, accompanied by a loss of the mud's low-end rheology - see yield point and gel strength data above.

From the results obtained in this study it was concluded that the upper temperature limit for rapeseed oil based drilling fluids was around 120C.

5 HIGH TEMPERATURE - HIGH PRESSURE ANALYSIS OF RAPESEED OIL BASED DRILLING FLUIDS

The drilling mud rheological properties quoted earlier in this report were obtained using the Fann, six-speed rheometer, at atmospheric pressure and 49°C. To determine the rheological properties of the fluids under real working conditions, a high temperature-high pressure rheometer was used, *ie* Schlumberger Dowell's Huxley-Bertram HTHP Viscometer.

The HT-HP conditions used were taken from a North Sea Well Plan Outline, *ie* Enterprise Oil's Nelson Field Development. This gave information on the drilling depths, formation types, bottom hole temperature and required mud weights.

The Well Plan was used to produce two trial drilling muds, *ie* a neat rapeseed oil formulation and a version containing Ultidrill, and also a temperature/pressure profile over which to test the fluids.

Briefly, two samples, *ie* mud A - a neat rapeseed oil based formulation, and mud B, *ie* an Ultidrill modified formulation were prepared. Their rheological properties over the temperature range 0 Bar to 338 Bar were determined. The results obtained are shown in Tables 6 and 7.

TABLE 6 HT-HP Analysis of Mud A

Rheological property	Temperature/Pressure Conditions					
	50°C/ 0 Bar	80°C/ 179 Bar	80°C/ 338 Bar	100°C/ 179 Bar	100°C/ 338 Bar	120°C/ 338 Bar
Plastic Viscosity (cP)	134.64	86.34	93.22	64.40	73.28	53.27
Yield Point (lb/100ft^2)	37.52	25.41	32.0	16.49	22.92	23.11
10 sec gel	25.41	14.40	23.74	7.18	16.85	16.85
10 min gel	34.61	22.88	33.79	12.7	25.41	31.90

TABLE 7 HT-HP Analysis of Mud B

Rheological property	Temperature/Pressure Conditions					
	50°C/ 0 Bar	80°C/ 179 Bar	80°C/ 338 Bar	100°C/ 179 Bar	100°C/ 338 Bar	120°C/ 338 Bar
Plastic Viscosity (cP)	69.72	57.49	64.72	36.44	38.81	32.77
Yield Point (lb/100ft^2)	31.77	19.39	16.25	10.86	10.01	7.26
10 sec gel	17.50	15.33	13.95	9.44	9.90	7.02
10 min gel	*	*	*	10.57	11.19	9.73

* These data were not recorded.

A discussion with the rheologist at Schlumberger Dowell Ltd indicated that the results gave no cause for concern and were typical of those obtained using traditional oil-based muds.

6 DRILLING MUD SPECIFICATIONS FOR ENTERPRISE OIL'S NELSON FIELD DEVELOPMENT

An extensive exercise was undertaken to develop rapeseed oil based drilling muds which met the requirements of the $12^1/4$" and 16" hole sections of Enterprise Oil's Nelson Field.

It was hoped at one stage that the Nelson Development would be used to field test the VOODOO mud system. Unfortunately a suitable well did not become available in this field. The production of mud, which met the Nelson Field requirements was, however, an extremely valuable exercise.

The required mud specifications are shown in Table 8, although the requirements of the $8^1/2$" hole section were not addressed, for completeness, they are also shown in the table.

TABLE 8 Nelson Field Drilling Mud Specifications

Mud Property	Hole Section/Specification		
	16"	$12^1/4$"	$8^1/2$"
Mud Weight (ppg)	12.0 - 12.5	14.0	10.0
Plastic Viscosity (cP)	40 - 50	50 - 60	28 - 35
Yield Point (lb/100 ft^2)	25 - 30	20 - 25	14 - 18
Fann 6 rpm Reading	16 - 18	14 - 16	>10
Electrical Stability (volts)	>400	>400	>300
Water Phase Salinity (g/l)	190	190	235
HT-HP Fluid Loss (ml)	<8.0	<5.0	<2.0

6.1 DEVELOPMENTS FOR $12^1/4$" HOLE SECTION

This hole section required the greatest mud weight and, overall, appeared the most technically demanding. For this reason it was the first to be studied.

6.1.1 Rapeseed Oil:Ultidrill 75:25 (v/v)

This was the usual diluent concentration used throughout the bulk of the research programme.

The formulation shown in Table 9 was produced, and hot-rolled for sixteen and seventy-two hours.

As the data shows, at this diluent concentration, the average plastic viscosity and average yield point of the formulation was greater than was acceptable.

In an attempt to overcome this problem, two modifications to the formulation were made:

(i) the organoclay content of the mud was reduced, *ie* from 3 ppb to 2 ppb and then to 1 ppb; and

(ii) the rapeseed: Ultidrill ratio was changed from 75:25 v/v to 65:35 v/v.

It was found that altering the organoclay content had no major effect on the mud properties, but increasing the Ultidrill content did significantly improve the situation.

TABLE 9 Rapeseed Oil/Ultidrill 75:25 (v/v)

Component	**Quantity (ppb)**		
Rapeseed Oil/Ultidrill Blend	194.6		
Emul HT	6.0		
Interdrill OW	1.0		
Truflo MVO	3.0		
Vistone	3.0		
$CaCl_2$ (83.5%)	7.35		
Water	25.29		
Barite	348.0		
Rheological Property	***BHR**	***AHR 72h, 120°C**	**Specification**
Apparent Viscosity (cP)	84	89	-
Plastic Viscosity (cP)	69	74	50 - 60
Yield Point (lb/100ft^2)	29.5	30	20 - 25
6 rpm	18	16	14 - 16
10 sec gel	18	14	-
10 min gel	23.5	16	-
Electrical stability (volts)	>2,000	1,344	>400
Percentage Hydrolysis	nil	14.5	

* Average of six repeats.

6.1.2 Rapeseed Oil:Ultidrill 65:35 v/v

Increasing the Ultidrill content of the base oil from 25% to 35% v/v, resulted in a decrease in the base oil apparent viscosity from 12.5 cP to 8 cP (49°C).

A formulation comprising this new base oil was prepared, its composition and properties are shown in Table 10.

As can be seen from the data in Table 10, increasing the Ultidrill content brought the plastic viscosity and yield point values in-line with the required specifications.

The only cause for concern at this point was the HTHP fluid loss characteristics of the mud. The prepared mud produced 11 ml of filtrate, with less than 5 ml being the requirement.

This situation was improved, with the replacement of Interdrill OW with Interdrill FL, *ie* a combined fluid-loss, oil-wetting and secondary emulsifier additive.

This had the effect of reducing the HTHP filtrate to 6.4 ml, *ie* still above the 5 ml limit, but a great improvement on the initial 11 ml produced.

This situation was further improved with the addition of 35 ppb of OCMA clay to the mud, this resulted in a fluid-loss of 2.6 ml.

TABLE 10 Rapeseed Oil:Ultidrill 65:35 v/v

Component	**Quantity (ppb)**			
Rapeseed Oil/Ultidrill Blend	191.3			
Emul HT	6.0			
Interdrill OW	1.0			
Truflo MVO	3.0			
Truvis	4.0			
$CaCl_2$ (83.5%)	7.31			
Water	25.71			
Barite	350.4			
Rheological Property	***BHR**	***AHR 16h, 120°C**	**AHR 72h, 120°C**	**Specification**
Apparent Viscosity (cP)	63	65.5	67.6	-
Plastic Viscosity (cP)	54	52	54	50 - 60
Yield Point ($lb/100ft^2$)	18	27	27	20 - 25
Fann 6 rpm reading	15	15	14.5	14 - 16
10 sec gel	15	14	13	-
10 min gel	20	18	15	-
Electrical stability (volts)	>2,000	1,700	1,600	>400
HT-HP Fluid Loss (ml)	-	11	-	<5.0
Percentage Hydrolysis	nil	1.5	16.6	

* Average of three repeats.

6.2 DEVELOPMENT FOR 16" HOLE SECTION

Based on the findings from the $12^1/4$" hole section development, the fluid produced for this section contained;

(i) a base oil comprising 65:35 v/v rapeseed oil:Ultidrill;

(ii) Interdrill FL; and

(iii) clay at 7 ppb.

The formulation shown in Table 11 was produced and characterised. For comparison, a similar formulation containing Finagreen, *ie* the ester based, commercially available drilling fluid base oil, was also prepared and characterised.

TABLE 11 16" Hole Section Formulation

Component	Quantity(ppb)				
Rapeseed Oil/Ultidrill Blend	195.7		-		
Finagreen	-		195.7		
Emul HT	10.0		10.0		
Interdrill FL	2.0		2.0		
Truvis	2.5		2.5		
OCMA Clay	7.0		7.0		
$CaCl_2$ (83.5%)	15.18		15.18		
Water	40.99		40.99		
Barite	230.8		230.8		
Rheological Property*	**BHR**	**AHR 16h, 120°C**	**BHR**	**AHR 16h, 120°C**	**Specification**
Apparent Viscosity (cP)	60.5	61	47	41.5	-
Plastic Viscosity (cP)	46	47	36.5	35	40 - 50
Yield Point (lb/100ft^2)	27.5	28	21.5	13.5	25 - 30
6 rpm reading	16	16	11	7	16 - 18
10 sec gel	15	15	10	8	-
10 min gel	18.5	18.5	12.5	9	-
Electrical stability (volts)	1307	970	1093	737	>400
HT-HP Fluid Loss (ml)	-	4.5	-	1.9	<8.0
Percentage Hydrolysis	nil	2.6	nil	2.7	-

* Average of six repeats.

The rapeseed oil based formulation comfortably met the specifications.

The Finagreen based fluids were generally 'thinner' than the rapeseed oil formulations, and this reflects the fact that Finagreen has a lower viscosity than the 65:35 v/v rapeseed oil: Ultidrill blend, *ie* 4.2 cP against 11.5 cP (all data at 40°C).

The Finagreen muds also had better HTHP fluid loss characteristics than the rapeseed oil samples, *ie* 1.9 ml versus 4.5 ml.

Interestingly, under these conditions, both base oils underwent a similar degree of ester hydrolysis.

6.2.1 Cement Contamination

During the drilling of a well, the steel casing which is used to line the borehole is cemented into place. There is a risk therefore, that a drilling mud may become contaminated with cement. For this reason it is standard practice to assess the stability of a drilling mud in the presence of cement.

This test is of particular significance to the VOODOO mud because of the known instability of rapeseed oil in the presence of lime, see Section 4.2.1.

Dry cement is mainly a mixture of calcium silicates. In the presence of water, however, a portion of these silicates form calcium hydroxide, *ie* lime.

The response of the rapeseed oil based and Finagreen based muds to increasing quantities of wet cement was assessed.

Wet cement contamination (1:1 water:cement) was in the range 2 - 8 ppb, and the formulations were hot-rolled at 120°C for sixteen hours.

The work is summarised in Table 12.

TABLE 12 Cement Contamination Study

Rheological Property*	Base Oil/Wet Cement Content (ppb)									
	Rapeseed Oil					Finagreen				
	0	2	4	6	8	0	2	4	6	8
Apparent Viscosity (cP)	61	62	62.5	97	Æ	41.5	44.5	45.5	46	46
Plastic Viscosity (cP)	47	47	45.5	68	Æ	35	39	37	38	35.5
Yield Point (lb/100ft^2)	28	32	34	55		13.5	10	15	16	20
Fann 6 rpm reading	16	16	17.5	32		7	6	10	8	9
10 sec gel	15	15	17.5	29		8	6	8.5	6.5	8
10 min gel	18.5	19	20	38		9	9	11	10	11
Electrical stability (volts)	970	956	985	988		737	693	788	631	649
HT-HP Fluid Loss (ml)	4.5	4.6	12	14.5		1.9	2.4	10.5	10.5	11
Percentage Hydrolysis	2.6	1.5	1.0	2.0	3.0	2.7	0.8	0.5	0.5	0.4

* Average of six repeats.

Æ Too viscous to measure.

The rapeseed oil proved to be stable to wet cement contamination up to levels of ca 4 ppb. At a contamination level of 6 ppb a noticeable increase in the viscosity of the fluid was observed, it did however remain a free-flowing liquid. At a cement slurry concentration of 8 ppb, after sixteen hours at 120°C, the sample was converted into a viscous paste which had to be spooned out of the ageing cell.

NB -It has been demonstrated, and reported that after extended ageing, *ie* 72 hours at 120°C, cement contaminated rapeseed oil based muds revert back to being fluids. These samples typically exhibit hydrolysis levels of ca 70% of available glycerides. It has also been observed that a high degree of hydrolysis generally results in a severe drop in viscosity. This may well be due to the organophilic clays losing their viscosifying power in the presence of the high concentration of fatty acids.

The Finagreen muds were more stable to cement content, and even at 8 ppb contamination remained relatively unchanged with respect to the uncontaminated mud.

Overall, it is expected that rapeseed oil based drilling fluids will tolerate ca 6 ppb of wet cement contamination, although a viscosity rise will be likely at this higher level. At wet cement concentrations higher than 6 ppb a severe thickening of the muds would be expected.

7 BIODEGRADABILITY AND MARINE TOXICITY

7.1 RAPESEED OIL BIODEGRADABILITY

Assessment of aerobic and anaerobic ready biodegradation was conducted by Schlumberger Dowell Ltd, using currently recommended and accepted methods. In these tests, substances are considered readily degradable if mineralisation exceeds 60% (gas removal or production) or 70% (organic carbon removal) during the test period.

Aerobic biodegradation potential of the rapeseed oil was measured in five replicates over 28 days following the OECD 301F protocol. Percentage degradation was determined from the ratio of measured oxygen demand to the theoretical oxygen demand of the test material.

The results are shown in Table 13.

TABLE 13 Percentage Aerobic Biodegradation of Rapeseed Oil

	Replicate Sample					
Exposure Time	**1**	**2**	**3**	**4**	**5**	**Average**
28 Days	60.7	57.4	59.2	66.3	62.1	61.1

These results indicate that rapeseed can be considered readily biodegradable.

Anaerobic degradation potential of the rapeseed oil was measured in five replicates over 56 days following the ISO CD 11734 protocol (equivalent to ECETOC 28). Percentage degradation was estimated from the ratio of inorganic carbon produced (increase in CO_2 and methane gas pressure and the concentration of dissolved inorganic carbon) to the amount of organic carbon present in the sample.

The results obtained are presented in Table 14.

TABLE 14 Percentage Anaerobic Degradation of Rapeseed Oil

	Replicate Sample					
Exposure Time	**1**	**2**	**3**	**4**	**5**	**Average**
56 Days	46.5	53.8	49.9	63.8	41.7	51.0

The results indicate that rapeseed oil does biodegrade anaerobically and, as sample 4 indicates, can be in excess of 60%.

7.2 TOXICITY TESTING

7.2.1 *Acartia tonsa*

Toxicity testing of rapeseed oil was carried out by Environment and Resource Technology (ERT) Ltd.

Four different brands of rapeseed oil (including a superdegummed variety) were subjected to screening tests using the marine copepod *Acartia tonsa*.

The test procedure used was as per the PARCOM (Paris Commission) guidelines for testing offshore chemicals.

In summary, it was found that the four rapeseed oil samples tested were all effectively non-toxic.

7.2.2 Toxicity Testing Requirements for Experimental Drilling Fluid

An application was made to MAFF, requesting permission to use an experimental rapeseed oil based drilling fluid to drill an offshore well. Before permission could be granted, MAFF required a detailed chemical breakdown of the drilling mud's components, and also data from specific, approved toxicity and bioaccumulation tests. The tests requested were:

(i) PARCOM protocolised toxicity testing of the whole mud formulation to *Skeletonema costatum*, *ie* an algal primary producer;

(ii) PARCOM protocolised toxicity testing of the whole mud formulation to *Corophium volutator*, *ie* a sediment dwelling organism;

(iii) the bioaccumulation potential, *ie* log P_{OW} value of the rapeseed oil using the OECD 117 method; and

(iv) the bioaccumulation potential of Ultidrill using the OECD 117 method.

These were to be carried out at GLP accredited laboratories.

The *Skeletonema* and *Corophium* toxicity results were determined by ERT Ltd.

The bioaccumulation potential of rapeseed oil and Ultidrill were determined by Hamilton Garrod Ltd (formerly Binnie Environmental Ltd).

A dialogue between IOE and MAFF was established, during which MAFF was given details of the VOODOO mud system, *ie* the identities and concentrations of all the potential components of the rapeseed oil based formulation.

MAFF concluded that before the granting of a temporary licence to use the VOODOO mud they would require toxicity data on a so-called **worst case** formulation, *ie* a mud with a high Ultidrill content, comprising a base oil which was 96:4 v/v Ultidrill:rapeseed oil.

This was carried out, and the results obtained are shown in Table 15.

For completeness, toxicity data were also obtained by IOE on a VOODOO mud comprising a base oil which was 65:35 v/v rapeseed oil:Ultidrill, as this formulation would be more typical of that used in the field. In addition a mud containing 100% edible grade rapeseed oil was tested against *Corophium*. These results are shown in Table 16 and 17 respectively.

TABLE 15 Toxicity Data for Mud Comprising a Base Oil 96:4 v/v Rapeseed:Ultidrill Oil

Test Species	Result
Skeletonema costatum	Algal growth not inhibited at addition rates up to 10,000 mg/l
Corophium volutator	10 day LC_{50} 914 mg/kg

TABLE 16 Toxicity Data for Mud Comprising a Base Oil 65:35 v/v Rapeseed:Ultidrill Oil

Test Species	Result
Skeletonema costatum	Maximum growth inhibition (2% inhibited) at 3,200 mg/l. (Some growth **enhancement** seen at other concentrations)
Corophium volutator	10 day LC_{50} 843 mg/kg

TABLE 17 Toxicity Data for Mud Comprising a Base Oil 100% Edible Grade Rapeseed Oil

Test Species	Result
Corophium volutator	10 day LC_{50} 5,099 mg/kg

As can be seen from the tables, the two muds comprising base oils 94:6 v/v Ultidrill:rapeseed oil and 65:35 v/v rapeseed oil:Ultidrill produced fairly similar data and were, in fact, statistically indistinguishable.

The *Corophium* data for the 100% rapeseed oil mud (Table 17) indicated an extremely high LC_{50} (*ie* low toxicity) for this formulation. This is a strong indication that the predicted inherent low toxicity of rapeseed oil is retained when in a full mud formulation.

The bioaccumulation potential of the rapeseed oil and the Ultidrill were determined using the OECD 117 method, *ie* an HPLC based technique.

The results obtained are shown in Table 18.

TABLE 18 Bioaccumulation Potential of Rapeseed Oil and Ultidrill

Base Oil	Log P_{OW}
Rapeseed Oil	>6 (10.2 - 10.4)*
Ultidrill	>6 (8.8 - 9.0)*
* A determination carried out by IOE, which extends the measurable range of log P_{OW} values, gave these results.	

Chemicals with low P_{OW} values of greater than 6 generally have the **potential** to bioaccumulate. This test does not however make a determination of any processes which might remove the substance from animal tissue, *eg* metabolism or depuration. A low P_{OW} value therefore only gives information on the **potential** bioaccumulation but not on the **actual** bioaccumulation.

This situation has been recognised by the regulatory authorities, and for full classification and licencing a base oil must be subjected to bioconcentration analysis, *ie* where living organisms (mussels) are exposed to the base oil and its up-take determined.

The data requested by MAFF, *ie* the toxicity results for the mud comprising a base oil 96:4 v/v Ultidrill:rapeseed oil (see Table 15) and the bioaccumulation data for Ultidrill and rapeseed oil, were forwarded to them.

On receipt of this data MAFF gave the **worst case** formulation the temporary OCNS classification B (restricted use). However, based on the data received, MAFF were prepared to give special dispensation to allow the mud to be used for a single well site. For the VOODOO mud to be moved to classification E (effectively unrestricted use within existing guidelines for product use), bioconcentration and biodegradation studies at a GLP accredited establishment would be required. It was considered that obtaining category E classification was outwith the scope of this **developmental stage** of the VOODOO project (and was also cost prohibitive) and hence this was not pursued.

The overall objective of this phase of the project was to obtain permission to carry out a single site trial with the VOODOO mud system, and this was achieved. Further, the extra data obtained, *ie* the aerobic and anaerobic biodegradability and the toxicity data shown in Table 16 and 17, indicate a very strong likelihood that full classification, *ie* licencing for routine commercial use, should be achievable.

8 ELASTOMER COMPATIBILITY

The effect of rapeseed oil and Ultidrill on commonly used elastomer sealing materials was investigated. Any changes in the mass, volume and thickness of the elastomers over a 742 hour (one month) test period were noted. The tests were carried out by Carless Refining and Marketing Ltd, and was based on the procedure described in ASTM D471.

The results obtained are shown in Table 19.

TABLE 19 Effect of Rapeseed Oil and Ultidrill on Elastomer Products

Base Oil/Effect	Elastomer					
	Silicone	Neoprene BS2752	Neoprene Commercial	Nitrile BS2751	Nitrile Commercial	Viton
Rapeseed Oil						
% Mass Change	-0.9	8.4	13.4	-5.7	5.2	0.7
% Volume Change	-1.6	14.3	27.4	-9.6	12.0	2.6
% Thickness Change	-2.0	2.0	8.7	-3.7	2.0	0.2
Ultidrill						
% Mass Change	46.7	3.0	17.9	-4.5	10.8	0.8
% Volume Change	90.7	9.7	45.3	-5.4	30.5	2.2
% Thickness Change	18.8	-0.5	17.0	-4.3	9.9	1.2
Rapeseed Oil:Ultidrill (65:35 v/v)						
% Mass Change	5.9	11.5	19.2	-5.6	8.7	1.1
% Volume Change	11.9	22.0	42.9	-8.8	21.6	3.1
% Thickness Change	1.5	2.3	15.0	-4.3	2.5	1.2

By comparison to neat Ultidrill, a drilling mud base oil with acceptable elastomer compatibility, neither the rapeseed oil, nor the rapeseed oil:Ultidrill blend exhibited severe elastomer incompatibility.

9 FIELD TRIAL

Towards the end of 1995 a suitable well was identified, *ie* Enterprise Oil's 53/5b-E. A Well Plan Outline for this development was provided, along with the technical specifications of the oil-base mud which had been used to drill a neighbouring well, *ie* 53/5b-4. These specifications are shown in Table 20.

TABLE 20 Mud Properties of Neighbouring Well

Rheological Property	Hole Section	
	$12^{1}/_{4}$"	$8^{1}/_{2}$"
Plastic Viscosity (cP)	37	40
Yield Point (lb/100 ft^2)	27	21
6 rpm	16	13
10 sec gel	24	18
10 min gel	44	45
Electrical Stability	650	680
Salinity (Cl^- g/l)	190	202
HTHP Fluid Loss (ml)	4.4	4.1
Mud Weight (ppg)	10.0	10.0 - 10.1

These data were used in the development of the muds for the proposed trial.

An extensive development programme was undertaken to produce muds with the required specifications, the formulations which exhibited the best physical properties are shown in Table 21.

The data were submitted to Enterprise Oil and were found, from a technical view point, to be acceptable. Agreement could not however be reached between Enterprise Oil and Schlumberger Dowell regarding the contractual arrangements for drilling and, unfortunately, the proposed trial did not proceed. Consequently, **the VOODOO mud is currently waiting for a suitable well to become available for field trialling.**

TABLE 21 Composition and Rheological Properties of Formulation for Intended Field Trial

Component	Quantity					
	$12^{1}/_{4}$"			$8^{1}/_{2}$"		
Rapeseed Oil	106			106		
Ultidrill	82.3			82.3		
Interdrill FL	2.0			2.0		
Truflo 100	3.0			3.0		
Interdrill S	5.0			5.0		
Travis	1.5			1.5		
$CaCl_2$ (83.5%)	23.53			21.35		
Water	59.31			59.70		
Barite	120.3			122.0		
Rheological Property	**BHR**	**AHR**	*	**BHR**	**AHR**	*
Apparent Viscosity (cP)	49.5	50.5	-	51.5	46	-
Plastic Viscosity (cP)	38	40	37	40	39	40
Yield Point Clb/100 ft^2	23	21	27	23	14	21
6 rpm	12	11	16	13	10	13
10 sec gel	11	10	24	10	9	18
10 min gel	-	13	44	-	12	45
Electrical Stability (volts)	11172	939	650	975	912	680
HTHP Fluid Loss (ml)	-	7.0	4.4	-	6.6	4.1

BHR - Before Hot Rolling, AHR - After Hot Rolling (120°C, 16 hours), * - Equivalent data from neighbouring well

10 INTERNATIONAL PATENT APPLICATION

To protect the intellectual property, and the rights for commercial exploitation of the VOODOO mud system, a patent was applied for.

Initially, a UK patent application was made which gave a priority date, *ie* the date of initial protection, of 26 March 1994. This application gave an initial 12 months cover in the UK. At the end of this period it was decided to extend the application to an International level, and hence an International application was made, *ie* a so-called PCT application. This gave cover in the seventy-eight countries participating in the Patent Cooperation Treaty (PCT). The application was then taken to the next stage of the procedure which involved its examination by the International Authority in Belgium, this extended the International cover to October 1996.

The initial opinion of the International Authority, included a request for some additional laboratory work to substantiate our claim that refined rapeseed oil must be used to minimise hydrolysis. The examiner also asked us to make more apparent how our invention differs from an existing US patent describing the use of vegetable oils as drilling mud base oils, *ie* US Patent 4 631 136 (Jones). These points have been addressed and we are awaiting the Authority's opinion.

The initial UK and subsequent PCT applications were compiled by a professional Patent Agent in the employ of Cruikshank and Fairweather, a company contracted by IOE to compile the patent application. The agent is confident that a full, international patent will be awarded in due course.

11 ADDITIONAL PROJECT EXPENSES

During the course of the project certain additional expenses were incurred which were not foreseen at the outset of the project.

The two sources of additional expense were:-

(i) Toxicity testing - During the lifetime of the project, the minimum testing requirements for a single site trial became more stringent and hence more costly.

An additional expense of £7,103 including VAT was incurred because of these stricter requirements.

(ii) Patenting - The administrative costs associated with pursuing an international patent application were more than expected. This was due to employing the services of a Patent Agent as opposed to compiling the document in-house. Due to the specialised legal nature of patenting, however, it was decided that using a Patent Agent gave the best chance of achieving a full patent which could withstand a legal challenge if required.

An additional expense of £9,215.22* including VAT was incurred.

* this includes an outstanding charge of £500 to cover the response to the International Authority.

To help cover these extra expenses incurred by the Institute, the industrial partners agreed to pay an additional £12,000 to IOE.

12 CONCLUSIONS

The main findings of the project are summarised below.

(i) Rapeseed oil (zero erucic acid variety) has an apparent viscosity of 25 cP (40°C) and is, therefore, considerably more viscous than conventional drilling mud base oils (typically 2 - 4 cP).

(ii) Rapeseed oil is compatible, *ie* is miscible, with these conventional base oils, and it was found that such fluids can be used effectively to reduce the rapeseed oil viscosity to more typical levels.

(iii) The ester bonds present in the rapeseed oil molecule undergo hydrolysis to yield fatty acids, di-and monoglycerides and glycerol. It was found that hydrolysis could be reduced by minimising the lime content of the formulation, *ie* a maximum concentration of 0.4 pounds per barrel, and also by using a refined grade of rapeseed oil.

(iv) The degree of refining of the rapeseed oil was found to have a major effect on its hydrolytic stability. During the refining process, the non-glyceride components (gums) are removed from the oil. Edible grade oil, which contains less than 0.1% of gums, was found to possess the necessary hydrolytic stability and hence is the recommended grade of oil for use in formulating oil base muds.

(v) The high temperature stability of the rapeseed oil muds was determined. The extent of hydrolysis occurring, at different ageing temperatures, being taken as the measure of the muds stability. It was found that the rapeseed oil underwent negligible hydrolysis at temperatures less than ca 100°C, and at 120°C the hydrolysis level was acceptable (6 - 10% of available glycerides). When the temperature was increased to 150°C however, over 70% of hydrolysis was detected. This indicated that the rapeseed oil muds had an upper temperature limit of ca 120°C.

(vi) The minimisation of rapeseed oil hydrolysis was a principal project objective. This was because at elevated fatty acid levels, *ie* the result of hydrolysis, the rheological profile of the mud changed. At increasing levels of fatty acid, the low-end rheology of the muds altered, exhibiting a significant decrease in their yield point and gel strength relative to the non-hydrolysed oil.

This phenomenon has been explained from a knowledge of the effect of fatty acids on the organophilic clays used to provide drilling mud rheological control. At elevated fatty acid levels, the quaternary ammonium compounds that coat the surface of the clay become displaced, resulting in the clay losing its organophilic nature and its viscosifying effects.

(vii) The compatibility of the neat rapeseed oil, and a rapeseed oil/Ultidrill blend with commonly used elastomer products was assessed. The results indicated that no adverse interactions should be expected.

(viii) Drilling muds were successfully formulated which met the specifications of Enterprise Oil's Nelson Field development. During this exercise it was found that the muds could tolerate a wet cement (1:1 water:cement) contamination level of 6 pounds per barrel. At contamination levels above this, however, the muds became extremely thick having the consistency of a paste.

A corresponding study where the ester product, Finagreen, was used as the base oil, indicated that this material could tolerate wet cement levels in excess of 8 pounds per barrel.

(ix) A study of the aerobic and anaerobic biodegradation of rapeseed oil was undertaken. The methods used were consistent with the recognised techniques, ie OECD 301F (aerobic) and ISO-CD11734 (anaerobic). The experimental procedures were not, however, carried out in a GLP accredited laboratory, and are therefore not acceptable to a regulator.

The average aerobic biodegradation was found to be 61% over a twenty-eight day period. The 'pass mark' for readily biodegradable substances is 60%.

The average anaerobic biodegradation was found to be 51% over a fifty-six day period. There is no current 'pass-mark' for anaerobic degradation but values of 50 - 60% are commonly found for synthetic drilling mud base oils.

(x) Toxicity testing of rapeseed oil (both partially and fully refined grades) was carried out by ERT Ltd. The test species used was the marine copepod *Acartia tonsa*.

It was found that both the partially refined grade (so-called superdegummed) and the edible grade were effectively non-toxic towards this organism.

(xi) An application was made to MAFF, requesting permission to use the VOODOO mud system to drill a single-site well. MAFF asked for a suite of toxicity and bioaccumulation tests to be completed, before any decision could be made.

The tests requested, and their results, were as follows:

(a) PARCOM protocolised toxicity testing of the whole mud formulation to the algal primary producer, *Skeletonema costatum*.

Result - 2% growth inhibition at 3,200 mg/l.

(b) PARCOM protocolised toxicity testing of the whole mud formulation to the sediment dwelling organism, *Corophium volutator*.

Result LC_{50} - 914 mg/kg.

(c) Bioaccumulation potential measurements, *ie* log P_{ow} values, of rapeseed oil and Ultidrill.

Result - rapeseed oil log P_{ow} >6
Ultidrill log P_{ow} >6

The data were passed to MAFF, and were found to be acceptable for a single-site trial.

Permission was given therefore to carry out a single site trial using the VOODOO mud system.

(xii) A proposed field trial, involving the drilling of Enterprise Oil's well 53/5b-E, was, for contractual reasons, not carried out. Rapeseed oil based fluids were however formulated which met the technical requirements of the well, and were deemed acceptable by Enterprise

Oil. The projects partners are currently waiting for another suitable well to become available.

(xiii) An international patent application was made, describing the major advances achieved during the project. The procedure was initiated in March 1994, and, if successful, will give cover from that date. The document was compiled by a professional Patent Agent who is confident a full patent will be granted in due course.

Application number - PCT/GB95/00680

13 ACHIEVEMENT OF GOALS

The researchers, in collaboration with their commercial partners, have investigated the potential for using rapeseed oil as a base fluid in drilling fluids of the type used to drill oil and gas wells offshore and **have successfully formulated a mud system that has**:

(i) **met an oil company's technical specification to drill an offshore well;**

(ii) **obtained a temporary government OCNS classification and permission to use the mud for a single well field trial.**

14 COMMERCIALISATION

The final part of the development process, **commercialisation**, may be divided into the following stages:

(i) **Field trial** (the researchers hoped this would form part of the research project);

(ii) **OCNS re-classification of the mud system to Group E** (this will cost approximately £12,000 and is outwith the scope of the original project);

(iii) **Licensing/commercialisation agreement** between Heriot-Watt University and the Commercial Partners (ideally to be completed prior to October 1996, when patent application would need significant financial investment to obtain international cover).

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