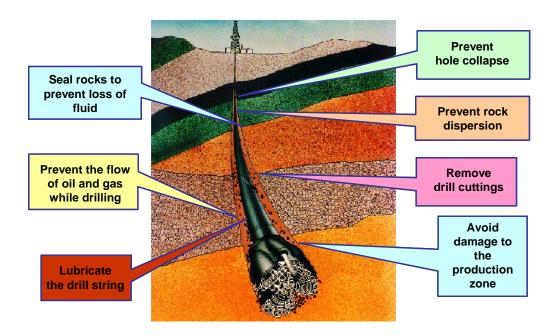
Base Oil Options for Onshore Drilling

By Don Van Slyke

Base Fluid Alternatives

As operators face increasingly demanding drilling, today's drilling fluids need to perform under challenging conditions while continuing to reduce their environmental footprint.

Non-aqueous fluids (NAF's) exhibit superior shale inhibition, borehole stability and lubricity compared with water-based drilling fluids. NAF's are widely regarded in the industry as the fluids of choice to drill the most difficult formations in deep, deviated, and/or complex wells, primarily because NAF's drill gauge boreholes through water-sensitive shale formations. Since major capital projects require drilling difficult wells, NAF's are critical to an operator's success.



Companies should be committed to operating in a clean and environmentally responsible manner that protects the health and safety of their employees and the public, - risk dollars, not people or the environment. Health risks and pollution hazards can be substantially minimized by using synthetic paraffins instead of diesel or distillates. When health, safety, long term liability, disposal cost, and drilling performance are factored in, the overall cost for drilling wells with these fluids is even lower than the cost for drilling with diesel.

There are many base oils that can be used in the continuous phase of NAF's for drilling wells onshore. This article will focus on the Oil and Gas Producers Association (OGP) Groups at the opposite ends of the spectrum in terms of environmental, health and safety:

- Group I includes diesel and straight run distillates, defined herein as fluids having 20 to 50% total aromatic content
- Group II includes mineral oils having medium aromatic contents
- Group III includes enhanced mineral oils and synthetic paraffins, defined herein as having less than 0.1% total aromatic content

Diesel has a relatively low flash point and an aromatic content that typically runs between 20 and 50%. Also included in the Group I category are straight run distillates, including Cutter D, Distillate 822, and Drillsol Plus. These distillates are primarily used in Canada, although they are starting to be applied in the U.S., particularly in North Dakota shale gas drilling. Advantages of distillates over diesel are that they are slightly cheaper and have higher flash points. Disadvantages of distillates compared to diesel are that they have about the same total aromatic content as diesel, are more viscous than diesel and some exhibit a black color from high asphaltene polynuclear aromatic (PAH) content. PAH's are the most carcinogenic components of oils hence they are highly regulated by environmental agencies such as EPA..

Group II fluids include mineral oils with medium aromatic contents. These fluids are falling out of use because they have higher aromatic contents than Group III fluids (with the associated HES disadvantages) yet their cost is not significantly lower than the cost of Group III fluids.

The high-volume commercial base fluid Saraline 185V meets the requirements for the OGP Group III category, the highest base fluid classification. It is available for use in the North America drilling fluids market.

Group III also includes other synthetic base fluids such as esters, internal olefins, and linear alpha olefins. These non-paraffin synthetics are primarily designed to meet specific offshore discharge regulatory requirements and are more expensive than Saraline 185V. Low aromatic content mineral oils such as Escaid 110 are included in Group III. These low aromatic mineral oils have a higher cycloparaffin and branched paraffin content. Hence they are less biodegradable that the paraffinic Saraline 185V, due to the relative difficulty for microbes to break down the molecules.

Saraline 185V is a Chevron-patented GTL synthetic paraffin base fluid that is one of the highest volume base oil products in the world. It is manufactured by Shell in Qatar and Malaysia. The Qatar product, made at the new Pearl GTL plant, has been shipped to the U.S. and stored in New Orleans to serve the North America market.

The Group III alternatives enhance the safety, health, and environmental properties of nonaqueous drilling fluids by providing ultra-low total aromatic content, ultra-low PAH content, and ultra-low benzene, toluene, ethylbenzene, xylenes (BTEX) content.

Field Case Histories

Saraline 185V has been used extensively worldwide, but its application in onshore drilling has been limited due to the perception that diesel and distillates result in lower well costs. While the unit cost per barrel for diesel and distillate base oils is lower, the overall well cost has been shown to be higher for diesel/distillates compared to Saraline 185V.

To strengthen the business case for using Saraline 185V instead of diesel/distillates, field trials were conducted that demonstrated the following advantages over diesel/distillates:

- Reduction in overall drilling cost per well
- Reduction in overall mud cost per well
- Reduction in disposal cost
- Improved health and safety
- Reduced vapors
- Reduced dermal exposure
- Increased environmental performance
- Lower ECD
- Reduced lost circulation
- Increased ROP
- Higher mud recovery
- Reduced base oil consumption
- Reduced oil retention on cuttings
- Decreased trip time
- Decreased rig time
- Improved rig personnel retention
- Increased longevity for elastomers
- Reduced long-term liability

In 2014 and 2015, Shell conducted a 4 well field trial in the Permian Basin, Texas, comparing the performance of Group III synthetic paraffin Saraline 185V with that of diesel used on 4 offset wells. Comprehensive measurements were made and extensive data were collected on drilling performance, environmental performance, waste management, cost, industrial health and hygiene. They found that Saraline 185V saved \$100,000 per well compared to diesel, even though the unit cost was about \$50 per barrel higher. The rate of penetration was 40% higher for Saraline 185V, which resulted in a decrease in rig time of 1-2 days per well. The trip time was 10-20% less with Saraline 185V. The base oil consumption for Saraline 185V was 40% lower than with diesel, the mud recovery was 58% higher, and the mud bill was 30% lower (exclusive of barite). The surface tension for Saraline 185V was much lower than that of diesel, as confirmed in sand bed flow tests. As a result, the oil retention on cuttings was lower for Saraline 185V as was the volume of drilled cuttings waste requiring treatment/disposal. There were no lost circulation events with Saraline 185V, while the diesel wells experienced some lost circulation incidents. Casing was landed successfully in the Saraline 185V wells, whereas in the diesel wells there were two instances of inability to land casing. The short term vapor exposure was 50x lower with Saraline 185V compared to diesel, and the 8 hour exposure was 4x lower. Dermal exposure as determined by doctors was 4x lower with Saraline 185V compared to

diesel. A survey sent to rig workers indicated much higher satisfaction when working with Saraline 185V compared to working with diesel.

Physical Properties

The physical properties of Group III fluid Saraline 185V, are compared with the properties of diesel in the table below.

	Diesel	Saraline 185v
Туре	Group I	Group III Synthetic Paraffin
Total Aromatics, wt%	37	.02
Kinematic Viscosity at 40 °C, cSt	3.4	2.66
Cold Flow Viscosity at 0 °C, cP		6.0
Polynuclear Aromatics, wt%	3-10	<.001
Flash Point, °C	66	89
Pour Point, °C	-10	-27
Density, g/cc	.85	.775
Aniline Point, °C	61	95

The lower viscosities of the Group III fluids result in significant improvements in drilling performance and reduction in drilling cost. Lower kinematic viscosity provides reduced frictional pressure drop, lower equivalent circulating density, better management of narrow margin fracture gradients, and enhanced rate of penetration. The low cold flow viscosity of the Group III fluids is particularly useful in deep water drilling, reducing surge and swab pressures and improving hydraulic performance of the drilling fluid.

The Group III fluids have higher flash points than diesel, which improves safety, reducing the chance of explosion or fire on the rig when high flowline temperatures are encountered. High flash points also reduce the exposure to vapors on the rig. The pour points of the Group III fluids are significantly lower than the pour point of diesel. This is particularly beneficial when transporting and handling the drilling fluid in cold climates such as those that are encountered in North America or Central Asia. The low pour point also improves drilling performance at low temperatures.

The higher aniline points with Group III fluids minimizes attack on elastomers and allows the fluid to be used with a wider variety of rig equipment.

The most significant improvement in Group III fluids is the lower aromatic content over diesel, both measured in total aromatics and polynuclear aromatics. Saraline 185V has 1,850 times lower aromatics than diesel. The lower aromatic content improves HES performance and reduces toxicity, as detailed in this paper. The concentration of toxic, carcinogenic, unbiodegradable polynuclear aromatics is about 10,000 times lower in Group III fluids compared with diesel.

Improved Drilling Performance and Cost Reduction

Group III base fluids are made to certain narrow physical and chemical specifications. In particular, synthetic paraffins within the Group III category are manufactured from pure components (methane). Diesel and distillates have no compositional specifications and need only to conform to a wide range of physical properties. Diesel is typically blended from several light and heavy streams available in refineries. Distillates are straight run products made by the continuous nonreactive distillation of crude oil to separate it into products in the order of their boiling points.

Due to the minimal processing used to manufacture diesel and distillates, they have thicker viscosities than fluids made with more rigorous processing, such as Group III base oils. Base fluids with thicker kinematic viscosities measured at 40 deg C typically result in thicker downhole mud viscosities during drilling.

Low base fluid viscosity means reduced drilling mud plastic viscosity (PV) and frictional pressure drop, lower surface pump pressure (SPP), enhanced rate of penetration (ROP), lower equivalent circulating density (ECD), and reduced risk of lost circulation (LC).

Reducing the difference between downhole ECD and mud weight is becoming more important as the wells that are drilled are becoming more challenging. In high temperature high pressure (HTHP) wells, deep water wells, extended reach wells, and wells in depleted reservoirs, the margins between pore pressure and fracture gradient may be very narrow. Low ECD may enable the drilling of otherwise unreachable target resources. Because ECD is directly proportional to the annular frictional pressure drop, it is important to minimize the pressure drop. There is also a minimal impact to drilling fluid rheology at low operating or mud line temperatures.

The cost of drilling a well is reduced with Group III fluids compared to Group I fluids due to the higher rates of penetration and other factors. Reduced viscosity at the bit should improve the rate of chip release, since a thinner fluid can enter fractures generated by bit action more quickly. Lower viscosity at the bit also improves bit hydraulics, since more horsepower is available due to reduced pressure losses.

Occupational Health and Industrial Hygiene

Recent evidence suggests that with diesel there are harmful short term and long term effects from worker exposure. Workers employed in drilling operations are often exposed to drilling

fluids either by skin contact or inhalation of aerosol and vapor. Contact is often unavoidable during use, either skin contact mainly associated with work on the drill floor or airborne contamination via vapor and mist in the mud room and shale shaker room. Since drillers regularly come in contact with the mud they use, implementation of the proper worker protection measures for diesel-based mud is necessary if this risk is to be minimized.

Field experience with diesel mud has shown that common complaints from workers include eye and skin irritation, allergic reactions, dizziness, headaches, and nausea. Aromatics in diesel are believed to contribute to worker discomfort. In addition, the low boiling point of diesel results in more vapor being produced over the mud pits.

Diesel is listed as moderately to highly toxic in skin tests on rabbits, and results in moderate to high skin irritation in humans. There are also chronic health concerns with diesel. Diesel is classified as carcinogenic by OSHA, IARD, and NTP. Diesel has produced positive skin cancer tests in animals. Benzene, currently a molecule of significant industrial hygiene and environmental concern as a potential carcinogen, is present in high levels (30-1000 ppm) in diesel.

Group III fluids have a low order of acute toxicity by the oral, dermal, and inhalation routes of exposure, are not labelled as potential carcinogens, are not expected to be skin sensitizers in humans, and are not mutagenic using in vitro or in vivo genotoxicity assays. Group III fluids result in improved rig hand retention due to the superior occupational health and industrial hygiene performance compared to diesel and distillates.

Working with fluids implies potential exposure to evaporative emissions. To help assess acceptable exposure, base fluids are assigned a specific Occupational Exposure Limit (OEL). The OEL is listed on each product's Material Safety Data Sheet (MSDS). The OEL is defined as the maximum airborne concentration of a substance that does not create an unreasonable safety risk for workers being exposed 8 hours/day, 5 days/week. It is expressed in units of mg material per cubic meter of air. Other human health attributes for Group III fluids, and the vapor OELs for Group III fluids Saraline 185V and Escaid 110 compared with Group I fluid diesel, are shown in the table below:

	Diesel	Saraline 185V	Escaid 110
OEL	200 mg/m ³		1200 mg/m ³
Acute Oral		LOW LD ₅₀ > 5 g/kg	LOW LD ₅₀ > 5 g/kg
Acute		LOW $LC_{50} > 5 mg/L$	LOW LC ₅₀ >Saturated vapor
Inhalation		(4h)	concentration
Inhalation TLV	100 ppm		300 ppm
Estimate			
Skin Irritation	Moderate/High	NON-IRRITANT	MILD PII = 1.08 to 1.58
Sensory		NON-IRRITANT	NON-IRRITANT Alaire
Irritation			Assay
Genotoxicity		NOT MUTAGENIC,	NEGATIVE Ames, In vitro
		NOT CLASTOGENIC	chromosome aberration, In
			vivo chromosome aberration

Subchronic		LOW Dosage levels of 750 mg/kg/day (highest dose tests) was considered to be the NOAEL for reproductive and systemic toxicity	LOW NOAEL = 1000 mg/kg/day (13-week oral) NOAEL = 900 ppm (12-week inhalation)
	Labeled as potential carcinogen	NOT EXPECTED TO BE CARCINOGENIC	NOT EXPECTED TO BE CARCINOGENIC Based on negative genotoxicity data and low subchronic toxicity

Note:

OEL: Occupational exposure limit

 LC_{50} : 50% Lethal concentration - is the concentration of a chemical in water that is estimated to produce mortality in 50% of a test population over a specific time period

LD₅₀: 50% Lethal dose – is the concentration of a chemical administered (e.g. milligrams) per kg of body weight that produces mortality in 50% of the group of test animals over a specific time period

PII: Primary Irritation Index

NOAEL: No observable adverse effect level. The highest exposure of a chemical having no adverse effects.

Ecotoxicity

Group III fluids have no acute toxicity effects on marine or fresh water species. They have been assessed in a diverse array of aquatic, sediment and terrestrial species tests. Because of the low water solubilities of these products, and the expected partitioning of residues to air, chronic exposure of aquatic organisms in the water column to residues of Group III fluids is unlikely. As a result, long-term adverse effects to aquatic organisms are not expected under single (e.g. accidental release) or intermittent release conditions.

For onshore applications, the high environmental performance of Group III fluids results in drill cuttings that are less expensive to dispose or remediate, and exhibit lower impacts to soil and groundwater than diesel/distillates.

Group III fluids are not classified for the environment under the European Union Dangerous Substance Directive (DSD) and Classification Labelling and Packaging of Substances and Mixtures (CLP), or the Globally Harmonized System of Classification and Labeling of Chemicals (GHS). In addition, Group III fluids are readily biodegradable per OECD 301F (freshwater) test methodology, which is accepted in global chemical regulatory programs such as GHS classification and REACH. Group III fluids also showed >60% biodegradation based on ThOD (theoretical oxygen demand) per OECD 306 (seawater) test methodology, indicating the potential for ultimate biodegradation in the marine environment. It is generally accepted that if a substance degrades in one media, e.g. freshwater or seawater, it will degrade in other media, e.g., soil, under most environmental conditions.

Ecotoxicity and biodegradation data for Group III fluids Saraline 185V and Escaid 110 are compared with data for diesel in the table below. Note that there is a huge difference in

ecotoxicity between diesel and Group III fluids Saraline 185V and Escaid 110. Furthermore, few test results are available for diesel because it is a given that it will perform poorly in ecotoxicity tests compared with fluids having negligible aromatic content. For example, the toxicity of diesel to Brown Shrimp is between 277 and 4,706 times higher than the toxicity of Escaid 110 to Brown Shrimp, according to the 96-hr LC₅₀ results. Likewise, the toxicity of diesel to Mysid Shrimp is over 500 times higher than the toxicity of Saraline 185V to Mysid Shrimp.

	Diesel	Saraline 185V	Escaid 110
Ecotoxicity			
Fish			
Oncorhynchus mykiss	96-hr LL ₅₀ = 6.6	96-hr LC ₅₀ >1,000 ppm	96-hr LL ₀ >10,000 ppm, Typical =
(Rainbow Trout)			100,000 ppm
Pimephales promelas	96-hr LL ₅₀ = 57		96-hr LL ₀ = 750 mg/l
(Fathead Minnow)			
Cyprinodon variegatus		96-hr LC ₅₀ >1,000 ppm	
(Sheepshead Minnow)			
Tilapia mossambica		96-hr LC ₅₀ = 145,000 ppm	96-hr LL ₅₀ = 31,200ppm
Mugil parsia		96-hr LC ₅₀ = 98,000 ppm	96-hr LL ₅₀ = 30,600ppm
Mugil cephalus (Mullet)		96-hr LC ₅₀ 86,500 ppm	
Pagrus auratus		96-hr LC ₅₀ >100,000 ppm	
(Snapper)			
Boleopthalmus boddarti		10-d LC ₅₀ = 235,000 mg/kg	10-d LC ₅₀ = 61,500 ppm
(Mud Skipper)			
Brachydanio rerio		96-hr LL ₅₀ = >1,000 mg/l	
(Zebrafish)			
Ctenogobius		96-hr LC ₅₀ >100,000 mg/l	
gymnanuchen (Goby)			
Leuciscus idus (Golden			48-hr LC ₅₀ >1,000 mg/l
Orfe)			
Notemigonus	10 mg/l		
crysoleucus (Golden			
Shiner)			
Invertebrates			
Crangon crangon	96-hr LC ₅₀ = 1.7-9.4 ppm		96-hr LC ₅₀ = 2,600 – 8,000 ppm
(Brown Shrimp)			
Chaetogammarus			96-hr LL ₀ = 10,000 ppm
marinus (Amphipod)			
Mysidopsis bahia	96-hr LC ₅₀ <50,000 ppm,	96-hr LC ₅₀ SPP	96-hr LL ₀ = 100,000 ppm
(Mysid Shrimp)	Typical = 2,000 ppm	>1,000,000 ppm	
Mysidopsis juniae		96-hr LC ₅₀ = 353, 553 ppm	96-hr LL ₅₀ >1,000,000 ppm
Penaeus indicus		96-hr LC ₅₀ = 67,000 ppm	
(Indian Prawn)			
Scylla serrate		10-d LC ₅₀ = 128,000 mg/kg	
(Mud Crab)			
Acartia tonsa		48-hr LC ₅₀ >1,000 mg/l	
(Copepod)			
Daphnia magna	EL ₅₀ = 1 ppm	48-hr EL ₅₀ > 1,000 mg/l	48-hr EC ₅₀ <100 mg/l

(Freshwater Flea)		
Corphium volutator	10-d LC ₅₀ =>20,000 (wet) >50,000 (dry)	10-d LC ₅₀ = 341 ppm
Lytechinus variegatus	24-28-hr CEO(I)I >1,000,000	
(Sea Urchin)	ppm No Chronic Effects	
Penaeus monodon	72-hr EC ₅₀ = 148,793 mg/l	
(Shrimp Larvae)		
Perna viridus (Green	96-hr LC ₅₀ = 200,000 mg/kg	
Mussel)		
Artemia nauplius (Brine	96-hr LC ₅₀ = 4,789 mg/l	
Shrimp)		
Penaeus vannamei	96-hr LC ₅₀ >100,000 mg/l	
(Pacific White Shrimp)		
Algae		
Skeletonema costatum	72-hr EC ₅₀ = 113,796 mg/l	72-hr NOEC= 815 mg/l
Nitzschia closterium	72-hr EC ₅₀ >83,300 ppm	
Environmental Fate		
Aerobic		
biodegradation		
(freshwater)		
OECD 301F	Readily biodegradable	64% in 28-d
OECD 306	72% in 28-d	
Aerobic		
biodegradation		
(seawater)		
OECD 306	62% in 28-d	67% in 28-d
Aerobic		
biodegradation (soil)		
OECD 307	Half-life (DT_{50}) = 21 days (based on 1000 mg/kg initial dose)	
Environmental		
Partitioning		
Octanol/Water Partition	>6.5	>6.5
Coefficient, LogKow		
(OECD 117)		
Bioconcentration Factor	35-d BCF= 3.2, Depuration Half Life = 21 days	
OECD 305 A-E (Blue		
Mussel)		
Note:		

Note:

LC_{50:} 50% Lethal concentration - is the concentration of a chemical estimated to produce mortality in 50% of a test population over a specific time period

 $LL_{50:}$ 50% Lethal loading – is the level of a chemical estimated to produce mortality in 50% of a test population over a specific time period. $LL_{50} = LC_{50}$ for soluble compounds

LL₀: Loading level where no lethal effects are observed at all loadings tested

EC₅₀: Median effective concentration - is the concentration of a chemical estimated to produce a specific effect in 50% of a population of test species after a specified length of exposure.

 EL_{50} : Median effective loading – is the level of a chemical estimated to produce a specific effect in 50% of a population of test species after a specified length of exposure. $EL_{50} = EC_{50}$ for soluble compounds

NOEC: No observable effect concentration

BCF: Bioconcentration factor

Saraline 185V is classified as 'not harmful' to aquatic organisms on the basis of the European Union Criteria. Its superior eco-toxicity performance is acknowledged with an OCNS (Offshore Chemical Notification Scheme for the North Sea) Group ranking of E – least potential hazard.

Hauling of cuttings containing diesel results in non water quality environmental impacts. Such impacts include air pollution from transportation, energy use during transportation, and disposal site factors. Diesel mud disposal often places toxic hydrocarbons and priority pollutants in landfills, where they can potentially leach into groundwater or otherwise leak out of the containment. The aromatic fraction of diesel contains compounds such as benzene, toluene and xylene which are partially soluble in water. There is also the question of whether sufficient capacity is available to handle cuttings disposal onshore. Waste volumes are high, - studies have shown that an 18:1 volume ratio of wash water to cuttings can be required for cleaning cuttings boxes.

In some states such as California, Group III base fluids are permitted to have a non-hazardous waste classification for both the mud and cuttings, and enable the cuttings to be disposed of in a non-hazardous waste site. Diesel cuttings will not pass the disposal law criteria so they must be disposed of in a hazardous waste site.

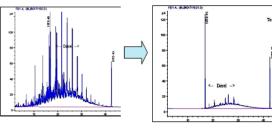
The OSHA Hazardous Communication Standard (HCS) for Oil & Gas Extraction, SIC 13, mandates that a mixture prepared from any component which carries a hazard warning must carry the same hazard warning if the mixture contains >1% of the hazardous component or >0.1% of the hazardous component if it is a potential carcinogen. Hence, commingling even small portions of diesel mud or cuttings with other non-hazardous waste will "spoil the batch".

The U.S. Clean Air Act (CAA) calls for monitoring and minimizing hazardous air pollutant (HAP) emissions to the air. Aromatic compounds such as benzene, toluene and xylenes are HAP's. Reduced HAP emissions result from Group III drilling operations due to rigorous hydrogenation/purification of the dearomatized base fluids. Odor is also improved with Group III base fluids due to the removal of sulfur.

Group III drilled cuttings can be bioremediated in a fraction of the time it takes to bioremediate diesel cuttings, due to the higher biodegradability and lower toxicity of the hydrocarbons that make up Group III fluids. As shown in the figure below, the aromatic fraction of diesel, which comprises between 20 and 50% of the fluid, does not readily biodegrade. This leaves a toxic "hump" of aromatic compounds behind, as shown on the GC fingerprint. Group III fluids do not have the aromatic hump. In particular, synthetic paraffins within Group III are readily biodegradable, so that bioremediation is a viable option for cuttings disposal.

Base Fluid Degradability

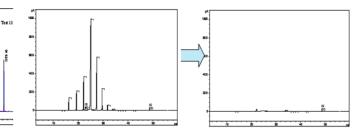
Group I: Diesel/Distillates





Remaining components toxic and nondegradable

Group III: Synthetic Paraffin



- ☑ Complete degradation
- ☑ No toxic remaining components