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Maximising Environmental Grease Compounds for Extreme High Pressure High Temperature Applications

Peter Pratelli, Technical Manager UK
Contributors: Don Oldiges, VP of Research & Development

Abstract

Jet-Lube's patented Environmentally Considered Formula (ECF) technology was developed to comply with the stringent North Sea environmental guidelines for offshore chemicals used on exploration drill rigs while maintaining the required performance standards. This paper explores the environmental properties of the binding grease, the constituent base oils, solid lubricants and additive chemistries to deliver a bio-degradable OSPAR compliant formula.

As conventional sources of oil and gas decline, operators are increasingly turning their attention to unexplored or underdeveloped areas with increasing focus on High Pressure High Temperature (HPHT) wells. Under such extreme conditions many items of equipment and tools simply cease to function. This imposes very real limitations on much of the technology currently available to help develop these reservoirs. Having developed a range of ECF drill collar and casing joint compounds Jet-Lube set about taking this technology a step further to develop a casing and tubing compound for extreme HPHT applications. By highly tuning existing market leading products and reformulating with new specially refined base oils, Jet-Lube had been able to develop a much improved product. This paper will focus on the challenges of delivering a bio-degradable product with such inherent instability for HPHT applications.

Commercial Background

The OSPAR Commission a successor to OSLO and Paris Commissions adopted strategies in 1998 to influence the protection and conservation of ecosystems and biological diversity in the North-East Atlantic. Particularly this manages use of hazardous chemicals in offshore and marine applications. Chemicals and lubricants used in offshore applications must achieve a permit to deck via reference to their Offshore Chemical Notification Scheme (OCNS) grading which is dependent on the chemical compositions, biodegradation, bioaccumulation and aquatic toxicities.

North Sea (UK) governed by The Centre for Environment, Fisheries and Aquaculture Science (CEFAS). Products are assigned an A to E rating with any relevant substation warnings for toxic components. E representing the best possible environmental performance.

Norwegian continental shelf governed by The State Pollution Control Authority (SFT). Colour based designations given from black to yellow. A green designation is given to water and specified inert materials that "Pose Little Or NO Risk" (PLONOR) to the environment. Yellow representing the best achievable designation for chemical mixtures such as thread compounds.

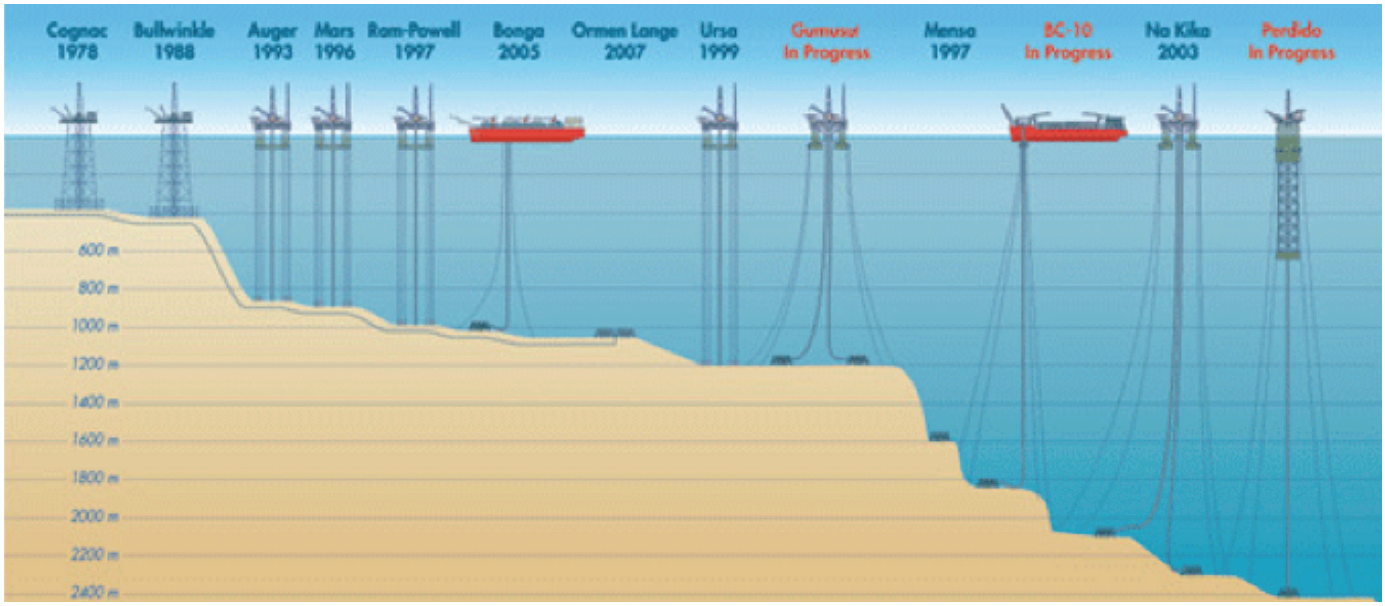


Figure 1. *Progression of off-shore drilling depths*

Hence operators are now obliged to consider the environmental profile of chemicals and lubricants used in offshore applications as a priority. Similar methodologies relate to Vessel General Permit (VGP) and other such environmental initiatives.

As conventional sources of oil and gas decline, operators are increasingly turning their attention to unexplored or underdeveloped areas. High temperatures and/or high pressures are often found in these uncharted territories, presenting complex challenges including casing buckling, accelerated drilling fluid chemical reactions and formation collapse. Historically High Pressure High Temperature (HPHT) wells were not considered achievable let alone commercially viable until the late 1990's. By their nature, high pressure fields contain more hydrocarbons than those with normal conditions but the risks are much greater.

Under such extreme conditions many items of equipment and tools simply cease to function. This imposes very real limitations on much of the technology currently available to help develop these reservoirs. The challenge therefore is to meet the tough application performance criteria and develop a product that is able to operate in high pressure and or high temperature wells within the OSPAR environmental certification.

Oilfield Thread Compounds

Jet-Lube has specialised in supplying oilfield thread compounds for over 65 years. Thread compounds are applied to tool joints and drill collars on drill strings preventing seizure / wear as well as API tubing and casing joints in well casings forming an integral sealing function. The performance of thread compounds is characterised by four primary aspects:

1. Sealability
2. Frictional / Make up characteristics
3. Galling resistance / anti-wear.
4. Drilling and production fluid compatibly

Thread compounds in drill string applications require controlled, higher frictional properties to protect against down-hole make-up where as a casing compound must form effective seals for API connection designs proportionally lower torque. For most proprietary mechanical seal designs the seal properties are intended to be provided by the connection design itself, so conventional thread compounds designed to seal API connections can interfere with the mechanical connections. For the duration of its use the compound will be expected to protect against wear, galling, seizure and corrosion ensuring easy break outs and long term protection of the drill pipe / casing many of which are made from high grade metal alloys and therefore represent significant value assets. Such alloys have much greater corrosion resistance but are more susceptible to galling and wear. As well tubing must occasionally be removed and replaced when well flow decreases anti seize characteristics must be retained. Thread compounds must not break down during use or it can result in high break-out torques and / or dry connections which increase the potential for wear and damage. Additionally drilling mud compositions often utilize high pH additives to reduce corrosion as well as various surfactants to suspend cutting debris. These combinations result in "alkaline cleaner" type properties which cause most grease types to dissociate with time and temperature and result in thread compound adhesion problems. Without a sufficient coating of thread compound connections will not attain the proper engagement nor will adequately seal or resist galling.

ECF Product Formulation

In order to meet the stringent requirements of the OCNS, Jet-Lube in cooperative development with VAM USA and Statoil developed an Environmentally Compliant Formula (ECF) product range. In order to achieve group E / Yellow, best in class environmental formulas jet-Lube had to consider:

1. Chemical composition – reformulate any toxic components
2. Biodegradation – 20-60% biodegradation in 28 days
3. Bioaccumulation – Log Pow < 3 or proof that the molecular weight exceeds 900
4. Aquatic toxicity - algae, crustacean, fish LC50 /EC50 >1000 ppm, sediment-dweller >10,000 ppm

Traditionally anti-seize compounds contain heavy metals to inhibit localised welding between similar metals during engagement, additionally anti-corrosion and anti-wear chemistries can be toxic to aquatic life. Many of the conventional additive types: copper, lead, zinc, Molybdenum disulphide, organophosphates and many sulphur compounds are wholly unsuitable to environmental applications. Inorganic alternatives were sort with many solid boundary lubricants were tested in combination with different particle sizes. Calcium fluoride with a hardness comparable to iron and good thermal stability in combination with Jet-Lube's patented micronised fibre additives **(EP0832173 A1)** yielded the desired frictional and galling resistance / anti-wear performance. To measures improvement in galling resistance and frictional properties a modification to the "Test Apparatus for Universal Friction Evaluation" outlined by the American Petroleum Institute (API) Recommended Practices 7A1 and 5A3 was utilised.

As with most Industrial lubricants the majority of the performance characteristics are intrinsically related to the base oil. To develop an inherently biodegradable product base oil selection is key, due to sulphur content and undefined chain length conventional mineral oil grades are unstable. Jet-Lube reviewed a range of base oils for suitability:

Initially Jet-Lube considered a biodegradable grease based on esters and aluminium complex thickeners. Group 5 oils where considered too expensive for this application. Since then extensive environmental studies on other synthetic, natural, petroleum base oils and blends have been completed. Using an optimised blend of vegetable oils and calcium sulfonate grease thickener we were able to deliver environmental performance while constraining costs within industry expectations **(EP2876151 A1 Patient Pending)**. For increased functionality a small amount of naphthenic oil (for enhanced low temperature flow properties) and PAO (added thermal stability) were added to optimise the formulation. Because of the calcite particles' lubricating properties, performance additives containing sulphur, phosphorous or zinc where not needed to enhance the extreme pressure functionality. The strong polar action of the sulphonate micelle and the calcite calcium carbonate yields superior corrosion resistance proprieties hence improving the formula's anti corrosion properties. Furthermore as an over-based grease (high total base number (TBN)) it is wholly compatible with high pH drilling muds. Being less soluble to drilling muds allows the thread compound to adhere to threads better than other grease types and less subject to dissociation by the "cleaner" properties of the drilling fluids.

Additionally, the massive molecules formed in the grease making process make bioaccumulation potential nil. Biodegradation by-products in the high molecular weight, near pseudo-polymers, may or may not result in a concern. The high hydrophobicity of calcium salts such as calcium 12-hydroxystearate or calcium sulfonate can make biodegradability much slower (as determined by OECD 306), but as such would also make bioaccumulation in individual organisms that much more unlikely in a marine environment.

Oil Type	Good	Bad
Vegetable Oil	• Polar nature lends to better lubricating properties • High viscosity index and flash point	• Hydrolytic stability and low temperature serviceability
Synthetic Oils		
Polyalphaolefins (PAO)	• Thermal stability	• Rubber / elastomer compatibility issues • Expensive
Esters	• Good Solubility • Antioxidant properties • Excellent high and low temperature properties	• Rubber / elastomer compatibility issues • Poorer hydrolytic stability • High temperature breaks down to form alcohols
Polyalkylene Polyglycols (PAG)	• Good for water based lubricants	• Emulsification issues with water • Poor additive solubility

HPHT

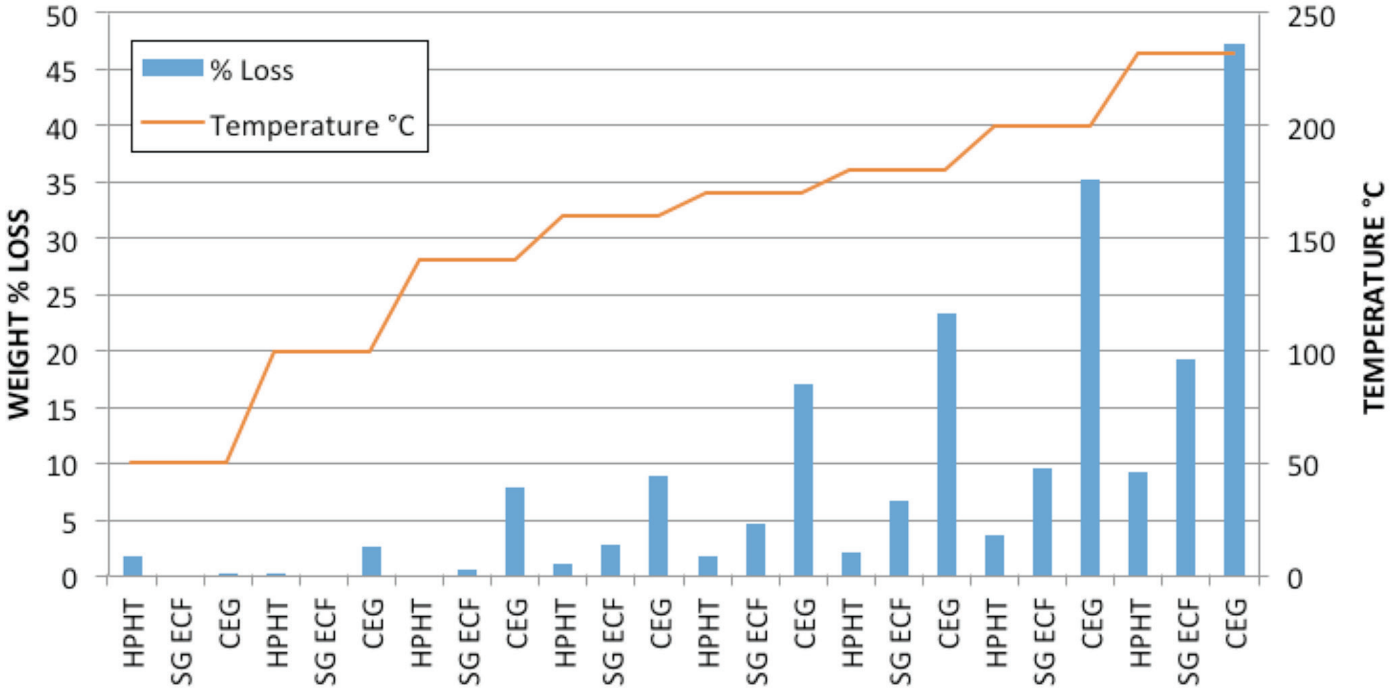
Jet-Lube currently offers a range of tubing and casing compounds which are used to seal joints and prevent seizing, corrosion, galling. Such casings are inserted after drilling to ensure the integrity of the well bore. In high temperature high pressure applications these compounds would be expected to function despite adverse conditions.

The goal therefore is to extend the performance of the ECF product range to reliably function at higher temperatures and / or higher pressures whilst maintaining best in class environmental performance. The closest comparable environmental grade, Seal-Guard ECF, operates up to 140°C, existing formulation attempts resulted in a loss in performance for more critical and extreme applications. The properties of Lead based API modified are well documented in the industry and favoured by many operators. Despite the obvious heavy metal toxicity of lead it has been used in casings throughout the industry for a great many years. During this time it has displayed excellent anti-welding and sealing properties and its coefficient of linear expansion is greater than that of the alloys used in the drilling industry. This aids the sealing properties at elevated temperatures. However, given increasing bio-toxicity & bioaccumulation concerns, particularly in reference to OSPAR compliance (lead listed by NSF on its list of priority substances) Jet-Lube has developed a number of dry lubricants to replicate the properties of lead in anti-seize compounds namely graphite, talc, calcium fluoride and micronized fibres. With no heavy metal content these products offer a much improved bio-toxicity rating and have been approved by European authorities for offshore use.

Fundamentally biodegradable products are intrinsically unstable, introducing increased stress factors like extreme temperatures and pressures accelerate degenerative process such as oxidation, nitration, cracking etc. Hence the HPHT had to be formulated to safeguard thermal stability. More generally genetic modifications of specific vegetable oils has led to some enhanced thermal stability. Whilst vegetable oils have proven functionality with existing ECF products an ester / PAO blend was optimised with high carbon chain lengths for enhanced performance. By adapting a blend of specially synthesised oils a proprietary formulation was optimised to deliver intrinsic thermal rigidity.

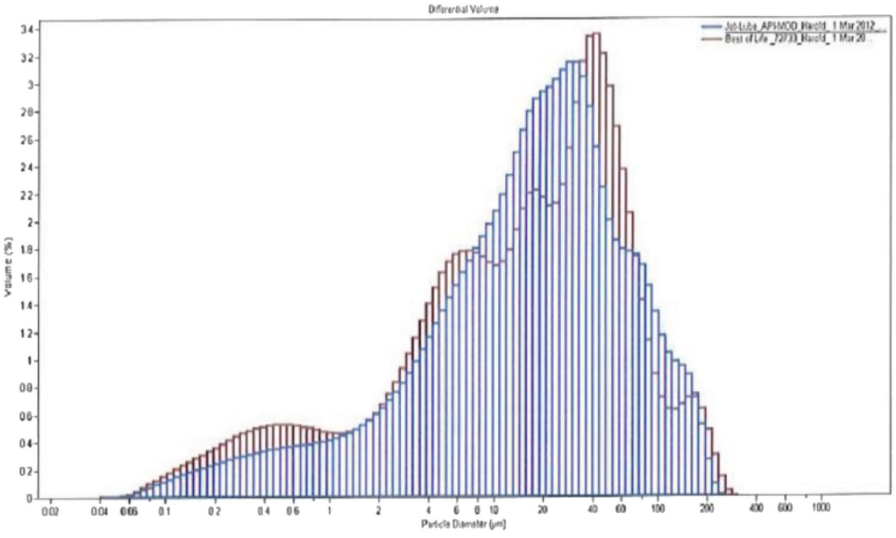
Feature	Seal-Guard ECF	HTHP	Benefit
Oil Type	vegetable oil with added Synthetic & naphthenic	Synthetic	Increased thermal stability
Dropping Point (°C)	198	>300	More stable
Flash Point (°C)	232	> 260	Less volatility
Pour Point (°C)	-29	-55	Brushable at lower temps
Biodegradability	Low viscosity	High viscosity	Higher viscosity slows biodegradation
Sheen	Fully saturated	Fully saturated	Sheen free on water

The below graph shows the percentage weight loss after 24 hours at temperature by reference to HPHT, Seal-Guard ECF and a Competitor Environmental Grade (CEG):



At high temperatures the product will not only be expected to remain stable but also to form an effective seal for casing joints and perform to the extreme internal pressures of the application. Well engineers go to great lengths to insure the integrity of their wells and failure is not considered an option in these types of applications. In further optimisation of solid lubricants particle size distribution was considered a key factor in delivering improved sealing properties, development formulations considered various different particle size combinations in relation to frictional profiles and sealing ability. By extending the particle size from 0-50 microns in Seal-Guard ECF to 0-200 microns in HPHT Jet-Lube had been able to deliver a more robust sealing ability comparable to its lead based counterpart. Field testing with Statoil is ongoing but initial results indicate a deliverable service enhancement of up to 230°C, some 90°C higher than any other environmental product currently available in the market. Furthermore this allows HPHT to be used on both 8-round & buttress thread types, as well as the proprietary mechanical seal thread forms.

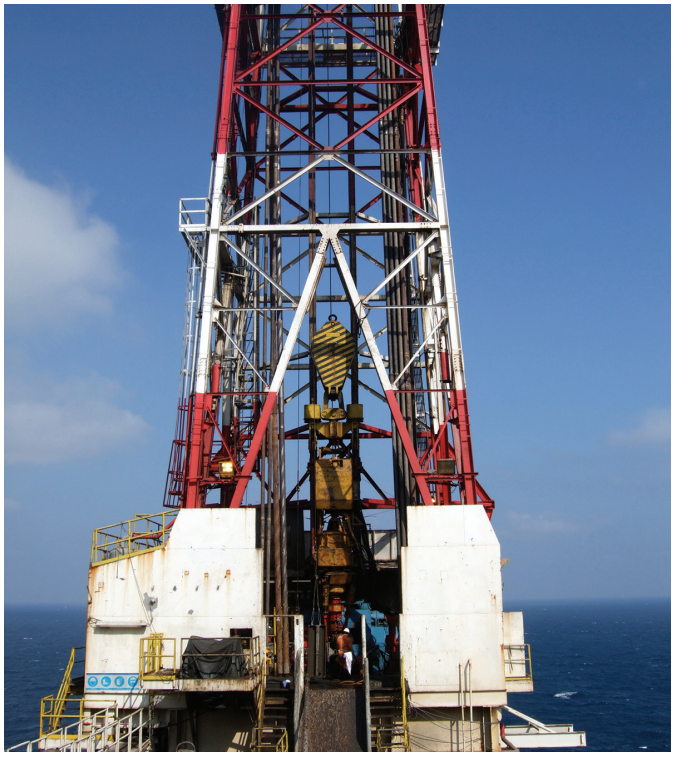
The below graph shows the particle size distribution in API-Modified, Jet-Lube used this profile to develop a refined practice sized distribution for HPHT:



Conclusion

By considering all components, re-addressing solid boundary lubricants, and base oil chemistries of the existing ECF product range, Jet-Lube's HPHT thread compound has succeeded in satisfying both the stringent OSPAR environmental performance criteria combined with the rigidity and robustness required to withstand the extreme service requirements of HPHT wells.

Feature	Seal-Guard ECF	HTHP	Benefit
Sealing up to (°C)	140	230	Increased temperature range
Components to make grease	13	7	Less variation
Components to make Sealant	7	5	Less variation
bioaccumulation potential, *Log P_{ow}*	molecular weight exceeds 900	molecular weight exceeds 900	Equivalent
Biodegradability OECD 306 – 28 days (%)	35	28	> 20
OCNS group / Norway	E / Yellow 2	E / Yellow 2	Equivalent
4 Ball Weld Point, kg of force	≥ 800	≥ 800	Equivalent
Coefficient of friction @ 55,000 psi	0.08	0.08	Equivalent



By reformulating away from heavy metal based compounds HPHT has a much lower density, this alone accounts for 50% greater coverage with the same mass. The use of vegetable oils in the existing ECF product range has not only delivered integral biodegradability, it is also a means of supporting more sustainable renewable hydrocarbon source.

In many industries, around 40 percent of a lubricant can be lost to the environment, given the particular aquatic type application the enhanced product biodegradability and aqua toxicity limits any pollution factors delivering the strategy of the OSPAR commission. As time progresses the Harmonized Offshore Chemical Notification Format (HOCNF) is quickly becoming a recognized international format included by some environmental agencies outside of the North-East Atlantic as well as in elements other marine type applications (Vessel General Permit (VGP)). This coupled with the Europe REACh initiative truly limits the propensity of harm or damage to the environment, in all a wholly sustainable future of efficient and truly environmentally friendly lubricants.

LINK
www.jet-lube.co.uk