Synthetic-Based Fluid Versus Oil Dust Suppressants

A Comparison of Environmental and Regulatory Issues

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1. EXECUTIVE SUMMARY

- Synthetic fluid-based dust suppressants and oil dust suppressants are not the same.
- Synthetic fluids and oil dust suppressants have different total costs of ownership, performance, affects on the environment, and the regulatory requirements, with the advantage going to synthetic fluids. Charts and graphs provide the narrative that explains the differing chemistries, performance and environmental impact.
- A substance is not synthetic unless it has been formed as the result of a chemical reaction created intentionally to produce it. A simple separation, purification or transformation does not result in a synthetic fluid as defined by the EPA.
- There are specific requirements that must be met with regard to spill prevention, control, storage, and countermeasure rules for non-transportation facilities that use, process, refine or consume oil.
- The rationale for using synthetic fluids and the development of two created specifically for dust control and soil stabilization are detailed in the following pages. Data analyses are included.
- In summary, a simple side-by-side chart compares synthetic fluid and oil dust suppressants in terms of application, amount of product required, delivery and cost of ownership.

2. INTRODUCTION

Some chemical liquids are synthetic fluids. Others are not; they are oil products. Synthetic fluids and oils are as different as apples and oranges.

The problem in the market is that manufacturers may present “oranges” (oils) as “apples” (synthetic fluids). This is troublesome for several reasons: The kind of dust suppressant a buyer selects affects performance, the environment, potential regulatory and safety consequence, and the wallet in terms of total cost of ownership.

2. WHAT IS A SYNTHETIC FLUID?

A synthetic material is a substance, pure or in a mixture, that has undergone at least one major chemical transformation (reaction) in its manufacturing process; it is the product of an intended chemical reaction and high temperature and pressures as well as a catalyst are usually required. A simple physical separation, purification or transformation (e.g. freezing, boiling) does not constitute a synthesis.

In 1990 the oil and gas extraction industry developed a class of synthetic materials called synthetic-based drilling fluids with which to formulate high-performing drilling fluids. These drilling fluids perform better than traditional oil-based fluids, with less environmental impact and greater worker safety.

To define synthetic, as it applies to drilling fluids, we reviewed the non-aqueous drilling fluid offshore disposal regulations as legislated in several parts of the world. In this document drilling fluids are classified as water-based fluids or non-aqueous based fluids.
Water based fluids consist of water, barite, clay, caustic soda, lignite, lignosulfonates and/or water-soluble polymers. They may also contain low concentrations of diesel fuel, mineral oil or other insoluble organic liquids at a concentration of a few percent to improve the lubricity of the mud and cuttings in difficult formations. EPA allows discharge of water based fluids mud and cuttings in water.

In non-aqueous based fluids, the continuous phase is a liquid hydrocarbon mixture or other insoluble organic chemical, which contains barite, clays, emulsifiers, water, calcium chloride, lignite, and lime. The three types of non-aqueous based fluids, based on the chemical composition of the base fluid in the mud are:

- Oil Based Fluids (OBFs)
- Enhanced Mineral Oil Based Fluids (EMOBFs)
- Synthetic Based Fluids (SBFs)

Oil based fluids contain diesel fuel or conventional mineral oil as the continuous phase. Mineral oils were originally developed as low-toxicity replacements for diesel fuel in oil based fluids in an attempt to reduce the negative impact on the environment; the EPA, however, does not allow the discharge of mud in the water, only the cuttings.

Enhanced mineral oil based fluids contain an enhanced mineral oil as the continuous phase. These are conventional paraffinic mineral oils that have been purified to remove most aromatic hydrocarbons, which are considered to be the most toxic components of oil based fluids and why the EPA does not permit the discharge of any mud from oil based fluids or enhanced mineral oil based fluids into the water.

In synthetic base fluids, the continuous liquid phase is a well-characterized synthetic organic compound.

Synthetic based fluids are classified into four categories:

- Hydrocarbon
- Ethers
- Esters
- Acetals

Synthetic hydrocarbons include:

- Normal Linear Paraffins (LPS)
- Linear Alpha Olefins (LEOS)
- Poly Alpha Olefins (PAOS)
- Internal Olefins (IOS).
Synthetic based fluids do not disperse in the water and do not increase turbidity. They are designed to be biodegradable under anaerobic conditions as well as aerobic environments. Biodegradation in both environments results in simple, non-toxic hydrocarbon products. From this information the EPA has come to the conclusion that a base fluid or continuous phase of a synthetic based fluid is a water-insoluble synthetic organic material. EPA (EPA 1996) defines a “synthetic material”, as applied to synthetic base drilling fluids, as:

“A material produced by the reaction of a specific purified chemical feedstock, as opposed to the traditional base fluids such as diesel and mineral oil which are derived from crude oil solely through physical separation processes. Physical separation processes include fractionation and distillation and/or minor chemical reactions such as cracking and hydro processing. Since they are synthesized by the reaction of purified compounds, synthetic materials suitable for use in drilling fluids are typically free of polycyclic aromatic hydrocarbons (PAHs), but tests sometimes report levels of PAH up to 0.001 weight percent PAH expressed as phenanthrene.”

Synthetic-based fluids must meet these effluent limitations guidelines for use in offshore drilling operations.

1. PAH Content - ≤ to 0.001 percent
2. Sediment Toxicity – as measured by the 10-day toxicity test (ASTM E1367-92) using a natural sediment or formulated sediment and Leptocheirus plumulosus as the test organism
3. Biodegradation – A process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment with aerobic and anaerobic conditions
4. Static Sheen Test – must pass

3. WHAT IS AN OIL?
To many, oil is a petroleum-based substance that at room temperature is a free-flowing liquid which floats on water. Today, however, the EPA has a very specific meaning for oil whether it is oil from petroleum or oil from plants.

i. Oil definitions
   a. Clean Water Act (CWA); Title 33 U.S.C. 26
      “Oil means oil of any kind or in any form, including, but not limited to, petroleum, fuel oil, sludge, oil refuse, and oil mixed with wastes other than dredged oil.”
   b. SPCC Reg 40 CFR 112.2
      “Oil means oil of any kind or in a any form, including, but not limited to: fats, oils, or greases of animal, fish, or marine mammal origin; vegetable oils, including oils from seeds, nuts, fruits, or kernels; and other oils and greases, including petroleum, fuel oil, sludge, synthetic oils, mineral oils, oil refuse, or oil mixed with wastes other than dredged spoil.”
   c. Oil Pollution Act (OPA 90); Title 33 U.S.C. 40
“Oil means oil of any kind or in any form, including petroleum, fuel oil, sludge, oil refuse, and oil mixed with wastes other than dredged spoil, but does not include any substance which is specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of section 101(14) of the Comprehensive Environmental Response, Compensations, and Liability Act (42 U.S.C. 9601) and which is subject to the provisions of that Act [42 U.S.C. 9601 et seq.]

In addition to the definition of oil per OPA 90 the law states:
Sec. 2720. Differentiation among fats, oils and greases.

ii. In general
“Except as provided in subsection (c) of this section, in issuing or enforcing any regulation or establishing any interpretation or guideline relating to the transportation, storage, discharge, release, emission, or disposal of a fat, oil or grease under any Federal law, the head of that Federal agency shall:
   a. Differentiate between and establish separate classes for– (A) animal fats, oils and greases, and fish and marine mammals, within the meaning of paragraph 2 of section 61(a) of title 13, and oils of vegetable origin, including oils from the seeds, nuts, and kernels referred to in paragraph (1)(a) of that section; (B) other oils and greases, including petroleum; and
   b. Apply standards to different classes of fats and oils based on considerations in subsection (b) of this section.

iii. Considerations
In differentiating between the class of fats, oils and greases described in subsection (a) (1)(A) of this (Oil Pollution Act (OPA 90); Title 33 U.S.C. 40 Sec. 2720). section and the class of oils and greases described in subsection (a)(1)(B) of this section, the head of the federal agency shall consider differences in the physical, chemical, biological and other properties and in the environmental effects of the classes.”

OPA 90 in essence recognizes that different chemistries require different handling. 40 CFR Parts 9 and 435 clearly differentiate between typical oil-based fluids and synthetic-based fluids.

4. SPILL PREVENTION, CONTROL, AND COUNTERMEASURE RULE
In November 2009, the EPA released the latest amendment to 40 CFR Part 112 better known as (SPCC) Rule. The rule regulates non-transportation-related onshore and offshore facilities (as defined by the Clean Water Act) that could reasonably be expected to discharge oil into navigable water of the US or adjoining shorelines. It defines several criteria used to determine who is covered, what facilities are covered, what covered facilities must do to prevent an oil spill, and what to do if an oil spill should occur.
A. Who Must Comply

Section 112.1 establishes the applicability of the SPCC rule by describing facility activities and equipment subject to the rule. Non-transportation-related facilities which fulfill the criteria are covered under the SPCC Rule.

- There is above-ground storage capacity for more than 1,320 US gallons of oil
- There is underground storage capacity for more than 42,000 US gallons of oil
- There is a reasonable expectation of discharge of oil into or upon navigable waters of the US or the adjoining shoreline
- Only containers with a capacity of 55 US gallons or greater are used in the calculation of capacity

B. Facilities

A covered facility is defined as any non-transportation related facility that stores, processes, refines, uses or consumes oil. The SPCC Rule lists potentially affected entities via industry sector and NAICS code. Some examples are:

- Electric Utility Plants NAICS 2211
- Food Manufacturing NAICS 311,312
- Transportation NAICS 481-488 (Airports 48819)
- Education NAICS 61

C. What Covered Facilities Must Do to Comply with SPCC

When a facility determines that it fulfills the requirement for stored oil or oil used at the facility and that the facility meets the NAICS criteria, the SPCC Rule defines what a covered facility must do with regard to:

i. Preventing Oil Spills

- Use suitable storage containers for stored oil
- Provide overfill protection
- Provide secondary containment which can be double-walled containers, dikes that contain largest expected size spill, or diversional structures to keep the oil from reaching navigable waters
- Inspection of containers, valves and secondary containment

ii. Preparing and Implementing the SPCC plan

Typically, and under older versions of SPCC Rule, all Plans had to be certified by a PE and meet very stringent requirements outlined in the Rule. However, in an effort to reduce burdens on industry especially when the incidence of catastrophic oil spills is
minimal, the EPA developed a tiered program for facilities which store or use fewer than 10,000 US gallons of oil. The smaller facilities can self-certify as one of two classifications:

**Tier I**

- Less than 10,000 US gallons of above-ground storage
- No discharges of greater than 1000 US gallons or no two discharges of greater than 42 US gallons in prior three years
- No single above-ground storage container of more than 5000 US gallons
- These facilities may use a much simplified plan template available from the EPA in the SPCC Rule and self-certify the plan

**Tier II**

- Less than 10,000 US gallons of above-ground storage
- No discharges of greater than 1000 US gallons or no two discharges of greater than 42 US gallons in prior three years
- Have an above-ground storage container of greater than or equal to 5000 US gallon capacity.
- These facilities have to follow the SPCC plan guidelines in the Rule, but can self-certify the plan.

These plans are maintained on site and must be available upon EPA request.

**D. What to Do in Case of a Spill**

Facilities must define a spill as it pertains to SPCC Rule. For an oil release to be defined as a spill it must meet the following criteria:

- The oil must reach navigable waters of the United States and only the amount of oil that actually reaches the water is considered a spill
- The spill is 1000 US gallons or greater in a single event in a 12-month period
- There are two separate spills of greater than 42 gallons in a 12 month period
- The oil spill violates some water quality standard
- The oil spill causes a sheen or film on the surface of the water.

If these criteria are met the facility must notify the National Response Center (NRC) which is staffed 24 hours a day. The facility must also notify state and local authorities as required.
5. **EK35 AND ENVIROKLEEN ARE SYNTHETIC FLUIDS – NOT OILS**

The basis for this statement comes from the way oil is defined by the Clean Water Act, SPCC and Oil Pollution Act, and the way a synthetic base fluid is described in 40 CFR Parts 9 and 435.

The synthetic base fluid used in EK35 and EnviroKleen is derived from a specific purified feedstock that undergoes major chemical reactions and molecular structure changes also known as hydroisomerization. This is opposed to non-synthetic oils which are subjected to a physical separation process but experience no molecular structural change. EK35 and EnviroKleen synthetic fluid meets the Effluent Limitations Guidelines by 40 CFR Parts 9 and 435.

The process of purified feedstock preparation, Part 1 and Part 2 and hydroisomerization used for EK35 and EnviroKleen is shown diagrammatically in Figures 1a, 1b and 2. The molecular structure changes during hydroisomerization are shown in Fig. 3 and 4.

Midwest sought a base fluid that is effective for both dust suppression and fines preservation – and also environmentally safe. After an extensive literature review, making tests in our lab, and evaluating options in the field, we chose a synthetic hydrocarbon fluid as the backbone for both products.

EK35 and EnviroKleen are synthetic fluids as defined by the EPA. As such, they do not have to be measured for compliance against regulatory requirements for oils. Companies choosing oil-based products for dust control, however, must adhere to stringent Oil Pollution Prevention, Spill Prevention, Control and Countermeasure (SPCC) regulations pertaining to storage, use and reporting.
Fig. 1a

Feedstock Preparation Part 1

- Q1 - Crude selection criteria (highest paraffin content)
- Q2 - Distillation check / GC (carbon number, S, N)
- Q3 - Aromatic level / UV absorbance (carbon number, viscosity, S, N)

Fig. 1b

Feedstock Preparation Part 2
Hydroisomerization Process

- Q4 - Q3 + mass spectroscopy (wax content, batch verification)
- Q5 - Aromatic level / UV absorbance, S, N clean-up
- Q6 - Catalyst check
- Q7 - Continuous on-line product check (every 4 hours)
- Q8 - Batch certification per product specification sheet

Fig. 2
Molecular Structure Comparison

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<th>Feedstock</th>
<th>Hydroisomerization</th>
<th>E-Family Synthetic Fluid</th>
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Fig. 3

Carbon Distribution

Fig. 4
6. **ANALYTICAL DATA**

The first three scans shown below use mass spectrometry (MS) to measure the mass-to-charge ratio of charged particles. It is used to determine particle mass and the elemental composition of a sample and for elucidating the chemical structures of molecules. MS works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratio.

Scan 1, below, is of the synthetic base fluid (as defined by the EPA) used in EnviroKleen and EK35; it shows a highly branched hydrocarbon that is easily broken apart when impacted by electrons. This ease of fragmentation is what makes synthetic fluids easily and cleanly biodegradable in nature and allows them to remain in the ocean when used in synthetic base fluid drilling muds. The highly branched hydrocarbons or iso-alkanes are not found in nature and can only be synthesized using the hydroisomerization techniques illustrated above (Figures 1-4).

The distinguishing features EK35 and EnviroKleen of this compound are:

- The aggregation of peaks below 100 m/z units indicates a highly branched hydrocarbon
- The highest peak at 57.1 m/z units represent a large population of isopropyl substitutions to the carbon chain backbone
- Lack of peaks at the higher end of the spectrum indicating a lack of straight chain hydrocarbons, particularly the barely visible peak at 276.3 m/z.
- Compare to the scan above of the E-family synthetic fluid
Scan 2, below, is of a competitor, a paraffin, or long-chain oil derived from petroleum distillation. Note the systematic loss of 14 m/z of the peaks. This represents the cleavage of each CH₂ unit in the straight hydrocarbon chain. This is a characteristic representation of petroleum distillate feedstock. Because straight chain hydrocarbons are resistant to bond cleaving, they are not easily biodegraded and are much more persistent in the environment than synthetic fluids.

That is why when mineral oils are used in drilling fluids, the cuttings may not be left in the ocean.

The distinguishing features of this compound are:

- The systematic loss of 14 m/z between peaks is indicative of a long straight hydrocarbon chain
- The prevalence of high-weight ion peaks indicate that the compound is not highly substituted or branched (few isopropyl groups)
- The molecular ion peak at 505 m/z shows that this compound is twice as heavy as the synthetic fluid illustrated above.
- Note the similarity of this scan to the feedstock scan in the carbon distribution scan (Figure 4) shown above and repeated below. The competitor’s is very similar to the feedstock used to synthesize the synthetic fluid in E-family products.
Mass spectrum of oil dust suppressant - X-axis = m/z (mass/charge ratio), Y-axis = intensity of peak. Note the 14m/z loss between peaks. This is an indication of breaking of the long straight chain hydrocarbon (loss of 1 carbon and 2 hydrogen atoms) or alkane or better known as mineral oil. These oils are found naturally. Compare Scan 2 to the feed stock used to manufacture synthetic based fluids. These straight chain oils are not easily broken or degraded in nature.
Mass spectrum of water contaminated by oil sands - x-axis = m/z (mass/charge), y-axis = intensity of peak. Note aggregation of high-intensity peaks between 300 and 450 m/z and indication of straight-chain hydrocarbons which occur naturally and are found in oils. Note similarities to Scan 2 of the competitive oil. Products of this chemistry are not easily broken or degraded in nature.
7. CONCLUSION
Synthetic-fluid-based dust suppressants perform better and have less of an environmental impact than oil-based dust suppressants. They also offer a lower overall cost of ownership. Nevertheless, manufacturers of oil fluids such as this competitor continue to claim that they are synthetic fluids and that they perform as well. This should become a substantial concern of buyers as new products expected to reach the market soon may make the same claims.

SYNTHETIC FLUIDS vs. OIL, A SIDE-BY-SIDE COMPARISON

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<th>SYNTHETIC-FLUID BASED</th>
<th>OIL</th>
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<tbody>
<tr>
<td>Where applied</td>
<td>250,000 ft² gravel runway</td>
<td>250,000 ft² gravel runway</td>
</tr>
<tr>
<td>Application rate</td>
<td>1 gallon / 40 ft²</td>
<td>1 gallon / 30 ft²</td>
</tr>
<tr>
<td>Gallons required</td>
<td>6250</td>
<td>8333</td>
</tr>
<tr>
<td>Delivery</td>
<td>275-gallon totes</td>
<td>275-gallon totes</td>
</tr>
<tr>
<td>Costs of ownership</td>
<td>Product Freight Double-walled totes or containment diking Oil spill containment materials SPCC Tier I Plan preparation and implementation Repeated maintenance Cost of a Reportable Incident</td>
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Without assigning dollar figures to the cost of use for the two options illustrated above, it is easy to see that the overall total cost of ownership will be greater when using oil for dust suppression. Even if the overall costs were equal for the two choices, should a spill occur or the oil enters the navigable waters of the United States, those costs would escalate and the biggest cost would be to the environment.