

## Review

# Biodegradation of mineral oils – A review

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The uses of the various kinds of mineral oils in various industrial situations have made them an indispensable ingredient of the industrialization and development that has characterized the past century. Recent focus on health, safety and the preservation of the environment has turned the searchlight to the effects of mineral oils on the environment when they are accidentally spilled, or intentionally disposed of. Biodegradation, which provides an indication of the persistence of a particular substance in the environment, is the yardstick for assessing the eco friendliness of substances. Due to the poor biodegradation rates observable for mineral oils, various methods of bioremediation are currently being researched, with the isolation of various microbial species with the ability to use up mineral oils as a carbon and energy source. Ultimately, vegetable oil based hydraulic fluids will come to the fore as a suitable and more environmentally friendly solution to the demand for hydraulic fluids.

**Key words:** Lubricant, environmental, transformer oil, additives.

## INTRODUCTION

Crude oils are naturally occurring, exceedingly complex mixtures, which consist predominantly of hydrocarbons, and contain sulfur, nitrogen, oxygen and metals as minor constituents. The petroleum industry, which holds a prime position in the modern world economy, is, in the main, centered on crude oil. The economic importance of crude oil is to be found in the numerous possible products obtainable from crude oil through refining – the uses of these products in the modern industrialized world justify the resources committed to its exploration and production. Motor fuels, domestic fuels, industrial fuels for heating and power generation as well lubricants are among the products derivable from crude oil.

The class of petroleum products known as mineral oils can be generally understood to include a variety of products which go by different names such as white oils, lubricating oils, light fuel oils, residual fuel oils, as well as transformer and cable oils (Gary and Handwerk, 2001). These various products have been applied ever since the discovery of crude oil. The recent worldwide emphasis on environmental preservation now raises questions which concern the long term effects of the use, accidental spills

and intentional disposal of industrial products such as mineral oils. Pressure is mounting to use more environmentally friendly products, especially in ecologically sensitive situations (Lea, 2005). Hence the biodegradability of mineral oils is of interest to a great many researchers, seeing that the environmental persistence of possibly toxic constituents of these mineral oils is fast becoming unacceptable.

## THE IDENTITY AND ORIGIN OF MINERAL OILS

The term “mineral oils” tends to be non-specific, and its usage in the literature could give rise to some confusion as it may be found to refer to various substances. However in this context, it is taken to refer to all oils which are made from dewaxed paraffin-based crude oils which are blended with additives to impart particular properties for specific uses. This classification is as against other oils such as Organophosphate esters and polyalphaolefin fluids ([www.atsdr.cdc.gov](http://www.atsdr.cdc.gov), 2008). Mineral oils include lubricant base oils (obtained from petroleum) and products derived from them ([www.ntp.niehs.nih.gov](http://www.ntp.niehs.nih.gov), 2003). Hence, their origin is petroleum – they are formulated from base petroleum stocks with about 10 – 25% additives. These additives consist of antioxidants and metal deactivators, detergents, dispersants, corro-

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sion inhibitors, rust inhibitors, amongst others (Farrington and Slater, 1997). The carbon number distribution and by extension the viscosity in mineral oil hydraulic fluids varies depending upon the anticipated application of the fluid. Generally however, C15 to C50 is a reasonably all encompassing range. Also, the higher the carbon number, the higher the viscosity of the fluid in question (www.atsdr.cdc.gov, 2008).

Mineral oils are composed of straight and branched chain paraffinic, naphthenic, and aromatic hydrocarbons with 15 or more carbons in a complex mixture. Generally, the physical properties of mineral oils depend on their composition in terms of carbon number distribution, and this is defined by the source of crude oil. Accordingly, these physical properties vary widely: boiling points generally range from 300 to 600°C, while specific gravities range from 0.820 for light paraffinic base/ process oils to just over 1.0 for high aromatic base/process oils. They are all generally insoluble in water and alcohol, but are soluble in benzene, chloroform, ether, carbon disulphide, and petroleum ether (www.ntp.niehs.nih.gov, 2003).

In most crude oil refineries, lubricating oil base stocks are obtained from the heavy vacuum gas oil fraction and reduced crude from paraffinic or naphthenic base crude oils. Reduced crude (bottoms from the atmospheric distillation unit) is processed in a propane deasphalting unit where asphaltenes are removed; following which it is processed in a blocked operation with the vacuum gas oils to give rise to lubricating oils base stocks, which form the basis for the wide range of mineral oils. Further details on the origin of mineral oils can be provided: the vacuum gas oils and deasphalted reduced crude stocks are first solvent extracted to remove the aromatic compounds and the dewaxed to improve the pour point. Then they are treated with special clays or high severity hydrotreating to improve their color and stability before they are blended into lubricating oils (Gary and Handwerk, 2001).

## USES OF MINERAL OILS

The first centers of large scale production of mineral oils were located in Pennsylvania and Baku. Generally, there has been an explosion of mineral oil based products globally over the last century due to the increasing demands of industrialization (Lea, 2005). Numerous useful products are obtainable from mineral base oils for numerous applications, and these are outlined below.

The uses of mineral oils includes applications such as engine oils, automotive and industrial gear oils, transmission fluids, hydraulic fluids, circulating and hydraulic oils, bearing oils and machine oils. Other uses are as machine-tool oils, compressor and refrigerator oils, textile machine oils, air tool oils, steam engine oils, metal-working oils, rust prevention oils transformer oils and so on and so forth (www.ntp.niehs.nih.gov, 2003). The list is almost endless, indicating that over the last century, it is

correct to say that mineral oil has been exploited to the full since its early discovery (Lea, 2005). Another use is found for mineral oils in medical applications, for we have oils that are known as medicinal white oils, which are essentially mixtures of highly refined paraffinic and naphthenic liquid hydrocarbons obtained from mineral crude oils through various refining steps including distillation, extraction and crystallization, with subsequent purification by acid and catalytic hydro treatment. They have medicinal applications – they have been taken orally as laxatives, and as used in many skin care products, as a suspending and levigating agent in sulfur based ointments, and in livestock vaccines (www.wikipedia.org, 2008). White mineral oils are also applied as release agents as well as glazing agents

## THE COMPOSITION OF MINERAL OILS - ADDITIVES

It must be noted that apart from base petroleum stocks, mineral oils in their commercial applications contain about 10 – 25% of substances known as additives (Farrington and Slater., 1997). These additives are necessary to impart properties that are considered appropriate to specific applications. These additives thus constitute a very important part of the composition of mineral oils (www.atsdr.cdc.gov, 2008), and include amongst others: “extreme pressure additives, which help prevent surface damage under severe loading (organic sulfur-, phosphorus-, and chlorine-containing compounds); anti-wear additives, which prevent wearing under light loads (fatty acids and derivatives, organophosphate esters); corrosion inhibitors, which prevent corrosion by oxygen and water (fatty acids, sulfonates, and salts of fatty acids); oxidation inhibitors, which inhibit oxidation of the hydraulic fluid (phenols, amines, and sulfides); defoam-ers, which prevent foam formation (silicone oils); viscosity index improvers, which reduce the dependence of viscosity on temperature (poly-alphaolefins, polymethacrylates, and polyalkylstyrenes); pour point depressants, which lower the pour point temperature (polymethacrylates and condensation products); demulsifiers, which allow separation of oil and water (ionogenic and non-ionogenic polar compounds); and dispersants, which prevent unwanted deposits (sulfonates and amides)” (www.atsdr.cdc.gov, 2008). The chemical nature and production methods of these additives are generally unknown as they are closely guarded trade secrets.

## THERMAL STABILITY OF MINERAL OILS

The term “thermal stability, when used in reference to lubricating oils may be defined as the resistance posed by the lubricant to either molecular breakdown, or some form of rearrangement at elevated temperatures in the absence of oxygen (Booser, 1984). It is a well observed fact that all oils will start to decompose even in the ab-

sence of oxygen when they are heated above a certain temperature. When heated, mineral oils break down to yield basically methane, ethane and ethylene (Stachowiak and Batchelor, 2005). More moles of methane are liberated than of ethane and ethylene (Booser, 1984).

Thermal stability of crude oil products, which includes the class of compounds known as mineral oils, determines their use and applicability in crude oil industry (Rychla et al., 2001). The improvement of the thermal stability of mineral oils is achieved right from the refining process. It is known that organonitrogen molecules are largely responsible for poor color and stability of base oils; hence the finishing processes undertaken during refining must necessarily involve operations which are effective for removing organonitrogen molecules (Mortier and Orszulik, 1997). Thermal stability may not be improved via the means of additives; rather, usually, additives used with lubricant base stocks have lower thermal stability than the base stocks themselves (Stachowiak and Batchelor, 2005). Thermal stability is also dependent on the length of usage (Karacan et al., 1999). Carbon to carbon single bonds are the most vulnerable points for thermal breakdown. Hence fluids such as mineral oils which are constituted of a substantial percentage of C-C single bonds exhibit a thermal stability of about 650 to 700°F. Synthetic oils, in general, exhibit better thermal stability than mineral oils (Stachowiak and Batchelor, 2005).

## **ENVIRONMENTAL AND HEALTH CONCERNS WITH MINERAL OILS**

In terms of environmental effects of mineral oils, each type of crude oil or refined product has distinct physical properties which affect the way the oil spreads and breaks down, and ultimately determines the hazard it may pose to marine and human life, and the likelihood that it would pose a threat to natural and manmade resources. Mineral oils are persistent and present a greater remediation challenge than lighter petroleum products (www.epa.gov, 2008).

This prospective hazard is recognized by many regulatory bodies; the Michigan Department of Environmental Quality for instance stipulates that used oils in liquid form cannot be disposed of by any of the following means:

- Dumped down drains or sewers or into surface or ground water
- Disposed of in land fills
- Burned in municipal solid waste incinerators or other incinerators without energy recovery or
- Used as dust control or weed control.

Under this regulation, used oil refers to petroleum-based products which are used as lubricating agents or in other protective applications.

The United States' Environmental Protection Agency

has laid down guidelines which stipulate that accessible oil be recovered in the event of a spill, and all contaminated soil be removed. This is expensive business; for instance a municipal electric utility in Iowa, USA spent over \$20 000 on spill remediation for a mere 20 gallon spill of PCB-contaminated transformer oil (www.safertransformers.org, 2008). Additionally, the EPA also requires that no visible oil sheen be evident downstream from facilities close to waterways. Another regulation requires that point discharges into waterways should not exceed 10 ppm of mineral-based oils (US Army Corps and Engineers, 1999)

As earlier stated, these various stringent regulations are as a result of the fact that mineral oils are generally recognized to cause pollution of soil and water when spilled accidentally or when disposed of, affecting plant and animal life. They cannot be regarded as readily biodegradable, and hence their harmful effects often persist in the environment (Cliff Lea). "Mineral-oil-based lubricating oils, greases, and hydraulic fluids....are usually toxic and not readily biodegradable, because of these characteristics, if these materials escape to the environment, the impacts tend to be cumulative and consequently harmful to plant, fish and wildlife" (US Army Corps and Engineers, 1999). The overall environmental hazard of lubricants and other mineral oils is not entirely determined by the mineral oil based base fluids, but more so on the several additives used in hydraulic fluids which contribute substantially to the toxicity of the spill. This increased toxicity is coupled with the physical effect of staining essential organs of animal life in aquatic environments (Broekhuizen et al., 2003). Additionally, by means of spills and improper disposal of mineral oils, the general population is potentially exposed to unused and used mineral oils which are present as environmental pollutants. Such exposure to untreated and mildly treated mineral oils has been linked to cancer (www.ntp.niehs.nih.gov, 2003).

## **THE BIODEGRADATION OF MINERAL OILS**

The notion of biodegradability conveys the meaning of the breaking down of complex, and possibly toxic material into simple and common forms, in which the elements carbon, hydrogen and oxygen exist or are simply associated. Whenever any substance is placed in the environment, it begins to undergo degradation due to the action of relevant substrate utilizing microorganisms. Every substance, irrespective of its complexity and toxicity is subject to this process. When used in the present context, it is referenced to a time frame. That is, for a given substance to be referred to as biodegradable, a specific time limit must be used as a reference (wiserenewables.com, 2006).

By definition, biodegradation is the chemical transformation of a substance caused by organisms or their enzymes. There are two major types of biodegradation –

**Table 1.** Ultimate Biodegradability Test (wiserenewables.com, 2006).

Ultimate Biodegradation tests: Test title	Measurements	Sponsoring organization
D5864, test method for the aerobic aquatic biodegradation of lubricants	Theoretical CO <sub>2</sub> (%)	ASTM
9429:1990, Technical corrigendum 1, water quality-evaluation in an aqueous medium of the "ultimate" biodegradation of organic compounds-method by analysis of released carbon dioxide	Theoretical CO <sub>2</sub> (%)	ISO
301B, CO <sub>2</sub> evolution test (modified Sturm test)	Theoretical CO <sub>2</sub> (%)	OECD
Aerobic aquatic biodegradation test	Theoretical CO <sub>2</sub> (%)	US EPA
C.4-C: Carbon dioxide (CO <sub>2</sub> ) evolution	Theoretical CO <sub>2</sub> (%)	EUC
L-33-A-934, biodegradability of two-stroke cycle outboard engine oils in CH <sub>2</sub> groups water (formerly L-33-T-82)	Loss of extractable (%)	CEC

Primary Biodegradation, which refers to the modification of a substance by microorganisms such that a change is caused in some specific measurable property of the substance (US Army Corps and Engineers, 1999). When the term primary biodegradation is used it refers to minimal transformation that alters the physical characteristics of a compound while leaving the molecule largely intact. Intermediary metabolites produced may however be more toxic than the original substrate (wiserenewables.com, 2006). Thus mineralization is the true aim. When this happens it is referred to as ultimate or complete biodegradation; which is the degradation achieved when a substance is totally utilized by microorganisms resulting in the production of carbon dioxide, methane, water, mineral salts, and new microbial cellular constituents (US Army Corps and Engineers, 1999).

Various methods exist for the testing of biodegradability of substances. Table 1 below indicates a number of tests amongst others for ultimate biodegradability in aerobic aquatic environments indicating their sponsoring organizations (Bioblend, 2008)

Biodegradability is assessed by following certain parameters which are considered to be indicative of the consumption of the test substance by microorganisms, or the production of simple basic compounds which indicate the mineralization of the test substance. Hence there are various biodegradability testing methods which measure the amount of carbon dioxide (or methane, for anaerobic cases) produced during a specified period; there are those which measure the loss of dissolved organic carbon for substances which are water soluble; those that measure the loss of hydrocarbon infrared bands (Bioblend, 2008); and there are yet others which measure the uptake of oxygen by the activities of microorganisms (the Biochemical Oxygen Demand, BOD).

However, when the reference is specifically to lubricants, there are 2 major methods of biodegradability testing, and these are outlined in brief below:

1. ASTM test method D 5864 determines lubricant biodegradation. This test determines the rate and extent of aerobic aquatic biodegradation of lubricants when exposed to an inoculum under laboratory

conditions. The inoculum may be the activated sewage-sludge from a domestic sewage-treatment plant, or it may be derived from soil or natural surface waters, or any combination of the three sources. The degree of biodegradability is measured by calculating the rate of conversion of the lubricant to CO<sub>2</sub>. A lubricant, hydraulic fluid or grease is classified as readily biodegradable when 60% or more of the test material carbon is converted to CO<sub>2</sub> in 28 days, as determined using this test method.

2. The most established test methods used by the lubricant industry for evaluating the biodegradability of their products are Method CEC-L-33-A-94 developed by the Coordinating European Council (CEC); Method OECD 301B, the Modified Sturm Test, developed by the Organization for Economic Cooperation and Development (OECD); and Method EPA 560/6-82-003, number CG-2000, the Shake Flask Test, adapted by the U.S. Environmental Protection Agency (EPA). These tests also determine the rate and extent of aerobic aquatic biodegradation under laboratory conditions. The Modified Sturm Test and Shake Flask Test also calculate the rate of conversion of the lubricant to CO<sub>2</sub>. The CEC test measures the disappearance of the lubricant by analyzing test material at various incubation times through infrared spectroscopy. Laboratory tests have shown that the degradation rates may vary widely among the various test methods indicated above (US Army Corps of Engineers, 1999).

Biodegradability tests based on the CEC method described above has certain trends which indicate that mineral oils, along with alkylated benzenes and polyalkeleneglycols among others, generally have poor biodegradability: between 0 – 40%. Specifically, mineral oil biodegradability varies from 15 – 35% as conducted by the CEC biodegradability test (wiserenewables, 2006).

## BIOREMEDIATION – THE CHALLENGE

Consequent on the poor biodegradability of mineral oils, remediation activities are required when spills occur. It

has been demonstrated that a variety of contaminants can be degraded by microbes, and that such biological processes are cost and clean-up effective, especially when compared to conventional pump and treat processes applied for the remediation of contaminated groundwater. Clean up efforts carried out by Biopract between 1997 and 2000 in Berlin for a 500 m<sup>2</sup> area, 10 m deep region contaminated by cable insulating oil. Bioremediation techniques were applied and an impressive biodegradation rate of 86% in a thousand days was recorded (Zittwitz et al., 2000).

A similar study to demonstrate the potentials of bioremediation of contaminated soils was carried out in Boucherville, Quebec, where a transformer oil spill had been recorded. The summary of the results is that on bioremediation, the site recorded a removal rate of 72% within 48 weeks (Biogenie, 1995).

In keeping with recorded successes on bioremediation efforts, research to optimize the process is ongoing with the isolation of strains of microorganisms which are found to have hydrocarbon degradative capabilities. Such microorganisms have enzyme systems which degrade and utilize oils as sources of carbon and hydrogen. In research carried out by Nwaogu et al. (2008) diesel oil was used as a source for the isolation of certain bacteria strains including *Bacillus subtilis*, and *Bacillus cereus*, which are found to possess hydrocarbon degrading capability (Nwaogu et al., 2008). Yet other studies have identified strains belonging to genus *Bacillus* as having impressive biodegradative ability, utilizing crude oil as the sole source of carbon and energy even under stressed environmental conditions (Khalida et al., 2006). Further studies carried out by Muratovba and Turkovskaia (2001) similarly isolated a series of microbial associations capable of degrading various petroleum oils, emulsols, and crude oil. Oil product degradation by these microbial associations was identified to be most efficient during aerobic flow cultivation. Under these conditions, oils were degraded by about 92%; also, certain parameters such as the brand of oil, the concentration of the oil, its degree of emulsification and aeration were found to have an effect on the microbial degradation of the oil (Muratovba et al., 2001). In another related study, surfactants belonging to the fatty acid-acylated amino acids were found to accelerate the microbial degradation of mineral oils.

The faster, more complete degradation of mineral oils is identified as being caused solely by interfacial activity (Riis et al., 2000).

## CONCLUSION

Mineral oils are very important products in the industrialized 21<sup>st</sup> century with such numerous applications that they may presently be described as indispensable. However, increasing environmental awareness has placed the spotlight on the persistence of the harmful

components of mineral oils in the environment, and their cumulative effects on ecosystems, especially in the light of their established poor biodegradability. Spills are inevitable, and the development of bioremediation processes utilizing isolated hydrocarbon degrading bacteria has gone a long way in improving the efficiency of spill cleanup. The poor biodegradability of mineral oils, coupled with the fact that remediation efforts always tend to be expensive has made the option of the development of environmentally friendly oils based primarily on vegetable oils an attractive one. The future will bring with it the improvement of the efficiency of biobased fluids in various applications, leading to the widespread use of these products; a situation which will no doubt be in the best interests of the global ecosystem to which we belong.

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