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Environmentally Acceptable Lubricants

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SECTION 1

INTRODUCTION

The purpose of this document is to describe the range of environmentally preferable lubricants that may be used as a best management practice (BMP) by operators of vessels covered under the Vessel General Permit for Discharges Incidental to the Normal Operation of Vessels (VGP)¹. Within this document, the term environmentally acceptable lubricant (EAL) is used to describe those lubricants that have been demonstrated to meet standards for biodegradability, toxicity and bioaccumulation potential that minimize their likely adverse consequences in the aquatic environment, compared to conventional lubricants. In contrast, lubricants that may be expected to have desirable environmental qualities, but have not been demonstrated to meet these standards, are referred to as environmentally friendly lubricants (EFLs) or biolubricants.

Lubricants lost from a vessel enter the aquatic environment, where serious damage to the aquatic ecosystem can occur. Consequently, there has been an emphasis on encouraging the use of EALs on vessels to protect the environment (Carter, 2009). Although their use is increasing, EALs comprise only a small percentage of the total lubricant market.

The significance of lubricant discharges (not accidental spills) to the aquatic ecosystem is substantial. The majority of ocean going ships operate with oil-lubricated stern tubes and use lubricating oils in a large number of applications in on-deck and underwater (submerged) machinery. Oil leakage from stern tubes, once considered a part of normal “operational consumption” of oil, has become an issue of concern and is now considered as oil pollution. Stern tube leakage is a significant source of lubricant oil inputs to the aquatic environment. A 2001 study commissioned by the European Commission DG Joint Research Centre revealed that routine unauthorized operational discharges of oil from ships in the Mediterranean Sea created more pollution than accidental spills (Pavlakakis et al., 2001). Stern tube leakage was identified as a major source of these discharges.

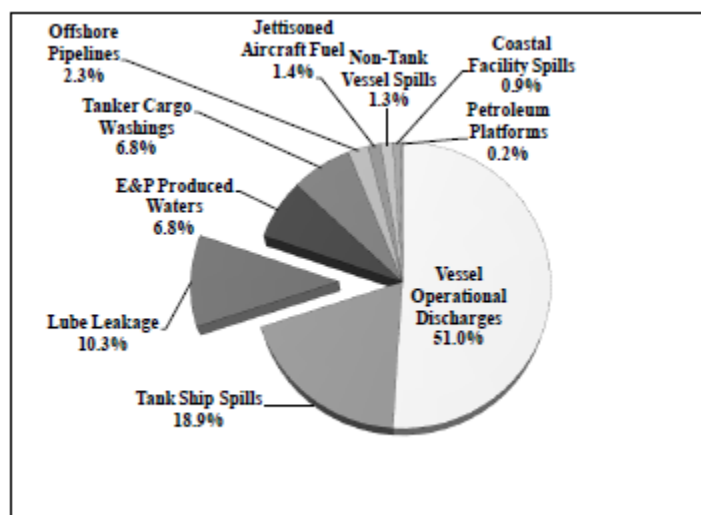
An analysis of data on oil consumption performed by a lubricant supplier indicated a range of average daily stern tube lubricant consumption rates for different vessels (Etkin, 2010). The average rate across vessel types was 2.6 liters per day, but ranged from less than 1 liter per day to 20 liters per day. Because it is common practice to use the lubricant supplied for the vessel’s main engines as the stern tube lubricant to minimize the number of lubricants held on board, the amount which is used in stern tubes and released to the sea is not recorded.

Engine oil formulations have the correct characteristics (e.g., viscosity) to fulfill the role of lubricants specifically formulated for stern tubes. However, engine oil additives, which can be up to 30% of the formulation, are strongly alkaline (to neutralize the acids formed during fuel combustion). Consequently, due to the nature of engine oil additives, this practice greatly increases the toxic effects of stern tube discharges.

¹ The 2008 VGP encourages vessel owners and operators to use environmentally preferable lubricants whenever possible.

In addition to spills and stern tube leakage, there are “operational inputs” of lubricant oils that occur due to continuous low-level discharges and leakages that occur during normal vessel operations in port. The sources of operational discharges include deck machinery and in-water (submerged) machinery. There are a number of systems situated below the waterline that must be lubricated. The main systems to consider are the stern tube bearing, thruster gearboxes, and horizontal stabilizers. All of these have pressurized lubricating oil systems that maintain a pressure higher than the surrounding sea. This ensures that no significant amount of seawater can enter the oil system, where it would compromise the unit’s reliability. However, any leakage of lubricant oil flows into the sea.

A 2010 study estimated the marine inputs of lubricant oils within the 4,708 ports and harbors of the world through stern tube leakage and operational discharges from marine shipping (Etkin, 2010). The study results indicate that commercial vessels make over 1.7 million port visits each year and leak 4.6 to 28.6 million liters of lubricating oil from stern tubes. In addition, 32.3 million liters of oil is introduced to marine waters from other operational discharges and leaks. In total, operational discharges (including stern tube leakage) input 36.9 to 61 million liters of lubricating oil into marine port waters annually – the equivalent of about one and a half Exxon Valdez-sized spills. Assuming that the higher estimate of stern tube leakage is representative of the inputs that may occur in port as well as in transit, the total estimated input of lubricating oil from leakage and operational discharges represents nearly 61 million liters annually worldwide. Leaks of lubricating oil represent 10 percent of the total oil inputs into marine waters, as estimated in the 2003 NRC Oil in the Sea study (see Figure 1). The total annual estimated response and damage costs for these leaks and operational discharges are estimated to be about \$322 million worldwide. Total estimated costs for the U.S. are estimated to be \$31 million annually (Etkin, 2010).



Based on Etkin, 2010 and NRC, 2003

Figure 1. Annual Oil Inputs into the Marine Environment

The following sections of this document describe the main types of EALs in current production; considerations for EALs in the aquatic environment; the standards for biodegradability, toxicity and bioaccumulation potential of EALs; the potential advantages and disadvantages of using EALs on board commercial vessels; and labeling programs.

1.1 MARKETING AND LABELING

Although EALs have been in commercial production for years, they comprise a small portion of the total lubricant market and are still regarded as niche products (Habereeder et al., 2008). The market for EALs continues to expand, particularly in Europe, where the use of such lubricants is being encouraged through a combination of tax breaks, purchasing subsidies, and national and international labeling programs based on well-defined criteria. Many lubricants are advertised as being environmentally preferable; however, currently there are no regulatory standards for EALs, and no internationally accepted term by which they are defined. To distinguish lubricants which have been shown to be both biodegradable and non-toxic according to acceptable test methods from those lubricants that are simply marketed as being “environmental” (or similar terminology), in their 1999 Lubricants and Hydraulic Fluids Manual, the US Army Corps of Engineers recommended use of the term “environmentally acceptable” (a term commonly used by American Society for Testing and Materials (ASTM) committees) to address environmental lubricants. Bioaccumulation potential was not addressed within this definition of EALs.

While numerous terms are presently used to advertise lubricants as having desirable environmental properties, there is growing consensus to use the term “environmentally acceptable” to denote a lubricant that is biodegradable, exhibits low toxicity to aquatic organisms and has a low potential for bioaccumulation. Although many tests for these qualities exist, there is also harmonization underway within the lubricant manufacturing community regarding the most appropriate standard testing methods for these and other qualities determined to be important for an EAL, such as the proportion of renewable (recyclable) materials used in manufacturing. An environmentally acceptable lubricant should still perform well in comparison to the conventional lubricant it replaces. This harmonization is being driven by national and international labeling programs, particularly in European nations where the testing procedures and criteria have been codified (Habereeder et al., 2008 and IENICA, 2004). These labeling requirements, while not regulated by law, have helped to clarify the difference between EAL and EFL products in the marketplace.

Because the majority of a lubricant is composed of the base oil, the base oil used in an EAL must be biodegradable. The three most common categories of biodegradable base oils are: 1) vegetable oils, 2) synthetic esters, and 3) polyalkylene glycols. Due to the low toxicities of these three types of base oils, aquatic toxicity exhibited by lubricants formulated from them is typically a consequence of the performance enhancing additives or thickening agents (found in greases) used in the formulation, which can vary widely.

SECTION 2

TYPES OF ENVIRONMENTALLY ACCEPTABLE LUBRICANTS

Environmentally acceptable lubricants are commonly classified according to the type of base oil used in their formulation. In general, lubricants consist of approximately 75 to 90 percent base oil. Greases contain approximately 10 percent thickening agent, which is usually a soap (Gow, 2009), in addition to the base oil. The remaining fraction of a lubricant formulation consists of performance enhancing additives. A lubricant formulation can include hundreds of additives, which address performance issues specific to their application and performance shortcomings of the base oil. Additives are commonly used to address oxidative aging, corrosion, high pressure, low or high temperature conditions, phase transition, shear, foaming, and hydrolysis (particularly for vegetable and synthetic ester-based oils) (Habereeder et al., 2008).

The number of additives that are compatible with vegetable oils, synthetic esters, or polyalkylene glycols is small relative to the number of additives that are compatible with conventional (mineral) base oils. However, this is changing as a result of increased emphasis on EAL development. Additive manufacturers are working more closely with the lubricant industry to design additives that are suitable for improving the performance of EALs that are more environmentally benign (Aluyor et al. 2009). For some of the more stringent labeling programs (see Section 5), additives used in EAL must be both ashless (i.e., containing no metals other than Ca, Na, K, Mg) and non-toxic (Habereeder et al. 2009). Among the soaps, calcium-based soaps are considered less toxic compared to other types (e.g., lithium-based), and soaps in general are considered less toxic than graphite thickeners (Gow, 2009).

2.1 VEGETABLE OILS

The main components of vegetable oils are triglycerides (natural esters), the precise chemical nature of which is dependent on both the plant species and strain from which the oil is obtained (Habereeder et al., 2008 and Nelson, 2000). Outside the U.S., rapeseed is the most commonly used crop for creating vegetable oil lubricants (Cuevas, 2005 and Habereeder et al., 2008). In the U.S., the most commonly used crops for producing vegetable oil lubricants are canola, soybeans, and sunflowers (Nelson, 2000).

Largely because of performance issues related to low thermo-oxidative stability and poor cold flow behavior, pure vegetable oil-based lubricants comprise a relatively small fraction of the biolubricant market, although recent research developments have shown promise for overcoming these shortcomings (Erhan et al., 2006 and Kabir et al., 2008). Another reason is that vegetable oil-based lubricants are much less available than synthetic esters (Bremmer and Plonsker, 2008). To date, their most common commercial applications include hydraulic fluid and wire rope grease.

2.2 SYNTHETIC ESTERS

Lubricants based on synthetic esters have been in production longer than any other class of biolubricant and were first used for jet engine lubrication in the 1950s. Synthetic esters can be prepared by the esterification of biobased materials (i.e., some combination of modified animal fat and vegetable oil). Because synthetic esters can be specifically tailored for their intended

application, they have many performance advantages over pure vegetable oils, and are used as the base oil in lubricants for many vessel applications, including hydraulic oil, stern tube oil, thruster oil, gear lubricant, and grease (ACE, 1999 and Habereeder et al., 2008). Synthetic esters-based EALs are developed and marketed by several major oil companies including British Petroleum, Chevron, Exxon/Mobil and Gulf, and are currently the most widely commercially available class of EAL.

2.3 POLYALKYLENE GLYCOLS

Polyalkylene glycols (PAG) are synthetic lubricant base oils, typically made by the polymerization of ethylene or propylene oxide (Brown, 1997). Depending on the precursor, they can be soluble in either oil (propylene oxide) or water (ethylene oxide) (Greaves, 2008 and Habereeder et al., 2008). Although they are made from petroleum-based materials, PAGs can be highly biodegradable, particularly the water soluble PAGs (Greaves, 2008; Sada et al., 2008; and Sada et al., 2009).

2.4 WATER

At least one company has developed a completely seawater-lubricated stern tube system that uses non-metallic bearings in place of metal bearings. This system is currently in place in over 500 commercial vessels, including several Carnival Corporation cruise ships (Carter, 2009).

SECTION 3

CONSIDERATIONS FOR EALS IN THE AQUATIC ENVIRONMENT

A number of factors must be considered when selecting lubricants for use in the aquatic environment. Vessels require a variety of lubricants for different applications and on-ship storage can be limited. Consequently, the most useful lubricants are those that can perform well in a variety of applications (Rana, 2001). Additionally, lubricants must be widely available; in the case of some larger ocean going vessels, compatible lubricants must be available at ports around the globe (Blanken, 2006).

Marine environments are characterized by high humidity conditions, and seawater ingress can pose serious lubrication problems in sealed compartments, such as stern tubes and hydraulic systems (Rana, 2001). Stern tube seals are highly susceptible to leakage, both from normal operations, including vibrations and misalignment, and from contact with nets or fishing lines (Sada et al., 2008 and Carter, 2009). The constant presence of seawater increases the potential for corrosion, requiring thicker greases to repel water and corrosion inhibitors to minimize corrosion following seawater ingress. In addition, lubricants subject to frequent contact with water have a greater likelihood of undergoing some degree of biodegradation (ACE, 1999).

3.1 THICKENING AGENTS

Stiffer greases (i.e., National Lubricating Grease Institute grade 3 or higher) are typically used in marine applications as they repel water more effectively. Lithium-based thickeners are the most commonly used thickening agents, as they are considered to have the best all-purpose formulation. Although they comprise a much smaller fraction of the grease market, calcium-based thickeners do perform well under cool, wet conditions, and are used in formulations for some marine applications (e.g., propeller housing and water pumps). Anhydrous calcium-based greases are becoming increasingly common in Europe, where there is a greater emphasis on adoption of EALs, because of their relatively low toxicity and better performance at higher temperatures (Gow, 2009).

3.2 ADVANTAGES AND DISADVANTAGES OF VEGETABLE-BASED EALS

In addition to their environmental benefits (i.e., high biodegradability and low aquatic toxicity), vegetable oils possess several advantageous performance qualities compared to mineral oils. They have a higher viscosity index (meaning they do not thin as readily at high temperatures) and they have a higher lubricity, or ability to reduce friction (Nelson, 2000; IENICA, 2004). Vegetable oil-based lubricants also have a high flash point, meaning they combust at higher temperatures than conventional mineral oils. They perform well at extreme pressures, and do not react with paints, seals, and varnishes (ACE, 1999).

Vegetable oils possess several major performance drawbacks, however, which have limited their use in the formulation of EALs. The primary limitations are (1) poor performance at both low and high temperatures and (2) oxidative instability (Erhan et al., 2006 and Habereeder et al., 2008). Vegetable oils thicken more than mineral oils at low temperatures and are subject to

increased oxidation at high temperatures, resulting in the need for more frequent oil changes. These shortcomings can be addressed with the use of selected additives for a formulation or through the selective breeding and use of high-oleic oils (i.e., oils that contain more oleic acid, a monounsaturated fat, and less polyunsaturated fats) that are less susceptible to oxidative instability. The use of selected additives can increase production costs and may decrease the overall environmental acceptability of the product (Nelson, 2000; Bremmer and Plonsker, 2008). In addition, vegetable oils remove mineral oil deposits, resulting in the need for more frequent oil filter service.

Vegetable oil lubricants are more expensive than comparable mineral oil lubricants, as a function of both higher base oil costs, as well as higher costs for the base oil-compatible additives (ACE, 1999). Although Miller (2008) stated that vegetable oil lubricants cost approximately double that of mineral base oils, more recent information obtained through personal communication with a major lubricant supplier suggests that the current cost premium for these biolubricants may be only 20% more. Changing from a mineral to a vegetable oil lubricant is relatively simple, as vegetable oils and mineral oils are compatible and vegetable oil lubricants will perform properly if some mineral oil residue remains. Because the overall formulations are less toxic, disposal costs are generally lower; however, this may not always be the case, as fewer disposal stations are able to accept spent biobased lubricants (ACE, 1999; Nelson, 2000; and Bremmer and Plonsker, 2008).

3.3 ADVANTAGES AND DISADVANTAGES OF SYNTHETIC ESTER-BASED EALS

Synthetic esters perform well across a wide range of temperatures, have a high viscosity index, possess high lubricity, provide corrosion protection, and have high oxidative stability (ACE, 1999 and Habereeder et al., 2008). Because they contain biobased material, many synthetic esters satisfy testing requirements for biodegradability and aquatic toxicity, although they tend to be less readily biodegradable than pure vegetable oil-based lubricants (WISE Solutions, 2006). Synthetic ester-based lubricants can be more or less toxic than vegetable oil-based lubricants, depending on the aquatic toxicity of the additives used in the formulation. The only notable performance issue with synthetic esters is that they are incompatible with some paints, finishes, and seal materials (ACE, 1999).

Synthetic esters are generally the most expensive class of EAL (Miller, 2008). Synthetic ester-based biolubricants cost approximately 2-3 times that for comparable conventional mineral oil-based lubricants. As the availability of synthetic ester-based EALs increases, this cost differential is expected to decline.

The relatively higher cost of synthetic esters is somewhat mitigated by their high oxidative stability, which results in longer lubricant life. This is particularly applicable to areas of the vessel that require more frequent lubricant changes (e.g., engine oil, hydraulic fluid, stern tube-thruster fluid). Synthetic esters are compatible with mineral oil, which reduces changeover costs, but similar to vegetable oils in that their effectiveness at removing mineral oil deposits can cause filters to clog during the period initially following lubricant changeover (ACE, 1999). Disposal costs are similar to those for vegetable oil-based lubricants.

3.4 ADVANTAGES AND DISADVANTAGES OF POLYALKYLENE GLYCOL-BASED EALS

Lubricants consisting of polyalkylene glycols (PAGs) have the best overall low- and high-temperature viscosity performance among all of the classes of biolubricants. For marine applications, water soluble PAG EALs are attractive because, in addition to their high biodegradability, they retain their performance characteristics following water influx better than other EALs; as a result, PAG EALs have received consideration as a stern tube lubricant (Sada et al., 2008; Sada et al., 2009). The water solubility of ethylene oxide-derived PAGs can improve performance relative to other lubricants by maintaining viscosity following some fraction of water influx (up to 20% in some laboratory tests), which can be of great importance for stern tube lubrication (Sada et al., 2008; Carter, 2009). PAGs also perform well in terms of lubricity, viscosity index, and corrosion protection. The relatively high viscosity and lubricity of PAGs has resulted in the recent development of PAG-based thruster lubricants (Sada et al., 2009).

Disadvantages associated with PAGs are that they are incompatible with mineral oils, as well as most paints, varnishes, and seals (ACE, 1999; Sura et al., 2008). Because of this incompatibility, they have the highest changeover costs of any class of EAL (Sada et al., 2008). Additionally, water soluble PAGs may demonstrate increased toxicity to aquatic organisms by directly entering the water column and sediments rather than remaining on the water column surface as a sheen (Habereeder et al., 2008).

3.5 AVAILABILITY AND COST OF EALS

At the present, the global availability of EALs for different marine applications is growing. One manufacturer of marine EALs, Castrol Bio Range, provided data demonstrating that stern tube and thruster lubricant, hydraulic fluids, gear lubricants and grease were available in the following global regions and countries (Pearce et al., 2010; Castrol Marine, 2011):

- Americas: USA;
- Northern Europe: Belgium, Denmark, Finland, France, Germany, Netherlands, Norway, Sweden, UK;
- Mediterranean: Italy, Spain, Turkey, UAE; and
- Asia-Pacific: China, Japan, Hong Kong, Singapore, Korea.

Market cost data for EALs are unavailable, because manufacturers consider such data to be proprietary marking information. The purchase prices of EALs are guarded closely by the manufacturers, and EPA has generally been unable to obtain publicly available cost information from EAL manufacturers. Operating costs for ship-owners and charterers using environmentally preferable lubricants are expected to increase modestly relative to conventional products, although there can be efficiency gains from longer life (e.g., reduced corrosive properties, enhance water contamination performance). However, the benefit of using environmentally preferable lubricants can be considerable in terms of reduced environmental impacts.

Some indication of the cost of EALs relative to conventional lubricants was provided by a major lubricant vendor and is tabulated in Table 1. Some specialized lubricants may have higher costs.

Table 1. Cost of EALs

Lubricant Base Oil	Ratio of EAL cost to Conventional Mineral Oil Lubricant Cost
Mineral Oil	1
Vegetable Oils	1.2
Synthetic Esters	2 to 3
Polyalkylene Glycols	2 to 3

An informal survey of websites for the boating supply distributors West Marine, Jamestown Distributors, Aerospace Lubricants, Inc. and Aqua Lube, demonstrates that semi-synthetic ester and full synthetic ester engine oil, gear oil, and greases are the most commonly available biolubricants for recreational vessel owners. The costs of full synthetic ester formulations (primarily two cycle and four stroke engine oils) range from 1.4-1.8 times the costs of comparable conventional (mineral oil) formulations. These distributor websites do not provide information as to whether any of the synthetic ester-based biolubricants meet certification standards that would classify them as EAL. For commercial vessels, relative pricing information for Gulf Oil marine lubricants reveals that costs for biolubricants advertised (synthetic gear oil, compressor oil, and coolant oil, the three synthetic lubricants), ranged from approximately 1.3-2.5 times (coolant oil) to 3.5-4.3 times (gear oil and compressor oil) the cost for comparable mineral oil products (Gulf Marine, 2010). It may be reasonable to assume that the cost premium for EALs is similar to these price ratios.

Many countries, primarily in Europe, encourage the manufacture and consumption of EALs. Examples are through tax exemptions on environmentally acceptable base oils, taxes on mineral oils, subsidies to consumers to cover the price difference between conventional and EALs, or preferential purchasing programs that require a percentage of certain classes of product to be made from renewable resources (Habereeder et al., 2008; IENICA, 2004; and WISE Solutions, 2006).

SECTION 4

DEFINING “ENVIRONMENTALLY ACCEPTABLE”

Lubricants may be labeled using a variety of terms to signify that they are environmentally friendly. Although EFLs are most likely to be tested for biodegradability, aquatic toxicity and bioaccumulation potential, there are numerous other methods, which vary in their sensitivity.

4.1 BIODEGRADABILITY

Biodegradability is a measure of the breakdown of a chemical (or a chemical mixture) by micro-organisms. *Primary* biodegradation is the loss of one or more active groups in a chemical compound that renders the compound inactive with regard to a particular function (Betton, 2009). Primary biodegradation may result in the conversion of a toxic compound into a less toxic or non-toxic compound. *Ultimate* biodegradation, also referred to as mineralization, is the process whereby a chemical compound is converted to carbon dioxide, water, and mineral salts (Betton, 2009).

In addition to primary and ultimate biodegradation, biodegradation is also defined by two other operational properties: inherent biodegradability and ready biodegradability. A compound is considered *inherently* biodegradable so long as it shows evidence of biodegradation in any test for biodegradability. *Readily* biodegradable is an operational definition that some fraction of a compound is ultimately biodegradable within a specific timeframe, as specified by a test method.

Common test methods, such as those developed by the Organization for Economic Cooperation and Development (OECD), the Coordinating European Council (CEC), and the American Society for Testing and Materials (ASTM), for determining lubricant biodegradability are OECD 301B (the Modified Strum test), ASTM D-5864, and CEC L-33-A-934. Both OECD 301B and ASTM D-5864 measure ready biodegradability, defined as the conversion of 60% of the material to CO₂ within a ten day window following the onset of biodegradation, which must occur within 28 days of test initiation (Willing, 2001). In contrast, the CEC method tests the overall biodegradability of hydrocarbon compounds and requires 80% or greater biodegradability as measured by the infrared absorbance of extractable lipophilic compounds (CEC, 1997 and WISE Solutions, 2006). Unlike the OECD and ASTM methods, the CEC method does not distinguish between primary and ultimate biodegradability, and is considered to be a less stringent test (Blanken, 2006).

Table 2 lists some of the internationally standardized test methods that measure biodegradability.

Table 2. Internationally Standardized Test Methods for Measuring Biodegradability

Test Type	Test Name	Measured Parameter ^a	Pass Level ^b	Method
Ready Biodegradability (A substance is considered to be inherently biodegradable using any of these tests if it shows ≥20% biodegradability within the test duration)	DDAT	DOC	≥70%	OECD 301A
	Strum test	CO ₂	≥60%	OECD 301B
	MITI test	DOC	≥70%	OECD 301C
	Closed bottle test	BOD/COD	≥60%	OECD 301D
	MOST	DOC	≥70%	OECD 301E
	Sapromat	BOD/COD	≥60%	OECD 301F
	Strum test	CO ₂	≥60%	ASTM D-5864
	Shake flask test	CO ₂	≥60%	EPA 560/6-82-003
	BODIS test	BOD/COD	≥60%	ISO 10708
Hydrocarbon degradability	CEC test	Infrared Spectrum	≥80%	CEC L-33-A-934
Screening tests (semi-official)	CO ₂ headspace test	CO ₂	≥60%	ISO 14593

Source: modified from Willing, 2001

a. DOC – dissolved organic carbon; CO₂ – carbon dioxide; BOD – biochemical oxygen demand; COD – chemical oxygen demand

b. Ready biodegradability is defined as complete mineralization of a compound into water, carbon dioxide, and mineral salts according to a specific test criterion. Pass levels indicate the percentage of complete mineralization (or ultimate biodegradation) as indicated by the “Measured Parameter” that must occur for a product to be classified as readily biodegradable.

Table 3 summarizes biodegradation rates for different lubricant base oils. Ester-based oils have a much greater inherent biodegradation rate due to the presence of carboxylic acid groups that bacteria can readily utilize (Mudge, 2010). These compounds are also more water soluble than compounds that do not contain polar functional groups, the absence of which can reduce their bioaccumulation potential.

Table 3. Summary of Differential Biodegradation Rates by Lubricant Base Oils

Lubricant base oil	Base oil source	Biodegradation
Mineral oil	Petroleum	Persistent / Inherently
Polyalkylene glycols (PAG)	Petroleum - synthesized hydrocarbon	Readily
Synthetic Ester	Synthesized from biological sources	Readily
Vegetable Oils	Naturally occurring vegetable oils	Readily

Source: Mudge, 2010

4.2 AQUATIC TOXICITY

In addition to possessing a certain percentage of readily biodegradable material, an EAL must also demonstrate low toxicity to aquatic organisms. Test methods to demonstrate toxicity include the OECD tests series 201-4, and 209-212; and corresponding USEPA environmental effect test guidelines from EPA 560/6-82-002. The most common aquatic toxicity tests for assessing EALs are the 72-hour growth test for algae (OECD 201), the 48-hour acute toxicity test for daphnia (OECD 202), and the 96-hour toxicity test for fish (OECD 203). Analogous USEPA tests are sections EG-8, EG-1, and EG-9 of EPA 560/6-82-002 for algae, daphnia, and fish, respectively. A listing of all of the OECD aquatic toxicity tests is included in Table 4.

Table 4. OECD Aquatic Toxicity Tests

Test Title, with Species	Test Number
Growth Inhibition Test, Alga	OECD 201
Acute Immobilization Test, <i>Daphnia</i> sp.	OECD 202
Acute Toxicity Test, Fish	OECD 203
Prolonged Toxicity Test: 14-Day Study, Fish	OECD 204
Respiration Inhibition Test, Bacteria	OECD 209
Early-Life Stage Toxicity Test, Fish	OECD 210
Reproduction Test, <i>Daphnia magna</i>	OECD 211
Short-term Toxicity Test on Embryo and Sac-fry Stages, Fish	OECD 212

In general, the vegetable oil and synthetic ester base oils have a low toxicity towards marine organisms with the LC₅₀ for fish toxicity reported as being ~10,000 ppm for fatty acid esters and glycerol esters (see Table 5) (van Broekhuizen, 2003). Water soluble PAGs may demonstrate increased toxicity to aquatic organisms by directly entering the water column and sediments rather than remaining on the water column surface as a sheen (Habereeder et al. 2008).

Table 5. Summary of Comparative Toxicity of Base Oils

Lubricant base oil	Base oil source	Toxicity
Mineral oil	Petroleum	High
Polyalkylene glycols (PAG)	Petroleum - synthesized hydrocarbon	Low ^a
Synthetic Ester	Synthesized from biological sources	Low
Vegetable Oils	Naturally occurring vegetable oils	Low

Source: Mudge, 2010

a. Solubility may increase the toxicity of some PAGs

As with many oily chemicals, the toxicity in some tests is not measurable as the LC₅₀ exceeds the water solubility of the compound (Mudge, 2010). In such cases, it is possible to induce physical effects such as smothering but this is not a chemical toxic effect. Some methodologies use the water-accommodated fraction, the part of the oil that disperse or dissolves in water, although this is not a true reflection of the entire oil behavior in the marine environment.

The petroleum-based oils have a greater toxicity to biota in the marine food chain compared to the other base oil sources (Mudge, 2010). This is related to the more rapid breakdown of petroleum-based oils once in the sea, which ultimately affects the potential for bioaccumulation. The toxicity of petroleum-based oils is also dependent upon additives used in formulations and metabolites produced in biodegradation.

The use of additives is dependent on the choice of base oil and the intended function of the lubricant (Mudge, 2010). However, several of the more toxic compounds in formulations are also the ones with poor degradability. The overall product toxicity may be significantly reduced by switching to a biologically-sourced base oil used in conjunction with low toxicity additives.

4.3 BIOACCUMULATION

The propensity of a substance to bioaccumulate is another property of a lubricant that is often considered in the qualification of a product as an EAL (Mudge, 2010). Bioaccumulation is the build-up of chemicals within the tissues of an organism over time. The longer the organism is exposed to a chemical and the longer the organism lives, the greater the accumulation of the chemical in the tissues (Mudge, 2010). If the chemical has a slow degradation rate or low depuration rate within an organism, concentrations of that chemical may build-up in the organism’s tissues and may eventually lead to adverse biological effects. It is, therefore, desirable to use compounds in formulations that do not bioaccumulate. It may not be possible to phase out all bioaccumulating compounds, but it is feasible to use chemicals that have a lower bioaccumulation potential, either through not being taken up as readily or by degrading more quickly both in the environment and in the organism.

The bioaccumulation potential of a compound is directly related to its water solubility; chemicals that are not water soluble tend to move into fatty tissues rather than staying in water. These lipophilic chemicals include most of the compounds used in the manufacture of the base oil in lubricants. The water solubility of a compound is related to the type of atoms in the molecule; compounds comprised solely of carbon and hydrogen tend to have the lowest solubility in water. Compounds of this type includes alkanes, which form almost 90% of the current base oil in conventional lubricant formulations. The inclusion of one or more oxygen atoms in a molecule will, in general, increase the water solubility and reduce bioaccumulation. Compounds with oxygen also tend to degrade more quickly in the environment or be excreted faster from organisms.

Many naturally-derived base oils used in lubricants are formulated around carboxylic acids, which increase water solubility and degradation; therefore, their bioaccumulation potential is reduced in comparison to alkane-based oils.

It has been assumed for some time that larger molecules are not bioaccumulated as they are unable to physically pass through the membranes of cells and be incorporated into the living cells (Arnot et al., 2010). Therefore, when designing lubricant formulations, the molecular size of the components of the base oil are considered as they will directly affect the rate of uptake. There has been several criteria proposed over the past few years to describe the point at which chemicals are no longer taken up in the body and bioaccumulated (Arnot et al., 2010). In an evaluation of data for esters, there was a strong link between the $\log K_{ow}$ (the logarithm of the partitioning coefficient of a substance in n-octanol and water) and the $\log BCF$ (a measure of the bioconcentration from water into aquatic organisms), while the other factors had less well-defined relationships. The selection criteria chosen by the Canadian Government and United Nations Environment Program (UNEP) (Canada, 2000 and UNEP, 2001) and the U.S. Environmental Protection Agency (USEPA, 1999) led to cut-off $\log K_{ow}$ values of ~ 5 . There is no single criterion to adequately describe the BCF; one study proposes a holistic approach integrating several factors, including measured uptake and elimination rates (Arnot et al., 2010).

Certain labeling programs, most notably the European Eco-label (see Section 5), require demonstration that a product is not bioaccumulative. This can be accomplished in a number of ways for organic compounds, such as measuring $\log K_{ow}$, or BCF. The two most common test

methods for establishing bioaccumulation potential are OECD 117 and 107. For these tests, the test substance is added to a mixture of octanol and water and its dissolution in each phase is detected using gas chromatography or an infra red detector. The bioaccumulation of the substance is measured by establishing its partition coefficient (expressed as $\log K_{ow}$) in octanol and water. Substances that have a tendency to bioaccumulate will preferentially dissolve in the octanol rather than the water, and octanol mimics the fatty tissue in an organism. Therefore, the greater the $\log K_{ow}$, the greater the likelihood that the substance will bioaccumulate.

Partition coefficients for the marine environment are normally measured on a log scale between 0-6. Substances with $\log K_{ow} < 3$ are deemed not to bioaccumulate and those with $\log K_{ow} > 3$ are deemed to be bioaccumulating.

Seawater may increase the likelihood of uptake by organisms in comparison to freshwater due to “salting out” of lipophilic substances. Therefore, although freshwater is used in these test methods, as long as conservative acceptance limits are set, they can be used as an indicator of bioaccumulation potential in the marine environment. The use of these test methods as an indicator of a substance’s bioaccumulation potential can negate the need to carry out *in vivo* or *in vitro* fish or mussel testing.

In summary, the level to which a component of the product is bioaccumulated in an organism is dependent on the environmental and biological half-lives of the compounds (some will degrade before being incorporated into an organism and some will be metabolized within the organism), as well as the lipophilic nature of the compounds (as measured by water solubility). Any component that has low water solubility may potentially bioaccumulate in an organism. In the case of lubricants, fatty acid-containing components have reduced bioaccumulation potential due to greater water solubility and higher biodegradation rates. This is one distinct advantage in using esters over the other carbon and hydrogen alone base oil types (see Table 6).

Table 6. Summary of Bioaccumulation Potential by Base Oil Types

Lubricant base oil	Base oil source	Potential for Bioaccumulation
Mineral oil	Petroleum	Yes
Polyalkylene glycols (PAG)	Petroleum - synthesized hydrocarbon	No
Synthetic Ester	Synthesized from biological sources	No
Vegetable Oils	Naturally occurring vegetable oils	No

Source: Mudge, 2010

4.4 SUMMARY OF ENVIRONMENTALLY ACCEPTABLE LUBRICANT CHARACTERISTICS

A summary of the major factors regarding biodegradation, toxicity and bioaccumulation potential, for each of the base oil types is shown in Table 7. In this table, the three major criteria are presented for each base oil and color-coded to indicate the environmental outcome. The biodegradability of a lubricant reflects that of the lubricant’s base oil, while the degree of aquatic toxicity is typically a consequence of the performance enhancing additives (or thickening agents) within the formulation. The base oils that degrade quickly are considered more preferable than those that do not rapidly degrade, although there might be a trade-off with regard to the depletion of oxygen during compound metabolism. The compounds that do not bioaccumulate and are

relatively less toxic are considered more preferable than those that bioaccumulate and have higher toxicities.

Table 7. Comparative Environmental Behavior of Lubricants by Base Oil Type

Lubricant base oil	Base oil source	Biodegradation	Potential for Bioaccumulation	Toxicity
Mineral oil	Petroleum	Persistent / Inherently	Yes	High
Polyalkylene glycols (PAG)	Petroleum - synthesized hydrocarbon	Readily	No	Low ^a
Synthetic Ester	Synthesized from biological sources	Readily	No	Low
Vegetable Oils	Naturally occurring vegetable oils	Readily	No	Low

Source: Mudge, 2010

a. Solubility may increase the toxicity of some PAGs

Currently, a majority of lubricant base oils (mineral oils) have the lowest biodegradation rate, a high potential for bioaccumulation, and a measurable toxicity towards marine organisms. In contrast, the base oils derived from oleochemicals (vegetable oils and synthetic esters) degrade faster, have a smaller residual, do not bioaccumulate appreciably and have a lower toxicity to marine organisms. PAG-based lubricants are also generally biodegradable and do not bioaccumulate; however, some PAGs may be more toxic due to their solubility in water. On the basis of this simple comparison, lower environmental impacts will arise if a greater proportion of base oils are manufactured from biologically-sourced materials.

SECTION 5

ENVIRONMENTALLY ACCEPTABLE LUBRICANT LABELING PROGRAM

To minimize confusion in the marketplace and to increase public awareness and create sensitivity for environmentally preferable products, national and international labeling programs have been developed, primarily in Europe (Habereeder et al., 2008). These labeling programs have defined and established methods to measure the properties of a lubricant that would qualify it as being environmentally acceptable. The labeling programs can aid the purchasing decisions of a vessel operator by helping to remove uncertainty. The principal national and international labeling certification programs for biolubricants and EALs are presented below.

5.1 NATIONAL LABELING PROGRAMS

5.1.1 Blue Angel

The first national labeling scheme for lubricants was the German Blue Angel label, developed in 1988. Criteria have been developed for several classes of lubricants, including hydraulic fluids, lubricating oils, and greases. In order to qualify for certification, a lubricant must possess the following characteristics: biodegradability; low toxicity to aquatic organisms; non-bioaccumulative; and no dangerous components (such as carcinogens or toxic substances as defined by Germany's Ordinance on Hazardous Substances). A product must also pass technical performance characteristics appropriate for its use. Biodegradability can be demonstrated using OECD tests 301B-301F to measure ultimate biodegradability or CEC L-33-A-934 to measure primary biodegradability. Blue Angel's requirement for ultimate biodegradability is the primary difference between the Blue Angel labeling certification program and other national and international certification programs. Aquatic toxicity is determined according to OECD 201-203.

Products receiving the Blue Angel certification must also pass a series of technical performance requirements that depend on the class of lubricant. Unlike some of the other labeling programs, the Blue Angel certification does not have any requirements for renewability; consequently, lubricants comprised completely of petroleum-sourced components can receive Blue Angel certification. Nevertheless, Blue Angel certification is considered rather stringent, and the proportion of lubricants receiving this certification remains low, with the majority being hydraulic fluids (Habereeder et al., 2008). A complete list of all lubricants that carry the Blue Angel certification can be found at http://www.blauer-engel.de/en/products_brands/search_products/search_for_products.php.

5.1.2 Swedish Standard

Another national labeling scheme for lubricants is the Swedish Standard, which includes standards for hydraulic fluids (SS 155434) and greases (SS 155470). Evaluation of a lubricant under the Swedish Standard involves testing for biodegradability and aquatic toxicity, as well as sensitizing properties of a lubricant formulation and its components (Habereeder et al., 2008). The Swedish Standard evaluates biodegradability using ISO test methods (e.g., ISO 9439), and has varying requirements, depending upon class, for renewable resources content (SP 2010). The

Swedish Standard is unique because it was conceived and developed as a collaborative project between government and industry. This program has more listed lubricant products, particularly hydraulic fluids, than any other national labeling program (IENICA, 2004).

5.2 INTERNATIONAL LABELING PROGRAMS

5.2.1 Nordic Swan

The first international labeling program for EALs was the Nordic Swan program, encompassing Norway, Sweden, Finland, Iceland, and Denmark. This program was initially introduced for hydraulic oil, two-stroke oil, grease, and transmission and gear oil (IENICA, 2004). The Nordic Swan certification addresses biodegradability, aquatic toxicity (OECD 201 and 202), technical performance, and renewability. The renewability requirements are the highest of all the labeling programs (e.g., at least 65% renewable content for hydraulic fluid, transmission fluid, gear oil, or grease, and at least 50% for two-stroke oil). Consequently, very few lubricants bear the Nordic Swan label (Habereeder et al., 2008).

5.2.2 European Eco-label

The European Union has adopted a single European Eco-label. The Eco-label is considered to be the first major advancement towards creating a single international standard, and is becoming the most generally accepted label. The Eco-label for lubricants was established in 2005, and includes hydraulic fluids, greases, and total loss lubricants, such as two-stroke oils. This labeling scheme consists of seven criteria encompassing biodegradability, aquatic toxicity, bioaccumulation, and the presence of certain classes of toxic substances (Habereeder et al., 2008). A complete list of all lubricants that carry the European Eco-Label can be found at <http://www.eco-label.com/default.htm>.

The ecological criteria for Eco-label lubricants aim at promoting products that have a reduced impact on the water and soil during their use and contain a large fraction of biologically-based material. Since this is the most widely accepted labeling program, the requirements for this labeling scheme are described in detail below.

5.2.2.1 Dangerous Materials

Before a lubricant can be considered for the Eco-label, it is determined that neither the formulation nor any of the main components are on the list of R-phrases (risk phrases) pertaining to environmental and human health hazards according to the European Union Dangerous Preparations Directive (IENICA, 2004). These include qualities such as explosiveness, flammability, carcinogenic potential, volatility, potential to cause birth defects, etc.

5.2.2.2 Toxicity

Aquatic toxicity can be evaluated either for the complete formulation and main compounds (those compounds comprising at least 5% of the formulation) or for each constituent substance. Greases must be evaluated for each constituent substance unless it can be shown that the thickening agent is at least inherently biodegradable (see below). All formulations and components must pass both OECD 201 and 202 for acute toxicity testing, and OECD 210 or 211 for chronic toxicity testing. If evaluated for the formulation and main constituents, the LC₅₀ (i.e.,

concentration of a compound or mixture that will kill half of the sample population of a specific test-organism in a specified period) of hydraulic fluids must be at least 100 mg/L and the LC₅₀ of greases, two-stroke oils, and all other total loss lubricants must be at least 1000 mg/L (European Commission, 2009). If the evaluation is based on each constituent substance, then constituents that comprise less than 20% of hydraulic fluids can have an LC₅₀ of 10-100 mg/L or have a no observed effect concentration (NOEC) of 1-10 mg/L; constituents that comprise less than 5% of hydraulic fluids can have an LC₅₀ of 1-10 mg/L or have a NOEC of 0.1-1 mg/L; and constituents that comprise less than 1% of hydraulic fluids can have an LC₅₀ of less than 1 mg/L or have a NOEC of 0-0.1 mg/L. For greases, two-stroke oils, and other total loss lubricants, the respective percentages are 25%, 1%, and 0.1% (European Commission, 2009).

5.2.2.3 Biodegradability and Bioaccumulation

Ninety percent or more of the total hydraulic oil formulation (75% for greases or two-stroke oils) must be ultimately biodegradable, as determined according to any of OECD tests 301 A-F, or equivalent. Less than 5% of the hydraulic oil formulation (20% for greases or two-stroke oils) must be inherently biodegradable. Inherent biodegradability can be defined as at least 20%, but less than 60% or 70% biodegradable (depending on the test), for any of OECD 301 A-F, or it can be defined as greater than 70% biodegradation in the OECD 302C test (or equivalent), or greater than 60% biodegradation in the ISO 14593 test (European Commission, 2009).

In addition to being biodegradable, a lubricant must not have the potential to be bioaccumulative. A lubricant is considered not potentially bioaccumulative if one of the following conditions is met: it has a molar mass greater than 800 g/mol or a molecular diameter greater than 1.5 nm; it has a log K_{ow} less than 3 or greater than 7; or it has a measured BCF less than 100 L/Kg (European Commission, 2004). Log K_{ow}, which can be assessed using OECD 107, 117, or 123, or calculated, can be used to demonstrate bioaccumulation potential for organic compounds only. For all other compounds, BCF must be measured using the flow-through fish test given by OECD 305 (European Commission, 2004).

5.2.2.4 Restricted Substances

Lubricant formulations must not include certain specific substances, including halogenated organic compounds, nitrite compounds, metals or metallic compounds (with the possible exception of sodium-, potassium-, magnesium-, lithium-, aluminum-, and calcium-based soaps) (European Commission, 2004).

5.2.2.5 Renewable Content

At least 50% of hydraulic oils and two-stroke oils, and at least 45% of greases, must consist of renewable materials, with renewable defined as vegetable oils or animal fats (European Commission, 2004). Given that 70-90% of a lubricant or lubricant grease is the formulation's base oil, this requirement effectively excludes mineral oil lubricants from Eco-label certification.

5.2.2.6 Other

The final criteria for the Eco-label are for technical performance, which are specific to the lubricant class in question.

5.2.3 **OSPAR**

The offshore oil and gas industry is highly regulated, particularly in the North Sea, compared to other marine industries (Pearce et al, 2010). Considerable attention is given to the chemicals used on and discharged from offshore oil facilities. Some of these chemicals, such as well chemicals, are deliberately discharged during normal use, similar to the discharge of total loss lubricants by the marine industry.

The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention)² is the current legal instrument guiding international cooperation on the protection of the marine environment of the North-East Atlantic. Work under the Convention is managed by the OSPAR Commission, which is made up by representatives of 15 contracting Governments and the European Commission (represents the European Union).

The standards for environmental compliance, which are defined within the OSPAR Harmonized Mandatory Control Scheme (HMCS) regulations, require component level testing of chemicals released to the marine environment for biodegradation, bioaccumulation, and toxicity. These standards, which apply to the North Sea, are being adopted by most other oil and gas regulators around the world (including Australia, Canada, India, Indonesia and New Zealand) as they are considered to be the most appropriate for measuring the overall impact of a substance – not just its persistence (Pearce et al., 2010). Although these regulations do not cover the shipping industry, they may be considered the most appropriate standards for measuring the impact of released chemicals in the marine environment.

The OSPAR standards measure environmental performance of chemicals in terms of persistence (biodegradation in seawater over a 28-day period, by OECD 306), bioaccumulation (evaluation by measuring K_{ow} using OECD 117 or 107) and marine toxicity to four North Sea species (algae, copepods, sediment reworkers and bottom-dwelling fish). Testing is carried out on each component, and must be conducted by an approved third-party laboratory. The OSPAR protocols for methods for the testing of chemicals used in the offshore oil industry are available online (OSPAR, 2006). The mechanisms set out in the HMCS to ensure and actively promote the continued shift towards the use of less hazardous substances (or preferably non-hazardous substances) are described in the OSPAR Decision 2000/2 on a Harmonised Mandatory Control System for the Use and Reduction of the Discharge of Offshore Chemicals (OSPAR, 2000).

5.3 **SUMMARY OF ENVIRONMENTALLY ACCEPTABLE LUBRICANT LABELING PROGRAMS**

A summary of the major EAL labeling programs discussed in this section (including biodegradation, toxicity, bioaccumulation potential and other criteria) is provided in Table 8.

² www.ospar.org

Table 8. Comparison of EAL Labeling Programs

EAL Labeling Program	Biodegradability	Aquatic Toxicity	Bioaccumulation	Other Criteria
Blue Angel (Germany)	OECD 301B-F (ultimate biodeg.) or CEC L-33-A-934 (primary biodeg.)	OECD 201-203	OECD 305 A-E or K_{ow}	Dangerous materials; Technical performance
Swedish Standard	ISO 9439	NA	None	Renewable content; Sensitizing properties
Nordic Swan	NA	OECD 201-202	None	Renewable content; Technical performance
European Eco-label	OECD 301 A-F (ultimate biodeg.), OECD 302C or ISO 14593	OECD 201 and 202 (acute) & OECD 210 or 211 (chronic)	OECD 107, 117 or 123 (K_{ow} for organic compounds) or OECD 305	Dangerous materials; Restricted substances; Renewable content; Technical performance
OSPAR	OECD 306 (degradation under marine conditions)	Marine toxicity to 4 species	OECD 117 or 107 (K_{ow})	

NA - Not available

SECTION 6

CONCLUSION

Because much of the lubricant lost from a vessel directly enters the aquatic environment, there is a greater focus on encouraging the implementation of EALs on vessels (see 2008 VGP, page 24) (Carter, 2009). For all applications where lubricants are likely to enter the water, EAL formulations using vegetable oils, biodegradable synthetic esters or biodegradable polyalkylene glycols as oil bases instead of mineral oils can offer significantly reduced environmental impacts across all applications. Although their use is increasing, EALs continue to comprise only a small percentage of the total lubricant market.

Among types of EALs used in vessels, hydraulic fluids are the most prevalent. Along with chain saw oil, more hydraulic fluids carry the Blue Angel and European Eco-label than any other class of lubricant. A major reason for the success of environmentally acceptable hydraulic fluid is that some of the performance issues associated with EALs in open systems (particularly those formulated with vegetable oil derived base oils), such as oxidation, temperature sensitivity, and biodegradation following exposure to water, are less problematic in this closed system (ACE, 1999).

Stern tube leakage is a significant source of lubricant oil inputs to the aquatic environment; therefore, the benefit of replacing mineral-oil-based stern tube lubricants with EALs is expected to be considerable. Because of the inevitability of leaks, stern tube lubricants are also subject to water influx and increased biodegradability associated with water contact. While still a niche market, environmentally acceptable stern tube lubricants formulated from PAGs have shown to perform as well as a conventional stern tube lubricant, with the additional benefit of maintained viscosity following water influx (Sada et al., 2009).

SECTION 7

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