

## Chapter 2

# Lubricant Additive Impacts on Human Health and the Environment

**Abstract** It is estimated that, at present, approximately 50 % of all lubricants sold worldwide end up in the environment via total loss applications, volatility, spills or accidents. More than 95 % of these materials are mineral oil based. In view of their high eco-toxicity and low biodegradability, mineral oil-based lubricants make up a considerable threat to the environment. While, most lubricants and hydraulic fluids based on plant oils are rapidly and completely biodegradable and are of low eco-toxicity; moreover, lubricants based on plant oils display excellent tribological properties and generally have very high viscosity indices and flashpoints. However, in order to compete with mineral-oil-based products, some of their inherent disadvantages must be corrected, such as their sensitivity to hydrolysis and oxidative attack, and their behavior at low temperatures. The chapter also makes effort to characterize the potential human health and environmental hazards of widely used classes of lubricating oil additives and poly-alpha-olefin (PAO) base fluids, and the related toxicity levels.

## 2.1 Introduction

Original equipment manufacturers (OEM) specifications for lubricant performance will continue to drive changes in formulations, with particular focus on lubricants' contribution to meeting fuel economy and emissions regulations leading to increased demands placed on related lubricant characteristics. Environmental concerns will continue to play a major role in lubricant formulation and use. Reduction of elements such as chlorine, phosphorus, sulfur, and metals has proceeded at a rapid pace over the past decade, particularly in automotive lubricants. Use of more environmentally friendly fuels, including renewable fuels, in both automotive and industrial engines will also drive changes in lubricant formulation and additive demand. For example, expanding use of biodiesel in the motor vehicle fuel pool will require better oxidation and corrosion protection from lubricants. In contrast, falling sulfur content in marine fuel oil may reduce the need for detergents in marine engine lubricants (Freedonia 2013).

A number of ways to improve the undesirable properties of native plant oils are being pursued by various researchers. While governments are putting regulations in place to enforce the use of bio-based fluids, for use in ecologically sensitive areas. Here effort is made to look at the key impact of additives on human health and the environment. The main classes of additives are: succinimide ashless dispersants, calcium sulphonates, calcium phenates, zinc dialkyldithiophosphates, oxidation inhibitors, and anti-wear inhibitors. Although lubricant additives do not pose a significant health risk to humans, lubricant additives do not readily biodegrade and may be persistent in the environment. Manufacturing advances are reducing the release of toxic by-products to the environment. The potential health effects of lubricant additives in humans can be determined in appropriate animal toxicity tests. This testing is an important tool to communicate accurately the human health and environmental hazards through the use of appropriate labels, Material Safety Data Sheets (MSDS), and employee training.

## 2.2 Environmental Effects of Used Oil

When the lubricants are drained from say engines, gearboxes, hydraulic systems, turbines and air compressors: the oil is contaminated with wear debris; the lubricating base oil has deteriorated and degraded to acids; the additives have decomposed into other chemical species; and process fluids such as degreasers and solvents have mixed into the used oil. It was also noted that used oil contains wear metals such as iron, tin and copper as well as lead from leaded petrol used by motorists. Zinc arises from the additive packages in lubricating oils. Many organic molecules arise from the breakdown of additives and base oils. The molecule potentially the most harmful is the polycyclic aromatic hydrocarbon (PAH) such as benz(a)pyrene and chrysene. Petrol engines generate the most PAH molecules per 1000 km, with diesel engines below that and two-stroke engines generating the least amount of PAHs.

Any release of used oil to the environment, by accident or otherwise, threatens ground soil and surface waters with oil contamination there by endangering drinking water supply and aquatic organisms. Used oil has been established that it can damage the environment in several different ways such as:

- Spilled oil tends to accumulate in the environment, causing soil and water pollution. Oil decomposes very slowly. It reduces the oxygen supply to the microorganisms that break the oil down into non-hazardous compounds.
- Toxic gases and harmful metallic dust particles are produced by the ordinary combustion of used oil. The high concentration of metal ions, lead, zinc, chromium and copper in used oil can be toxic to ecological systems and to human health if they are emitted from the exhaust stack of uncontrolled burners and furnaces.

- Some of the additives used in lubricants can contaminate the environment e.g., zinc dialkyl dithiophosphates, molybdenum disulphide, and other organo-metallic compounds.
- Certain compounds in used oil—e.g., poly-aromatic hydrocarbons (PAHs)—can be very dangerous to one's health. Some are carcinogenic and mutagenic. The PAH content of engine oil increases with operating time, because the PAH formed during combustion in petrol engines accumulates in the oil.
- Lubricating oil is transformed by the high temperatures and stress of an engine's operation. This results in oxidation, nitration, cracking of polymers and decomposition of organ-metallic compounds.
- Other contaminants also accumulate in oil during use—fuel, antifreeze/coolant, water, wear metals, metal oxides and combustion products.

Thus in summary, in summary if used oil is disposed in an irresponsible manner it may cause great danger to the human resources like water supply. The environmental effects of used oil can be classified as human health effects, wetlands and wildlife effects, burning waste effects, marine and fresh water organisms effects, and effects of using waste oil as dust control.

### 2.3 Environmental Impacts

An important cause of soil biodiversity loss in urban areas is the pollution of soils by petroleum products. Engine lubricating oil is a major product of petroleum which helps the engine move smoothly. Spent or waste engine oil is oil that has been used, and as a result contaminated by chemical impurities which contribute to chronic hazards including mutagenicity and carcinogenicity as well as environmental hazards with global ramifications. Waste engine lubricating oil is oil that has served its service properties in a vehicle withdrawn from the meant area of application and considered not fit for initial purpose. Waste engine oil is a mixture of several different chemicals including low and high molecular weight aliphatic hydrocarbons, aromatic hydrocarbons, polychlorinated biphenyls, chloro dibenzofurans, lubricative additives, decomposition products and heavy metal contaminants such as aluminum, chromium, lead, manganese, nickel and silicon that come from engine parts as they wear down.

Waste engine oil has also been shown to create an unsatisfactory condition for life in the soil. At the impacted site arthropod assemblage and abundance was much lower, suggesting that spent lubricating oil from car engines demonstrated profound effect on the arthropod species. The absence of myriapod species as well as the generally low individual numbers of other arthropods at the contaminated sites may be explained by habitat transformation which resulted in biodiversity loss and elimination of species in the habitat. At the impacted site arthropod assemblage and abundance was much lower, suggesting that spent lubricating oil from car engines demonstrated profound effect on the arthropod species.

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According to literature reports, varying amounts of lubricants at present, end up in the environment. For example, heavy duty marine engines require both a cylinder lubricant and a crankcase lubricant. The cylinder lubricant requires a very high level of detergency to cope with acids produced in the combustion of lower quality marine fuels, while water separation and deposit control are most important for the crankcase oil. Natural gas engines contend with higher temperatures and high levels of nitrogen oxides (known as nitration). Sulfur containing EP additives can be further described by their content of “active” sulfur. Active sulfur refers to the tendency of sulfur to react chemically at low temperatures. High active sulfur content is desirable when EP performance is needed at comparatively low temperature, but can also lead to corrosion, particularly of copper. Extreme pressure additives are produced by a number of companies, and sold as part of additive packages as well as individual additive components (Freedonia 2013).

There are many different modes of action through which an oil or lubricant may adversely affect species and these include: direct toxicity of oil or lubricant components, especially to the liver and kidneys in mammals and fish. And indirect toxicity by reducing the breeding success and by passage of compounds into the young or through suppression of the immune system. This may be through bioaccumulation or bio-concentration of compounds over a long period of time.

In the USA 32 % ( $432 \times 10^6$  gallons of  $1351 \times 10^6$  gallons) of lubricating oils ended up in landfills or were dumped. It is claimed that 50 % of all lubricants sold worldwide end up in the environment via total loss, spillage and volatility. Estimates for the loss of hydraulic fluids are as high as 70–80 %. Most problematic are uncontrolled losses via broken hydraulic hoses or accidents whereby large quantities of fluids escape into the environment. They contaminate soil, surface, ground- and drinking water and also the air.

While, lubricants and hydraulic fluids based on plant oils are generally rapidly and completely biodegradable and are also of low eco-toxicity. At present the use of pure native plant oils is limited to total loss applications (lubricants for chainsaws, concrete mould release oils) and those with very low thermal stress. Hydraulic fluids are of increasing importance for applications in environmentally sensitive areas where a potential total loss could be encountered, such as excavators, earthmoving equipment and tractors, in agricultural and forestry applications and in fresh water (groundwater) sensitive areas. Mineral oils are toxic for mammals, fish and bacteria. Considering the sump capacities of such machinery (up to 1000 l) the ecological impact is obvious—as are the economics of the resulting clean up operations.

Although it seems obvious that the increased use of rapidly biodegradable lubricants would be of considerable ecological and economical advantage, the present market share of these materials is relatively small. For hydraulic fluids this amount is increasing more rapidly, with estimates ranging from 25 to 75 %.

Technical performance, acceptable price and ecological compatibility will constitute the basis for future developments along these lines. From some studies, it seems that bio lubricants are already available for the majority of applications and that the technical performance is comparable and sometimes even better than for conventional lubricants. As they display:

- excellent tribological properties (ester functions stick well to metal surfaces)
- lower friction coefficients than mineral-oil-based fluids
- lower evaporation (Noack)—up to 20 % less than mineral-oil-based fluids
- higher viscosity index (multi-range oils)
- excellent biodegradability
- high flashpoints
- low water pollution classification.

Their technical properties are thus largely comparable with mineral-oil-based fluids. However, they are thermally less stable than mineral oils, sensitive to hydrolysis and oxidative attack, and their low-temperature behavior is frequently unsatisfactory. For the development of lubricants and hydraulic fluids on the basis of renewable resources such as native plant oils one will always have to make a compromise between the performance based on the chemical structure and the desired biodegradability and eco-toxicity. All lubricants and hydraulic fluids are composed of so-called base fluids and additives.

Major arguments for environmentally acceptable plant-oil-based lubricants and hydraulic fluids are (a) high biodegradability and (b) low eco-toxicity. Yet in spite of these criteria the term environmentally acceptable lubricants must be properly defined, especially for formulated oils. A formulated oil consisting of a highly biodegradable base fluid in combination with toxic additives environmentally is not acceptable: while the bulk of fluid is indeed biodegradable, the overall lubricant is not. The lower the degree of un-saturation, the longer is the lifetime. Saturated synthetic esters are clearly the most stable ester materials at present. However, in many cases the biodegradability is less than satisfactory. At present it seems that the best compromise between performance, price and biodegradability are high oleic oils. These can be obtained either by cultivation (selective breeding), with high oleic sunflower oil (90 % + oleic acid) being the most prominent example, followed in the future possibly by high oleic rapeseed and soybean (selective breeding or GMO). Alternatively, chemical modifications of commodities such as rapeseed oil or biodiesel would be an interesting alternative.

## 2.4 Effect of Used Oil on Soil

Waste lubricating oil having been contaminated with impurities in the course of usage and handling, contain toxic and harmful substances such as benzene, lead, cadmium, polycyclic aromatic hydrocarbons (PAHs), zinc, arsenic, polychlorinated biphenyls (PCBs) etc. which are hazardous and detrimental to the

soil and the surrounding environment. The environment must be protected against pollution by lubricants and hydraulic fluids based on mineral oils. This is, of course, best done by preventing undesirable losses and by reclaiming and reusing lubricants. Alternatively, environmentally acceptable lubricants and hydraulic fluids should be used whenever and wherever possible. Increase in demand for cars, heavy duty automobiles, generators etc. throughout the year, led to increase in demand for lubricating oils, and this resulted in the generation of large oil irrespective of the type and source of collection, is sometimes dumped into the soil causing harmful or toxic materials to percolate through the soil thus contaminating the soil and thereby changing the physical and chemical properties. It is also sometimes dumped down drain, sewers, disrupting the operations at waste water treatment plants (Udonne and Onwuma 2014).

Sample analyses were done on two samples and the results indicated that the presence of lubricating oil in one of the samples had altered the soil chemistry, and thus resulted in the adverse effects on the physical and chemical properties of the soil. Table 2.1 shows how the physical properties of were altered, when looking at properties like bulk density, capillarity, porosity, and water holding capacity.

While on a separate set of samples, the presence of waste oil had an equally adverse effects on the chemical properties of the soil as shown on Table 2.2. Waste lubricants reduced the pH thereby making the soil more acidic. There was considerable reduction in potassium content in the contaminated soil, as well as increase in carbon contents this being attributed to carbon present in waste oil. An increase in moisture was also noted, as originated from used oil.

Thus it was amply shown by experiments that waste lubricating oils can significantly and adversely affect physical and chemical properties of the soil making it less productive, due to the various contaminants within the used

**Table 2.1** Effects of waste lubricating oil on physical properties of soil

Parameters	Uncontaminated soil sample 'A'	Contaminated soil sample 'B'
Bulk density (g/cm <sup>3</sup> )	1.10	1.15
Soil capilarity (cm/h)	8.10	0.04
Soil porosity (ml)	110	80
Water holding capacity (WHC) (ml)	55.0	15.0

**Table 2.2** Effects of waste lubricating oil on the chemical properties of soil

Parameters	Uncontaminated soil sample 'A'	Contaminated soil sample 'B'
Soil pH	6.5	6.0
Phosphorus content (ppm)	80	40
Potassium content (ppm)	98	60
Organic carbon	2.15	3.05
Moisture content (%)	3.5	9.9

lubricants such as OCBs, PAHs, benzene, lead, arsenic, zinc etc. which are the cause for soil contamination unlike virgin oil.

## 2.5 Future Development of Eco-friendly Lubricants

In general terms, the cost of biodegradable lubricants and hydraulic fluids is—depending on the product quality—frequently higher than that of comparable mineral-oil-based products. Since the price level is also dependent on the corresponding additivation and the amounts purchased, differences. Generally, the price of rapeseed oil is much lower than that of synthetic esters, with differences of up to 200 %. However, the price differences have to be seen also in relation to differences in quality and extended lifetime (i.e., extended periods between oil changes). The current differences in prices between bio-based and mineral-oil-based fluids may, however, become irrelevant if one looks into the very near future. It can be predicted that mineral oil production will reach its peak. Since bio-lubricants are already available for numerous applications, with performance being well comparable and sometimes even better than those of mineral oil products—combined with the methods for chemical derivatizations increasingly being developed—plant oils are an attractive alternative as raw materials for future lubricants.

## 2.6 Chemistry of Lubricant Additives and Their Toxicology to Humans

Neither mineral nor synthetic base oils can satisfy today's lubricant performance requirements without using additives. Additives are chemical substances, in most part synthetic, which are used in lubricant formulations to adjust a broad of spectrum of properties by enhancing what is desired and suppressing what is unwanted. Many additives are multifunctional products that may exhibit synergistic or antagonistic behavior when mixed together. As a rule of thumb, additives do not add. This makes balancing and optimization of additive systems a challenging task.

The increasing focus on energy efficiency and environmental safety of lubricants poses new challenges for lubricant formulators, preventing or restricting the use of certain time-proven chemistries, such as ZDDP in engine oil or boric acid in MWF formulations. At the same time, it stimulates the search for new classes of additives, including all-organic ashless friction modifiers, nano-additives, and bio-based super lubricity additives, as well as fundamental studies into how individual additives work.

Exposure to lubricating oil additives usually occurs by skin contact with finished oils that contain the additives. On rare occasions, workers may be

exposed to the neat additive in the manufacturing and blending plants or during transportation. The criteria for identifying the hazards of petroleum additives are based on those of the EU Dangerous Substances Directive or the US OSHA Hazard Communication Standard. The risks are normally classified as below:

- Acute oral toxicity
- Acute dermal toxicity
- Eye irritation
- Skin irritation
- Skin sensitization.

The interpretation of test results for other toxicity end points, such as genotoxicity, reproductive and developmental toxicity, and target organ effects, requires the evaluation of expert toxicologists to determine the potential hazards.

**Ashless succinimide dispersants:** The most widely used and manufactured lubricating oil additives are ashless succinimide dispersants (Fig. 2.1). They are used at levels approaching 50 % in all automotive crankcase additive packages. They are also found in marine, railroad diesel, natural gas-fuelled engine and air- and water-cooled two-cycle engine lubricants. Frequently, additive suppliers will functionalise succinimides with additional materials, such as boric acid (borated succinimides) and organic acids (oxalic, mono short-chain alkyl, terephthalic, etc.).

**Toxicity of succinimide ashless dispersants:** They are not considered harmful if swallowed or absorbed through the skin. They are neither eye nor skin irritants, and they do not cause an allergic skin reaction based on guinea-pig sensitization tests. Unlike mono succinimides and borated succinimides, which gave negative results in the Ames, succinimides functionalized with organic compounds are positive.

**Sulphonates and phenates:** Sulphonates and phenates are important members of the group of additives known as metallic detergents. Sulphonates are used in virtually all types of lubricants, while phenates are used primarily in marine, railroad, and automotive crankcase oils. Sulphonates are prepared either from the sulphonation of lubricant oil (natural sulphonates) or from the sulphonation of synthetically prepared C<sub>16</sub> and greater alkylbenzenes (synthetic sulphonates). Sulphonates can be prepared as calcium, magnesium, or, less importantly, barium and sodium salts. Sulphonates are prepared in order to produce either low over based (LOB) or high overbased (HOB) products (Fig. 2.2). The basic metallic carbonate over basing is present in HOB sulphonates as a reverse micelle (Fig. 2.2).

**Toxicity of sulphonates and phenates:** Calcium sulphonates are generally not hazardous but there is some concern with skin sensitization potential of calcium sulphates. These materials are not considered harmful if swallowed or absorbed through the skin. They are neither eye nor skin irritants. They do not cause serious systemic effects in subchronic toxicity tests.

**Zinc dialkyldithiophosphates:** Zinc dialkyldithiophosphates (ZDTPs) are the most popular multifunctional additives used (Fig. 2.3). They act as anti-oxidants, anti-wear agents, and corrosion inhibitors. ZDTPs are made by the reaction of alcohols, phosphorus pentasulphide (P<sub>2</sub>S<sub>5</sub>), and zinc oxide. The type of alcohol

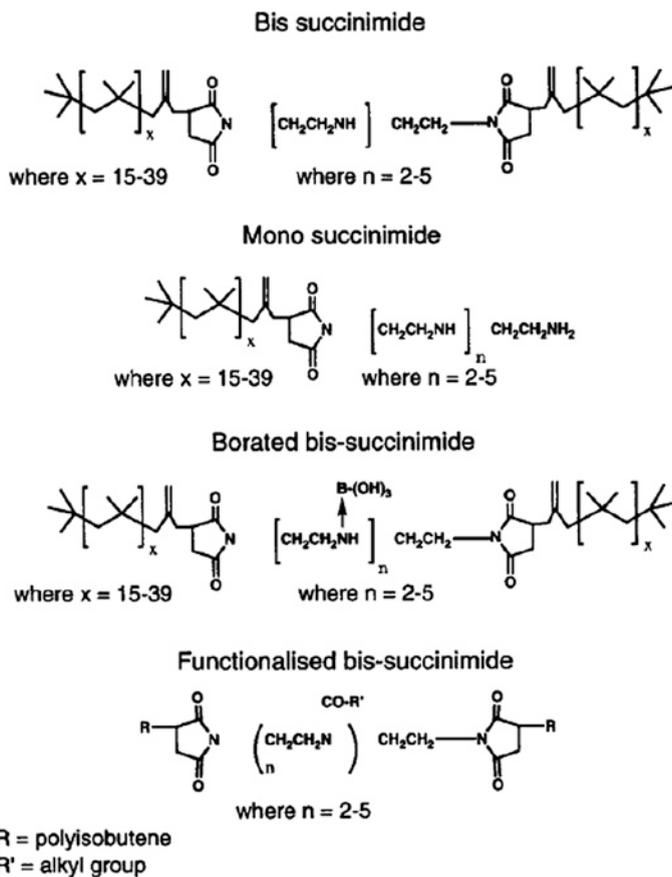
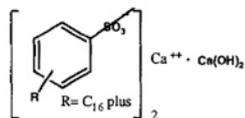
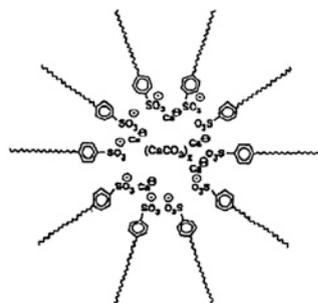


Fig. 2.1 Ashless succinimide dispersants

Low-overbased calcium sulphonate



High-overbased calcium sulphonate reverse micelle



High-overbased calcium sulphonate

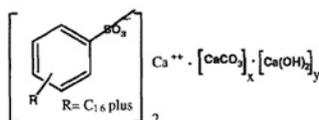


Fig. 2.2 Calcium sulphonates

Fig. 2.3 Zinc dialkyldithiophosphates

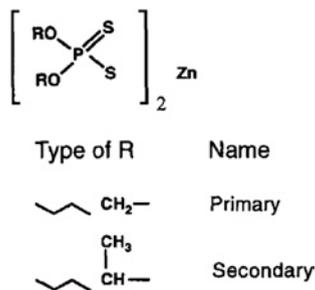
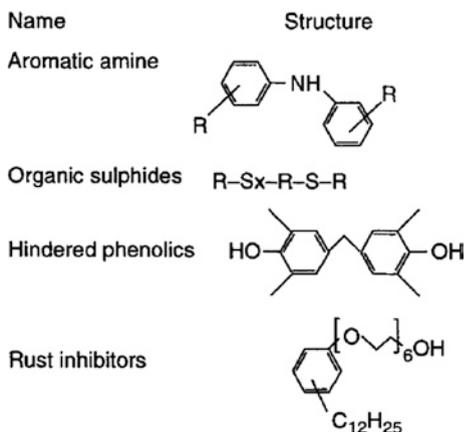


Fig. 2.4 Ashless inhibitors



used to make a ZDTP can vary. Low molecular weight  $C_{3-6}$  secondary alcohols are used to prepare ZDTPs for use in automotive lubricants. These additives decompose at low temperatures, thus acting as very good wear inhibitors. Industrial oil applications use ZDTPs made from primary  $C_{4-8}$  alcohols. In these types of ZDTPs, oxidation performance is enhanced relative to secondary ZDTPs.

**Toxicity of Zinc dialkyldithiophosphates:** The primary human health hazard of concern with ZDTPs is their eye irritation potential though not irritating to the skin. It was found out that ZDTPs are mutagenic. Further work showed that the mutagenicity of ZDTPs was due to the presence of zinc.

**Rust inhibitors:** Rust inhibitors such as the one shown in Fig. 2.4 are used in a variety of industrial and crankcase lubricants. Organic fatty acids made from a variety of natural and synthetic sources are also used extensively in the lubricant industry as rust inhibitors.

**Toxicity of rust inhibitors:** They are not expected to be harmful if swallowed or absorbed through the skin. They are neither eye nor skin irritants, and they do not cause allergic skin reactions. The molybdenum-nitrogen complex is not mutagenic, and it does not cause serious systemic effects in subchronic toxicity tests.

Products such as demulsifiers, friction modifiers, antifoam agents, pour point depressants, and viscosity index improvers are combined with the additive classes discussed above to formulate performance additive packages which are sold to lubricant manufacturers around the world. Lubricant manufacturers formulate finished lubricant products using refinery produced lubricant base stocks, PAOs, and other synthetically derived base stocks.

## 2.7 Lubricant Additives and Their Hazards to the Environment

As given in Fig. 2.5 below gives a chronological view of the development of the main additive families since 1930s to present. These developments have been driven by new specification demands imposed by engine design changes, which in turn are a response to consumer demand and emissions requirements. Base oils or synthetic base stocks alone cannot provide all the engine lubricant functions required by a modern gasoline or diesel engine. Over the last eighty years a number of chemical additives have been developed to enhance base stock properties, overcome their deficiencies and provide the new performance levels required by the technological evolution of engines or by new regulations (ATC 2007). Lubricant additives fall into two categories:

- those protecting metal surfaces in the engine, such as anti-wear, anti-rust, anticorrosion and friction modifier additives; and,
- those reinforcing base stock performance, such as antioxidants, dispersants, viscosity modifiers and pour point depressants.

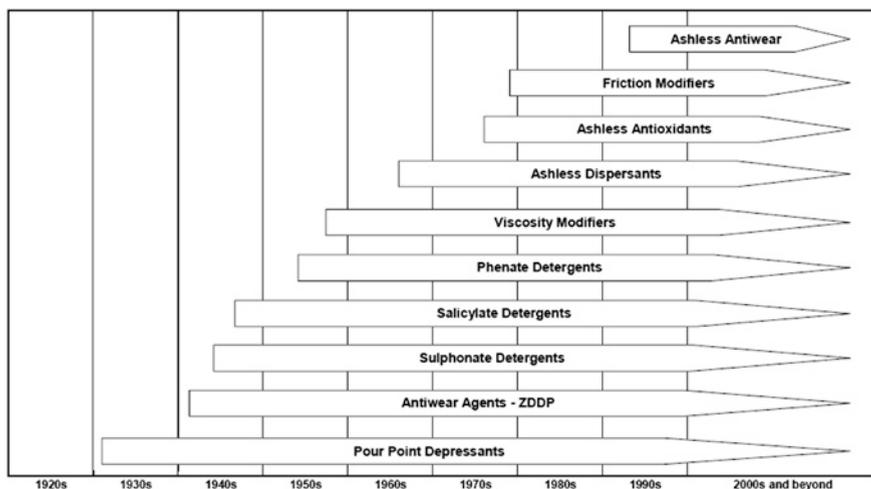


Fig. 2.5 Development of lubricant additives (ATC 2007)

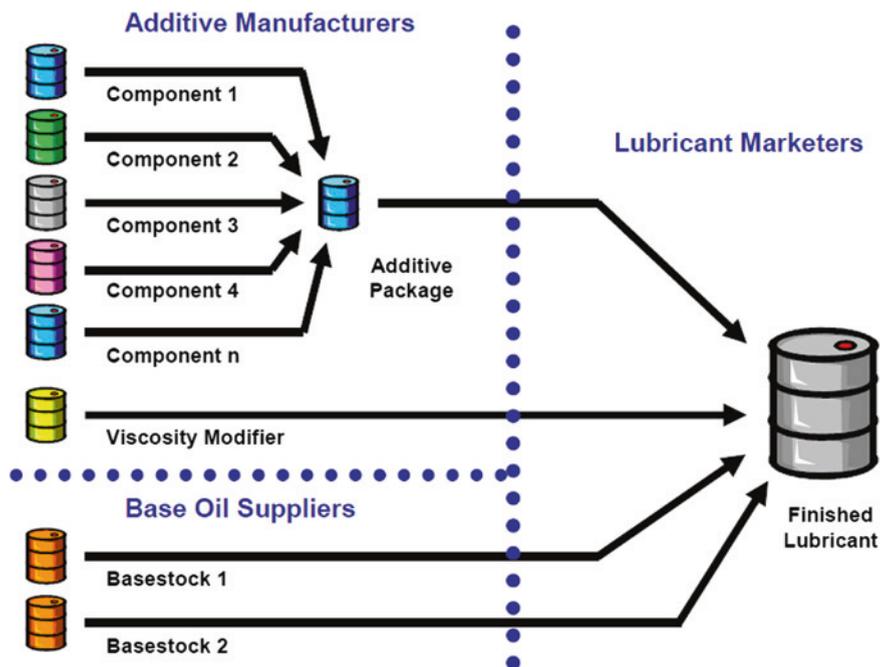


Fig. 2.6 Component additive package formulation

Finished lubricants contain a number of individual additive components—typically about eight but ranging from five to fifteen. Some or all may be blended individually into the lubricant base stock during manufacture. More typically, the components are pre-blended by the additive manufacturer into a performance additive package which is sold to the lubricant marketer. The viscosity modifier, which is a major component of multi-grade crankcase lubricants, is usually purchased and blended separately by the lubricant marketer. Figure 2.6 illustrates this schematically.

The majority of lubricant additives are of low mammalian toxicity and are typically less harmful when ingested than familiar household products. Some lubricant additives are suspected of being harmful to aquatic organisms and most show a degree of persistence but these additives are typically of low water solubility and when handled and disposed of according to manufacturers' recommendations are considered not to present a significant environmental risk.

The composition of the crankcase lubricant changes during use. Some additives are chemically changed or even destroyed as part of their functionality, and any contaminants of combustion generated during the course of engine operation which are not swept into the exhaust stream are neutralized and dispersed within the lubricant. It is widely accepted that used oil drained from the engine sump will contain poly aromatic hydrocarbons (PAHs) generated by the combustion process

and this waste is suspected to pose a carcinogen risk through accidental skin contact. Users are normally advised against inappropriate contact or disposal of used lubricants to minimize the environmental and human risks from used oil.

Lubricant additives can be released into the environment during manufacture, transport, and usage, and therefore it is necessary to evaluate these materials for their potential in causing adverse environmental effects. We use a standard approach to environmental hazard characterization that evaluates lubricant additives based on the following three criteria of environmental effects:

- the material's toxicity to sensitive environmental organisms,
- the material's relative persistence in the environment measured by its degradation rate,
- the material's potential to accumulate in the food chain.

Though all materials are evaluated for their potential in causing toxicity in both aquatic and terrestrial environments, actual toxicity testing is usually performed on aquatic organisms because they show greater sensitivity to materials than do terrestrial organisms. This is due to the fact that aquatic organisms are closely associated with their aqueous environment, and they are usually exposed to much higher concentrations of released materials for longer periods of time. Further, more adequate toxicity assessments can be made on terrestrial organisms by extrapolating the mammalian toxicity data for the material.

The following aquatic toxicity thresholds are generally recognized for classifying and labeling materials worldwide based on the amount of material required to produce adverse effects on representative aquatic test organisms (fish, aquatic invertebrates, and algae) when additives are directly added to the test water (Table 2.3).

When a lubricant additive is directly added to water, the test organisms are exposed to different fractions of the additive. These include the water-soluble portion, portions that form dispersions or emulsions, and the insoluble fraction which lies on the surface of the water or coats the container. Therefore, the effects observed on the organisms could be influenced by the non-soluble fractions of the material which may cause fouling (physical coating due to contact with the test organisms). Fouling effects may interfere with the observation of toxic effects and

**Table 2.3** Relative substance toxicity

Relative substance toxicity	EC <sub>50</sub> * (range (mg/l))
Relatively harmless	>1000
Practically non-toxic	>100–1000
Slightly toxic	>10.0–100
Moderately toxic	>1.0–10.0
Highly toxic	<1.0

\*EC<sub>50</sub> is defined as the concentration of material that would affect 50 % of the test organisms during the exposure period. The greater the EC<sub>50</sub> the lower the toxicity of the material

can be assessed by reviewing the physical/chemical properties of the lubricant additives.

These data show that lubricant additives are practically non-toxic to aquatic test organisms, except for ZDTPs and hindered phenolics. ZDTPs are moderately toxic to aquatic organisms. Hindered phenolics are highly toxic, but are used in finished oils at use levels of less than 1 %. The activated sludge inhibition test results indicate that none of the lubricant additives that were tested would disrupt the operation of waste water treatment facilities or adversely affect micro organisms in the environment.

### 2.8 Ultimate Fate of Lubricant Additives

All lubricants, as identified in the previous section are here followed through to their ultimate fate in the air, water or soil compartments. Other industry partners have placed increasing emphasis on the reuse and safe disposal of used oil. OEMs have given much emphasis over the last five years to the recycling of used engine oil. The re-refining of used oils has also increased.

In above diagram (Fig. 2.7) effort was made to trace the fate of crankcase lubricants from sale through to the environmental compartments. The environmental pathways for lubricants used in the passenger car and truck sectors are the same. Thus crankcase lubricant additives also follow these same general pathways, to their ultimate fate in the air, water or soil compartments. Crankcase

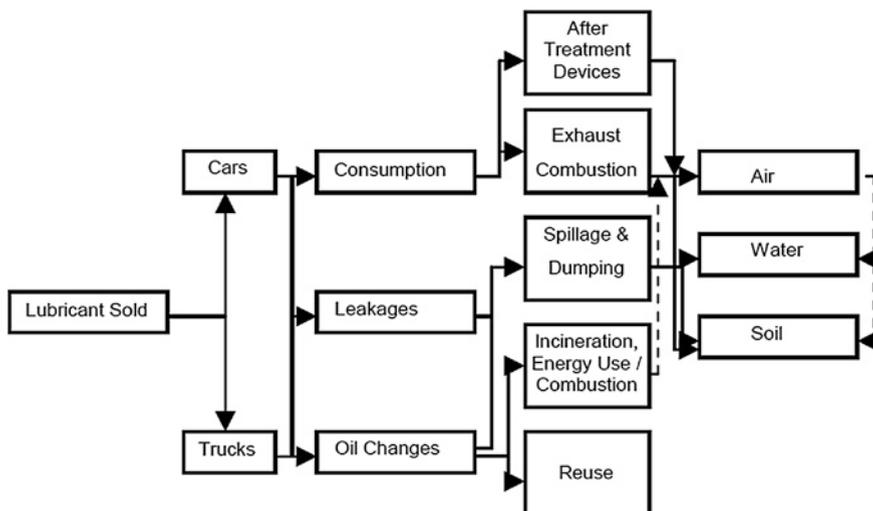


Fig. 2.7 Flow diagram on fate of lubricants

lubricants enter the engine when either the sump is filled or when the engine is topped up. They leave the engine:

- when drained, as used oil or
- as leakage through seals or gaskets during use or
- via lubricant consumption down the tailpipe as gaseous emissions (combustion products or particulates).

If the vehicle is fitted with a particulate trap, the incombustible portion of the lubricant in the exhaust will be trapped by this filter. Broken lines in Fig. 2.7 show that a portion of used oil which is collected and burnt or incinerated contributes to emissions in the air compartment—and that, ultimately, some emissions to the air compartment end in the soil or water compartments. The lubricant leaves the engine down the tailpipe as emissions of either combustion products (gases or vapor) or particulates (which will be collected if a particulate trap is fitted). A portion of the lubricant (and fuel) combustion products is entrained and re-dispersed in the crankcase lubricant itself, or forms deposits in the engine. Leakage past seals or gaskets is estimated to be negligible for both cars and trucks. The environmental routes of this portion of the lubricant are to the water and soil compartments.

Used oil should be drained from the crankcase, collected and re-refined and re-used, or disposed of suitably. Approximately 75 % of lubricants sold (2000 k tons) is drained as used oil at oil changes. This includes oil from scrap vehicles. A significant proportion (estimated 47 %) of that collected is used as fuel oil or incinerated for energy value or disposal. Regeneration represents an estimated 24 % of the total waste oil. Additives in oils properly disposed of by these routes end up as solids for landfill, used in cement or as gaseous emissions. However, approximately 28 % of used oil is still unaccounted for and may be dumped into the soil and water compartments, or burnt entering the air compartment. The proportions going to the various pathways are illustrated in Fig. 2.8.

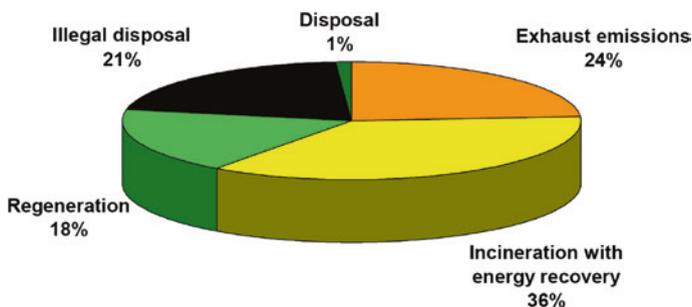


Fig. 2.8 Fate of lubricants

## 2.9 Biodegradation of Additives

If lubricant additives (or finished lubricants) are not consumed by combustion in an engine or recycled, we must concern ourselves with environmental fate. One possible measure of environmental fate is biodegradation. It is an important factor for determining the fate of lubricant additives in the environment together with water solubility, volatility, absorption to suspended solids, sediment and soil, hydrolysis, and photolysis. Although the biodegradation process is really a series of microbial-mediated processes which involve many kinds of microorganisms acting in concert to degrade both the materials and their degradation by-products, none of the current ready biodegradability tests adequately measures the entire process. In any of these tests, only the initial and terminal stages of the process are measured, i.e., primary and ultimate biodegradation.

Ultimate biodegradation, or loss of parent material from the test media through conversion into carbon dioxide and water (i.e., the extent of material mineralization), is determined in ready biodegradation tests that measure either carbon dioxide evolution from the test media or oxygen utilization (consumption) in the test media. In these tests, the criteria for designating materials 'readily biodegradable' is that more than 60 % of the carbon in the material has evolved as carbon dioxide in the test system, or that more than 60 % of the theoretical oxygen demand has been consumed in the test media, at the end of the 21–28 day tests.

For the majority of lubricant additives, degradation rates are usually very low because they have very limited water solubility, usually less than 1 mg/l. This limits their bioavailability to microorganisms and increases the length of time in which they will degrade. In addition, their very large molecular weights make them tend to partition from water to solids and organic matter where they are not readily accessible to microbial degradation processes. Currently the EU is concerned that slowly degradable materials may cause long-term harm to the environment due to their persistence. But a material's persistence in the environment is only an indicator of its fate, and not its effect on the environment. It has yet to be determined if rapidly or slowly degraded materials are really more environmentally desirable for a given use or disposal of a material. Rapidly degradable materials may deplete the available dissolved oxygen in the immediate environment and thereby indirectly affecting aquatic organisms through suffocation, or they may degrade rapidly into by-products that may be considerably more toxic to aquatic species than the parent materials.

There is a clear need for continued efforts to develop more relevant biodegradation tests that assess the biodegradability of lubricant additives under realistic environmental conditions as well as to develop better techniques of interpreting the data from these tests to provide realistic assessments of environmental effects of lubricant additives.

## 2.10 Bio-concentration of Additives

Materials that accumulate in the food chain to the extent they can cause adverse environmental and human health effects are cause for concern. The extent to which materials accumulate in organisms is expressed as the bio-concentration factor (BCF). In aquatic environments, BCF is defined as the ratio of the concentration of the material in the aquatic organism at equilibrium to the concentration of the material in the water. Generally, the less water soluble a material is, the greater its accumulation in the lipid tissues of aquatic organisms.

However, these tests were developed for materials consisting of single defined chemicals, not for materials like lubricant additives which are actually mixtures with a range of log Kow. Thus it is technically difficult to measure analytically all of the components of lubricant additives in fish bio-concentration tests and generally we rely on marker compounds in the lubricant-additive matrix. The testing of lubricant additives is further complicated by the fact that many components of lubricant additives are quite similar to naturally produced materials within the fish, thus interpretation of tissue residue results can be extremely difficult.

## 2.11 The Future of Additive Technology

The performance of synthetic sulphonates has matched the performance of natural sulphonates for most applications, but with the corresponding environmental benefits. An effort has been under way to replace diesel fuel and kerosene used to prepare drilling muds with fluids that may be less harmful. PAOs offer an advantage because they show significant biodegradation using the CEC L-33-T-82 biodegradation method, are stable under basic and acidic drilling conditions, and are much cheaper than more expensive esters and ethers.

Lubricant additive technology seeks to enhance performance of base fluids derived from a variety of crude oils. These lubricants can then be used with a wide variety of fuels derived from different crude oils and processes. Optimum use of petroleum resources is thus achieved. Lubricant additives are engine design components, enabling the continuing evolution of engine design to provide increasingly efficient and more environmentally-friendly vehicles. Lubricant additives provide high performance engineering for the consumer and ensure reliability, longevity and optimal performance of the vehicle. Lubricant additives are considered to be of low environmental risk, however there is need for ongoing health and safety reviews.

## 2.12 Conclusion

Considerable effort was spent to understand the potential human health and environmental hazards of lubricating oil additives, and these efforts have been described in this chapter. Future efforts will involve continuing to meet the human health and eco-toxicity requirements of new technology and meeting, to the fullest extent possible, the product stewardship and responsible care initiatives of industrial organizations and global regulatory agencies. There will be a special focus on understanding bio-accumulation and biodegradation of lubricants in the environment as our industry meets the challenges of the twenty-first century.

### *Revision Questions*

1. *State three major hazards of additives on the environment*
2. *Name four classes of additive chemicals and explain their potential toxicity to humans.*
3. *What do understand by bio-degradation?*
4. *What physical nature of additives limits their bio-degradability?*
5. *Explain what is meant by bio-concentration effect of additives on aquatic life.*

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