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EMISSION SCENARIO DOCUMENT ON LUBRICANTS AND LUBRICANT ADDITIVES

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EMISSION SCENARIO DOCUMENT ON LUBRICANTS AND LUBRICANT ADDITIVES

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Organisation for Economic Co-operation and Development

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Explanatory notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals used in lubricants to assist in the estimation of releases of chemicals into the environment.

This ESD should be seen as a ‘living’ document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other that the lead (the United Kingdom). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The comments will also be made available to users within the OECD web-site (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

Coverage

This ESD provides information on lubricants used in three areas – automotive lubricants, hydraulic fluids and metal working (cutting) fluids. The relevant industry categories are IC 8 (metal extraction, refining and processing industry) and IC 9 (mineral oil and fuel industry), although lubricants find their end use in a wide range of industrial areas. The use categories are UC 29 (heat transfer fluids), UC 30 (hydraulic fluids and additives) and UC 35 (lubricants and additives).

The document covers releases form the formulation of lubricants, from lubricants in use through their service life (many lubricants tending to have use over extended periods of time), and from the treatment of waste lubricants. Information included relates to both the base fluids and the additives used to modify the existing properties or introduce new ones, and emissions of both may be estimated. The document addresses releases to air, water soil and solid waste as appropriate for the various life cycle steps.

How this document was developed

The document is based on a report produced by the Building Research Establishment for the UK Environment Agency entitled ‘Use Category Document – Lubricants and lubricant additives’. The original purpose of the document was to provide information to be used in risk assessments for new and existing substances in the EU. Information for the original report was largely provided by practitioners in the industry with a wide breadth of knowledge and experience. Published sources are cited where appropriate, but most of the information did not come from such sources and was based on this knowledge and experience. Unless a specific source is cited for a piece of information, it should be assumed to be derived from the experience of the original authors. The information was collected for the original report over the period 1994-1997.

The OECD Task Force on Environmental Exposure Assessment selected this original document as suitable for development as an OECD-wide emission scenario document by revising it with additional information including where possible information from countries outside the EU. Prior to circulation, information from a report from The Netherlands, entitled ‘EUSES Use Category Document. Automotive fuels, lubricants and additives’ was incorporated, in particular in relation to releases from lubricant blending processes. The formal consultation took place in 2000.

Comments on the document were received from Germany, the United States and Switzerland. Germany provided the INFU/UBA report ‘Emission Scenario Document - Metal Extraction Industry, Refining and Processing Industry IC 8: Subcategory Metal Processing. Assessment of the Environmental Releases of Chemicals used in Metal Cutting and Forming Fluids’, and information from this has been incorporated into the current document, in particular in relation to the treatment of waste metal working fluids. The US EPA provided a draft generic scenario for automotive lubricants as well as other comments, and Switzerland provided scenarios for estimating releases to roadside soil and water.

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1. INTRODUCTION AND OVERVIEW OF THE LUBRICANT INDUSTRY

1.1 Introduction

1. This document provides information on the use and potential release to the environment of substances used in lubricants. Such information can be used in the risk assessment of new and existing substances in situations where specific information on a substance or process is not available.

2. The document is based on a report produced for the UK Environment Agency entitled ‘Use Category Document - Lubricants and Lubricant Additives’ and incorporates additional information from a report from RIVM in The Netherlands entitled ‘EUSES Use Category Document. Automotive fuels, lubricants and additives’ and from the INFU/UBA (Germany) report ‘Emission Scenario Document – Metal Extraction Industry, Refining and Processing Industry IC8: Subcategory Metal Processing. Assessment of the Environmental Releases of Chemicals used in Metal Cutting and Forming Fluids’. All of these reports were produced in order to provide information for the assessment of exposure in risk assessments for new and existing substances in the EU. The descriptions of the industry structure in the current document are largely based on the situation in the UK. Figures and suggested default values refer mainly to the UK with values from The Netherlands and Germany (noted as such). In some areas wider information on Europe has been included. Information from a generic scenario for lube oil additives produced by the US EPA is also included, mainly in the sections on automotive lubricants. Additional scenarios to estimate emissions to roadside soil and water were provided by Switzerland. The reader should note that the data for the original reports were gathered some time ago, mostly from 1994-1997 in the case of the UK document, and there may have been changes in some areas since this time.

3. This document gives an overview of the lubricant industry including a description of the types of base fluids and additives used. Three main categories of lubricant are considered. These are automotive lubricants, hydraulic fluids and metal-working lubricants. The formulation of lubricants and their additives is described and information is provided on possible release during formulation of lubricant additive packages and lubricants themselves. The relevant information and example calculations are in Section 5.

4. The report provides information on the amount of lubricant used, the releases of a substance during use of a lubricant, the form of release and the amount released for each of these categories. Waste treatment and recycling of lubricants is also considered. Flow diagrams are included for each lubricant category considered which aim to help the reader to locate relevant information (Appendix A).

5. The amount of information included varies for the different categories of lubricant. This is in part due to the availability of information, and in part due to the different natures of the use areas. For all categories the information on formulation of packages and blending of lubricants should allow the estimation of representative local releases for these steps (examples are given in Section 5). Releases of automotive lubricants to the environment are described largely in terms of the fate of these lubricants as used in the UK. This information could be used to estimate regional releases, particularly for widely used substances - an example is included in Section 6 – but not for emissions on a local scale. Information from the US on releases from automotive servicing locations is included.

6. Hydraulic fluids are used in such a wide range of machinery that it would be very difficult to develop any realistic scenarios for releases on the local scale during their working life. The information on the overall fate of these fluids could be used to estimate releases on a larger scale, and an example is given in Section 7.

7. For cutting fluids the use area is more closely defined, and the information presented can be used to calculate releases from representative sites on a local scale as well as on the regional scale. Examples are included in Section 8.

8. The Use Categories relevant to this ESD are UC 29 (heat transferring agents), UC 30 (hydraulic fluids and additives) and UC 35 (lubricants and additives). The most relevant Industry Categories are IC 9 (mineral oil and fuel industry), and IC 8 (metal extraction, refining and processing industry) for metal cutting fluids.

1.2 Overview of the lubricant industry

9. There are some 60 manufacturers of lubricants currently operating in the UK. They may be conveniently classified as 'multi-nationals', 'majors' and 'independents'. The multinationals are those fully-integrated oil companies which operate in all sectors of the oil industry, including exploration, extraction, refining, blending, distribution and marketing. The only base oil manufacturers in the UK are Mobil, Esso, BP and Shell. The majors are the specialist lubricant companies, such as Castrol, Fuchs etc., whose market share is as significant as that of the multi-nationals. The independents are the smaller lubricant companies whose principal business area is normally in lubricants, but some have other non-lubricant business areas such as fuels, or niche markets such as road-marking products, janitorial products, etc.

10. Some of the independents concentrate mainly or entirely in one specialist area of the market, e.g. greases, metalworking fluids etc. These companies normally provide other lubricant companies with their specialist products, in addition to supplying their own direct customers. As an example, although the majority of lubricant companies will offer a range of greases for sale, there are only some half dozen grease manufacturers in the UK. Specialist companies will often procure for resale more generalist products from other lubricants companies to supplement their own product range.

11. Note: A number of substantial lubricants companies who trade under their own name are in fact owned by the multinationals. Their tonnages have therefore been included in the Multinational category. This situation is expected to be very similar in other countries.

12. Manufacturing tonnages of all the various organisations range from some 500 to 100,000 tonnes/year. Table 1.1 summarises the market share, capacities and typical size of plant.

13. A number of other non-lubricant products are traditionally manufactured and supplied mainly by lubricants companies. These products include corrosion protectives, industrial waxes and process oils, which are supplied either for use as ingredients to be incorporated into other products, such as rubber extenders or printing ink oils, or for use by the general manufacturing industry.

Table 1.1 Summary of the UK lubricants industry

Manufacturers of lubricants	Market share %	Production tonnes/year	Typical plant size tonnes/year
Multinationals	62.5	500,000	30,000-100,000
Majors	25	200,000	10,000-30,000
Independents	12.5	100,000	500-10,000
TOTAL		800,000	

14. There are a number of major suppliers allied to the lubricants industry. They can be divided into two groups: those whose products are specifically intended for the lubricants industry; and others who provide general 'commodity-type' chemicals that are also used in other industries. The large additive companies in the first group are mainly concerned with supplying additives for automotive lubricants as this sector is the largest in terms of volume of additives.

15. Lubricants may be sold directly by the manufacturer to the end user, but may also be supplied via a third party. These may be authorised distributors, whose main business may well be in another area, such as fuels. Suppliers of equipment allied to the manufacturing industry such as machine tools may well also supply their own brand-name range of lubricants. Automotive lubricants are also available from garage forecourts, or from high-street shops.

16. In the United States around thirty companies produce lubricant additive chemicals, or packages of additives. These are sold to lube oil blending facilities. A few large companies both manufacture additives and blend them into oils.

17. There are two trade organisations involved with the UK lubricants industry, namely the British Lubricants Federation (BLF), and the Union of European Independent Lubricant manufacturers (UEIL). The BLF membership, which currently represents some 90-95% of the industry, is comprised of those companies who manufacture or supply lubricants, or are otherwise associated with the lubricants industry, e.g. suppliers of additives, base oils, packaging, bulk storage, synthetic fluid bases etc., and also re-refiners and other organisations with specific areas of interest in the lubricants industry. The UEIL is a European organisation, whose membership spans the EC countries, but is restricted to independents only, and is therefore not representative of the whole lubricants industry.

18. The total UK market for lubricants is currently in the order of 800,000 tonnes/year. Base oil production in the UK is approximately double this figure; the UK is a net exporter of finished lubricants, and significant amounts of base oil are sold directly to overseas markets. The overall use of lubricants in the UK in the three main areas covered by this report, and the types of additives that may be present in these lubricants are illustrated in Figure 1.

19. Statistics relating to the lubricants industry (see Table 1.2) have historically been published by the Institute of Petroleum based on information gathered by the UK Petroleum Industries Association. However, these figures are of limited usefulness due to the significant number of companies who did not report. This situation is now improving, as more and more of the previously non-reporting companies are being successfully encouraged to report. Pan-European figures are now being dealt with by a recently-formed European organisation, Europalub. The product categorisation has also been improved, and it is anticipated that quantitative and qualitative accuracy of lubricants statistics reports will improve significantly.

Table 1.2 Lubricant oils and greases - 1994 UK PIA statistics

End-use	**Consumption (tonnes)**
Automotive	316,507
Industrial	301,889
Aviation	2,784
Marine	58,085
Greases	12,084
Fuel oil sold as lubricants	639
Deliveries to blending companies not submitting returns	102,554
TOTAL	794,542

Notes for Table 1.2:

Automotive - includes commercial and retail multigrade and monograde oils, transmission and speciality oils, also greases.
Industrial - includes hydraulic oils, compressor oils, metal-working fluids, (neat and water-based) quenching oils, process oils, mould oils, turbine oils, transformer oils, heat transformer oils, general machine oils, industrial gear oils, white oils etc.
Aviation - includes aviation greases
Greases - includes industrial and marine
Fuel oil sold as lubricants - includes, for example, gas oil used in mould release agents
Deliveries to blending companies not submitting returns - lubricating oils and greases distributed to specialist blending companies for formulating products for automotive, industrial, agricultural and marine applications.

Figure 1: Lubricant usage in the UK

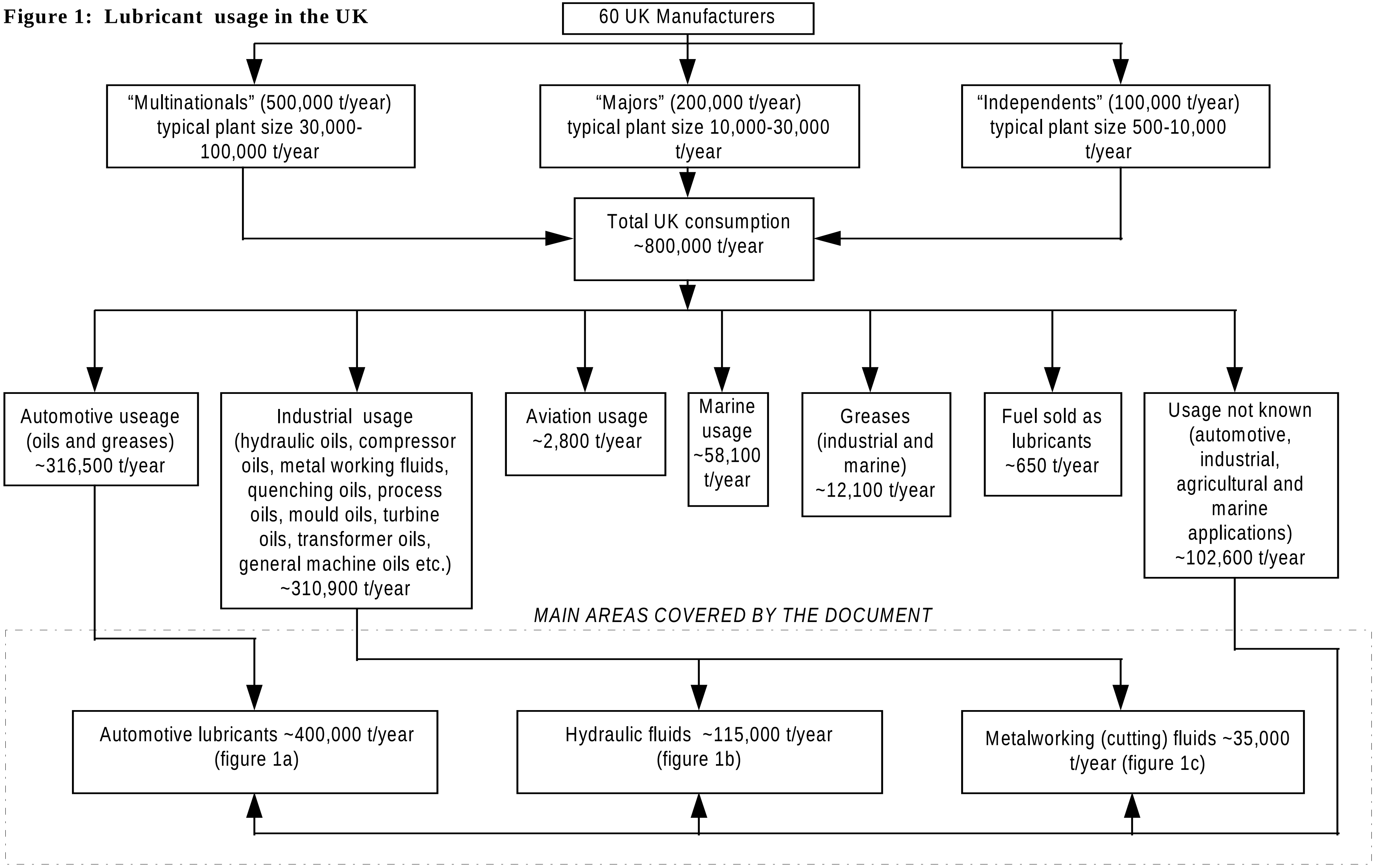
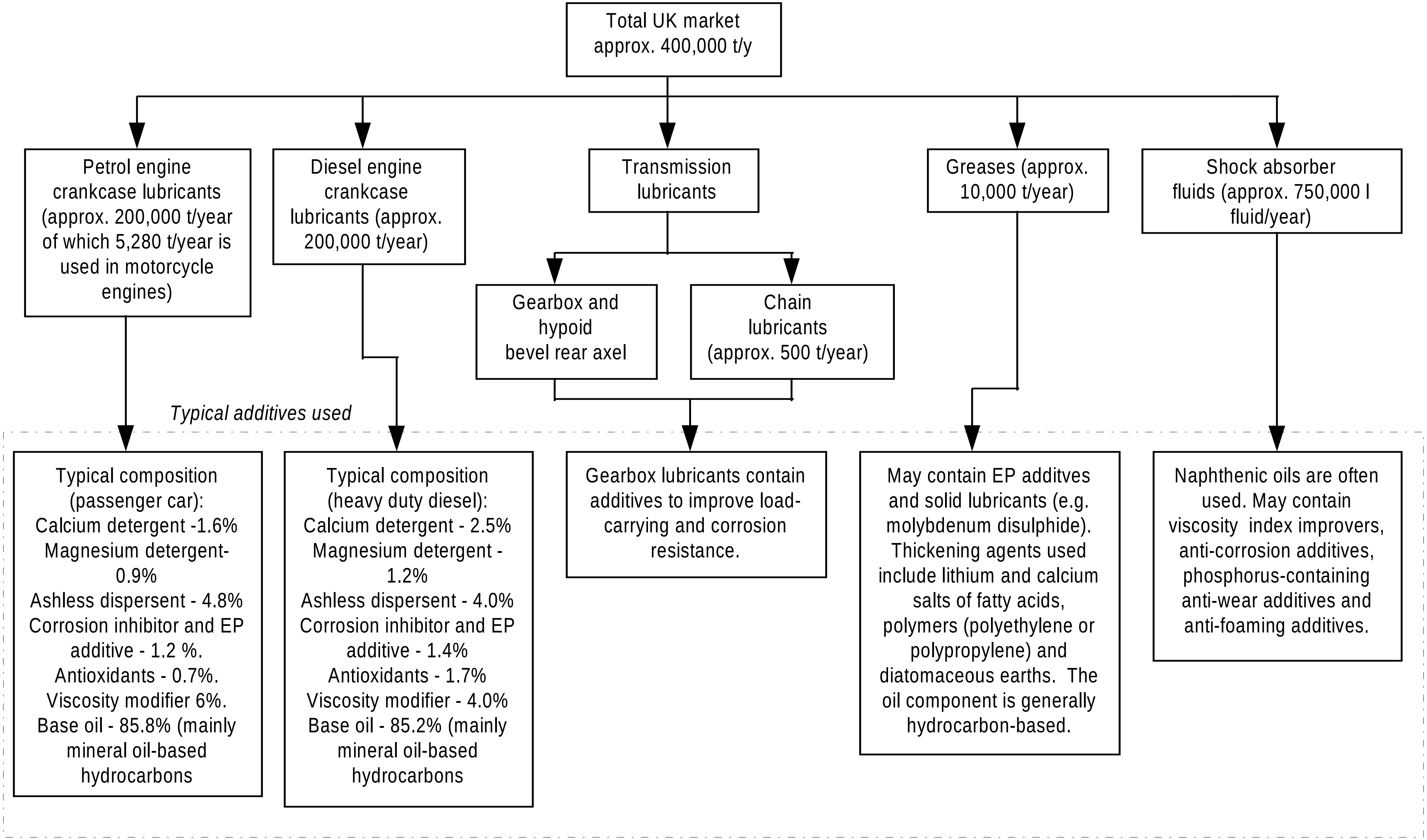


Figure 1a: Use of automotive lubricants in the UK



Typical composition (passenger car):
Calcium detergent -1.6%
Magnesium detergent- 0.9%
Ashless dispersent - 4.8%
Corrosion inhibitor and EP additive - 1.2 %.
Antioxidants - 0.7%.
Viscosity modifier 6%.
Base oil - 85.8% (mainly mineral oil-based hydrocarbons

Typical composition (heavy duty diesel):
Calcium detergent - 2.5%
Magnesium detergent - 1.2%
Ashless dispersent - 4.0%
Corrosion inhibitor and EP additive - 1.4%
Antioxidants - 1.7%
Viscosity modifier - 4.0%
Base oil - 85.2% (mainly mineral oil-based hydrocarbons

Gearbox lubricants contain additives to improve load-carrying and corrosion resistance.

May contain EP additves and solid lubricants (e.g. molybdenum disulphide). Thickening agents used include lithium and calcium salts of fatty acids, polymers (polyethylene or polypropylene) and diatomaceous earths. The oil component is generally hydrocarbon-based.

Naphthenic oils are often used. May contain viscosity index improvers, anti-corrosion additives, phosphorus-containing anti-wear additives and anti-foaming additives.

Figure 1b: Use of hydraulic fluids in the UK

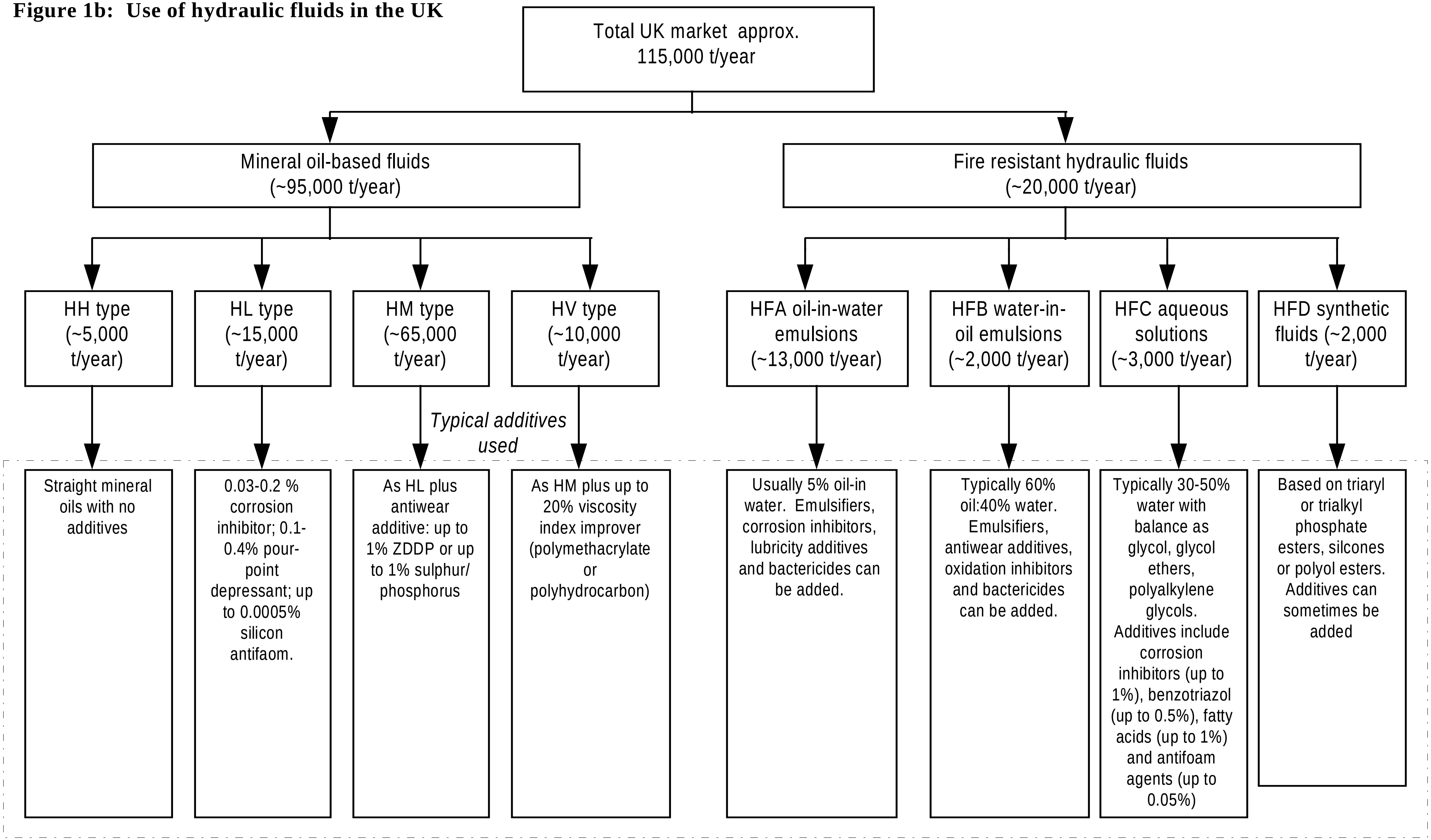
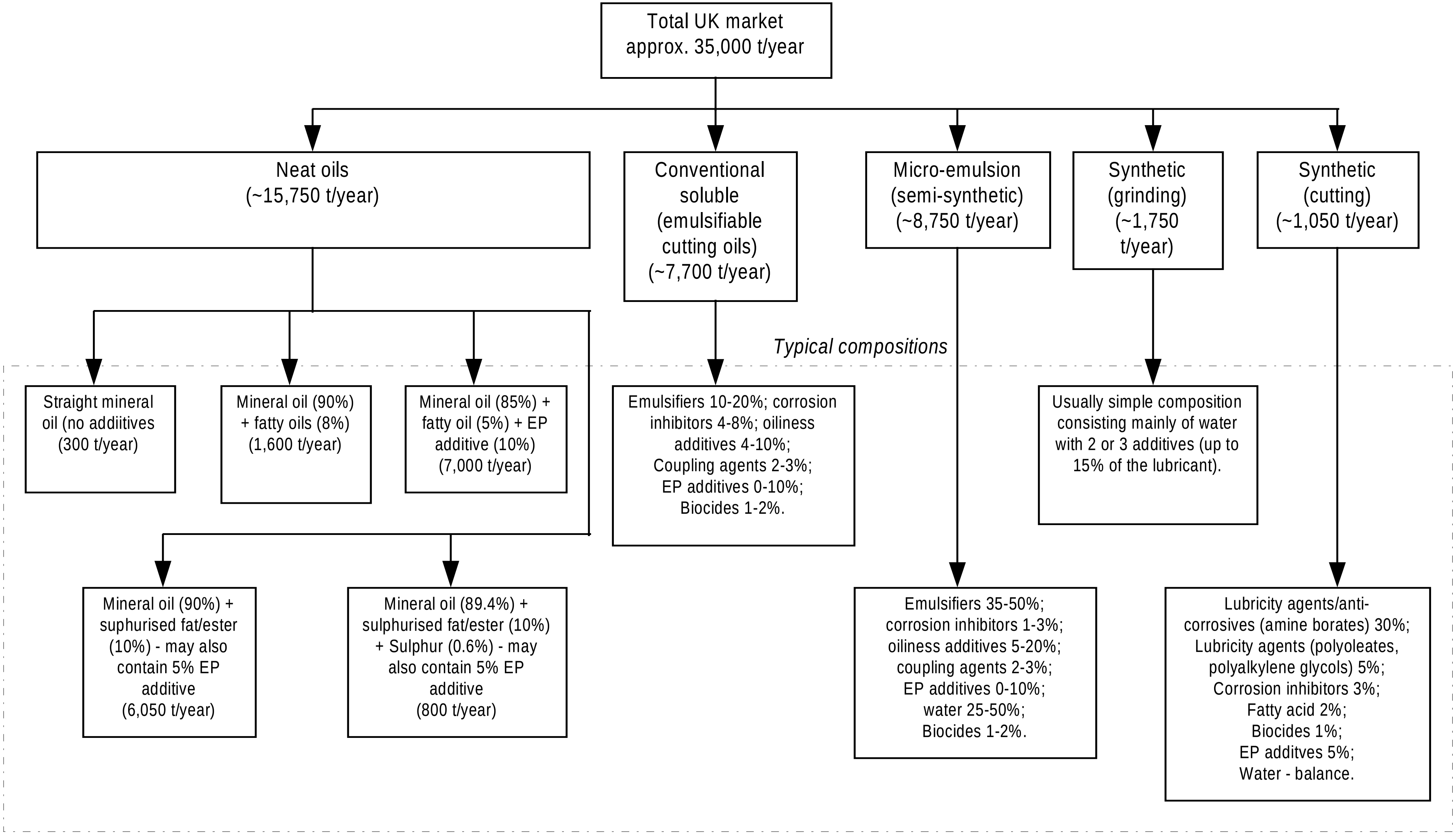


Figure 1c: Use of metalworking (cutting) fluids in the UK



2. OVERVIEW OF LUBRICANTS AND THEIR ADDITIVES

2.1 Introduction

20. A lubricant is a material, being either a solid, liquid or gas, the purpose of which is to reduce friction between surfaces in relative motion with each other. However, it is generally accepted that the term "lubricant", certainly in terms of statistical reporting for example, can be applied to a wider range of products, including power and heat transmission media, dielectric fluids, process oils etc. An example included in this wider scope of the definition is a hydraulic oil, which is one of the categories of product covered by this report.

21. In addition to the primary function of a true lubricant, i.e. the reduction of friction, lubricants can perform a number of additional functions, depending on the process and working environment. These other functions include the removal of heat and wear particles from the load carrying zone, as a sealant to prevent the ingress of foreign materials into the lubrication clearance zone, the protection of lubricated components against corrosion, the introduction of controlled frictional characteristics into systems which rely upon certain levels of friction for correct operation, etc.

22. In the reduction of friction, it is possible to distinguish between two types of lubrication, total lubrication and deficient lubrication. In the case of the former, the moving components are completely separated by a lubricant film, and do not come into contact with each other. This process can be further sub-divided into hydrodynamic lubrication (where the lubricant film thickness is maintained by the relative movement between components) or hydrostatic lubrication (where the lubricant film thickness is maintained by external pressurisation). In the case of deficient lubrication, the sliding surfaces may come into direct contact, whereupon frictional reduction is achieved by adsorption or chemisorption processes which occur on the surfaces of the moving components.

23. All lubricants consist of a lubricant base, which may contain additives which can either modify the inherent properties of the lubricant base or impart new properties which may include lubricating properties, e.g. extreme-pressure performance, or non-lubricating properties, e.g. dispersency, detergency, antioxidants etc. In general, the properties of the base fluid are more important for total lubrication, whereas the properties of the additives are particularly important during deficient lubrication.

24. Lubricant bases include mineral oils derived from petroleum fractions, synthetic oils derived from a variety of polymer types, oils derived from naturally-occurring products, such as vegetable oils, solid lubricants, and gases. The application of gases is almost entirely confined to the use of compressed air to separate moving components, and, along with other specialised bearing types, e.g. magnetic bearings, is outside the scope of this overview and will not be considered further.

25. A glossary of terms and description of specific lubricant properties is given in Appendix B.

2.2 Lubricant base fluids

2.2.1 Petroleum-based fluids

26. By far the most common base fluids used in lubricants are those derived from mineral oil. The refining processes necessary to manufacture such products may be briefly described as follows:

a) Distillation under atmospheric pressure - removes the lower-boiling components from crude oil.

b) Distillation under reduced pressure - the feedstock for this process is the residue from the previous atmospheric distillation process (atmospheric residue), which is then subjected to further distillation to produce a series of fractions of different flash-points and viscosities, and also a residue. These can then be used as the source materials for the production of lubricant basestocks.

c) Refining - the various distillates from the vacuum unit contain undesirable components which lead to premature degradation of the lubricant, i.e. darkening, viscosity increase, formation of acids and sludge, etc. These components may be removed by further processing, normally involving either acid treatment, solvent extraction or hydrogenation. The various refining processes yield products with differing characteristics. Additional processing may involve deasphalting (to remove asphaltenes), de-waxing (to remove high-melting point paraffins), contact with diatomaceous earth (to improve colour), etc.

27. The refining stages described above mainly involve separation processes, i.e. the segregation and purification of those compounds which possess the characteristics required for lubricant basestocks. However, refinery reforming processes are also used in the production of lubricant basestocks. Reforming processes differ from separation processes in that new compounds, possessing the required characteristics, are formed rather than extracted. These are not necessarily present in crude oil, or may only be present in small amounts. For example, the catalytic hydrocracking of slack waxes from dewaxing plants, followed by vacuum redistillation and solvent de-waxing can produce lubricant basestocks with extremely high viscosity indices. These products are known as "super-refined" oils or "VHVI" (very high viscosity-index) oils. The physical characteristics and in some cases, the chemical nature of these products resembles those of synthetic hydrocarbons (see 2.2.2 below).

28. The manufacture of lubricant basestocks is almost entirely confined to the major oil companies. Since the various companies will have developed or adopted their own particular variants of the manufacturing process, and will be using different sources of crude oil, the properties of the lubricant basestocks available from different suppliers may differ. In many cases, such differences in the properties can be compensated for during the lubricant blending operation. In other cases, however, it may be that the properties of a certain basestock are unique and essential to the requirements of a particular lubricant, and the basestock may not then be interchangeable with that from another supplier.

29. Lubricant basestocks are mainly characterised by viscosity and viscosity index (VI), and by differences in the predominant molecular type, i.e. paraffinic, naphthenic or aromatic, determined by differences in the refining process and/or feedstock.

30. **Paraffinic base oils** consist mainly of fully saturated straight- and branched-chain hydrocarbons with the general formula C_nH_{2n+2}.

31. Their advantages as lubricants are that they are stable and have good viscosity temperature characteristics, i.e. a high viscosity index, meaning a slow reduction in viscosity with increase in

temperature. Their disadvantages are relatively low polarity and correspondingly poorer solvency characteristics. This is not desirable for certain categories of lubricants, e.g. soluble metalworking fluids, greases etc. where base oil with higher polarities are preferable. Poor low temperature properties are due to the separation of wax crystals and consequent solidification at relatively high temperatures which results in high 'pour-points' and 'cloud points', necessitating the incorporation of pour-point depressants.

32. **Naphthenic base oils** are saturated polycyclic hydrocarbons with or without aliphatic side chains. They have better low temperature properties than the paraffinic oils, i.e. separation of wax crystals occurs at a lower temperature. However they are less stable than paraffinic oils and therefore more susceptible to oxidative degradation. This is due to the strain inherent in a ring formation as opposed to a linear molecule. They also have poor viscosity/temperature characteristics.

33. Differences in the properties of the different compounds determine the end-use of that basestock, e.g. paraffinic basestocks with their high viscosity indices are more suitable for the production of automotive crankcase oils, naphthenic basestocks with their higher polarity are more useful for the manufacture of greases and soluble oils.

34. **Aromatic base oils** are basically compounds containing aromatic rings with or without saturated side chains. They have high polarity and solvency power and for this reason they find use mainly as process oils, for example as printing ink oils or as rubber extenders. Their main disadvantage is that their general stability is poor. Indeed, part of the refining process in base oil manufacture consists of the removal of aromatics from both paraffinic and naphthenic base oils. For this reason the aromatics are often referred to as 'aromatic extracts', the refined residue being termed the 'raffinate'. They are little used in lubricants.

2.2.2 Base fluids not directly derived from petroleum

35. Since synthetic fluids are produced under closely-controlled conditions, the degree of variation in molecular size, chain length and chain branching in synthetically-produced fluids is much less than that which normally occurs in basestocks extracted from crude oil. Consequently, the physical characteristics of such products can be more closely controlled. Also, certain synthetic species may exhibit properties which are superior to those of hydrocarbons derived from mineral oils. The use of such fluids has introduced a whole new lubricants technology, since additive performance, so essential to the overall performance of many lubricants, can vary significantly according to the particular type of synthetic fluid used as the lubricant base. A number of different types of synthetic fluids have been used for lubricant basestocks, and the more important are described below:

2.2.2.1 Esters of carboxylic acids

36. Ester oils are one of the most widely used of all synthetic oils. Four types of ester molecules or their combinations have been found to be particularly suited as lubricant components:

- Esters of branched or straight chain primary alcohols with straight-chain dicarboxylic acids.
- Esters of branched chain monocarboxylic acids and straight chain diols or polyalkylene glycols.
- Esters of straight-chain primary alcohols with branched-chain dicarboxylic acids.
- Esters of neopentyl polyols with monocarboxylic acids.

37. Esters generally show good viscosity-temperature (VT) characteristics, have high resistance to oxidative degradation, and also possess low pour-points. For more specialised applications, ester oils containing sulphur and also fluorine have also found use.

2.2.2.2 Synthetic hydrocarbons

38. Saturated linear aliphatic hydrocarbons have low viscosities but good VT characteristics. The viscosities increase with increasing chain length, as does the pour-point and viscosity index (VI). For a given molecular weight, the presence of side chains leads to an increase in viscosity and a decrease in pour-point and VI. The length and position of the side chains have an influence on all three characteristics. In order to reach a high VI, lubricant hydrocarbons should ideally have straight chains, be completely saturated for good oxidation resistance and stability, and crystallise only at low temperatures. There is obviously considerable scope for improving the characteristics of hydrocarbons to render them more suitable for use as lubricant basestocks. This is normally achieved by the three main processes described below:

Polymerisation of Olefins

39. Polymerisation of alpha-olefins yields hydrocarbons with particularly favourable VT characteristics, and the VI increases with the increasing number of carbon atoms of the monomer (see Table 2.1).

Table 2.1 Lubricant characteristics achieved from the polymerisation of olefins

Polymerisation of.....	**VI**	**Other characteristics**
Ethylene	up to 125	Low pour-point
Propylene	110	Poor thermal stability
Equimolecular mix of ethylene and propylene	up to 140	Low pour-point Good oxidation resistance and stability
Butene	120	Low pour-point Moderate resistance to oxidation

40. The presence of branches or rings in the polymer structure has a negative effect on the viscosity index. The polymerisation processes and catalysts used are therefore designed to avoid the formation of these structural features. The polymerisation of higher olefins can lead to products which closely approach the ideal for a hydrocarbon lubricating oil basestock.

Condensation Products of Aromatics with Chlorinated Paraffins or Olefins

41. Condensation of chlorinated paraffins with aromatic hydrocarbons has been used in the past to produce lubricating oils. However, the products did not have good VI values, and the process has now been largely discontinued, except in certain specific instances where products of certain characteristics are required, or where certain feedstocks are available.

Synthetic Oils from Chlorinated Hydrocarbons

42. Hydrocarbons with VI values of up to 125 can be obtained by a dechlorinating condensation catalytic process.

2.2.2.3 Polyethers

43. Polyalkylene glycols have found extensive use as lubricants, particularly the polyethylene and propylene glycols and their copolymers, their mono- and diether, ester-ethers, and diesters. They tend to be used in the field of speciality lubricants, such as brake fluids, hydraulic oils and metal cutting fluids because of their different solvency properties to hydrocarbons. They are divided into water-soluble or water insoluble types, their miscibility with water increasing with the number of ethylene oxide units in the molecule. Different products can be obtained by varying the ratio of the alkylene oxides, the end groups, and the molecular masses. Although some of the products have high flash and fire points, they can be prone to thermal decomposition. Antioxidant additives such as phenyl-alpha-naphthylamine are effective in improving stability, at least up to the standard of petroleum-derived products, but polyglycols are generally not used as, for example, crankcase lubricant bases because of their corrosion instability in the presence of acidic fuel combustion products.

44. Polyphenyl ethers are particularly suited as high temperature and radiation-resistant hydraulic fluids and lubricants. They have also been used for high temperature lubrication of bearings and for gear lubrication. In comparison with the polyalkylene glycols, the introduction of aromatic radicals increases the stability and negatively affects the VT characteristics.

45. Perfluoropolyalkyl ethers, tetrahydrofuran polymers and polythioether oils have also been used as lubricant base fluids.

2.2.2.4 Phosphoric acid esters

46. Tertiary esters of phosphoric acid with alcohols or phenols have gained importance as plasticisers, fire-resistant hydraulic fluids, compressor oils, oil and fuel additives and as synthetic lubricants. They are divided into triaryl, trialkyl or alkylaryl phosphates, the physical properties depending strongly upon the nature of the hydroxyl component. The lubricating properties of these products are excellent, particularly under conditions of boundary, or deficient, lubrication. In these situations, the lubricating properties appear to be due to chemical reactions involving the phosphorus, rather than to the physical characteristics of the products. They also have good miscibility properties and can therefore be used with most types of additives.

2.2.2.5 Silicone oils and silicate esters

47. Silicone oils are straight-chain polymers of the alkyl- or arylsiloxane series, the properties of which are determined by the molecular mass and the nature of the side chains. They have relatively high boiling-points, low volatilities and high flashpoints, particularly in comparison with hydrocarbon oils. VT properties are excellent, but their lubricant properties are more suited to rolling bearing applications than to sliding friction. They may also be used in applications where chemical inertness is required.

48. In contrast to the silicones, silicate esters do not contain Si-C bonds; all hydrocarbon radicals are linked to the Si atom via an oxygen atom. The properties therefore differ markedly from those of the silicone oils. Although low volatility and excellent viscosity-temperature characteristics make them suitable for lubricant purposes, their applications are limited by poor hydrolytic stability.

49. These base fluids are not used in Germany.

2.2.2.6 Halogenated hydrocarbons and halocarbons

50. Polychlorohydrocarbons and chlorocarbons with aromatic or aliphatic structures are very stable and incombustible, and have been used as lubricants, hydraulic oils, insulating oils and heat transfer fluids.

Their usefulness is limited, however, by poor VT characteristics. Aliphatic fluoro- and chlorofluorocarbon oils have exceptional stability against chemical influences, and are used as lubricants and liquid transfer media. Although VT properties are poor, they have high oxidation stability, low corrosivity, good low-temperature characteristics, and outstanding boundary lubrication properties. The lubrication properties of halogenated base fluids are due to the formation of chemical intermediate compounds (chlorides) by a reaction between the metal surfaces and the chlorine in the lubricant base. These compounds are only formed under conditions of high temperature and pressure, but their presence can reduce the friction between sliding surfaces. The situation is similar to that of the reaction of chlorine in chlorinated extreme-pressure additives (see Section 2.3.5). The reduction in friction in this situation is much more marked than that which could be achieved by hydrodynamic lubrication which is dependant upon the physical properties of the lubricant base.

51. Chlorinated hydrocarbons are no longer used in Germany as base fluids (or additives) for industrial lubricants, hydraulic fluids or heat transfer fluids.

2.2.2.7 Miscellaneous

52. In addition to the main groups of synthetic lubricants listed above, a variety of other types have also been used. These include ferrocene derivatives, aromatic amines, heterocyclic nitrogen, boron and phosphorus compounds, and derivatives of urea.

2.2.3 Natural products

53. Vegetable oils are finding increasing use as lubricant bases, especially in environmentally-sensitive areas. Vegetable oils are naturally-occurring triglycerides of long-chain fatty acids. They are biodegradable and have low toxicity, so they are ideal for total loss lubricants, but like all such esters, they are prone to hydrolysis or saponification at the ester linkage under certain conditions. Biodegradation while in use is also possible if water is admitted. To date, this inherent instability has restricted their adoption as lubricant bases, but recent developments, particularly in the Scandinavian countries, have resulted in the availability of vegetable oil-based products of superior performance by careful selection of the source oil and by the incorporation of specific additives. Other developments include the genetic engineering of plants with the intention of yielding oils with the specific characteristics required for a lubricant basestock.

54. The most common sources include castor oil, rapeseed oil, olive oil, coconut oil and palm oil. In Europe, rapeseed oil is used. Crude vegetable oils are refined after extraction by removing free fatty acids, bleaching and steam stripping under vacuum to remove odour, flavour and some colour-forming products. The selection of oils to produce a lubricant base is on the basis of obtaining the correct balance between fluidity, melting-point, stability and cost.

2.2.4 Water

55. Water is used as a lubricant base for certain hydraulic fluids, also simple metalworking fluids such as grinding fluids which have a mainly coolant function.

2.3 Additives

56. The function of an additive is to modify the inherent properties of the base fluid (low-temperature properties, VT characteristics, etc.), or confer new properties (emulsion- forming tendency, anti-corrosion properties, extreme pressure lubrication properties, etc.). The properties required depend on the application of the lubricant. It is likely that a high degree of stability, i.e. resistance to oxidative degradation breakdown is universally desirable, but other characteristics may be more specific to the end-use.

57. Some additives affect the physical properties of the base fluid, others have a chemical effect. Additives can assist each other, resulting in a synergistic effect, or they can lead to antagonistic effects. Many modern additives are supplied as a pre-mixed package having several functions and thus the possibility of antagonism is reduced.

2.3.1 Oxidation inhibitors (antioxidants, metal deactivators)

58. Oxidation of petroleum hydrocarbons proceeds by a radical chain mechanism via alkyl and peroxy radicals after an induction period, the length of which depends upon the degree of refining of the oil.

59. Oxidation reactions can result in premature degradation of the base fluid (i.e. the formation of acids, gums, lacquers, varnishes and sludges) at prolonged high temperatures. Mineral oil fractions already contain natural inhibitors in the form of sulphur and nitrogen compounds, aromatics or partially hydrogenated aromatics, phenolic oxidation products, etc., which delay oxidation and impart good ageing properties. However, when the mineral oil is subjected to a high degree of refining, these materials can be lost along with those having less-desirable characteristics.

60. Compounds which interrupt the radical chain mechanism of the autooxidation process by removal of the radicals and/or decomposition of the peroxides are termed oxidation inhibitors or antioxidants.

61. Such compounds include “hindered phenols” (e.g. dibutyl-p-cresol), certain amines (e.g. phenyl alpha-naphthylamine), sulphur and phosphorus or compounds containing both of these elements, metal phenates such as the alkaline earth metal compounds of phenol disulphides, zinc compounds of thiophosphates and carbamates (e.g. zinc dialkyldithiophosphate). This last compound also confers anti-wear properties to an oil and is an good example of a multi-functional additive.

62. Initiation of radical chains by ionising radiation can be reduced by including compounds which absorb in the wavelength range 300-400 nm (e.g. hydroxydiphenyl ketones, hydroxyphenylbenzotriazoles).

63. Metal compounds can have either an oxidising or a reducing effect. They can accumulate in the oil as a result of surface abrasion or by the corrosive action of acidic oxidation products. They can be "complexed" with a suitable additive and thus prevented from contributing to further oxidative degradation.

2.3.2 Viscosity modifiers

64. Viscosity modifiers (VM) are additives which alter the viscosity-temperature (VT) characteristics of oils, i.e. they change the rate of decrease of viscosity with temperature. They normally consist of linear polymer molecules which can be either coiled up or stretched out depending on the concentration in the base fluid and the solvency in the base fluid. As the solubility of the polymer in the base fluid increases with temperature the polymer molecules change from a coiled state to a stretched state, thereby exerting an increasing thickening effect as the temperature increases. The degree of thickening effect is not sufficient to fully compensate for the normal reduction of viscosity with increasing temperature, but the presence of the polymer does exert a retarding effect upon this rate of change.

65. The average molecular mass of such polymers lies in the range 10,000 to 100,000; the solubility in the oil decreases with increasing molecular mass. VI polymers can be degraded by mechanical stress, and by thermal and oxidative breakdown.

66. Examples of viscosity modifiers are polyisobutenes, polymethacrylic acid esters, diene polymers, polyolefins and polyalkylstyrenes.

2.3.3 Pour-point depressants

67. As the temperature of a mineral oil is reduced, the less-soluble constituents such as the paraffin waxes fall out of solution and exert a gelling effect on the remaining oil which reduces its fluidity. The pour-point is described as the temperature at which the oil ceases to flow under specified test conditions. The low-temperature properties of the oil can be improved by deep dewaxing, which removes those constituents with the greatest tendency to precipitate at low temperatures. Since this process adds to the refining costs, in practice such oils are only partially dewaxed to achieve pour-points in the region of -15°C. If lower pour-points are required then these are more readily achieved by the addition of additives which depress the pour-point. The additive has no effect upon the precipitation temperature of the separated wax; it acts instead by modifying the external shape and size of the separated crystals, thereby reducing the tendency to crystal growth and subsequent agglomerisation of the crystals into a network-like structure.

68. Pour-point depressants consist of a long alkyl group, which is included into the growing wax crystal immediately after the nucleation stage, together with side chains or groups which hinder subsequent crystal growth. They must also be resistant to oxidation and have good thermal stability and shear resistance. Care must be taken to ensure that the pour-point depressant used is compatible with any viscosity modifier.

69. High molecular-weight aliphatic petroleum fractions and metal soaps (particularly aluminium) have in the past been used, but those in current use are typically polymerisation and condensation products such as bicyclic aromatics with several long alkyl chains. Some pour-point depressants also act as viscosity modifiers, e.g. polymethacrylates. Long chain alkyl phenols and phthalic-acid dialkylaryl esters have also been proposed. Copolymers of vinyl acetate and ethylene or of 1,2-epoxyalkanes are also used.

2.3.4 Detergents and dispersants

70. Detergents and dispersants represent some 50% of all additives used (detergents 20% and dispersants 30%).

71. The purpose of detergents is to keep oil-insoluble combustion products in suspension, and to prevent the agglomeration of resinous and asphalt-like oxidation products. Thus, they prevent the formation of deposits on metal surfaces, oil thickening and sludge deposition, and also prevent corrosive wear by neutralising acidic products of combustion. They are usually oil-soluble or finely-dispersed metal soaps of organic acids. Detergents can react with hydroxyacids, formed during oxidation of the oil, and thus prevent the deposition of these compounds which would otherwise form resins.

72. Dispersants are ash-free organic compounds which prevent the flocculation and coagulation of colloidal particles. They act by causing an electrostatic repulsion between particles onto whose surfaces they have been adsorbed. However, since their dispersing power is not sufficient to prevent the formation of deposits in the engine, extra dissolving power is needed. This is provided by the detergents. There is in fact no sharp distinction between the action of dispersants and detergents.

73. The cleaning action of detergents is due to the orientated adsorption onto the metal surface, and a chemical reaction with the surface with the formation of metal soaps. Since they are deliberately manufactured using excess alkali, they also neutralise acids, nitrogen oxides, sulphur dioxide and trioxide resulting from combustion. In practice, a detergent additive package will consist of a combination of a

metal-soap together with an ash-free detergent. In order to meet the requirements, detergent additives need to contain:

- polar (hydrophilic) groups (e.g. sulphonate, hydroxyl, mercapto, carboxylic or carbonamide groups);
- oleophilic aliphatic, cycloaliphatic or alkylaromatic hydrocarbon radicals which provide oil solubility; and
- one or several metal ions or amino groups.

74. Conventional detergents consist of an acidic substrate such as sulphonates, phenates, salicylates, thiophosphonates, neutralised with an alkaline base such as an alkaline earth metal hydroxide or carbonate, e.g. calcium hydroxide. However, using appropriate processing conditions, it is possible to produce stable oil-soluble sulphonates containing many times as much metal (by a factor of 10 or more of the stoichiometric quantity) as that present in normal sulphonates. These 'over-based' (also known as hyper- or superbased) detergents, possess unusually high detergency power, as well as having a high capacity to neutralise acidic contaminants such as combustion by-products from fuels containing sulphur. They are particularly useful for diesel engine lubricants, due to the relatively greater amounts of acidic combustion products which are generated compared with petrol engines. Metal salts of alkylphenols, alkylphenyl sulphides and salicylates are also used.

2.3.5 Extreme pressure (EP) additives

75. In order to perform adequately under conditions where the loading is such that the hydrodynamic film is broken down, e.g. in heavily-loaded gear teeth, lubricants are fortified with extreme-pressure (EP) additives. Under conditions of high loading and deficient lubrication, the rough surfaces of the metal become welded to each other, so that metal particles are torn from the surfaces as the relative movement continues and pressure relaxation occurs (wear). Such a situation can be avoided by the inclusion of extreme-pressure agents which form metal compounds with the metal surfaces. These are solid under normal conditions, but become liquid under high-pressure and temperature, allowing sliding to take place. The primary elements involved in the formulation of EP additives are phosphorus, sulphur and chlorine.

- **Phosphorus**

76. Organic phosphorus compounds act as EP agents by forming metal phosphides on metallic surfaces which are in relative motion at high temperatures. Although the element phosphorus is the key ingredient, the nature of the organic compound which contains the phosphorus influences the effectiveness of the EP activity. Alkyl phosphates are better than aryl phosphates, tributyl phosphate is better than tricresyl phosphate. ZDDP (zinc dialkyldithiophosphate) in particular is widely used.

- **Sulphur**

77. Sulphur may be used as an EP agent either in the neat form, in which it is soluble to a limited extent in mineral oil, or as an organic compound. A sulphide layer is formed at the metal surface at 200°C which not only prevents direct contact between the sliding surfaces, but which also has a lower surface-to-surface coefficient of friction compared to steel. Elemental sulphur is more effective than organic compounds of sulphur, but leads to corrosion and staining of yellow metals. The most effective sulphur compounds are those with polysulphide bridges in which the sulphur atoms are present in a labile form, such as sulphurised polyisobutene, polypropylene, polystyrene and sulphurised fatty oils such as

rapeseed oil, cottonseed oil or soya bean oil. Disulphides such as dibenzyl disulphide, butylphenol disulphide are used but are less effective.

- **Chlorine**

78. Chlorine compounds, used in industrial applications only, coat the metal surfaces with a chloride film under high-pressure conditions, and in the presence of traces of moisture. The main compounds involved are chlorinated paraffins, where the effectiveness of the EP activity is dependent upon the degree of chlorination rather than on the chain-length of the paraffin. A range of chlorinated paraffins is used in components of straight and emulsifiable metal-working lubricants as well as gear oils for industrial and automotive applications. The selection of chlorinated paraffin and the level of additive depends on the type of application and the severity of the operation (Kirk-Othmer, 1993). In practice, chlorinated paraffins with a chlorine content of 40-70% wt are used. Such compounds are, however, sensitive to light and moisture. Also, chlorine-containing EP additives can lead to severe corrosion of the metal surfaces due to the formation of hydrogen chloride.

79. The chloroparaffins used in this area are generally of C_{10}-C_{13} chain length (short chain chlorinated paraffins). There is likely to be a general decline in the amount of short chain chlorinated paraffins used in Europe, particularly in the metalworking industry, due to environmental concerns over these substances. All European countries party to Osparcom, except Portugal and the UK, have agreed to phase out all short-chain chlorinated paraffins by 2004 and to phase out use in metalworking fluids by 1999 (ECN, 1995). The costs of disposal of chlorine containing waste oils are also contributing to a general decline in use of chlorinated additives. In Germany there are very few (exceptional) cases where chlorinated paraffins are still used in metal working lubricants, largely due to legislation on waste oil disposal and on ecological concerns.

80. Compounds containing combinations of the elements described above, such as chlorine-sulphur compounds, phosphorus-sulphur compounds and chlorine-phosphorus have also been used with success. Organic nitrogen compounds such as nitroaromatics, aminophenol derivatives of naphthenic acids and esters of carbamic acid have also been used as EP agents. EP additives are often used in combination with each other for maximum overall effectiveness.

81. Corrosion inhibitors can interfere with the effectiveness of EP additives due to competition for the active surface sites.

82. Polar substances, the action of which is based purely on adsorption, are less effective than true EP additives.

2.3.6 Friction modifiers

83. These additives generally act by forming thin layers on the friction surfaces due to physical adsorption, and consist of polar oil-soluble molecules such as fatty alcohols, amides or salts. The effect increases with increasing molecular weight and in the order alcohol < ester < unsaturated acid. Since the effect drops when the temperature reaches the melting-point of the compound, they are generally used in preventing stick-slip oscillations during start-up and shut-down of sliding metal surfaces subject to high loads, and in the reduction of friction to improve fuel consumption.

2.3.7 Anti-foam agents

84. Foaming is not only detrimental to the lubricating properties of an oil, but can also increase oxidation rates. The foaming tendency is dependent upon the surface tension of the oil, which is influenced to some extent by the degree of refining and also by the presence of surface-active additives such as

detergents, EP additives and corrosion inhibitors, which can significantly increase the foaming tendency of the oil. The purpose of anti-foam additives is to enhance the separation of air bubbles from the oil phase. Liquid silicones are most effective, but for maximum effect the silicone chosen must be insoluble but finely dispersed in the oil. The presence of silicones is not always desirable, since adhesion problems of coatings on machined metal surfaces can occur, so polyethylene glycol ethers and sulphides and polyether siloxanes may also be used.

2.3.8 Demulsifiers

85. In the presence of water, lubricating oils can form relatively stable water-in-oil emulsions which can interfere with their operation. The emulsions can be broken by altering the interfacial tension between the oil and the water by the inclusion of appropriate surface-active substances such as dinonylnaphthalenesulphonates in the form of their alkali or alkaline-earth salts.

2.3.9 Corrosion inhibitors

86. Corrosion can be prevented by protecting the metallic surface from access by water and oxygen by the formation of a non-metallic protective layer. Such protection can be afforded by both physical and chemical inhibitors. Mineral oil alone allows permeation by oxygen as well as water and is thus not completely effective in preventing corrosion.

87. There are three kinds of corrosion inhibitors - physical, chemical and those that are effective in the vapour phase. They are described below.

Physical

88. Physical inhibitors are molecules with long alkyl chains and with polar groups which adsorb onto the metal surface to form a densely-packed, orientated hydrophobic layer. Typical inhibitors include the following:

- • Basic nitrogen compounds such as the tertiary amines or their salts of benzoic, salicylic and naphthenic acids; esters of fatty, naphthenic or dicarboxylic acids with triethanolamine; alkaline-earth phthalylalkylamides; aminodicarboxylic acids; dicyclohexylamine; and diamides of heterocyclic hydroxylamines and their esters.

- • Amides of saturated and unsaturated fatty acids with alkanolamines, alkylamines, sarcosine or imidazolines.

- • Phosphoric acid derivatives such as the diarylphosphates and thiophosphoric acid esters, and the neutral salts of primary n-alkyl amines or of cycloalkylamines with dialkylphosphates.

- • Sulphonic acids and sulphur compounds such as basic alkaline-earth sulphonates and mono- and dialkylarylsulphonates.

- • Carboxylic acid derivatives such as wool fat (lanolin) and its combinations with oil-soluble sulphonates have been in use for many years. Naphthenic acids in the form of their heavy metal salts are effective, but some such as lead naphthenate are being discontinued on health grounds. They are no longer used in Germany in metal working fluids. Oxidised waxes, dicarboxylic acids, maleic acid, unsaturated fatty acids, hydroxy fatty acids have been used with success as well as special products such as pentaerythritol and sorbitan monooleates, o-stearoylalkylolamines and polyisobutenylsuccinic acid derivatives.

Chemical

89. Chemical inhibitors react with the metal surface and form protective layers which alter the electrochemical potential. These include fatty acids, although these are only effective in the presence of water or other polar compounds since in nonpolar media the acids are present as dimers which do not react with the metal.

90. Typical chemical inhibitors or metal passivators include zinc dialkyldithiophosphates (rarely used in Germany), dialkyldithiocarbamates and benzotriazoles.

Vapour phase

91. Corrosion inhibitors which are effective in the vapour phase have gained in importance. They are carboxylic acids with 8-10 carbon atoms or volatile nitrogen compounds which can act as a base, and can be added to tanks, crankcases etc. in order to protect the metal surfaces.

2.3.10 Emulsifiers and emulsifying aids

92. Emulsifiers and emulsifying aids are included in the formulations of soluble oils used in metalworking applications, fire-resistant hydraulic oils, quenching oils, etc. They have a structure containing both hydrophobic and hydrophilic groups, and act by reducing the interfacial surface tension, thereby assisting in the formation and stabilisation of oil-in-water and water-in-oil emulsions depending on the requirement. The hydrophobic part of the molecule consists of a hydrocarbon radical, the hydrophilic part depends on whether the emulsifier is anionic, cationic or non-ionic. The activity of the emulsifiers depends upon the pH and hardness of the water.

93. Anion-active emulsifiers normally consist of alkaline salts of long-chain, usually unsaturated carboxylic acids such as mixtures of oleic acid, tallow-oil fatty acids, naphthenic acids etc., and of synthetic carboxylic acids and sulphonamides.

94. Cation-active emulsifiers all belong either to the long-chain alkylated ammonium salts, such as dimethyl-dodecyl-benzylammonium chloride, or to the imidazolinium salts.

95. Non-ionic emulsifiers almost entirely contain polythene oxide radicals such as the alkyl-, alkylaryl-, acyl-, alkylamino- and acylaminopolyglycols as well as long-chain acylated mono- and diethanolamines. (Note that the use of diethanolamine has virtually ceased in Germany due to restrictions on the use of secondary amines.)

2.3.11 Solid lubricants

96. Solid lubricants may be applied in the dry state, but are generally added to oil-based lubricants in the form of finely-divided dispersions or suspensions. They have therefore been categorised as an additive for the purposes of this report.

97. Solid lubricants are necessary for lubrication under extreme conditions, such as very high temperatures, aggressive chemicals such as acids, liquid oxygen, fuels, solvents, and also high-energy radiation. They are most suited to relatively slow-moving high loads, and also in situations where specific properties such as electrical conductivity are required.

98. The most common solid lubricant is graphite, either natural or artificial, the lubricating properties of which are mainly derived from its layered lattice structure, where van der Waals forces between adjacent layers permit movement, whilst the strong bonds within the layers resist penetration by

asperities in the sliding surfaces. The low frictional properties of graphite layers also depend upon adsorbed films, particularly of water vapour.

99. Molybdenum disulphide possesses a lamellar structure where, again, the van der Waals forces between the sulphur layers permit easy relative movement between lamellae. The strong ionic bond between molybdenum and sulphur resists penetration by asperities in the sliding surfaces. Unlike graphite, the lubricating properties are not dependent upon adsorbed films, and therefore this material functions equally well in a vacuum. The sulphur layers also adhere strongly to metal surfaces. In the absence of an oxidising atmosphere, molybdenum disulphide retains its lubricating properties up to 800°C.

100. Combinations of graphite and molybdenum disulphide show synergistic effects, the relative proportions for maximum effectiveness varying with temperature.

101. Other solid lubricants include borax, cadmium chloride, boron nitride, lead iodide, cobalt chloride, silver sulphate, zinc stearate, heavy-metal sulphides, selenides and tellurides. Solid lubricants can be used in powder form, or as suspensions, pastes or lacquers.

2.3.12 Cosmetic additives

102. Cosmetic additives include dyes, fluorescent additives, de-blooming agents etc. The paraffinic Pennsylvanian oils, which had a natural green fluorescence, were highly-regarded as lubricants during the early part of the century, and even today such fluorescence is regarded as a sign of good quality. Most of the substances which give rise to such colouration are now removed by the refining process. However, as marketers have recognised the association of appearance and perceived quality, also the advantages of brand identification by colour, dyes are often used to impart a unique appearance to certain categories of lubricants, mainly automotive oils.

103. These dyes normally consist of water-insoluble, oil-soluble azo dyestuffs, such as 1-(2,4-dimethylbenzeneazo)-2-hydroxy-naphthalene (red) or 2,3-dimethyl-4-(2-hydroxy-1-azonaphthyl)-azobenzene (reddish-brown).

2.3.13 Other additives

104. Preservatives are added to certain lubricants, notably emulsifiable cutting oils, in order to inhibit microbial growth and thereby prolong the working life of the lubricant. Suitable preservatives include imidazolines, amidoacetals, hexahydrotriazines, oxazolidine derivatives, O-formals, phenoxy alcohols and isothiazolone derivatives.

105. Tackiness additives are used to improve the adhesive characteristics of lubricants in order to reduce losses by drainage, dripping, spraying or centrifugal throw-off. These additives normally consist of high molecular-weight hydrocarbon polymers, such as polybutenes.

106. Odourants are added to mask the natural odour of lubricants in order to improve their acceptability in situations where there is potential for olfactory exposure. These products include substances such as pine and citronella oils.

107. Coupling agents are chemicals such as hexylene glycol, higher molecular weight glycols and glycol ethers which are highly miscible in both aqueous and non-aqueous phases. They are added to maintain the homogeneity of products such as soluble oil concentrates which contain small quantities of water resulting from the manufacturing process. They function by partitioning between the oil and water phases, thereby improving the mutual miscibility of the two phases.

2.4 Lubricant categories

108. Three main lubricant categories will be considered in this document. These are automotive lubricants, hydraulic fluids and metal-cutting fluids. Flow diagrams which describe the use of these lubricants and show where to find information in the document are given in Appendix A.

2.4.1 Automotive lubricants

109. These may be sub-divided into the following main categories:

- Petrol-engine crankcase lubricants
- Diesel-engine crankcase lubricants
- Transmission lubricants
- Greases
- Shock absorber fluids

110. The vast majority of automotive lubricants are the crankcase lubricants; these products also have the greatest potential for environmental release during use. Grease, shock-absorber fluids, etc. are generally contained in sealed-for-life systems and therefore the potential for release only arises on disposal.

2.4.1.1 Petrol engine crankcase lubricants

111. The vast majority of petrol engines currently use the traditional reciprocating 4-stroke cycle. Other variants such as the Wankel design and the Orbital 2-stroke, despite continuing development, have not yet achieved significant market penetration.

112. Although the car population continues to escalate, the production of engine oils has not increased at the same rate, due to reduced consumption rates in the engine, and also the adoption of more extended drain intervals.

113. The requirements of engine oils include:

High viscosity index
High oxidation resistance
Low volatility
Low pour-point
Good boundary lubrication performance
Detergent activity
Dispersant properties
Catalytic converter compatibility
Acidic by-product neutralisation capability
High shear stability

114. The **viscosity classification** was developed in the US by the Society of Automotive Engineers (SAE). The classification covers both monograde oils (where the viscosity limits are specified at 100°C only) and multigrade oils (where the viscosity limits are specified at both 100°C and a sub-zero temperature depending upon the actual grade being tested). Testing to the approved specification is

straightforward and uses comparatively basic test equipment, and is within the capability of the average lubricant blender.

115. The main issuers of the **performance specifications** are:

- API - American Petroleum Institute
- MIL - USA Military Specifications
- CCMC - Comité des Constructeurs d'Automobiles du Marché Commun - now obsolete
- ACEA - Association des Constructeurs Européen des Automobiles
- Mercedes Benz
- Volkswagen

116. The vast majority of engine oils are still based on mineral oil-based hydrocarbons, mainly those derived from conventional refining processes, although increasing use is being made of the hydrocracked "super-refined" or "VHVI" oils in order to achieve the necessary performance characteristics. Some oils based on synthetics fluids such as the polyalphaolefins are also being increasingly used, despite the significant price differential. The characteristics of the base fluids are enhanced or extended by the addition of specific additives as described in the previous section.

2.4.1.2 Diesel engine crankcase lubricants

117. Diesel engines, although having been used in commercial vehicles for many years, are currently becoming increasingly popular in the passenger car market. The requirements of diesel engine lubricants are in many ways similar to those of the petrol engine variety. However at present, diesel fuel has a higher sulphur content than petrol, so the process of combustion produces a larger amount of acidic by-products. Therefore the corrosion- inhibition properties of the lubricant need enhancement. Diesel engines are more prone to produce sludge and deposits than the petrol variety, and the lubricant detergency requirement characteristics are correspondingly greater.

2.4.1.3 Transmission lubricants

118. These are used for the lubrication of gearboxes (manual and automatic) and for the hypoid bevel rear axles (conventional and limited-slip). Each type of application calls for a lubricant with particular characteristics. Generally, separate lubricants are supplied for the separate applications although, in some applications, standardisation occurs (see below). Permanent oil fill ('lubricated for life') has been standard practice with back axles for many years, and is becoming increasingly more common with gearboxes.

119. Lubricants for manual gearboxes are normally of the multigrade variety, and contain additives to improve load-carrying and humidity-corrosion resistance. Due to the high operating temperature of automatic gearboxes, these lubricants require additional long term stability characteristics, higher oxidation resistance and also frictional characteristics which are compatible with the requirements of the friction clutches in such equipment.

120. Lubricants for hypoid bevel final drive units require additives which provide the necessary lubrication requirements of the combined sliding/rolling action of the hypoid bevel gear teeth. These oils are generally not compatible with the requirements of gearbox oils since the additive treat level would

cause too high a wear rate in the synchronisation cones. In certain front-wheel drive vehicles the same lubricant is used for the engine, gearbox and final drive components. The transmission components in such cases are designed to be compatible with the characteristics of the crankcase lubricant. One of the earlier examples was the Mini, introduced in 1969 which used a common engine/gearbox lubrication system. Many modifications and improvements in both the engine/gearbox design and in the lubricants themselves have since taken place, which have to a certain extent overcome the basic disadvantages of such multipurpose lubricants.

121. However, the use of a single lubricant to perform many functions has been standard practice in certain use categories for many years. For example, 'Super Tractor Universal Oils' is a standard term for a product which may be used to fulfil all the lubrication requirements of an agricultural tractor, including the engine, gearbox, hydraulic equipment and wet clutches. This simplification of the lubrication requirements is preferred by farmers since lubricant stocks can be more easily rationalised, and the possibilities of using an oil in an incorrect application are minimised. The engineering design of a tractor in terms of materials used for the engine, gear components and oil seals, also the loading and stresses of the various components, takes into account the limitations of the use of a single lubricant.

122. The disadvantages of this approach are:

- such a lubricant can be a compromise product, not necessarily providing the optimum lubrication in all areas that could be achieved by using several single-purpose lubricants.
- the cost of the lubricant reflects the most severe application, i.e. in the engine. There is a performance 'give-away' when using the same lubricant in a less demanding application such as the hydraulic system.

123. However, in this case, the perception of the customer is that the advantages outweigh the disadvantages.

124. Chain lubricants used for exposed motorcycle chain transmissions will eventually be totally discharged to water, since they are washed off under wet conditions. There are a number of varieties of chain lubricants, ranging from the solid petrolata type, which is applied in the molten form, to the more commonly-used liquids, often applied from an aerosol. The overall tonnage is uncertain, but is unlikely to exceed 500 tonnes/year in the UK.

2.4.1.4 Greases

125. Greases are used in situations where it is not feasible to provide an oil supply, e.g. in wheel bearings, constant-velocity joints, steering components, etc. Greases, which are essentially oils plus a thickening agent, lubricate components by means of the slow release of oil from the grease structure. Many of the greases used in automotive applications contain additional EP (extreme pressure) agents, as well as solid lubricants such as molybdenum disulphide. Grease thickening agents include alkali-metal soaps (normally lithium and calcium) of fatty acids (normally 12-hydroxystearic acid), polymers (normally polyethylene or polypropylene), diatomaceous earths and a variety of other materials used in specialised applications. The oil component is normally hydrocarbon-based, but certain synthetic fluids (polyalkylene glycols, silicones etc.) are used again for more specialised applications. Very soft (semi-fluid) greases are specified in place of gear oils by some manufacturers.

126. The amount of grease manufactured in the UK is approximately 30,000 tonnes/year; one third of this is exported. The lower UKPIA figure is likely to be an underestimate. Of the 20,000 tonnes/year sold in the UK, the split between automotive and industrial is approximately 50/50.

127. Greases are commonly used in sealed-for-life components in which they do not degrade appreciably. They also do not leak and so do not need to be topped up or replaced. Thus their environmental impact during use is likely to be low.

128. Vehicle dismantlers habitually drain off all fluids such as engine oils, radiators, gearboxes, back axles, before dismantling or scrapping the vehicle. This is done partly as the used oil has a value, either to be sold to a waste oil collector or to be used in-house as a heating fuel, and partly because the spillage of lubricants from scrapped vehicles can pose a housekeeping problem. Grease in prepacked bearings, and oil in sealed shock-absorbers is not removed, but scrapped with the vehicle. Where the particular components are re-melted these lubricants would ultimately be emitted to the atmosphere in a partially combusted or oxidised form. Otherwise the components and the lubricants they contain are disposed of to landfill.

2.4.1.5 Shock absorber fluids

129. The purpose of shock absorbers (also known at dampers, dash-pots) is to convert vibrational energy into heat and thus have a dampening effect upon the vibration, i.e. will decrease the amplitude of vibration and also the vibration period and frequency compared with an undamped system. Early dampers relied on dry frictional plates which were subjected to spring compression pressure to obtain the required degree of damping. Modern systems, which are generally sealed-for-life, consist of oil-filled reservoirs, where the oil is forced between chambers through narrow apertures or control valves. The oil is heated to 60-100°C during this process. The shock absorber fluids are generally based on mineral oil, although synthetic oils may be used where particularly high performance is required. The requirements of the fluid are as follows:

Operational at low temperatures
Good VT characteristics
Low volatility at maximum working pressure
Non-foaming characteristics
Anti-corrosion properties
Anti-wear properties

130. In practice, naphthenic oils are often used because of the good low temperature characteristics. The VT properties are improved by the addition of shear-stable VI improvers. Anti-corrosion additives, phosphorus-containing anti-wear additives and anti-foaming additives are also generally incorporated.

131. Approximately 750,000 litres of fluid per annum are currently used in filling UK-manufactured shock absorbers. In the UK, fluid-filled shock absorbers are currently disposed of with the vehicle at the time of breaking without draining out the fluid. It is the intention in Germany to introduce legislation which will require fluid-filled shock absorbers to be drained before disposal, and for the oil to be disposed of after suitable treatment. We can anticipate that this requirement may be introduced into the UK in the future.

2.4.2 Hydraulic fluids

132. Fluids intended for the hydrokinetic transmission of power are termed power transmission fluids. Those intended for hydrostatic power transmission are termed hydraulic fluids. Fluids used in shock absorbing systems, used to suppress vibrations and as energy converters, represent a special case of hydraulic fluid. Hydraulic fluids are used widely in machine tools, steering gear, load manipulating equipment, the transmission of pressure in land, sea, and airborne craft, as well as for comfort hydraulics and for brake systems. The range in operating conditions can be extreme, requiring a whole variety of fluids with differing characteristics.

133. The main properties of importance in a hydraulic fluid are the viscosities at working and start-up temperatures, viscosity index, compressibility, seal and metal compatibility, corrosion and wear resistance, also air entrainment and foaming characteristics. For non-aqueous systems, water separability and demulsification ability are also important for some products while detergency, or the capacity to carry extraneous material, is important for others. There may be other requirements, such as non-flammability, depending on the working environment.

134. Most hydraulic fluids are based on mineral oils, although aqueous systems (with and without additives), emulsions and synthetic fluids are commonly used. The separate categories are detailed below.

2.4.2.1 Hydraulic fluids based on mineral oil

135. Paraffinic oils are normally used because the higher viscosity index, compared with naphthenic oils, is advantageous in most hydraulic fluid applications because the working temperature of a hydraulic fluid operating at even low or moderate pressures is generally some 40 to 50°C above the start-up temperature. The pressure/viscosity relationship of the two types of oil differ - the viscosity of the naphthenic oils under high pressure increasing more rapidly than that of the paraffinic oils. This can be an advantage, however, when starting up at low temperatures where paraffinic oils cannot be employed because of problems with cloud and pour-points.

136. In simple applications, where there is no special requirement for ageing, corrosion, wear, foaming tendency, etc., additive-free refined mineral oils can be used. For more demanding applications, additives are necessary to improve and extend the properties of the mineral oil base fluid. A highly critical factor in hydraulic systems is the absence of particulate material. Consequently, hydraulic oils are filtered to a high degree, both during manufacture, and during use by filtration units incorporated into the hydraulic system. In certain circumstances, specialised additives imparting controlled stick/slip properties are incorporated. For applications involving extreme fluctuations in temperature, or where the systems are particularly sensitive to viscosity changes in the oil, high VI oils are required, which are formulated from suitably high VI basestocks, or which incorporate VI improving additives.

2.4.2.2 Hydraulic oils based on vegetable oils

137. These products are normally based on rapeseed oils and rapeseed oil esters and may also contain synthetic esters. Their use is normally confined to environmentally-sensitive locations. Traditionally, such products have inferior performance in many aspects compared with mineral oil products, particularly in terms of oxidation stability, sealing compatibility, VI, degradability, hydrolysis, etc. However, recent developments have led to significant improvements (see Section 2.3.3).

2.4.2.3 Fire-resistant hydraulic fluids

138. The use of fire-resistant hydraulic fluids is necessary in working environments such as foundries, steel mills and coal mines, for obvious safety reasons. Fire risks as a result of hydraulic system leakages can be greatly reduced by the use of fire-resistant fluids. The different types of fluids are:

- **Non-aqueous fire-resistant hydraulic fluids**

139. These normally consist of silicones, polychlorinated biphenyls and phosphoric acid esters. Silicones are used only for very specialised applications because of their high cost. The polychlorinated biphenyls have now been almost completely withdrawn because of potential toxicity problems. The phosphate esters are based on the trialkyl or triaryl phosphates, or mixtures of both types. Although they have better VIs and a lower vapour pressure than mineral oil equivalents, seal materials must be

specifically designed for such products, the fluorohydrocarbon elastomers being most suitable. Oxidation stability is good but the hydrolytic stability can be poor for certain fluid compositions.

- **Water-miscible fire-resistant hydraulic fluids**

140. These consist of oil-in-water emulsions, water-in-oil (invert) emulsions, polymer-thickened aqueous solutions and the so-called high water-based hydraulic fluids, the water content of all of these products being responsible for the low flammability. The use of water alone as a hydraulic fluid would lead to excessive wear rates, corrosion problems, etc. In addition to use in critical applications where a low flammability product is required, they may also be used in situations where high leakage rates necessitate the use of low-cost products, or where environmental considerations do not permit the use of mineral oils. However, where recovery/disposal of fluids is subject to waste regulation this latter is not an option.

141. The compositions of the oil-in-water emulsion products are similar to those of the emulsifiable cutting oils described in Section 2.4.3.2. Such products have in fact been used as low-cost hydraulic fluids. In environmentally-sensitive areas where emulsions are expected to be biodegradable, the emulsifiers need to be carefully specified and the mineral oil may be replaced by more suitable fluids.

142. Water-in-oil emulsions are used less frequently (and not at all in Germany), and mostly in situations where improved lubricity is required compared with the more conventional oil-in-water emulsion. The characteristics of these products are closer to those of a mineral oil. If the product is inadvertently subjected to high temperatures and a possible flammable environment the emulsified water flashes into steam and exerts a flame-quenching effect.

143. The polymer-thickened fluids contain mixtures of glycol, water-soluble glycol ethers and polyglycols together with the normal anti-oxidants and anti-rust agents. The water content needs to be at least 35% in order to be classified as a fire-resistant fluid.

144. High water-based hydraulic fluids (HWBHF) are a comparatively recent innovation (within the last 10 years). They consist of water containing approximately 5% of an additive concentrate which provides the required lubricity and anti-corrosion performance.

145. During use, emulsions normally require continuous attention in terms of filtration and stability monitoring. Regular controlled dosing with bactericides and fungicides is also advisable. During extended shut-down periods, the hydraulic system needs to be air-purged to avoid the build-up of anaerobic bacteria.

2.4.2.4 Brake fluids for road vehicles

146. These normally consist of mixtures of polyglycol ethers and polyglycols together with antioxidants and rust-preventing agents. In certain cases, mineral oils are still used, although on a decreasing level. In other cases, silicone fluids are used in order to overcome problems associated with the hygroscopic nature of polyglycols.

147. The main requirements of such fluids are:

- Low viscosity and good flow properties at low temperatures;
- Low bubble-forming tendency at high temperatures;
- High thermal and oxidation stability;
- Compatibility with metals and elastomers;

- Compatibility and miscibility with water without affecting the operation of the hydraulic system.

2.4.3 Metal-working lubricants (cutting fluids)

148. Metal-working processes involve either metal-cutting operations, such as turning, drilling, milling, planing, and grinding, or metal-forming operations, such as rolling, pressing, and deep-drawing. All these operations involve friction between the tool and the workpiece, resulting in wear of the cutting/forming tool, heat generation, and the possibility of adverse effects on the surface quality of the workpiece. All of these undesirable effects can be overcome to some extent by the use of lubricants. References to metal cutting fluids in this document should be taken to relate to the whole range of metal working processes unless specific processes are identified.

149. In metal-cutting operations, the lubricant performs all or some of several functions, i.e., coolant, removal of metal swarf, reduction of friction and therefore reduction of wear and heat generation, and also corrosion prevention. Lubricants for metal working operations fall into a number of categories, as listed below.

2.4.3.1 Neat cutting oils

150. Neat oils are the most expensive of cutting oils, and are used when a high degree of surface finish and accuracy is required. High temperatures and pressures are involved in the cutting operation, the geometry of which does not permit hydrodynamic lubrication. In order to maintain the necessary oil film essential for lubrication, cutting oils normally contain active ingredients which adsorb onto the surface of the metal to form a chemisorbed layer, although neat mineral oils can be used in cases where the requirement is mainly for cooling and flushing purposes involving machining of metals which are easily cut.

151. The additives used vary with the severity of the cutting operation. For the less-demanding operations, fatty acids provide adequate lubricity. For the more demanding operations, oil-soluble additives containing chlorine, phosphorus and/or sulphur (either neat or as a sulphurised fat) are necessary. At the elevated temperatures involved, these additives react with the metal surface to form metal chlorides, phosphides and sulphides respectively, all of which lower the friction between the cutting tool and the workpiece.

152. Organic chlorine compounds react with the metal surface at around 180°C. These additives are readily hydrolysed, however, and precautions must be taken to counter the potential corrosion problems when machining ferrous metals. The use of chlorine-containing compounds has in general reduced in recent years.

153. Organic phosphorus additives react with the metal surface at temperatures ranging from 200 to 700°C. Their purpose is primarily to protect the cutting tool. They are also used in the formulation of multipurpose lubricants, i.e. those which may also be used as gear and hydraulic oils.

154. Sulphur and sulphur compounds are used for heavy and extra-heavy duty cutting operations at medium speeds. Although they react more slowly with the metal surface, they have a high load-carrying capacity and shear strength and are stable up to 1000°C. They are not used for the machining of yellow metals due to the formation of copper sulphide which causes staining of the metal surface.

155. When required combinations of all of the above may be used for special applications.

2.4.3.2 Emulsifiable cutting oils

156. In cases where cooling of the cutting operation is the primary requirement, the ideal medium should have a high specific heat, good thermal conductivity and a high latent heat of evaporation. Water meets all of these thermodynamic requirements, but is a poor lubricant, hence the inclusion of mineral oil is necessary in the form of an emulsion. Since emulsions of oil in water are inherently unstable, the use of emulsifying additives is necessary.

157. A typical emulsifiable cutting oil formulation will therefore contain a mineral oil, emulsifiers and additives to improve the corrosion protection (e.g. alkanolamides), and/or additives which reduce the foaming tendency (e.g. polyethylene glycol ethers). For the more arduous operations, the oils can also contain additives such as fatty oils and extreme-pressure additives which include chlorine (reduced in recent years), sulphur and or phosphorus compounds.

158. Since oil-in-water emulsions provide an ideal growth environment for a range of micro-organisms, biocide additives such as triazines are also added to prevent deterioration of the working fluid and extend its useful working life. Naphthenic oils are more suited to the preparation of emulsions than paraffinic. The oil contents of emulsions are normally between 2 and 5%, although concentrations above 10% can be used for heavy cutting operations. Water quality is important for optimum emulsion stability, hardness and pH being the most important factors. Emulsion appearance is dependent upon droplet size. Milky emulsions have a droplet size of ca. 2 µm, whilst in transparent emulsions the droplets are smaller than 0.05 µm. "Semi-synthetic" emulsions may contain higher levels of emulsifiers producing finer emulsions, and the oil can also be partially substituted by a synthetic fluid. Emulsifiable oils are normally supplied in neat form, for subsequent dilution with water by the customer.

2.4.3.3 Water-based or synthetic cutting fluids

159. These products do not contain mineral oil. In the case of water-based products their lubricant properties are entirely derived from the additives present. In the past these were mainly anti-corrosion additives such as sodium nitrite and triethanolamine in water, which were used for many years in operations such as grinding where cooling is the primary requirement. These additives systems have now been largely discontinued on health grounds. The technology of water-based products has now become much more sophisticated, and the range of their application increased. These products now contain non-ionic surfactants, soaps of natural or synthetic fatty acids, polyalkylene glycols etc., and can be used for a variety of metal-cutting operations, even those requiring heavy duty cutting fluids.

3. RELEASE DURING FORMULATION OF ADDITIVE PACKAGES

3.1 General

160. Blending of additives is typically carried out in a batch operation involving up to twenty components, mainly in liquid form and supplied to the process in bulk or drums. The packages produced are used mainly in automotive applications. The components are known as intermediates in the lubricant industry Regulations in the UK.

161. Operational systems are designed and documented for management control of waste, minimisation of operator exposure and accident or spill prevention (bunded and segregated tanks). Preventative maintenance systems are designed to maximise equipment utilisation and efficiency, including all environmental controls and arrestment plant.

3.2 The blending process

162. Additive blending is generally carried out at elevated temperatures between 50 and 90°C because of the viscosity characteristics of many of the intermediates. The temperatures and volatility of some of the intermediates create emissions to atmosphere which are generally lower than those seen in lube oil blending plants. The wide range of products that are blended does increase the proportionate use of drummed additions.

163. The blending process itself can be more critical for additives than for lubricants in that intermediates are generally surface active materials. This surface activity with the subsequent physical interactions means that the order of addition of the intermediates can be critical. Controls are in place to prevent overheating blends during and after mixing as this could lead to chemical degradation.

3.2.1 Emissions to air

164. Although additive blending is not part of the prescribed process under the Environmental Protection Act 1990 in the UK, intermediate storage for subsequent blending may be. Any emissions to air will, therefore, be controlled and monitored. Maximum release levels are prescribed locally, and will vary depending upon local environmental factors. Parameters controlled may include hydrogen chloride, volatile organic compounds, particulate matter, total amines etc.

165. Controls such as wet scrubbing may be required under certain circumstances.

166. Where necessary emissions from drummed intermediates are controlled during the emptying process by engineered systems which discharge through the same environment control system as that for the blend process.

167. In the case of some specialist additives, the equipment incorporates vent condensers to control reactions not only for environmental protection but also to maximise yields.

3.2.2 Emissions to water

168. To eliminate any environmental impact from accidental spills, blend drainage systems are separated from any domestic foul drains. The blend drains, where appropriate, will be connected to the chemical plant system and have appropriate abatement equipment such as skimmers or effluent treatment plant. The final discharge from this process is into controlled waters and is maintained within locally prescribed limits, which may, where appropriate, include biological oxygen demand, suspended solids, hydrocarbon oil, pH, temperature etc.

169. There is no use of water in the additive blending process. Losses from the blending process can be kept to a minimum through careful housekeeping and planning. The mixing vessels are rinsed with oil to remove residual additives and the oil recycled. By sequencing the composition of batches carefully the residues can be used in the following product. These factors in combination with the controls on such processes mean that in the UK emissions are expected to be negligible.

4 COMPOSITION OF LUBRICANTS IN USE

4.1 Introduction

170. It is necessary at this stage to distinguish between automotive and industrial (hydraulic oils, cutting oils) since the two categories are entirely different in the manner in which they are specified, formulated, handled and recovered.

4.2 Automotive

171. Crankcase fluids are by far the largest single category of automotive lubricants. They are formulated to meet both viscosity and international performance specifications.

172. The performance specifications for crankcase oils are very complex, and require the use of engine test facilities which are well beyond the capability of the average lubricant blender. These facilities would only be available at the development establishments of the performance package suppliers and of the major oil companies. Consequently, the engine test development costs are at least £400,000, and it is not expected that the lubricant blender would test against the performance specification. In practice, the performance additive supplier would develop a package (i.e. a blend of chemicals) or packages to meet the performance requirements. This formulation would be thoroughly engine-tested. The formulation (i.e. percentage limits of the performance additives together with the elemental concentrations) would be supplied to the lubricant blender, who would blend according to the given formulation, and check against the elemental concentration limits specified. It can therefore be appreciated that, since the additive suppliers have invested substantially both in direct finance and in technical know-how, detailed composition of the additive packages are not disclosed. However, the formulations currently in use are classifiable in broad terms as shown in Table 4.1 (derived from ATC, 1994). The table contains values for the content of an additive type in the lubricant which can be used in the absence of specific information.

173. Formulations specifically devised for passenger car diesel engines are approximately intermediate between the two types of formulations quoted in Table 4.1; a mid-point can be used. However, oils specifically introduced for passenger car diesel engine use have not been universally adopted. Oils intended for petrol engine use are commonly used, and will give a satisfactory performance, but are not as good as a purpose-designed oil.

174. It is standard practice to change passenger diesel oils at approximately twice the frequency of petrol engine oils although for many cars the interval is now the same as that for petrol engines. At present, 6.5% of the present car population are diesels (22% of 1994 new car sales in the UK were diesels). Thus 12% of automotive oils are used in passenger car diesel vehicles, i.e. 24,000 tonnes/year although as already stated, not all of this will be purpose-designed oil.

175. The passenger car motor oil information in Table 4.1 is for leaded and unleaded petrol application. When unleaded petrol was first introduced, a 'black sludge' problem occurred in petrol engines, which appeared to be associated with the use of unleaded petrol. Further extensive checks

confirmed that the problem was only partially fuel-related with engine design and the type of crankcase ventilation also contributing factors. It was possible to reformulate the lubricant to eliminate the problem.

Table 4.1 Weighted average automotive crankcase lubricant components for Europe[a] (from ATC 1994)

Additive component	**Passenger car motor oil (PCMO) (%wt)**[b]	**Heavy duty diesel oil (HDDO) (%wt)**[b]
Detergents:		
- calcium detergents	2	**3**
- magnesium detergents	1.2	**1.5**
- others	2	**3**
Dispersant	**5.5**	4.5
Corrosion inhibitor:		
- zinc dithiophosphate	1.5	**1.75**
- others	1.5	**3**
Extreme pressure (EP) additive:		
- zinc dithiophosphate	1.5	**1.75**
- others	1.5	**1.75**
Anti-oxidants	1	**2.25**
Viscosity modifier	**7.5**	5.5
Others:		
- no specification	**7.5**	5.5
- antifoam additive	0.003	**0.003**
- anti-rust additive	1.5	**3**
- antiwear additive	1.5	**1.75**
- dye	0.001	**0.001**
- friction modifiers (anti-friction additives)	0.5	**0.5**
- metal deactivators	1.5	**1.75**
- “inhibitor”	1.5	**3**
Total UK market (approx)	200,000 tonnes/year	200,000 tonnes/year

a - Different chemistries are used by different companies so the contents of additives can vary significantly in different lubricants. For example, some lubricants may contain only calcium detergent with no magnesium detergent. Monograde oils are also available which do not contain viscosity modifiers.

b - Values in bold should be used where PCMO or HDDO has not been specified explicitly.

176. The total UK market in motorcycle lubricants is 6,000 tonnes/year. Of this, 60% (3,600 tonnes/year) is used in 4-stroke engines, where the general environmental emission impact is similar to that of petrol automotive engines. The remaining 40% (2,400 tonnes/year) is used in 2-stroke engines, split 70/30 between engine and gearbox (1,680 and 720 tonnes/year respectively). In 2-stroke engines the engine oil is either mixed with petrol or directly injected into the engine and exits with the exhaust gases. In both cases, the environmental fate of the lubricant is the same, i.e. it will be combusted during use.

177. Looking to the future, there are likely to be some minor changes to the formulations given above as a result of:

- Change to low-sulphur fuel for heavy duty diesel oils (HDDOs).
- An increase in the proportion of diesel-powered passenger cars.
- Requirements for catalyst compatibility.
- Increasingly stringent emission requirements.

178. There may be, for example, some change when a particular performance test for PCMOs which uses leaded fuel is dropped or replaced. Likewise, there may be some change on the diesel side to reflect the change to a lower sulphur fuel. However it is anticipated that sulphur contents outside Europe may well stay at high levels for some time yet. As many lubricant formulations are designed for international markets the broad pattern of formulation described will be relevant for at least another 5 years.

179. There are more similarities than differences between PCMOs and HDDOs. Any changes in market share will have only a small effect on the components used in the formulations.

180. Oil additives from different manufacturers achieve the required performance levels by using a variety of different chemistries (or combinations of additives), each manufacturer tending to specialise in a particular approach. However, the chemistries are not incompatible; oils of different makes may be mixed with each other without detrimental effects. The vehicle supplier has no control over which grade the motorist may use for 'topping up' purposes, other than by stipulating the specification of the oil needed. Therefore a situation of incompatible chemistries would not be acceptable.

181. There have been concerns about lubricant compatibility with catalysts for at least 10 years, these being mostly related to the phosphorus content. During this period, however, the catalyst manufacturers have made substantial progress in reducing the sensitivity of their products, and at the same time engine manufacturers have greatly reduced oil consumption.

182. The overall conclusion is that any formulation changes will be relatively minor, and will not unduly affect the overall additive balance.

4.3 Hydraulic fluids

4.3.1 Mineral oil-based fluids

183. Mineral oil fluids account for over 80% of all fluids used in industrial hydraulic systems. These fluids are formulated to conform to a series of ISO (International Standards Organisation) viscosity specifications. As with the automotive oils, the viscosity classification implies no quality performance. The performance levels of mineral oil-based hydraulic oils are comparatively simple, and are designated by the ISO system into four categories, i.e. HH, HL, HM and HV. Table 4.2 gives a summary of overall quantities produced in the UK and the additives they contain. A different classification system based on the DIN standard 51524 is used in Germany. Rough equivalences between the systems are noted.

4.3.1.1 HH type

184. These are non-inhibited fluids and consist of straight mineral oils containing no additives. They are used in undemanding systems such as hand-operated hydraulic jacks or in systems which may be prone to high leakage rates.

185. This type of fluid corresponds to a type C lubricant under the DIN system (under a different standard to that mentioned above) and such fluids are not used as hydraulic fluids in Germany.

Table 4.2 Summary of market and additives for mineral oil based hydraulic fluids

Type	UK Market tonnes/year	% Additives
HH	5,000	None
HL	15,000	0.03-0.2% corrosion inhibitor 0.1-0.4% pour-point depressant up to 0.0005% wt silicone anti-foam
HM	65,000	As HL plus antiwear additive up to 1% ZDDP for EP and corrosion inhibitor or up to 1% sulphur/phosphorus additive
HV	10,000	As HM plus up to 20% VI improver - polymethacrylate or polyhydrocarbon
TOTAL	95,000	

Note: ZDDP – zinc dalkyldithiophosphate

The relative use of these fluids differs between countries. For example, HM fluids are particularly important in Germany (as HLP and HLPD types) but are predominantly zinc-free.

4.3.1.2 HL type

186. These contain additives which inhibit against rust, corrosion and oxidation. Since they do not offer good anti-wear performance, they are not now widely used. The DIN system has a roughly similar category.

187. Typical formulations contain from 0.03 to 0.20% of a rust/corrosion inhibitor, e.g. an alkylated organic (succinic) acid/ester in addition to the base oil. If necessary, a pour-point depressant (0.1 to 0.4%) and up to 5 ppm of a silicone anti-foam may be added.

4.3.1.3 HM type

188. These are the most widely used fluids and contain anti-wear additives in addition to the above HL requirements. However, in this range there are marked performance differences between a 'standard' and a 'superior' quality hydraulic fluid. About 90% of the market uses zinc based antiwear additives, but ashless S/P esters can also be used. The trend towards higher pressure, more responsive systems results in closer tolerances in the components, leading to cleaner fluids filtered through much smaller pore size, typically micron, filters. The modern additive package often contains up to twelve separate components to meet all the performance requirements, including air release, foaming, thermal stability, hydrolytic stability, wet and dry filterability and pump testing.

189. Typical formulations for a zinc-containing product contain up to 1% of the cost-effective EP and anti-corrosion agent, zinc dialkyldithiophosphate (ZDDP). However, it has been established that even when the more hydrolytically-stable secondary alkyldithiophosphate is used, the incorporation of ZDDP in hydraulic oils can lead to filterability problems due to the formation of oil-insoluble products if any water

is present. If the filtration requirement is for retention of particles exceeding 5 microns then a non-zinc hydraulic oil must be used. Non-zinc formulations for improved filterability would contain similar levels of a sulphur/phosphorus additive either in combination, such as triphenylthiophosphate, or as separate additives such as tributylphosphate with a sulphurised fat. There is now an increasing interest in the fine filterability of hydraulic oils. This is particularly important for numerically-controlled machine tools where the close tolerances required for a fine surface finish are only attainable when the machine tools index accurately for each metal cutting operation undertaken.

190. In Germany, HLP and HLPD-type oils correspond to this group – HLPD type fluids contain additional detergent/dispersant additives. Fluids in Germany are now predominantly zinc free.

4.3.1.4 HV type

191. These are essentially HM Type fluids with improved viscosity/temperature characteristics. Some improvement in the VT characteristics can be achieved by the use of a suitably-high VI base oil, but the use of a specific VI additive is normally necessary to achieve the desired VT characteristics. Up to 20% of a viscosity modifier can be added to lift the VI and this is usually a polymethacrylate or polyhydrocarbon.

192. These fluids are called HVLP-type fluids in Germany. HVLPD fluids are similar, with added detergent/dispersant.

4.3.2 Fire resistant hydraulic fluids

193. These are characterised by the 'HF' category, with additional letters to denote the type:-

- HFA - Oil-in-water emulsions containing typically 5% v/v oil. (~ 13,000 tonnes/year)
- HFB - Water-in-oil emulsions containing typically 40% v/v water. (~ 2,000 tonnes/year)
- HFC - Aqueous solutions containing soluble polymers which increase the viscosity. (~ 3,000 tonnes/year)
- HFD - Synthetic fluids containing no water. (~ 2,000 tonnes/year)

194. Table 4.3 summarises the overall quantity of these chemicals used, and their additive constituents.

4.3.2.1 HFA oil-in-water emulsions

195. These emulsions are a dispersion of oil in water to a maximum of 20% but more usually around 5%, in the form of fine droplets up to 5 microns in diameter. The emulsion is stabilised by the incorporation of emulsifiers similar to those used in the soluble cutting fluids i.e. natural and synthetic sodium petroleum sulphonates, in addition to corrosion inhibitors, lubricity additives, bactericides, etc.

4.3.2.2 HFB water-in-oil emulsions

196. These are less commonly-used than the HFA type. They consist of approximately 40% water and 60% oil, the emulsion again being stabilised by the incorporation of the appropriate type of emulsifier, albeit at lower levels than in the HFA type. The dispersion of oil droplets (1 to 2 microns diameter) is produced by specialised manufacturing techniques. The oil component again contains anti-wear additives, oxidation and corrosion inhibitors, also bactericides. These fluids are not used in hydraulic fluids in Germany.

4.3.2.3 HFC aqueous polymer (also known as water-glycol) solutions

197. These solutions contain between 35 and 50% wt/wt water, with the balance being mainly glycol, water-soluble glycol ethers and polyalkylene glycols.

Table 4.3 Summary of market and components for fire resistant hydraulic fluids

Type	**UK Market tonnes/year**	**% Components in fluid as used**
HFA	13,000	Oil - usually 5% (vol), can be up to 20%; water 80-95% emulsifiers - natural/synthetic sodium petroleum sulphonates corrosion inhibitors lubricity additives bactericides etc.
HFB	2,000	Oil 60%; water 40% (vol) emulsifiers antiwear additives oxidation inhibitors bactericides
HFC	3,000	30-50% water (wt) balance - glycol, glycol ethers, polyalkylene glycols corrosion inhibitors, e.g. triethanolamine up to 1%, benzotriazole up to 0.5%, fatty acids (lauric acid) up to 1% anti-foam agents up to 0.05%
HFD	2,000	Synthetics - triaryl or trialkyl phosphate esters or silicones or polyol esters additives are sometimes added to these fluids
TOTAL	20,000	

Note: HFB fluids are not used in Germany.

4.3.2.4 HFD non-aqueous fluids

198. These include a variety of types of product, mainly based on triaryl or trialkyl phosphate esters, but silicones are also used for certain specialised applications. Polyol esters are also used e.g. for industrial robots performing welding operations.

4.4 Metalworking (cutting) fluids

199. It is estimated that there are some 50,000+ businesses using metalworking fluids in the UK. These include not only engineering companies but the maintenance departments of large companies and organisations in industrial and other sectors.

200. Metalworking fluids are divided into five different categories as shown in Table 4.4 below. In general, the neat oils are basically simple blends of up to about six ingredients, and can be identified in a reasonably straightforward fashion. The water-miscible fluids (categories 2-5 above) are very different. Not only are they more complex in composition, containing as many as 15-20 ingredients, but there is a wide diversity in the number and nature of the individual additives. Many companies are involved in the

manufacture of these types of products, including a number of specialist companies, and details of individual formulations are not obtainable except under conditions of strict confidence. Many hundreds of combinations of the different ingredients are possible, so the information given below is therefore a broad overview of the general types of formulations which are in current use.

Table 4.4 Consumption of the different categories of metalworking fluid in the UK

	Tonnes/year (approx)	**%**
1. Neat oils	15,750	45
2. Conventional soluble (milky emulsion)	7,700	22
3. Micro-emulsion (semi-synthetic)	8,750	25
4. Synthetic (grinding)	1,750	5
5. Synthetic (cutting)	1,050	3
TOTAL	35,000	

4.4.1 Neat oils (15,750 tonnes/year)

201. Neat cutting oils are variously formulated to meet a variety of different applications. They consist of mineral oils, fortified to meet the necessary requirements. Their typical composition is shown in Table 4.5 below.

202. More details on the uses of the various compositions are given below.

- Straight mineral oil (no additives) - Used only for the low demanding operations, e.g. high-speed blanking of thin laminates.

- Mineral oils plus fatty oils - Used for light duty machining on cast iron, aluminium, brass and magnesium.

- Mineral oils plus fatty oils plus chlorinated paraffin - Used for machining operations such as low severity turning, drilling and tapping, ferrous and non-ferrous form grinding, broaching (with higher chlorine contents).

- Mineral oil plus sulphurised fat - Used for machining ferrous alloys with low to medium machinability at medium to high operational severity, gear cutting, threading.

- Mineral oil plus sulphurised fat/ester plus free sulphur - Used for extremely arduous machining operations on tough ferrous alloys, tapping, broaching, deep hole drilling.

Table 4.5 Typical composition of neat oils

Type and composition of neat oil	UK market tonnes/year
Straight mineral oil	300
Mineral oil and fatty oils Mineral oil - 90% Lard/rapeseed oil - 8%	1,600
Mineral oil, fatty oil and chlorinated paraffins Mineral oil - 85% Lard/rapeseed oil - 5% Chlorinated paraffins - 10%	7,000
Mineral oil and sulphurised fat Mineral oil - 90% Sulphurised fat/ester - 10% (may also contain chlorinated paraffins - 5%)	6,050
Mineral oil, sulphurised fat and free sulphur Mineral oil - 89.4% Sulphurised fat/ester - 10% Sulphur - 0.6% (may also contain chlorinated paraffins - 5%)	800
TOTAL	15,750

Note: composition given is that of fluids ready to use.

As described earlier (Section 2.3.5), the use of short-chain chlorinated paraffins in metalworking fluids is likely to decline in the next few years. However, medium and long-chained chlorinated paraffins may still be used in metalworking fluids.

203. In Germany these types of fluids are described as non-water miscible cooling lubricants. Information on the composition of such fluids as used in Germany is presented in Table 4.6.

4.4.2 Conventional soluble oils (milky emulsion) (7,700 tonnes/year)

204. These oils are used for lower duty general machining operations. The composition of these fluids is described in Table 4.7.

205. In use, these fluids are mixed with water to give an emulsion containing typically 5% of the fluid. The oil particle size is between 2 and 10 microns.

206. Table 4.8 below shows examples of additives suitable for use in emulsifiable cutting oils.

Table 4.6 Composition of non-water miscible cooling lubricants (Germany)

Component	Content
Basic oil	87-95%
Sulphur	~0.5%
Sulphurised ester or sulphurised olefin	3-6%
Organophosphorus compounds and calcium sulphonate	0-3%
Carbon acid ester (friction modifier)	0-3%
Mist inhibiting agent	0.5-1%
Antioxidant	~0.2%

Table 4.7 Weighted average composition of emulsifiable cutting oils

Component	%	Tonnes/year
Emulsifiers	10-20	1540 max
Corrosion inhibitors	4-8	616 max
Oiliness agents	4-10	770 max
Coupling agents	2-3	231 max
Extreme-pressure additives	0-10	770 max
Water (from neutralisation reaction)	1-2	
Biocides	1-2	154 max
Mineral oil	Balance	Balance
TOTAL		7700

207. The list of additives in Table 4.8 shows the wide variety that may be used in emulsifiable cutting oils. In contrast to automotive additives, where there is a limited range of standards which have stringent requirements, there is much more freedom for manufacturers to choose different additives and a much wider range of applications for which the oils can be used.

208. The examples of additives listed may be used together in various combinations; they are also used in the semi-synthetic fluids detailed below.

209. These types of lubricant are described as traditional emulsifiable cooling lubricants in Germany. Information on the composition of such fluids in Germany is given in Table 4.9. The information relates to the concentrated forms of the fluids. Dilution of these fluids may depend on the operation for which they are being used. Table 4.10 has examples of dilutions for different metal working processes. In the absence of any specific information, a dilution of 1:20 (concentrate:water) is suggested.

Table 4.8 Examples of typical additives for emulsifiable cutting oils

Corrosion inhibitors Triethanolamine Alcohol amines Amine borates	Coupling agents Butyl glycol Hexylene glycol
Amine dicarboxylate Aryl sulphamido carboxylic acid Alkyl amido carboxylic acid Calcium sulphonate	Extreme-pressure additives Sulphurised oils/fats/esters Chlorinated paraffins Neat sulphur Polysulphides
Emulsifiers Petroleum sulphonates* Synthetic sulphonates* Sulphonate base Alkyl sulphamido carboxylic salt Octyl phenol ethoxylate Nonyl phenol ethoxylate Alkali fatty acid soap 2:1 Diethanolamine fatty acid amide 2:1 Diethanolamine fatty amide Glyceryl mono-oleate Sorbitan mono-oleate	Biocides Hexahydro-1,3,5-tris (2-hydroxy ethyl)-5-triazine 4,4-dimethyloxazolidine 3,4,4-trimethyloxazolidine 2-bromo-2-nitro-1,3-propanediol 4-(2-nitrobutyl)-morpholine 4,4'-(2-ethyl-2-nitro-methylene)dimorpholine 2-hydroxymethyl-2-nitro-1,3-propanediol Poly{oxyethylene(dimethyl imino)ethylene} dichloride Potassium dimethyldithiocarbamate 2-(thiocyanomethylthio)-benzothiazole Hexahydro-1,3,5-tris-(2-hydroxyethyl)-s-triazine 1-(3-chloroallyl)-3,4,7-triaza-1-azoniaadamantane chloride o-phenylphenol Sodium o-phenylphenate
Oiliness agents Inverse soluble ester Complexed polymeric fatty acid Sulphated castor oil	

Block copolymer ethylene diamine	1,2-benzisothiazolin-3-one
Block Copolymer	Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine
Reverse block copolymer	Sodium 2-pyridinethiol-1-oxide
Poly alkylene glycol	5-chloro-2-methyl-4-isothiazoline-3-one
Triethanolamine/acid polyglycol	2-methyl-4-isothiazolin-3-one
Phosphate ester - low phenol	2-n-octyl-4-isothiazolin-3-one
Phosphate ester - alcohol	Hexahydro-1,3,5-tris (2-hydroxy ethyl)-s-triazine)
Phosphate ester - phenol	
Amphoteric carboxylic salt	
Imidazoline	

*Note: Sulphonates are the products of the neutralisation of a sulphonic acid with a metallic base. Petroleum sulphonates were formerly the by-products of the sulphuric acid treatment of oil fractions in the manufacture of white oils. However, they are now the principal product. Their structure is not completely known, and depends upon the source of the crude oil, containing varying proportions of aliphatic, naphthenic and aromatic hydrocarbons. Synthetic sulphonates were originally derived from the residues resulting from the manufacture of dodecyl benzene. These residues were converted into sulphonic acids, which were normally derivatives of benzene with long alkyl substituents. The starting material for synthetic sulphonates now consists of carefully selected hydrocarbon components. The majority of sulphonate detergents are in the form of calcium, magnesium and sodium. The alkaline earth derivatives are used in crankcase oil formulations, whereas the sodium derivative is used in emulsifiable cutting oils.

Table 4.9 Composition of traditional emulsifiable cooling lubricants (Germany)

Component	Content
Basic oil	~60%
Emulsifier (anionic)	15-20%
Solubiliser	~5%
Friction modifier	0-5%
Aliphatic acids	~5%
Corrosion protection agent	~5%
Neutralization agent	0-3%
Bactericide	~4%
Fungicide	0-1%

Note: content refers to that of the concentrate, not of the lubricant as used.

Table 4.10 Mixing ratios for cooling lubricant emulsions for different processes

Cutting process	Concentration	Concentrate:water
Broaching	10 - 20	1:10 - 1:5
Thread cutting	5 - 10	1:20 - 1:10
Deep hole drilling	10 - 20	1:10 - 1:5
Parting off	5 - 10	1:20 - 1:10
Milling, cylindrical milling	5 - 10	1:20 - 1:10
Turning, drilling, automation work	3 - 10	1:33 - 1:10
Sawing	5 - 20	1:20 - 1:5
Tool grinding	3 - 6	1:33 - 1:17
Cylindrical grinding	2 - 5	1:50 - 1:20
Centreless grinding	3 - 6	1:33 - 1:17
Surface grinding	2 - 5	1:50 - 1:20

4.4.3 Semi-synthetic soluble oils (transparent emulsion) (8,750 tonnes/year)

210. These products have better cooling and wetting properties than conventional soluble oils and permit the use of higher speeds and feed rates in machining operations. Droplet size is conventionally less than 2 microns. Their average composition is described in Table 4.11.

211. The roughly equivalent category of fluids in Germany is semi-synthetic emulsifiable cooling lubricants. Information on the composition of such fluids in Germany is given in Table 4.12. The information relates to the concentrated forms of the fluids. As above, dilution of these fluids may depend on the operation for which they are being used and Table 4.10 has examples of dilutions for different metal working processes. In the absence of any specific information, a dilution of 1:20 (concentrate:water) is suggested.

Table 4.11 Average composition of semi-synthetic cutting oils

Component	%
Emulsifiers	35-50
Oiliness agents	5-20
Corrosion inhibitors	1-3
Coupling agents	2-3
Extreme pressure additives	0-10
Water	25-50
Biocides*	1-2
Mineral oil#	Balance

Notes:Composition relates to the fluids as used.* - such as hexatriazines, semi-acetals, parachlorometacresol, etc. # - in the semi-synthetic fluids, part of the mineral oil may be substituted by a synthetic fluid e.g. polyalkylene glycol.

Table 4.12 Composition of semi-synthetic emulsifiable cooling lubricants (Germany)

Component	Content
Basic oil	~30%
Emulsifier (non-ionic)	10-15%
Solubiliser	~5%
Corrosion protection, bacteriostatic agent	20-25%
Boric acid (biocide)	0-3%
Carbon acid (emulsifier, corrosion protection, cutting facilitation)	5-15%
Corrosion protection	0-10%
Bactericide	0-5%
Fungicide	0-1%
Water	0-10%

Note: contents refers to that of the concentrate, not of the lubricant as used.

4.4.4 Synthetic fluids (grinding) (1750 tonnes/year)

212. These are generally relatively simple products, consisting of aqueous solutions of up to two or three ingredients. The main purpose is cooling, rather than lubrication, therefore water containing anti-corrosion additives is sufficient. Such additives typically comprise 15% of the lubricant (262 tonnes/year).

213. Note: These types of simple and cost-effective fluids have normally been formulated to contain sodium nitrite and triethanolamine. Due to the possibility of the formation of nitrosamines (see HSE publication EH/49) during use, availability of this type of product has almost disappeared on health and safety grounds. No entirely satisfactory alternatives are available, so machiners are using the more sophisticated and expensive products described in Section 4.4.5 below. This type of fluid is not used in Germany.

4.4.5 Synthetic fluids (cutting) (1,050 tonnes/year)

214. Depending on formulation, these products can be used for a variety of machining operations including relatively heavy duty machining and grinding. Again, the formulation possibilities are numerous, but they are all characterised by an absence of mineral oil, being based on water (Table 4.13).

Table 4.13 Typical composition of synthetic cutting fluids

Component	%	Tonnes/year
Lubricity agents/anti-corrosives (amine borates - water soluble)	30	315
Lubricity agents (polyglycol oleates, polyaklylene glycols - water soluble)	5	52.5
Corrosion inhibitors (ethylenediaminetetraacetic acid, diethanolamine, triethanolamine, benzotriazole, tolyltriazole)	3	31.5
Fatty acid	2	21
Biocides	1	11
Extreme pressure additives (phosphate esters - water soluble)	5	52.5
Water	balance	

Note: Content relates to that of the fluid as used.

215. The approximate equivalent of these fluids in Germany are aqueous cooling lubricants (mineral oil free). Information on the composition of these fluids is presented in Table 4.14, relating to the concentrated form of the fluid. As above, dilution of these fluids may depend on the operation for which they are being used and Table 4.10 has examples of dilutions for different metal working processes. In the absence of any specific information, a dilution of 1:20 (concentrate:water) is suggested.

Table 4.14 Composition of aqueous cooling lubricants (mineral oil free) (Germany)

Component	Content
Corrosion protection	20-40%
Neutralization agent (soaping)	15-25%
Solubiliser	10-20%
Friction modifier	5-10%
Water	5-30%
Biocide	3-4%
Fungicide	0-1%

Note: contents refers to that of the concentrate, not of the lubricant as used.

5 RELEASES DURING FORMULATION OF LUBRICANTS

5.1 General

216. The term 'blending' is applied to a lubricant formulating process which involves the simple mixing of two or more components. Where a chemical reaction stage is involved, e.g. during the production of a typical soap-thickened grease, the term 'manufacture' is used.

217. The blending process of a batch-blending operation is briefly described as follows:

218. In order to achieve the desired viscosity in the final product, it is normal to use a mixture of at least two base oils of different viscosities. The required quantities of base oils are introduced into the production vessel using flow meters. It is standard practice to add the lower-viscosity base oil first, followed by the higher-viscosity base oil. If required, the base oils are heated to the specified blending temperature, which is normally a maximum of 60°C. However, many blending plants now carry out the blending operation at ambient temperature, since the saving in heat energy outweighs the increased energy demands of the more prolonged mixing required at the lower temperature. Once the base oil is blended, any necessary additives are added.

219. Liquid additives which are used in substantial quantities are normally stored in bulk, and are metered in, as for the base oils. Smaller quantities may be added directly to the blending vessel via a hatch or man-hole, either in the neat form, or pre-diluted with additional base oil. The pre-dilution may be carried out as a separate operation involving the production of a batch of an additive concentrate, or alternatively some of the base oil from the blend vessel may be pumped into an adjoining decanting vessel. The additive is added to the base oil in the decanting vessel and mixed until homogeneous. The mixture is then pumped back into the main blending vessel.

220. Solid additives which are soluble in the base oil are almost always pre-dissolved in a smaller quantity of base oil before addition to the actual blend. The relatively high energy input into a smaller concentrate preparation speeds up the process of solution. Also a sample can be checked to ensure that the additive is completely dissolved before the concentrate is added back to the main vessel.

221. Some additives, both solid and liquid, are not necessarily soluble in, or miscible with, the base fluid. Examples of such solid additives include graphite and molybdenum disulphide. Normally these additives are of colloidal dimensions to prevent premature separation and are supplied pre-dispersed in a base oil. If the additives are added to the blend in the form of a non-colloidal dry powder, precautions must be taken to ensure that the blend is adequately mixed up to and during the filling-off process to ensure no separation of the blend occurs prior to the filling operation. The use of non-colloidal, insoluble solid additives is confined to grease products.

222. Immiscible liquid additives include, for example, silicone type anti-foaming agents. These products, in order to be effective, need to be substantially insoluble but readily dispersible in the base fluid. Again, such products are normally supplied to the blender as a concentrate pre-dispersed in the base fluid. A range of base fluids may be used to ensure compatibility.

223. Many additives, particularly viscosity modifiers, are difficult to handle on account of their high viscosity. Such additives are pre-heated prior to blending to facilitate their transfer and also to speed up the mixing process. When stored in bulk, additives are normally heated by steam coils in the base of the bulk storage tank. When stored in packages, normally 205 litre steel drums, the additives are heated after removal of the bung closures, by placing in a suitable plant oven which is normally heated by steam or

electricity. Alternatively, they may be heated by placing on a hot-plate, or by surrounding the drum with an electrically-heated jacket or induction-type heater.

224. The blending vessels are normally mixed using conventional paddle mixers or jet mixers, sometimes in combination with re-circulation. Other methods include air sparging, pulse-air mixing, high-shear mixing and passing the fluid through a convoluted chamber to induce turbulence.

225. As an alternative to the batch-blending process described above, continuous or in-line blending can be used in the larger plants. Continuous blending processes, whilst common in the US, are rare in the UK where the volume requirement for lubricants does not justify the use of such equipment.

5.2 Emissions from plant during the blending process

226. Plant emissions are considered under three categories, namely emissions to the atmosphere, aqueous discharges to drain and solid waste.

5.2.1 Emissions to the atmosphere

227. These include emissions of both mists, vapour and particulate materials resulting from the process of formulation.

5.2.1.1 Automotive crankcase lubricants

228. Low volatility at elevated temperatures is an essential requirement in these lubricants as they are designed for use at a bulk liquid temperature of around 80°C, although transient temperatures, particularly in high-performance vehicles fitted with turbo-chargers, can be very much higher. There are specified procedures (DIN 51 581) for measuring volatility.

229. Due to this requirement for low volatility at high working temperatures, the volatility of the base oil and of the other additives used in the formulation of crankcase oils will need to be extremely low at ambient temperatures. The generation of significant quantities of vapour during a formulation process at ambient temperature is therefore virtually non-existent. Also, because of the relatively low energy inputs during the mixing process, the generation of oil mists is also virtually non-existent.

230. Any emissions to the atmosphere will be limited to the following source possibilities:

- **Vapours emitted from bulk storage tank vents from tanks containing base oil and additives**

231. Base oils used in the manufacture of automotive crankcase lubricants do not require heated storage. Their vapour pressures at ambient temperatures are so low (less than 10^{-6} mbar [= 10^{-4} Pa or 1.5 x 10^{-7} mmHg] for a 150 Solvent Neutral Base Oil which is the lower viscosity component of a typical automotive crankcase oil) that vapour emissions from the storage tanks are negligible.

232. Certain of the additives for automotive crankcase lubricants do require heated storage to maintain the viscosity within the limits which are readily pumpable. These additives are normally the viscosity modifiers which consist of relatively high molecular weight polymers. The vapour pressures of these products are again very low and of the same order as those of the base oils.

- **Vapour/mists generated during the transfer of additive from drums into the blending or pre-blending vessel**

And

- **Vapour emitted from open drums of additives during the pre-heating stage**

233. Plant heating ovens are not normally equipped with positive venting as the materials needing pre-heating are relatively involatile and do not give rise to significant quantities of vapour. The most volatile component of lubricant additives is often the base oil in which they are dissolved (see below). Any associated vapours therefore tend to accumulate in the area of the workplace. With the introduction of the COSHH (Control of Substances Hazardous to Health) Regulations in 1988 (in the UK) much evidence has been obtained on workplace exposure levels to oil mists and vapours from both fixed plant monitors and from the use of personal monitors. In the UK the Statutory Occupational Exposure Standards which apply to Oil Mists (General) in the Workplace are as follows (EH40/94):

8 hour TWA(Time Weighted Average)	5 mg/m^3 LTEL (Long term exposure limit)
10 min TWA	10 mg/m^3 STEL (Short-term exposure limit)

234. From a survey of BLF member companies, exposure levels of below 1 mg/m^3 have been habitually recorded for the LTEL. Typical plant general ventilation systems (where present) have an extraction volume of up to 2 m^3/sec for an average size plant. The relative concentrations of the constituents of the mists will be in proportion to their concentrations in the product formulation (i.e. the composition of mechanically generated mists should resemble that of the bulk fluid). The composition of the vapour (and that of any condensation aerosol) will be in proportion to vapour pressure of the components of the bulk fluid.

- **Vapours/mists generated during the blending process**

235. Vessels used for the blending of automotive crankcase lubricants are not normally equipped with local exhaust ventilation since the generation of mists and vapours, particularly at ambient temperatures, is insufficient to warrant such preventative measures. Emissions are therefore covered by the COSHH monitoring described above.

- **Emissions of particulate materials**

236. Particulate materials are very rarely used in the formulation of automotive crankcase lubricants. Probably the only example of the use of such a material is the addition of powdered dyestuff to the product. This again is unusual since such dyes are normally supplied in the form of a liquid concentrate. The occurrence of the use of powdered dyes in the formulation of crankcase lubricants is so small that any emissions arising from this source can be discounted.

- **Gear oils and greases**

237. The environmental emissions associated with the manufacture of gear oils would be intermediate between the situation for engine oils and that for oil-based hydraulic fluids.

238. The environmental impact associated with the manufacture of grease differs in that there is a significant discharge to the atmosphere. By far the most common grease used in automotive applications is a lithium soap-based grease. This is normally manufactured by saponifying hydrogenated castor oil with lithium hydroxide under pressure. During the saponification process, and during the transfer of the soap base to the finishing vessel, there is a discharge of mainly steam which contains small quantities of

glycerol and some free fatty acids, to the atmosphere. Most grease plants are situated in areas where the emission does not pose a problem to any neighbouring establishments. However, at least one plant in the UK has installed a comprehensive emission control system, consisting of a venturi-scrubber, followed by a trickle-filter bed, in order to prevent the emission of such constituents to the atmosphere. The grease is cooled before the addition of any additives.

5.2.1.2 Hydraulic fluids

239. Hydraulic fluids operate at lower temperatures compared with the automotive lubricants; also they operate in sealed systems rather than in positively ventilated systems as in the case of the automotive lubricants. Hence the requirement for low volatility is not as important as it is in the case of the automotive products. In general, however, hydraulic fluids based on mineral oil use base oils with similar volatility characteristics to those used in the formulation of automotive crankcase lubricants. Usually the additive contents of these hydraulic fluids are considerably lower than those of the automotive lubricants. However, a very limited number of additives (notably coupling agents) have been found to have a volatility appreciably greater than those used in the automotive oils. These additives are the exception rather than the rule and can be disregarded in the overall situation.

240. The vast majority of hydraulic fluids are based on mineral oils, to which the emission considerations detailed below apply. The same considerations apply to hydraulic fluids based on vegetable oils. Also, Section 2.4.2.3 refers to fire-resistant hydraulic fluids, which are used in far smaller amounts.

241. In the case of fire-resistant fluids based on non-aqueous fluids, the same general considerations detailed above apply, although the volatility of these products is likely to be even lower than that of the oil-based variety.

242. In the case of the water-in-oil emulsions, the emulsifying additives can contain coupling agents with a relatively high volatility. These products would normally then be prepared in blending vessels equipped with local exhaust ventilation. However, in view of the extremely limited use of this type of product, the overall emission potential is correspondingly low.

243. In the case of the water-glycol type of product, the general considerations detailed above for oil-based products apply, although there is some use of powdered additives, e.g. benzotriazole or tolyltriazole. Again, in view of the extremely limited use of this type of product, the overall emission potential is correspondingly low.

- **Vapours emitted from bulk storage tank vents from tanks containing base oil and additives**

244. Base oils and additives used in the manufacture of hydraulic fluids do not require heated storage. Their vapour pressures at ambient temperatures are so low that vapour emissions from the storage tanks are negligible.

- **Vapour/mists generated during the transfer of additive from drums to the blending or pre-blending vessel**

245. Emissions are covered by the COSHH monitoring described earlier in section 5.2.1.1, i.e. plant and personal monitoring exercises confirm that the levels of vapour involved are extremely low.

- **Vapour emitted from open drums of additives during the pre-heating stage**

246. It is not necessary to pre-heat drums of hydraulic fluid additives prior to use therefore there is no emission potential.

- **Vapours/mists generated during the blending process**

247. Vessels used for the blending of hydraulic fluids are not normally equipped with local exhaust ventilation since the generation of mists and vapours, particularly at ambient temperatures, is insufficient to warrant such preventative measures. Emissions are therefore covered by the COSHH monitoring described above.

- **Emissions of particulate materials**

248. Particulate materials are not used in the formulation of oil-based hydraulic fluids.

5.2.1.3 Metalworking fluids (cutting oils)

- **Neat cutting oils**

249. The additives used in neat cutting oils are occasionally sufficiently viscous to require some mild pre-heating before blending. Again, the vapour pressures involved are low, and similar to those of the base oils. An exception to the general blending operations described previously is the addition of neat sulphur to cutting oils. This can be accomplished by using a concentrate containing free sulphur dissolved in a suitable base oil. However, because of the limited solubility of sulphur in oil (<1%) these solutions have a tendency to precipitate out. Therefore, the addition of sulphur used to be performed at the blending plant by adding flowers of sulphur (pure sulphur in a finely-divided powder form) to a series of aliquots of the base oil which was preheated to a high temperature (normally 115°C if steam heating was used). A high-shear mixer such as a Silverson mixer was used to disperse and dissolve the sulphur, and the sulphur concentrate was then added back to the main blend. The process was repeated until the required level of sulphur was obtained. The potential for volatile, particulate and mist emission from this process was significant, and the operation was always conducted in a vessel fitted with local exhaust ventilation. It is now general practice to add active sulphur in the form of a polysulphide solution, which contains up to 40% sulphur. Sources of this material are now readily available, and the blending process does not now present the potential environmental hazards involved in the handling of neat sulphur as was previously the case.

- **Soluble (emulsifiable) cutting oils**

250. The general considerations for neat cutting oils mainly apply. However, a significant difference in emission potential compared with neat oils is due to the incorporation of coupling agents in the soluble oils. These coupling agents, for example hexylene glycol, are relatively volatile. If the blending process is carried out at an elevated temperature, the mix is cooled to at least below 30°C before the coupling agent is added. This minimises any losses during the process, but the average loss is estimated at a maximum of 10% of this type of additive.

- **Semi-synthetic and synthetic cutting oils**

251. Simple synthetics normally consist of organic and inorganic salts dissolved in water. The blending process is normally carried out at ambient temperature, and the nature of any particulate material is such that dust emission does not occur during the blending process.

252. The more complex fluids will contain, in addition, water-soluble synthetic chemical lubricants, normally polymers such as polyalkylene glycols, which may require some degree of pre-heating to reduce the viscosity. The vapour pressures are again low, even at elevated temperatures, and any losses would be negligible.

5.2.1.4 Calculation of emissions to air

253. From the discussions above, the amounts of oil and additives released to air are expected to be small in the majority of cases. In the absence of more specific information (such as that for soluble cutting fluids) it is suggested that a maximum concentration in air of 1 mg/m^3 is assumed. The following sections indicate how to calculate the quantity of substance (base oil or additive) emitted to the atmosphere. These calculations assume there is no treatment of the air to remove the substances.

- **Base oils**

254. In order to convert the concentration in air to an emission rate the ventilation or air exchange rate is needed. In Section 5.2.1.1 the ventilation rate of an average-size plant is given as 2 m^3/sec (this is taken to be a plant of 30,000 tonnes capacity, which is the largest size suggested for a 'major' lubricants producer in Section 1.2). This is equivalent to 7,200 m^3/hour or 57,600 m^3/day for an 8-hour day. For a concentration in air of 1 mg/m^3 this gives an emission rate of ~58 g/day, which could be used as a basic figure.

255. If more specific information is available then this could be used to replace some or all of the suggested values. An expression for the daily emission can be written as follows:

$$Elocal_{blend,air,\ base} = V_{effective\_air} \times N_{air\_exchange} \times Temission_{blend} \times C_{oil\_in\_air} \times 10^{-6}$$

Explanation of symbols:

$Elocal_{blend,air,\ base}$	= emission rate of base oil to air from blending	[kg.day^{-1}]	
$V_{effective\_air}$	= effective volume of air in the blending plant	[m^3]	suggested default 2400 m^3, which corresponds to a site blending 30,000 tonnes of lubricant per year
$N_{air\_exchange}$	= number of air exchanges per hour	[h^{-1}]	suggested default 3
$Temission_{blend}$	= number of hours worked per day	[h.day^{-1}]	suggested default 8
$C_{oil\_in\_air}$	= concentration of oil in air	[mg/m$^{3]}$	suggested default 1 mg/m^3

256. The effective volume of air in the plant will be related to the capacity for lubricant blending, but is not expected to double for double the capacity. A relationship between the air volume and capacity has been developed as follows:

$$V_{effective\_air} = a * CAPACITY_{site} + b$$

where the capacity is the annual capacity in tonnes, and the constants a and b have the values 0.05 and 750 m^3 respectively. This equation could be used to estimate the air volume to be used.

257. Alternatively the air volume could be estimated from information on the ventilation rate ($FLOW_{air}$, m^3/sec) and the air exchange rate $N_{air\_exchange}$ (exchanges per hour) if these are known:

$$V_{effective\_air} = FLOW_{air} * 3600 / N_{air\_exchange}$$

258. As an example, consider the largest size of multinational plant in Section 1.2, at 100,000 tonnes. From the formula $V_{effective\_air} = a * CAPACITY + b$, the air volume is calculated to be 5750 m^3. The emission rate is therefore (using the suggested default values for the other parameters):

$$Elocal_{blend,\ air,\ base} = 5750 * 3 * 8 * 1 * 10^{-6} = 0.14 \text{ kg/day}$$

- **Additives**

259. As noted in Section 5.2.1.1, the amount of additive in the air emissions will depend on the vapour pressures of the various components. In order to calculate these emissions, a number of assumptions have to be made:

1. The base oil may be considered as a single substance (so only one molecular weight is applicable).

2. The ideal gas law applies.
3. When an additive is added, a binary system is produced to which Raoult's law can be applied (with the two components being the additive and the rest of the oil treated as base oil).

260. In order to carry out the calculations, the vapour pressures and molecular weights of the base oils and the additive are needed. The values for the additive should be available, and are represented as VP_{add} and $MOLW_{add}$ respectively. Values for the three most likely base oil types have been estimated (see Appendix C) and are included in Table 5.1 with the symbols VP_{base} and $MOLW_{base}$ respectively.

Table 5.1 Suggested molecular weights and vapour pressure values for base oils

Base oil type	**Molecular weight ($MOLW_{base}$)**	**Vapour pressure (VP_{base}, units Pa)**
Paraffinic	625	0.004
Organic esters	400	0.006
Synthetic hydrocarbons	800	0.003

261. The first step is the calculation of the mole fraction of the additive and base oil in the lubricant. If the content of the additive in the lubricant is F_{add} (%) by weight, then in 1 kg of lubricant there are 0.01* F_{add} kg of additive and (1-0.01* F_{add}) kg of base oil. The required mole fractions are therefore:

mole fraction base oil = $m_{b,fluid} = 1 - m_{a,fluid}$

$$\text{mole fraction additive} = m_{a,\ fluid} = \frac{0.01F_{add}/MOLW_{add}}{(0.01F_{add}/MOLW_{add}) + (1 - 0.01F_{add})/MOLW_{base}}$$

From Raoult's law the partial pressures of additive and base oil are:

Additive: $p_a = m_{a,fluid} * VP_{add}$

Base oil: $p_b = m_{b,fluid} * VP_{base}$

Hence the mole fraction of the additive in the vapour is:

$$m_{a,vapour} = p_a/(p_a + p_b)$$

$$= \frac{m_{a,fluid} * VP_{add}}{m_{a,fluid} * VP_{add} + m_{b,fluid} * VP_{base}}$$

If the number of moles of additive in the vapour in 1 m^3 of air is χ and the number of moles of base oil is γ, then

$$m_{a,vapour} = \frac{\chi}{\chi + \gamma}$$

and rearranging gives

$$\chi = \frac{m_{a,vapour} * \gamma}{1 - m_{a,vapour}}$$

The number of moles of base oil in 1 m^3 of air can be estimated by assuming that the concentration is solely the oil; hence

$$\gamma = C_{add\_in\_air} * 10^{-3} / MOLW_{base}$$

and hence χ can be calculated. The concentration of the additive in air ($C_{add\_in\_air}$) is given by $\chi * MOLW_{add} * 10^3$ (mg/m^3) and can be used in the same equation as for the base oil emissions:

$$Elocal_{blend,air,add} = V_{effective\_air} \times N_{air\_exchange} \times Temission_{blend} \times C_{add\_in\_air} \times 10^{-6} \text{ kg/day}$$

Symbols used in this section:

$Elocal_{blend,air,\ add}$	= emission rate of additive to air from blending	[kg.day^{-1}]	
$MOLW_{base}$	= molecular weight of base oil	[g.mole^{-1}]	specific information or Table 5.1
$MOLW_{add}$	= molecular weight of additivc	[g.mole^{-1}]	substance information
VP_{base}	= vapour pressure of base oil	[Pa]	specific information or Table 5.1
VP_{add}	= vapour pressure of additive	[Pa]	susbtance information
F_{add}	= additive content in lubricant as formulated	[%]	Specific information, or Tables in Section 4 as appropriate
$C_{add\_in\_air}$	= concentration of additive in air	[mg.m^{-3}]	calculated

Other symbols as in previous section.

- **Example**

For this example, an extreme pressure additive in automotive lubricants is considered.
The properties of the additive are:

Molecular weight ($MOLW_{add}$) = 500
Vapour pressure (VP_{add}) = 3x10^{-4} Pa.
Content in lubricant (F_{add}) = 1.5% (from Table 4.1)

The base oil is taken to be paraffinic; the relevant properties from Table 5.1 are:

Molecular weight ($MOLW_{base}$) = 625
Vapour pressure (VP_{base}) = $4x10^{-3}$ Pa

From this information, the lubricant composition is:

Moles of additive = (0.01 * 1.5)/500 = $3x10^{-5}$
Moles of base oil = (1-0.01 * 1.5)/625 = $1.6x10^{-3}$

The corresponding mole fractions for the fluid are:

$m_{a,fluid} = 0.019$
$m_{b,fluid} = 0.981$

The partial pressures are:

Additive, $p_a = 0.019 * 3x10^{-4} = 5.7x10^{-6}$ Pa
Base oil, $p_b = 0.981 * 4x10^{-3} = 3.9x10^{-3}$ Pa

Hence the mole fraction of additive in the vapour is:

$m_{a,vapour} = 1.46x10^{-3}$

The number of moles of base oil in 1 m^3 of air, assuming a concentration of 1 mg/m^3, is:

$\gamma = 1 * 10^{-3}/625 = 1.6x10^{-6}$

Hence the number of moles of additive in 1 m^3 is:

$\chi = (1.46x10^{-3} * 1.6x10^{-6}) / (1-1.46x10^{-3}) = 2.3x10^{-9}$

and

$C_{add\_in\_air} = 2.3x10^{-9} * 500 * 10^3 = 1.15x10^{-3}$ mg/m^3.

Using this result in the equation for emissions

$$Elocal_{blend,air} = V_{effective\_air} \times N_{air\_exchange} \times Temission_{blend} \times C_{add\_in\_air} \times 10^{-6} \text{ kg/day}$$

and assuming the suggested default values for the other parameters gives the following result:

$E = 2400 * 3 * 8 * 1.15x10^{-3} * 10^{-6} = 7x10^{-5}$ kg/day.

- **Annual emissions**

262. These emission estimates are for daily emissions. There may be a need to estimate annual emissions as well. For the base fluids, it is probably reasonable to assume that they will be used throughout the year and hence usage over 300 days is appropriate. For additives, the tonnage of the additive available should be considered. Two possible approaches based on experiences in The Netherlands and the UK are suggested. In both cases the quantity of lubricant which can be formulated using the known amount of additive at the specified content needs to be determined. For example, if 200 tonnes of an additive are used at a content of 2% in the lubricant, then the maximum amount of lubricant which could be formulated

using this additive is 10,000 tonnes. The first proposal is that for a lubricant tonnage of less than 1,000 tonnes, a production period of 50 days is assumed. For a tonnage between 1,000 and 5,000 tonnes 100 days production is assumed, and for greater than 5,000 tonnes a 300 day period is assumed.

263. As an alternative, the quantity of lubricant could be compared with the capacity of the typical plant, assumed to be 30,000 tonnes if no other information available. For the example above, the quantity of lubricant is one-third of the capacity. It could hence be assumed that the lubricant would be produced for one third of the time, ie 100 days. This method will probably under-estimate the number of days, as it is unlikely that a large site would produce only one specific lubricant at a time.

5.2.2 Liquid waste from blending plants

5.2.2.1 Waste product

264. A certain amount of waste product will always be generated at any lubricants blending plant. Off-specification product which cannot be rectified, such as line flushings and vessel flushings, add to the accumulation of waste. However, the lubricants industry currently operates to very tight margins, and such waste product is in the main re-used and not disposed of.

265. Off-specification material can be down-graded to a product of lower specification, even though this may entail some quality 'give-away'. Alternatively, it can be blended away in a series of subsequent batches of the same or similar product, the addition rate of the off-specification product would have been pre-determined so as not to jeopardise product quality.

266. The generation of line flushings is minimised by the use of dedicated or piggable pipework; any flushings would normally be stored and added back to a suitable subsequent blend or blends.

267. The generation of vessel flushings is minimised by the use of dedicated blending vessels, restricted to a single blend 'family'. Products belonging to a blend family are similar in general composition, and therefore some degree of 'carry-over' is permissible between successive batches of product. The main blend families are:

Straight base oils - No additives
Hydraulic oils, compressor oils
Zinc-free hydraulic oils, compressor oils
Automotive and diesel crankcase oils, automatic transmission fluids
Zinc-free engine oils
Extreme pressure gear oils (leaded)*
Extreme pressure gear oils (non-leaded)*
Neat cutting oils
Oils containing fats
Low flash-point oils
Soluble oils
Synthetic (water-based fluids)
Synthetic (polymer-based) fluids

Note: * 'leaded' refers to the oil not the fuel. Lead is very effective as an extreme pressure agent but its use will gradually reduce, primarily due to new regulations.

268. Vessel flushings normally arise from the changing of duty of a vessel from one blend family to another. Again, the flushings would be stored and added back to the next suitable product.

269. It will be seen that any product waste which would be generated from a blending plant is almost 100% re-usable. Loss rate of a maximum of 2% are the norm for many oil blending plants. Large plants (≥25,000 tonnes/year, of which there are about 6 in the UK), with sophisticated flushing and pigging systems generally record loss rates of below 1%. Any that cannot be used would be sold off to a licensed waste carrier for disposal or reuse (see Section 9). The plant losses of 2% maximum would consist of irrecoverable waste oil which would be collected by a contractor together with losses to drain (see section 5.2.2.2).

5.2.2.2 Waste effluent

270. The generation of waste effluent from blending plants is highly dependent upon factors such as housekeeping, plant maintenance, etc. Blending plants are normally equipped with oil capture and recovery systems, e.g. plate interceptors, which prevent the unrestricted passage of free oil into the drainage system and thereby to the sewage treatment plant. Recovered oil is skimmed off or diverted to an oil collection tank, the waste oil is collected at intervals by a licensed waste carrier. The vast majority of the additives would remain in the oil.

271. In the UK, the regulatory authority is the Environment Agency (EA), which stipulates that 'no visible physically separable dispersed oil or emulsified oil shall be present' in effluent. In practice, this equates to about 5 ppm of oil in water. Discharge consent limits can however vary throughout the country according to the specific requirements of the local authority. The figure of 5 ppm oil is generally regarded as the maximum acceptable level by most local authorities since at this level the residual oil becomes visible as a contaminant, but lower levels can be demanded in situations where there is possible contamination of e.g. inland waterways. The vast majority of blend plants operate well within the acceptable level of 5 ppm. Regular sampling and analysis by local authorities ensures compliance, since non-compliers are fined and persistent non-compliances can result in plant closure. 5 ppm therefore represents a realistic worst case. A typical COD content would be 600 ppm. Factors affecting such limits can include the total effluent volume, the quantitative and qualitative loading of the relevant effluent treatment plant, restrictions on the final quality of the treated effluent, etc. Total plant effluent volumes are related to the surface area occupied by the plant (rainfall capture potential), the geographical location of the plant and also the frequency and extent of housekeeping operation such as yard washing.

272. Floor surfaces which become contaminated with oil, which may occur due to seepage and leaks from pumping, are generally cleaned by mechanical scrubbing together with a suitable solvent, e.g. kerosene. The solvent is then sorbed onto sawdust or a propriety sorbent, which is shovelled up and transferred into sacks for disposal as solid waste to landfill.

273. The only major potential problem area involves the possibility of spillage to drain of any emulsifiable cutting fluids. Such products, if allowed to enter the oil/water separator system, can result in the solubilisation of substantial amounts of separated oil, with consequent contamination of the aqueous effluent. For this reason, any lubricant plant involved in the production of such products is normally well-bunded, and the drainage system is physically separated from the normal plant system. Major spills and accidental releases are not covered by this report.

274. A reasonable worst case estimate of loss to water within the blending plant for the UK would be 0.25%. This would be before the operation of any interceptor treatment as described above. The eventual discharge of oil would be a maximum of 5 ppm, the limit of visibility. As an indication of the volume of water in which such a discharge will occur, a site in the UK producing 10,000 tonnes of lubricants has an

annual total aqueous discharge of 10^6 litres. This is equivalent to 100 litres per tonne of lubricant. The discharge of 5 ppm of base oil is equivalent to an emission factor of $5\text{x}10^{-4}$ kg/tonne lubricant.

275. As far as the additives are concerned, the extent to which they are removed will depend on their partitioning properties. A worst case assumption would be that all the additive was released in the water. As noted above, the majority of additives would be expected to remain in the oil. Experimental measurements on the additive of interest in the actual oil-water system would be preferred. If this is not available, an estimate of the partitioning can be made, based on the following assumptions:

1. The base oil has similar partitioning properties to those of octanol.

2. The oil-water separation system allows time for equilibration between the oil phase and the water phase.

276. The release figures from above are also used, so that the release of oil to water within the plant is 0.25%, and the maximum concentration of oil in water leaving the plant is 5 ppm.

277. If the content of the additive in the lubricant is F_{add} (%), then the amount of additive in 1 kg of lubricant is $0.01 \times F_{add}$ kg. The maximum release of lubricant is 0.25%, or 2.5 kg per tonne of lubricant. So the maximum release of additive is $0.025 \times F_{add}$ kg per tonne.

278. If the density of the lubricant is $RHO_{lubricant}$ kg/l then the concentration of additive in the lubricant is

$$C_{add\_in\_lubricant} = 0.01 \times F_{add} \times RHO_{lubricant} \text{ kg/l.}$$

279. Note that this is the concentration of the additive in the lubricant as formulated. In the sections on metal working lubricants, a distinction is made for some types of lubricant between the concentrated form and the lubricant as used. For those types of fluid the concentrated form is being considered here.

Assuming a value of 0.9 kg/l for the density, $C_{add\_in\_lubricant} = 9\text{x}10^{-3} \times F_{add}$ kg/l.

Using the octanol-water partition coefficient of the additive Kow as a measure of the partitioning between the base oil and water

$$K_{ow} = \frac{\text{concentration in oil phase } (C_{add\_in\_lubricant})}{\text{concentration in water phase } (C_{add\_in\_water})}$$

and hence $C_{add\_in\_water} = C_{add\_in\_lubricant}/K_{ow}$

thus

$$C_{add\_in\_water} = 9\text{x}10^{-3} \times F_{add}/\text{Kow kg/l}$$

Water use per tonne is 100 litres, (from above) so the loss of additive per tonne of lubricant is $0.9 \times F_{add}/K_{ow}$.

280. This is the loss of additive dissolved in water. There will also be loss of additive in the oil which is released in water. The maximum level of oil in water is taken to be 5 ppm, or 5 mg oil per litre of water. The concentration of the additive in oil will be that in the formulated lubricant as a maximum; this is F_{add} (%), or $0.01 \times F_{add}$ kg additive per kg oil. Therefore in 1 litre of water there are $5\text{x}10^{-6} \times 0.01 \times F_{add}$ or $5\text{x}10^{-8}$

$\times F_{add}$ kg of additive. The typical water usage per tonne of lubricant produced is 100 litres, so the release of additive in oil per tonne is $5x10^{-6} \times F_{add}$.

281. The combined release in water (as dissolved substance and in oil) is

$$F_{blend,\ water,\ add} = 0.9\times F_{add}/K_{ow} + 5x10^{-6} F_{add} = F_{add} \times(5x10^{-6} + 0.9/K_{ow}).$$

282. This approach gives a reasonable estimate for high values of Kow, but at low values the results exceed the maximum possible release estimated above - for example, a Kow of 1 gives a release of $0.9 \times F_{add}$ kg per tonne, while the maximum possible release is $0.025 \times F_{add}$ kg. In order to accommodate the lower values of Kow, the calculation needs to take into account the relative volumes of the oil and water.

283. The amount of additive lost per tonne of lubricant is $0.025\times F_{add}$ kg. Let

$Q_{add,\ oil}$ = mass of additive in oil phase
$Q_{add,\ water}$ = mass of additive in water phase
V_{oil} = volume of oil phase
V_{water} = volume of water phase

Then

$$K_{ow} = \frac{Q_{add,\ oil} / V_{oil}}{Q_{add,water} / V_{water}}$$

and $Q_{add,\ oil} + Q_{add,\ water} = 0.025\times F_{add}$

From above, the volume of water per tonne is 100 litres, i.e. V_{water} = 100 l. The amount of oil is 0.25%, or 2.5 kg; at a density of 0.9 kg/l this is a volume of 2.8 litres, ie V_{oil} = 2.8 l. Hence

$$K_{ow} = \frac{Q_{add,oil} / 2.8}{Q_{add,water} / 100}$$

and rearranging, $Q_{add,\ oil} = 0.028 \times K_{ow} \times Q_{add,\ water}$

Also, $Q_{add,\ oil} = 0.025 \times F_{add} - Q_{add,\ water}$

Hence: $0.028 \times K_{ow} \times Q_{add,\ water} = 0.025 \times F_{add} - Q_{add,\ water}$

And so the mass of additive released in water (in kg) per tonne of lubricant produced is given by:

$$Q_{add\ ,water} = F_{blend,\ add\_in\_water} = \frac{0.025\times F_{add}}{0.028\times K_{ow} + 1}$$

There will also be some release of additive in the oil released to water from the plant; this will more significant at higher values of Kow. The mass of additive in the total oil volume per tonne of lubricant is

$Q_{add, oil} = 0.025 \times F_{add} - Q_{add, water}$

or

$$Q_{add, oil} = 0.025 \times F_{add} \left(\frac{0.028 \times K_{ow}}{0.028 \times K_{ow} + 1} \right)$$

Only a fraction of this oil is released to water, as the concentration of oil in water is 5 ppm as a maximum. In 100 litres of water this is 500 mg, which is 500 mg/2.5 kg of the total amount of oil, or a fraction of $2x10^{-4}$. Hence the amount of additive released to water through oil per tonne of lubricant (the emission rate) is $2x10^{-4} \times m_o$, or:

$$Q_{add, oil} = F_{blend,add\_in\_oil} = 5 \times 10^{-6} \times F_{add} \left(\frac{0.028 \times K_{ow}}{0.028 \times K_{ow} + 1} \right)$$

As the Q_{add} quantities are expressed per tonne of lubricant they are equivalent to emission factors.

- **Summary**

The derived equations for emission factors for releases to water from lubricant blending are as follows.

$F_{blend, water, base} = 5x10^{-4}$ kg/tonne of lubricant

$$F_{blend, add\_in\_water} = \frac{0.025 \times F_{add}}{0.028 \times K_{ow} + 1}$$

$$F_{blend, add\_in\_oil} = 5 \times 10^{-6} \times F_{add} \left(\frac{0.028 \times K_{ow}}{0.028 \times K_{ow} + 1} \right)$$

Where log Kow is greater than 3, simplified equations can be used:

$F_{blend, add\_in\_water} = 0.9 \text{ x } F_{add}/Kow$

$F_{blend, add\_in\_oil} = 5x10^{-6} * F_{add}$

For both cases, the total emission factor is:

$F_{blend, water} = F_{blend, add\_in\_water} + F_{blend, add\_in\_oil}$

Explanation of symbols:

$F_{blend, water}$	= emission factor to water from blending	[kg.tonne^{-1}]	Per tonne of lubricant blended
F_{blend, add_in_water}	= emission factor to water in water	[kg.tonne^{-1}]	Per tonne of lubricant blended

	phase from blending		
$F_{\text{blend, add\_in\_oil}}$	= emission factor to water in oil phase from blending	[kg.tonne^{-1}]	Per tonne of lubricant blended
F_{add}	= additive content in lubricant as formulated	[%]	Specific information, or Tables in Section 4 as appropriate
K_{ow}	= octanol-water partition coefficient		From substance information

These estimates of release have to be multiplied by the daily production tonnage at a site to estimate the daily release, and by the number of days of operation for the annual releases. The same comments as above for the air releases apply here.

- **Example**

284. As an example of the calculation method, consider a neat cutting oil, containing 10% chlorinated paraffin. The additive is present at 10% by weight, and the log Kow value is taken as 6.5. The base oil is a paraffinic mineral oil. Using the full equation for $F_{\text{blend, add\_in\_water}}$ from above:

$$F_{\text{blend, add\_in\_water}} = \frac{0.025 * 10}{0.028 * 10^{6.5} + 1}$$

$$= 2.8\text{x}10^{-6} \text{ kg/tonne}$$

$$= 2.8 \text{ mg/tonne lubricant.}$$

From the equation for the release in oil, $F_{\text{blend, add\_in\_oil}}$ is calculated as

$$F_{\text{blend, add\_in\_oil}} = 5\text{x}10^{-6} * 10\left(\frac{0.028 * 10^{6.5}}{0.028 * 10^{6.5} + 1}\right)$$

$$= 50 \text{ mg/tonne}$$

Hence the total amount released is 53 mg/tonne.

285. Table 4.5 indicates that the total UK production of this type of cutting fluid is 7,000 tonnes per year. Assuming that all of the fluid produced contained the same additive, the two methods for estimating the number of days of production in Section 5.2.1.4 give 300 days or 70 days. These correspond to daily production quantities of 23 tonnes and 100 tonnes respectively, and to daily releases of 1.2 g or 5.3 g respectively. The annual release is calculated as 371 g/year.

5.2.2.3 Residues in drums of additives

286. Current requirements by drum reconditioners in the UK are that for drums to be classified as 'empty' they must contain less than 1% by weight of residue. Many additives are viscous in nature, and appreciable quantities can remain in the drums if no special precautions are taken. Since the cost of additives is generally very much higher than the cost of the base oil, lubricant blenders take care to ensure that the minimum quantities of additives remain in the drum. In practice, once the contents of an additive drum have been removed, normally by inserting a standpipe, base oil is transferred back to the drum in order to dilute any residue and flush the drum before sucking the contents back. Thus if the maximum of

1% of the additive package is left in the drum initially, this will be diluted 100-fold with base oil on rinsing. When this oil is removed the drum will then contain a maximum of 1% of the diluted additive in oil, with a maximum additive package content of 0.01%. The drums will then be sent to drum reconditioners for complete cleaning. On arrival at the reconditioning plant, drums are examined to assess the thickness, physical condition and previous contents before being categorised and designated for the type of reconditioning required. Drums are reconditioned by cleaning internally and externally with an aqueous caustic solution or by furnace cleaning and shot blasting. In the US, all drums containing petroleum-based materials are furnace cleaned in re-conditioning.

5.2.3 Solid waste from blending plants

287. Solid waste product from lubricant blend plants is normally confined to greases and waxes. Section 2.4.1.5 refers to an annual UK production tonnage of some 30,000 tonnes of grease. An upper level of waste grease of, say, 1.5% would therefore correspond to some 450 tonnes per annum of scrap grease. However, scrap grease is often used for low demand applications such as a cheap anti-corrosion protective or for smearing onto paint-booths. The actual amount scrapped to landfill in the UK is probably in the region of 250-300 tonnes per annum.

5.3 Summary

288. Lubricant blending plants, unlike lubricant refineries or recycling plants, are not regarded as 'Prescribed Processes' by the Environment Agency in the UK. Atmospheric emissions of VOCs (volatile organic compounds) are extremely low because of the generally involatile nature of lubricants and their associated additives.

289. The oil contents of aqueous waste from lubricants plants are normally maintained within the consent limits, according to in-house monitoring records. The effluents are also monitored externally by the appropriate local water company. Due to the comparatively high viscosity of most lubricants (compared with e.g. motor spirit or water), accidental spillages are normally readily contained.

290. The greatest loss a manufacturer would tolerate would be in the region of 1%, and a maximum of 2%. Of this, by far the greatest part would be in controlled losses, i.e. off-spec material that could not be reused. This would then be sold to contractors. The other loss would be to drum reconditioners. Overall, losses to the atmosphere are expected to arise only from pre-heating and blending and to be very low. Methods to estimate these releases have been developed. A worst case estimate for loss of additive to drain in the UK would be 0.25%, assuming all the additive partitions into water. Losses of oil to drain are not expected to exceed 5 ppm. Methods have been developed to estimate releases of base oil and additives to water and to take account of partitioning between oil and water. Solid waste is confined to greases and waxes and will be approximately 250 - 300 tonnes per year in the UK.

6 AUTOMOTIVE LUBRICANTS AND ADDITIVES

291. Information in this section is based on experience in the UK. The fate of used oil in particular may be different in other countries. If more specific information relating to the region of interest is available then this should be used.

6.1 Possible losses during use

292. Loss of lubricant during use has decreased dramatically during the past few years due to a number of factors, including improvements in the lubricants, in fuel and in the vehicles themselves. The improvements achieved in passenger car crankcase lubricants over the years can be seen in oil consumption statistics. For vehicles of model years 1949 and 1972 the oil consumption was 0.5 and 0.25 l/1000 km respectively. For vehicles of model year 1992 the oil consumption is between 0.1 l/1000 km and 0.01 l/1000 km. However this reduction in losses from individual vehicles is offset at least in part by the increasing number of vehicles in use.

293. It has been estimated that 25% (weighted average) of lubricants used in both passenger cars and commercial vehicles is consumed during use. Most of the used lubricant is present in the exhaust gases as either combustion products or particulates. 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. A small amount (~ 0.5%) is lost as a result of leakage.

294. Positive crankcase ventilation is designed to eliminate the emission of any vapourised lubricant from the engine by connecting the crankcase breather to the inlet manifold. Any vapourised lubricant is then subjected to the combustion process before discharge to the atmosphere in the exhaust gases. (See also Section 6.5).

6.2 Frequency of dosage/renewal

295. Oil changes are specified by the vehicle manufacturer. They are generally based upon vehicle mileage, with scope for more frequent changes during particularly arduous use, e.g. dusty climates, short journeys involving frequent stopping and cold-starting, low annual mileage, etc. For low mileage vehicles, where the annual mileage is below the mileage interval specified for oil changes, the manufacturer will generally recommend that the oil is changed on an annual basis, rather than at the specified mileage. However, the vast majority of vehicles in the UK are subjected to oil changes at the normal recommended mileage, and, for the purposes of this report, this situation is assumed valid for the total vehicle population. Figures for the amounts of used oil from road vehicles are given in Table 6.1.

296. Losses in charging and waste oil in containers amounts to approximately 6,000 tonnes/year in the UK. Approximately 500 tonnes/year are released to waste water, 4,000 tonnes/year to landfill and 1,500 tonnes/year are reused.

Table 6.1 Weighted average quantities of used oil from road vehicles

	Passenger cars (petrol)	**Passenger cars (diesel)**	**Commercial heavy duty diesel**
Oil change (km)	15,000	10,000 (5,000 - 15,000)	15,000 (5,000 - 45,000)
Oil flush	No	No	No
Sump capacity (l)	4	4	30
Annual mileage (km)	19,300	24,200	96,600
Oil changes per year	1.3	2.4	6.4
Used oil per car per year (l)	5.2	9.6	193.2
No. vehicles*	18,091,800	2,010,200	535,000
Used oil per year (l)	9.4×10^7	1.9×10^7	1.03×10^8

* DoT Transport Statistics for Great Britain - 1994. Based on the assumption that diesel vehicles account for 10% of all cars and commercial heavy duty diesel include goods vehicles and public transport vehicles.

6.3 Form in which lubricant is discharged

6.3.1 Used oil

6.3.1.1 Base oil degradation

297. The ageing of mineral oils occurs through thermal stress or oxidative changes of the base oil, which are accelerated by high temperatures. Oxygen is readily soluble in mineral oil and rapidly diffuses throughout the oil. Oxidation proceeds by the formation of peroxides by a free radical chain mechanism.

298. The rate of degradation of and the degradation products formed from the base oil will depend upon the extent of refining:

* Mildly refined oils are inclined towards sludge formation (high molecular-weight oxidised products) and less to the formation of acids, because they contain a relatively large amount of sulphur-containing components which act as natural inhibitors by decomposing peroxides and preventing further oxidation.

* Highly refined oils form acids more readily since the natural inhibitors are removed during the refining process.

299. In both cases, degradation products can consist of a variety of oxidised components of the base oil, including free acids, aldehydes, ketones and alcohols. Secondary reactions leading to an increase in viscosity as a result of an increase in molecular size include condensation and polymerisation. Loss of the lighter components by evaporation can also lead to an increase in viscosity.

300. Also of note is the production of polycyclic aromatics which are present in virgin base oil in negligible quantities and are generated and do accumulate in petrol (not diesel) engines. This is primarily a human health problem.

6.3.1.2 Additive changes

301. Typical changes in additive chemistry in used engine oil are shown in Table 6.2 below.

Table 6.2 Changes in additive chemistry after oil use (ATC 1993)

Additive component	**% changed[a]**	**Changed to**
Detergent	46	Adsorbed film on small particles kept in suspension. Calcium and magnesium carbonate, calcium and magnesium sulphates/neutralisation products including bound water.
Ashless dispersant	16	Adsorbed film on small particles kept in suspension. Neutralisation by acidic combustion species.
Zinc dialkyldithiophosphate	45	Phosphates, thiophosphates, metal sulphides, mercaptan metal salts, zinc pyrophosphate, zinc sulphide, zinc oxide. Adsorption and chemisorption on metallic engine surfaces of chemical decomposition products of ZDDP
Antioxidant	45	Formation of oxidation product. Thermal decomposition.
Viscosity modifier	9	Thermal decomposition products. Mechanically sheared polymer.

a - the % changes refer to the physical or chemical change to the active ingredient content of the additive at the end of the oil drain period, and not to the total additive which contains diluent oil.

302. Changes to the composition of lubricant lost before the end of the oil drain period, e.g. by leakage, will be proportional to the mileage covered.

6.3.2 Exhaust emissions

303. This section describes the fate of the lubricant and additives consumed during use. The following general assumptions are made:

- Base oil and additives are burnt at the same rate. (This suggests that the additive content of drained oil is the same as in the unused lubricant. In practice, the additive content of the used lubricant is normally greater than the additive content of the unused lubricant, since the volatility of the base oil is generally higher than that of the additives.)
- All nitrogen in the lubricant is converted to oxides of nitrogen.
- All the additive metals burnt during combustion contribute to particulate formation.
- The amount of combusted lubricant which contributes to engine deposits is insignificant compared with the total combustion products.
- A small percentage of the lubricant additive carbon contributes to particulate formation in petrol engines.

304. Not all combustion products pass through the exhaust system, some are captured by the crankcase lubricant (blowby and positive crankcase ventilation systems)

305. The following sections give more details based on the elements contained in the additives.

- **Carbon**

306. In both petrol and diesel engines the contribution from additives is small. For petrol, the most significant contribution (hydrocarbons and nitric oxides) is just 0.4% of the regulated emission level. For diesels, the major contribution is to particulate emissions, where up to 15% of the regulated weight may originate from the lubricant additives.

307. On the basis of ATC and industry statistics (ATC, 1993; Volkswagen 19XX), it is assumed that: 20% of lubricant consumed in trucks contributes to particulates, 20% goes to CO, 20% to hydrocarbons, 5% remains suspended in the oil and the remainder is burnt to CO_2. For gasoline engines, 5% of the lubricant consumed contributes to particulates, 5% goes to CO, 5% to hydrocarbons, 1% remains suspended in the oil and the remainder is burnt to CO_2. These figures vary widely in practice, according to operating conditions (i.e. idling when stationary, running under full load, etc.).

308. The fate of fuel carbon during combustion is:

	Particulates	CO_2	CO	HC
Cars (non-catalyst)	0.1% wt.	88.0	11.2	0.7
Trucks (")	0.3	99.0	0.6	0.1

309. Additive carbon contributes similarly in proportion to the emission categories above.

310. The attainment of reduced emission levels by suitable engine design and operating conditions is dependent upon lubricant technology.

- **Nitrogen**

311. Lubricants contain only low levels of nitrogen. As a reasonable worst case, it is assumed that additive nitrogen contributes to the regulated nitric oxide emissions, but in practice the contribution is very small compared with that from the atmospheric nitrogen which is combined during the combustion process.

- **Metals**

312. It is assumed that all additive metals burnt during combustion contribute to particulate composition. Magnesium and calcium form sulphates, zinc forms zinc oxide and zinc pyrophosphate.

- **Chlorine**

313. Crankcase lubricants no longer contain chlorine as a deliberately added functional component. However, some important classes of additive (some detergents, ashless dispersants, etc.) contain traces of chlorine as a by-product of the manufacturing process. Also, road-salting operations can result in the contribution of traces of chlorine to engine oil. Studies have since shown that the trace amounts of chlorine present in commercial engine lubricants do not contribute to vehicle dioxin and furan emissions, within the detection limits and test capabilities currently available. The current level of chlorine in used motor oil is around 200-300 ppm, which emanates mainly from additives, although not deliberately added as such.

- **Phosphorus**

314. Ashless anti-wear additives occasionally contain phosphorus but the most common source of phosphorus is from zinc dialkyldithiophosphate, which is typically present in PCMOs at 1.2% and in HDDOs at 1.4%. This level is not considered to be detrimental to catalyst life.

6.4 Concentration of chemical in discharge

315. Table 6.3 contains information on the typical elemental composition of used engine oil.

Table 6.3: Typical composition ranges of used engine oil

Element/chemical	Concentration (ppm)	Comments
Sulphur	1,000-10,000	From additives and base oil
Calcium	1,500-2,000	From additives
Magnesium	130-900	From additives
Phosphorus	880-1,400	From additives
Zinc	1,000-1,100	From additives
Nitrogen	80	From additives
Copper	30-75	Wear element
Tin	15-60	Wear element
Iron	80-100	Wear element
Lead	300-700	From fuel (diminishing)
Chlorine	250-3,000	Scavenger/contaminant

316. Details of the nature of the degraded additives are given in Section 6.3.

6.5 Volume of discharge - fate in environment

317. The fate of used automotive crankcase oils is summarised in Table 6.4. The figures in this section all relate to the UK unless noted.

318. There will be a certain amount of loss due to spillage when crankcases are filled and due to a residue of oil remaining in the containers. This is estimated to be 1.5% of the total. i.e. 6000 tonnes/year.

319. According to ATC estimates (ATC, 1993), some 25% of the lubricant is consumed during use (this includes loss due to leakage). This figure is based on historical evidence and may be on the high side, bearing in mind recent improvements in engine design and sealing. Of this, lubricant which is combusted and discharged with the exhaust emissions amounts to up to 100,000 tonnes/year, i.e. emission to atmosphere of largely combusted lubricant, although there will be a significant proportion of unburnt lubricant in emissions from older engines (Pereira et al, 1983).

320. ATC have estimated that 1% (4,000 tonnes/year) of lubricant is lost due to leakage. Further information would be needed in order to be able to consider local emissions to road surfaces, or the impact

on the local environment at the edge of a road (this would also apply to other types of chemical such as those used in rubber in tyres). It is suggested that the leaked oil is assumed to be largely washed from the road surface by rainwater, and can be treated as a diffuse emission to surface water or soil. The composition will vary according to the lubricant mileage of the depositing vehicle. Alternative scenarios to calculate a concentration in run-off water or in roadside soils are included in Appendix D.

321. The 298,000 tonnes/year of drained lubricant is distributed as follows:

- Up to 100,000 tonnes/year is used in-house mainly for heating. Some 40,000 tonnes/year is used in garages and workshops alone since they have an internal supply of cheap heating fuel in the form of used engine oil. Some garages sell surplus collected oil since the quantity collected often exceeds their own requirements. This is probably sold to a variety of neighbouring industrial factories in the vicinity of the particular garage, who would welcome the opportunity of a cheap form of heating. Although all such forms of heating are registered with the local authorities, and should conform to exhaust emission regulations, the situation is difficult to police. Exhaust emissions are likely to contain small quantities of lead, and possibly even dioxins due to contamination by chlorine in the waste oil (up to 1500 ppm). The lead emission situation will improve as the use of unleaded fuel increases. Vehicle dismantlers drain fluids from vehicles before dismantling/scrapping, but the fate of the drained lubricant varies between establishments. The more professional organisations use some of the drainings as a direct fuel source, and sell off any surplus to waste oil collectors. Waste oil is used for boiler plant and air heaters and for direct processes such as cement kilns, roadstone kilns, fluidised beds and incinerators. Smaller operators dispose of the lubricant in a variety of ways.

- 55,000 - 106,000 tonnes/year is collected, laundered, and used as fuel oil by oil recyclers who undertake simple laundering and then resell. The oil may be blended with other fuel oil. Thus there will be emissions of oxidised components to the atmosphere.

- 86,000 - 137,000 tonnes/year of total used oil is unaccounted for. The largest single contribution is probably from DIY car maintenance, and the majority is likely to be poured down drains, over soil, or put in a container and disposed of to municipal waste. With the increasing sophistication of vehicle technology, i.e. computerised engine management systems, the extent of DIY maintenance is likely to diminish. Also, with the tendency to smaller sump capacities and more extended oil drain intervals, the amount of waste oil which is unaccounted for is likely to diminish.

322. Small amounts of used engine oil are used for other purposes such as corrosion protectives, wood preservatives, mould release agents for concrete shuttering, etc. although these practices are likely to diminish as the hazards of used engine oil become better appreciated.

Table 6.4: Summary of fate of automotive crankcase oils in the UK

	Quantity inUK tonnes/year	% of total	Environmental fate (release factor)
Spillage losses on charging/oil left in containers	500 4,000 1,500	0.125 1 0.375	wastewater ($F_{\text{filling, wastewater}}$) landfill ($F_{\text{filling, landfill}}$) waste oil for re-use($F_{\text{filling, re-use}}$)
Consumed in use[a]	96,000 4,000	24 1	exhaust emissions to air, largely combusted ($F_{\text{serv, burned}}$) leakages to soil/water ($F_{\text{serv, soil}}$ or $F_{\text{serv, water}}$)
Used oil	100,000[b] 55,000-106,000[c] 86,000-137,000[d]	25 13.75-26.5 21.5-34.25	Re-used as fuel oil in house ($F_{\text{disp, re-use in house}}$) Re-used as fuel oil after treatment ($F_{\text{disp, re-use after treat}}$) Home use: disposed to wastewater/soil/landfill ($F_{\text{disp, watewater}}$ or $F_{\text{disp, soil}}$ or $F_{\text{disp, landfill}}$)
TOTAL UK market	400,000		

Notes:

a - ATC, 1993. Lubricant Additives and the Environment. Additive Technical Committee Document 49.

b - Warren Spring Laboratory, Feb 1983. 'The Combustion of Waste Oil and Emission Measurements. ISBN 0 85624 333 7.

c - The total collected for use as fuel oil would include companies which subject the collected oil to a laundering process before offering it for use as a fuel oil component.

d - UKPIA/BLF, June 1994. Used Luboil Report. UKPIA/BLF Working group.

Also - Bardos RP, Barton J et al, June 1994. Market Barriers to Materials Reclamation and Recycling, Chapter 11, Waste Mineral Oil. Warren Spring Laboratory Report LR861(MR).

323. Looking at the wider picture than the UK, ATC (1993) estimated that around one third of the automotive lubricants used in OECD Europe were lost by spillage and dumping. There are incentives in place in some countries to try to reduce or prevent these losses. These include

- taxes and subsidies
- obligations on vendors
- restrictions on over-the-counter sales
- transportation franchises
- collection sites and kerbside pickup
- public procurement
- public education.

324. There are also differences between countries in the way that oil changes take place. In some countries, oil changes are mostly carried out by motorists themselves (‘do it yourself’) while in other countries this is mainly carried out at vehicle workshops and service stations.

325. Of the used engine oil which is collected in OECD Europe (about 40% of that used), half is incinerated and half re-refined or reused (ATC 1993).

326. The disposition of used crankcase lubricating oils in the US is given in Table 6.5 (data from 1988). This information is taken from the USEPA draft scenario for lubricant additives (US EPA 2000). Based on practices in the US, the draft scenario document considers that emissions to the environment from crankcase lubricant oil disposal are negligible.

Table 6.5 Disposition of used lubricating oils in the US

0 Disposition	1 Auto service stations		2 Do-it-yourself	
	3 Mgal/year	4 % of total	5 Mgal/year	6 % of total
7 Burned	8 258	9 83.2	10 8	11 4.1
12 Lube oil and non-fuel	13 28	14 9.0	15 10	16 5.2
17 Dumped	18 15	19 4.8	20 118	21 60.8
22 Landfilled	23 5	24 1.6	25 58	26 29.9
27 Road oiling	28 4	29 1.3	30 0	31 0
32 **Total used oil handled**	33 310	34	35 194	36

Note: 1 m^3 = 264.2 gal.

6.6 On-site waste treatment

327. On-site treatment is not applicable to these products.

6.7 Example release calculation

328. Antioxidant in crankcase oil for passenger cars

Total usage in EU	2,000 tonnes per year
Concentration in lubricant	1% (Table 4.1)

329. Disperse release are calculated from the use and disposal of lubricant.

Loss through spillage on filling	= 1.5% made up of (Table 6.4):
0.125% to water ($F_{filling, wastewater}$)	= 2.5 tonnes antioxidant
1% to landfill ($F_{filling, landfill}$)	= 20 tonnes antioxidant
0.375% to waste ($F_{filling, re-use}$)	= 7.5 tonnes antioxidant (re-used)
Loss in use (whole lubricant)	= 25% made up of (Table 6.4):
24% burnt ($F_{serv, burned}$)	= 480 tonnes antioxidant
1% leakage to soil/water ($F_{serv, soil}$ or $F_{serv, water}$)	= 20 tonnes antioxidant

330. The lubricant is drained from the crankcase at the end of its working life. The fate of the drained lubricant is described in Table 6.4. However, degradation of the antioxidant during use also has to be considered ($Fadditive_{serv\_elim}$). Table 6.2 indicates a degradation of 45% for antioxidants. The percentages in Table 6.4 refer to the original quantity of lubricant and so need to be reduced by 45% to take account of the degradation of the antioxidant in this example. The results are shown in Table 6.6.

331. These releases apply to the whole of the EU. One tenth of these could be used as the input to a $PEC_{regional}$ calculation. For example, the regional losses to waste water from filling ($RELEASEreg_{proc, waste-water}$ considering this as a processing step) would be 250 kg/year; losses to soil during use ($RELEASEreg_{serv, soil}$) would be 2 tonnes/year assuming an even split between soil and water; and the losses on disposal ($RELEASEreg_{disp, waste-water}$ and $RELEASEreg_{disp, soil}$) would be 7.9-15.9 tonnes/year (assuming an even split between water, soil and landfill).

Table 6.6 Fate of drained lubricant (example calculation)

Fate	% of original lubricant	% of antioxidant	Quantity of antioxidant (tonnes)
Fuel oil in house	25	13.8	275
Fuel oil after treatment	13.75-26.5	7.6-14.6	152-292
Unaccounted for - to waste water/soil/landfill	21.5-34.25	11.8-18.8	236-376

7. HYDRAULIC FLUIDS AND ADDITIVES

7.1 Losses during use

332. Unlike crankcase oils, hydraulic oils are used in a wide diversity of applications, which makes generalisation difficult. Since by the nature of the type of equipment used, hydraulic fluid systems are generally efficiently sealed, losses during use are generally very low apart from major but temporary losses arising from leakages from burst pipes, etc. This type of loss is very dependent upon the type of system used; systems subject to the possibility of significant fluid losses generally utilise low-cost fluids such as oil-in-water emulsions, or HH type mineral fluids. Proportional losses during use for this type of product therefore tend to be higher compared with the other types of fluid. Certain processes, e.g. plastics moulding, do make provision for the collection and recycling of leaked hydraulic fluid.

333. Since the fluids do not become excessively contaminated or degraded during use, as in the case of the automotive lubricants, it can be assumed that additive losses are in direct proportion to the total oil lost. Losses will be to soil, water or waste oil contractors depending on the application.

7.2 Frequency of dosage

7.2.1 Mineral oil based hydraulic fluids

334. Frequency of renewal is dependent upon a number of factors.

335. The lower specification (HH) fluids are generally used in the less demanding applications, or in situations where major losses can be anticipated. There are therefore huge differences between the replenishment intervals. For simple applications, e.g. hand-operated hydraulic jacks, the hydraulic fluid may very well never be replaced during the life-time of the equipment. Conversely, where loss rates are high, due to poor maintenance, dosing frequency may well be as frequent as monthly or even weekly. Since these fluids do not contain additives which could be subject to depletion, lubricant renewal is generally carried out to restore volumes to normal operating levels only, and not to restore fluid performance.

336. Since volumes of these fluids currently used are now low (See Section 4), and there are no additive components to consider, the establishment of an average replenishment period is not of major significance. For the purposes of this report, a replenishment period of 12 months is assumed.

337. HL fluids, although again not now generally used, are nevertheless designed to have an extended working life compared with HH fluids. The average replenishment period for these fluids is probably about 5 years.

338. HM fluids, which is the largest category, are used in more sophisticated equipment and under more arduous conditions than the previous types. They are likely to be subject to more rigorous planned maintenance schedules, and, in the larger organisations, to be subjected to reconditioning, either on-site or off-site. Such reconditioning is generally carried out on an annual basis, during planned annual

shut-downs, for example, and the additive levels would be boosted to restore the performance of the fluid. Complete fluid replacement is likely to occur at typically 5-year intervals.

339. HV fluids are used for the most sophisticated equipment, and maintenance of fluid performance is critical. These fluids are again subjected to reconditioning at 6-month intervals, and replacement at 3-year intervals.

7.2.2 Non-mineral oil based fluids

7.2.2.1 HFA-type fluids (oil-in-water emulsions)

340. These fluids are the cheapest form of fire-resistant hydraulic fluid variety, and are generally replaced or 'topped-up' comparatively frequently, since they tend to be used in situations where loss rates can be significant. Complete fluid replenishment is likely to occur at intervals of approximately 3 months. Additive boosting during service is not normal.

7.2.2.2 HFB-type fluids (water-in-oil emulsions)

341. These fluids are more expensive than the HFA type, as they have higher oil contents, so they are generally used in situations requiring a higher degree of lubricity, and where loss rates are much lower. Fluid replacement is generally carried out in order to restore the water content of the fluid, which must be at least 35% in order to maintain the fire-resistant properties. Water loss rates will be influenced by the bulk fluid temperature and the adequacy of sealing of the system. These fluids are used mainly in the mining industry, and they are normally monitored and renewed at approximately 12-monthly intervals, depending on conditions. Additive boosting during service, including restoration of the water content, is not carried out, since the manufacture of these fluids is not straightforward and requires specialised techniques.

7.2.2.3 HFC-type fluids (water-glycol fluids)

342. Unlike the previous types of fluid, HFC fluids are generally monitored and the properties restored by additive boosting when required. Again, water contents need to be maintained above 35% to maintain the fire-resistance properties. However, since these fluids are simple solutions, water content may be restored by the addition of the appropriate amount of de-ionised or distilled water to the fluid reservoir. Also, the pH of the fluid tends to decrease during service, which tends to reduce the effect of certain inhibitors in the fluid formulation. Thus boosting of the alkalinity reserve of the fluid by the addition of suitable additive is sometimes carried out.

343. Such monitoring and additive replenishment or water make-up if necessary, is generally carried out on a 3-monthly basis, complete fluid replacement depends upon the operating conditions and on the condition of the equipment, but is normal at intervals of about 2 years.

7.2.2.4 HFD-type fluids

344. These fluids consist of a number of different chemical types, and are used in a variety of situations. Phosphate ester fluids are the most common, and can also be subjected to re-conditioning in a similar way to the more sophisticated mineral oil fluids. Because of the wide variety of applications, generalisation is difficult, but phosphate ester fluids are generally reconditioned or replaced at intervals of 12 months, depending upon the degree of acid accumulation. Additive boosting is normal at the time of reconditioning, but not during use.

345. With regard to other types of HFD fluids, generalisation in terms of replenishment intervals is not possible due to the variety of types involved. However, since the volumes involved are very small, this is of little practical significance.

7.3 Form in which lubricant is discharged

7.3.1 Mineral oil based fluids

7.3.1.1 HH fluids

346. These fluids do not contain additives as such, and consist only of straight mineral oils. The fluids are not expected to degrade to any marked extent, service life generally being determined by contamination rather than by degradation. The small quantities of degradation products which are present are as described in 6.3.1.1 above. Polychlorinated aromatics are not produced.

7.3.1.2 HL fluids

347. These fluids contain organic oxidation and corrosion inhibitors which are subject to thermal and oxidative degradation.

7.3.1.3 HM fluids

348. These fluids contain anti-wear additives in addition, which would result in the formation of small amounts of, e.g. phosphates, thiophosphates, metal sulphides, mercaptan metal salts, zinc pyrophosphate, zinc sulphide and zinc oxide. Since the bulk temperature of the fluid is not sufficiently high to evaporate any accumulated water, zinc dialkyldithiophosphate can also undergo a certain amount of hydrolysis.

7.3.1.4 HV fluids

349. These products are similar to the HM fluids with the addition of VI improvers. These additives can degrade by mechanical shearing resulting in shorter-chain polymers, but the rate of degradation in hydraulic oils is low.

7.3.2 Fire resistant hydraulic fluids

350. In general, the additives in all classes of fire-resistant hydraulic fluids are little changed during the working life of the fluid; fluid life generally being limited by an accumulation of contaminants rather than by any deterioration in performance.

7.4 Concentration of chemical in discharge

7.4.1 Mineral oil based fluids

351. The chemical composition of the used lubricant is similar to that of the fresh fluid, since little degradation takes place. The fluids are eventually rendered unfit for further service due to a build-up of contaminants, including seal wear particles, dislodged debris, coating particles, together with some degradation products, e.g. phosphates, thiophosphates, metal sulphides, mercaptan metal salts, zinc pyrophosphate, zinc sulphide and zinc oxide.

7.4.2 Oil-in-water emulsions (HFA or SFA fluids)

352. The chemical composition of the used lubricant is similar to that of the fresh fluid, since little degradation takes place. The fluids are eventually rendered unfit for further service due to a build-up of contaminants, including seal wear particles, dislodged debris, coating particles, microbiological contamination, etc.

7.4.3 Water-in-oil emulsions (HFB fluids)

353. As for 7.4.2 above.

354. Note for 7.4.2 and 7.4.3: It is preferable to 'split' emulsions before disposal to minimise the volume of liquid waste. It is estimated that approximately 35% of emulsions are split before disposal, either by the user or by a disposal contractor. The majority of emulsion is disposed of directly to drain without splitting. If the emulsion is split, then the additives would predominantly (i.e. over 90%) partition into the oil phase. The composition of the two phases will then depend on the physical-chemical properties of the substance and on the method of emulsion-splitting used, i.e. chemical, physical, or biological. The composition of the aqueous phase is normally acceptable to local authorities for direct disposal and so the oil content would probably be less than 5 ppm. The oil phase would normally be collected by a waste oil contractor. Synthetic fluids are generally mixed in with emulsions at the disposal stage since companies would not normally operate using synthetics only.

7.4.4 Water glycol fluids (HFC fluids)

355. Concentrations of chemicals in used fluids are similar to those of unused fluids.

7.4.5 Non water based fluids (HFD fluids)

356. Concentrations of chemicals in used fluids are similar to those of unused fluids.

7.5 Volume of discharge

357. Table 7.1 summarises the discharges of hydraulic fluids to the environment. Note that these figures are for the UK, and the distribution in other countries may differ significantly, especially in the fate of waste fluids.

Table 7.1 Summary of the percentage discharges of hydraulic fluids

Type and market (tonnes/year)	Replacement/ reconditioning rate	Loss in use (%)		Used oil (%)	Waste (%)		
		soil ($F_{serv, soil}$)	water ($F_{serv, water}$)	(F_{rec})	Chemical ($F_{disp, treated}$)	General ($F_{disp, landfill}$)	Drain ($F_{disp, wastewater}$)
HH (5,000)	1 year - estimate	16	4	50		30	
HL (15,000)	5 years	12	3	82		3	
HM (65,000)	5 years, additive boost/ reconditioning ~ annually	8	2	89		1	
HV (10,000)	3 years, additive boost/ reconditioning ~ 6 months	4	1	95			
HFA (13,000)	3 months	5	45			27	23
HFB (2,000)	1 year	2.7	0.3	60			37
HFC (3,000)	2 years, reconditioning ~ 3 months	1.5	13.5		50		35
HFD (2,000)	12 months reconditioning or replacement	1.4	0.6		98		
TOTAL (115,000)							

Notes:

- Used oil refers to oil collected by licensed contractor and reused (an estimated 10% is lost in recycling).
- Waste is the fluid remaining at the end of useful life which is not collected and reused.
- Chemical waste is disposed of according to type, e.g. solvents would be re-distilled, by a licensed contractor.
- General waste means municipal waste - i.e. generally landfill

358. The figures in Table 3.3 are considered to be realistic worst case values. The possibility of releases to the environment depends on the type of equipment in which the hydraulic fluid is used, and is highest for use in off-road and agricultural equipment. Fluid losses on industrial sites are more likely to contained and managed within the plant. This is reflected to some extent in the values in the table and the further comments below, as the type of fluid used may vary between the different situations. However for uses which are predominantly in an industrial location these are likely to be over-estimates.

359. A significant proportion of low-cost HH fluids are lost during use, mainly due to inadequate maintenance. In the case of off-highway and agricultural equipment, much of this is likely to be deposited in the soil. Only about 50% is likely to be collected and sold as waste oil, most of the remainder tends to be regarded as general waste, and is likely to end up as land-fill.

360. The pattern for the higher specification HL grades is broadly similar, but a much higher proportion is collected and sold for reuse.

361. In the case of the HM grades, although the quantities lost during use are very significant, due to equipment leakages much of this may well end up as an inadvertent diluent for neat cutting oils, or as 'tramp oil' in water-based cutting fluids. (Tramp oil is contamination oil, i.e. leaked from other applications, which tends to sit on top of emulsified oil.) In the case of the former, the eventual environmental fate will be determined by that of the neat cutting oil. In the latter case, excess tramp oil is sometimes separated off, and segregated as oil waste. Smaller amounts will either be eventually discharged to drain or will partition with the separated oil in any subsequent emulsion-splitting process. Most of the used oil will be reclaimed for use as fuel oil.

362. The pattern for the HV oil is similar to that of the HM oils, although as these oils tend to be used in the more modern and sophisticated equipment, loss rates during use due to leakage are generally lower.

363. HFA fluids are the cheapest form of fire-resistant fluid, and high loss rates due to leakage can be tolerated. Due to the low oil content (2-5%) spent fluid is not normally subjected to splitting before disposal. The spent fluid is likely to be evenly distributed between soil/ landfill and water.

364. HFB fluids contain much higher oil contents, and the majority are split before disposal. The distribution of additives depends on the physical chemical properties and on the method of splitting.

365. HFC fluids can suffer significant losses during use, which are likely to be included with the water drain quantities. Some spent fluid is disposed of as chemical waste.

366. HFD fluids are normally segregated after use and disposed of as chemical waste. Leakage rates are generally well-controlled because of the high costs of these products.

7.6 On-site waste treatment

7.6.1 Mineral oil hydraulic fluids

367. The lower duty fluids (HH and HL), are not normally subjected to any maintenance or treatment operations.

368. The HM and HV types, however, which commonly form part of a large centralised hydraulic system, are subjected to regular inspection and maintenance. Inspection consists of determining the particulate contamination, water content, acidity and viscosity.

7.6.1.1 Particulate content

369. Cleanliness requirements for hydraulic fluids are given in Table 7.2 below.

Table 7.2 Cleanliness requirements for hydraulic fluids

System	**Number of particles > 5µm per 100 ml**	**NAS 1638 Class**
Very critical systems	4,000	4
Critical machine tools	10,000	5
Machine tools with servo systems	40,000	7
Large industrial systems and earth moving equipment	500,000	11
Non-critical systems, but where contamination is to be avoided	1,000,000	12

370. The maintenance of fluid cleanliness levels is a major factor in the reliability of hydraulic systems. Contamination arises from the generation of seal wear particles, from dislodged debris, from coating particles, from ingress of dust particles through breathing of the system and from the accumulation of acid sludge due to oxidation of the fluid. Cleanliness levels are maintained by the incorporation into the system of suitable filters, either of the depth type (felt or fibre layer), surface type (pleated paper), or of the edge type (stacked disc). Most systems use 25 micron filters, but in critical situations, filters of mesh size down to 1 micron are employed, in conjunction with pre-filters (typically 10 micron) to remove the bulk of the debris, thereby avoiding the blinding of the fine filter. If chemical filter agents are used, these are usually replaced in service. In other types, a periodic back wash dislodges the residue on the filters. Some edge type filters are fitted with a rotating blade which scrapes off the contaminants through an occasional turn of the screw. Filter beds of a finely-divided diatomaceous earth (Fullers Earth) are often used if ultra-fine filtration is required. (All external reprocessors would normally use Fullers Earth treatment; however, this section deals with on-site waste treatment where the operation is not normally as comprehensive as that of an external reprocessor). The disadvantage with this type of filter is that some additives in the fluid also tend to be extracted. Also, if the fluid contains a detergent additive, some of the 'earth' may be taken up into circulation and act as an abrasive. No filtration system is effective in removing the slimy sedimentation caused by bacterial contamination. The only effective remedy is to replace the fluid, after emptying and flushing with a bactericide.

7.6.1.2 Water content

371. The levels of water are normally controlled by the regular draining of the system, and should in any case never normally exceed 0.5%. Some systems can tolerate higher levels of water (up to 2%), but there is a consequent risk of erosion occurring in spool valves and the life of ball and roller bearings may also be reduced due to fatigue. Ingress of salt water can be most deleterious to the system. The presence of salt can be removed by water-washing the fluid followed by centrifugation, but this practice can also extract some of the performance-enhancing additives from the fluid, in which case the oil must be replaced. The discarded oil may be used in less critical applications.

7.6.1.3 Soluble acids

372. If the neutralisation value (NV) of the fluid exceeds 0.5 mg KOH/g, the oil must be re-processed (See Section 9) or changed. NVs of this magnitude will also indicate that the anti-wear performance of the oil has deteriorated.

7.6.1.4 Viscosity

373. With the exception of HV oils, where reductions in viscosity can occur as a result of the shear-instability of the viscosity index improving additives, changes in viscosity are normally due to contamination by other mineral oil products.

7.6.2 Fire resistant hydraulic fluids

7.6.2.1 HFA fluids (oil-in-water emulsions)

374. For treatment prior to disposal see Section 8.6.2 below (Emulsifiable cutting oils).

7.6.2.2 HFB fluids (water-in-oil emulsions)

375. For treatment prior to disposal see Section 8.6.2 below (Emulsifiable cutting oils).

7.6.2.3 HFC fluids (water glycol fluids)

376. HFC fluids can become contaminated with mineral oil in which case the fluid is drained out of the system. After allowing to stand, the separated oil is skimmed off, and the fluid returned for re-use. Apart from the possible need to top up the water content, no other treatment is normally required during the working life of the fluid.

7.6.2.4 HFD fluids

377. These fluids are not normally subjected to any on-site treatment apart from filtration.

7.7 Example release calculation

378. Anti-foaming agent in HFC-type hydraulic fluid

Total EU usage of anti-foaming agent = 1 tonne/year
Concentration in fluid = 0.05 % (Table 4.3)

379. Thus the total amount of fluid containing this additive is 2,000 tonnes/year.

Disperse release from use and disposal of lubricant

380. Table 7.1 contains estimates of the proportions of hydraulic fluid released or disposed of by various routes. Applying the values for HFC-type fluids for this example gives the following (all quantities refer to the additive):

Release to water during use ($F_{serv,\ water}$) = 13.5% = 0.135 tonnes/year
Release to soil during use ($F_{serv,\ soil}$) = 1.5% = 0.015 tonnes/year
Disposal of as chemical waste ($F_{disp,\ treated}$) = 50% = 0.5 tonnes/year
Disposal of to drain ($F_{disp,\ wastewater}$) = 35% = 0.35 tonnes/year

381. These releases apply to the whole of the EU. One tenth of these could be used as the basis for calculation of a regional PEC. So the regional releases would be: $RELEASEreg_{serv,\ water}$ 13.5 kg/year; $RELEASEreg_{serv,\ soil}$ 1.5 kg/year; $RELEASEreg_{disp,\ waste\text{-}water}$ 35 kg/year.

8 METALWORKING FLUIDS AND ADDITIVES

8.1 Losses during use

382. This section considers releases from the sites where cutting fluids are used. The degree to which such releases are important will vary between different countries and to some degree with the size of the operations. In Germany, for example, losses from equipment in use are collected and sent to external treatment sites for disposal. The use of completely encapsulated machine tools helps to make this possible. In these situations, releases from the waste treatment sites will be more significant, and releases from the actual use sites are considered to be negligible. In other countries, for example in the UK, larger sites may collect releases or treat them on site, but emissions to the environment can occur from smaller sites. Section 8.6 deals with estimating releases from waste treatment sites. The following sections are largely based on UK experience.

8.1.1 Neat oils

383. 'Drag-out' losses (losses of lubricant caused by adhesion of lubricant to cutting swarf and millings) and losses due to the generation of oil mists account for the major losses of neat cutting oils during use. Up to 270 litres of oil per tonne of swarf can be lost by drag-out, although a figure of 30-50 litres per tonne is more typical. The recovery and subsequent recycling of lubricant from swarf is a standardised part of the operation, particularly by larger users, due to the comparatively high costs of cutting oils. The loss figures per day for neat oils are dependent more upon the effectiveness of the swarf recovery system than on the size of the shop.

384. A study (Evans et al, 1989) involved a machining facility which contained plant, machinery and metal-cutting processes functioning on a scale which was typical of that found in many large production engineering operations. The workshop employed a large centralised cutting oil system incorporating automatic swarf management. Careful monitoring of the use of the cutting oil revealed that an average of 38% was replaced annually by incidental oil additions and by oil top-up to adjust for oil losses, although a figure of 50% is thought to be more typical and reasonably representative of the majority of machining operations. (See Section 8.5.)

385. Proportioning the total loss between drag-out and oil mist generation is not easy. Measurements of oil mist concentrations are beset with a number of problems, although more attention is now being given to this topic since the introduction of the Occupational Exposure Standard for Mineral Oils of 5 mg/m^3 (8 hour Time Weighted Average) and 10 mg/m^3 (10 minute TWA). The main problem is that current sampling and analytical techniques are not capable of distinguishing between oil mists and oil vapours. Although this is not of significance when determining the total losses arising from use of the product, there are obvious health implications. The rate of generation of oil mists varies widely according to the machining process involved, and the composition also varies according to whether the mist is generated as a result of evaporation followed by condensation, or by mechanical dispersion. The composition of the oil mist invariably varies greatly from that of the parent material. The particle size also depends upon the method of generation, e.g. thermally generated oil mists contain more particles in the respirable range than

those resulting from mechanical generation. Generation of oil mists can be reduced by the incorporation of anti-misting agents in the cutting oil, which is now a fairly standardised practice.

386. From Section 4, the amount of neat oil produced per annum is 15,750 tonnes, therefore the total loss of neat oil amounts to ca. 8,000 tonnes/year during machining operations.

8.1.2 Emulsifiable and synthetic fluids (coolants)

387. Since these products are far cheaper than the mineral oil cutting fluids, recovery and re-use has not received nearly as much attention. Coolants are the lowest-cost item in the metalworking budget, amounting to less than 0.5% of the overall estimated costs. However, these products are much more susceptible to degradation during use, particularly by micro-organisms. Attention has therefore been mainly directed towards prolonging the useful life of such products.

388. Because of the nature of these products, the loss pattern differs from that of the neat oil products. Losses by evaporation and by mist generation are far higher compared with the neat oil variety. However, the vapours and mists generated tend to have a higher water content than the bulk material, therefore the oil losses are not necessarily in proportion to the total losses. Adhesion to swarf is less than in the case of the neat oils because of the low viscosity. However because no attempt is normally made to recover lubricant from swarf, the overall losses in this area are greater when compared to the neat oils, where the lubricant is recovered and recycled.

8.2 Frequency of dosage

8.2.1 Neat oils

389. The frequency of replenishment is dependent upon the workload together with the efficiency of the equipment used to separate cutting oil from swarf. Up to 270 litres of oil can remain on one tonne of swarf, although a figure of 30-50 litres/tonne is more normal. A large organisation, where the throughput is sufficient to warrant the installation of sophisticated separation systems, will replenish the lubricant at a rate of approximately 50% per year. Neat cutting oils do not readily degrade in service, but become contaminated by an accumulation of metal fines, etc., which can accelerate degradation. They are then normally reprocessed on site or by an external facility. Reprocessing normally occurs at a frequency of between 1 and 6 times per year depending on throughput and contamination levels (in modern plants in Germany, the preparation and upkeep of these oils is effectively a continuous process). Additives may be added at reprocessing to restore the original levels. In practice, additives are not depleted to any extent by the cutting action, but additive dilution often occurs if the cutting oil becomes contaminated with hydraulic oils, slideway oils, or any other lubricants as a result of leakage. The cutting fluid is finally replaced when the degree of degradation renders it unfit for further service, but this period can extend from 1 year to 5 years.

390. Table 8.1 contains information on the loss of lubricant and the reprocessing/replacement frequency for different sizes of operation. By calculation, if large shops represent 40% of the market of 15,750 tonnes/year, then they would consume approximately 6,300 tonnes/year. Similarly, medium and small shops would each consume approximately 4,725 tonnes/year respectively.

Table 8.1 Loss and replacement frequencies of neat oils

	Loss of lubricant per annum %	Reprocessing frequency	Replacement frequency
Large machine shop with sophisticated swarf treatment (40% of market)	50	1-6 times per year	5 years
Medium machine shop with basic swarf treatment (30% of market)	75	Twice yearly	2-3 years
Small machine shop with no swarf treatment (30% of market)	100	Not applicable	1 year

8.2.2 Emulsifiable and synthetic fluids (coolants)

391. It is not normally economic to recover coolants from swarf, because the lubricant consists mainly of water. The general practice is to allow the coolant to drain off before the swarf is despatched. However, because the emulsified oil provides a growth medium for certain types of micro-organisms, the fluid does degrade during use at a rate determined mainly by the general housekeeping of the establishment. It is important to maintain the correct concentration of oil to water and, in practice, the rate of water loss by evaporation is to some extent compensated by preferential removal of the oil phase by drag-out losses. Fluid concentrations are routinely monitored, either by 'splitting' the emulsion in the laboratory and measuring the oil/water ratio, or more simply by measuring the refractive index of the emulsion, which is related to the oil content. The correct concentration levels can be regained by adding water or emulsifiable oil as appropriate. The fluid can also become unsuitable for use as a result of excessive microbial contamination. Since certain biocides degrade during use, the fluid can often be recovered, on a temporary basis at least, by the addition of further biocide. Micro-organisms may adapt to a particular biocide so it is often more effective to top up the system with a different type of biocide. The rate of degradation is also influenced by contamination by waste materials such as dirt, food or other organic material. The rate of degradation can also be influenced by the design of the system, which should ideally be free of regions where the coolant can stagnate.

392. Again, generalisation is difficult on account of the diversity of systems, workshop practices and the scale of the operation. An average replenishment rate of ~10% per week is typical to compensate for loss of fluid by swarf dragout, evaporative losses, leaks, etc. Since there is a preferential loss of water by evaporation, the replenishment package used is often a diluted version of the original oil concentration, typically 50% of the normal working concentration of the emulsion or synthetic fluid.

8.3 Form in which lubricant is discharged

393. The rate of degradation of additives in cutting oils is generally low; the service life of these products being generally limited by the accumulation of contaminants rather than by reduced performance.

8.3.1 Neat oils

394. These products accumulate contaminants such as sludge, moisture and metal fines during use which limit their service life. Degradation of oxidation inhibitors can result in sludge formation; anti-wear

and EP additives can be degraded as a result of chemical reaction with the metal surfaces. The proportion degraded is low in comparison with the initial concentration, but the accumulation of lower molecular weight acidic material containing sulphur and chlorine can be detrimental.

395. Some years ago, a study (Eyres, 1981) confirmed that there was a small degree of accumulation of polycyclic aromatics in used cutting oils, but the levels were not regarded as presenting any significant hazard to health.

8.3.2 Emulsifiable and synthetic fluids

396. The service life of these types of fluid is normally limited by the accumulation of microbial contamination, since oil emulsions provide a rich growth media for a variety of micro-organisms. Species common to metalworking fluids (MWFs) are shown in Table 8.2 below. Control of the microbial population is exercised by the inclusion of biocides in the MWF formulation. Principle chemical classes of biocide are also shown in Table 8.2 below.

Table 8.2 Bacteria and fungi common to MWFs and principal classes of biocides

Bacteria	**Fungi**	**Biocides**
Citrobacter freundi Desulphovibrio sp Enterobacter cloacae Escherichia coli Klebsiella pneumoniae Proteus mirabilis Pseudomonas aeruginosa	Candida sp Cephalosporium sp Fusarium sp	Alkane derivatives Formaldehyde condensates Isothiazolines Morpholine compounds Oxazolidine compounds Phenols Pyridine derivatives Quaternary ammonium compounds

8.4 Concentration of chemical in discharge

8.4.1 Neat oils

397. Concentrations of chemicals in used fluids are similar to those of unused fluids.

8.4.2 Emulsifiable fluids

398. Due to preferential evaporation of the water component, additive levels tend to increase with fluid use. The situation is contained by adding make-up fluid (approximately 10% of original fluid volume) which is normally at 50% of the concentration of the unused fluid. Thus at discharge, as a certain amount of time will have passed since the last addition of make-up fluid, the additive levels will be somewhat higher (e.g. 110%) than the original fluid.

8.4.3 Synthetic fluids

399. The concentrations of chemicals in used synthetic fluids are similar to those in unused fluids.

8.5 Volume of discharge

8.5.1 Neat oils

400. There are distinct differences in disposal patterns between large machine shops, with comprehensive internal reprocessing facilities for removing and recycling oil adhering to swarf, and smaller machine shops where the working practices are rather different. Misting/evaporation losses can be minimised by suitable ducting arrangements, where the mist droplets can coalesce, or vapour condense, and the collected liquid is returned to the reservoir. Losses in this area are generally low due to the low volatility of the neat oil at ambient temperatures. Oil splashed onto overalls will be transferred eventually to water waste. Losses due to leakages will probably be contained as oil waste in the larger premises, but possibly go to water waste in the small premises. Losses on external reprocessing due to line flushing, etc. are generally some 10% per treatment, and are therefore significant when such treatment is regularly practised. Because of the scope for recycling the oil recovered from the swarf, topping-up is less frequent, and a significant proportion of the lubricant is eventually discarded as waste oil. About 10% of any swarf, with any adhering lubricant, is generally used as landfill, but by far the major proportion is re-melted and re-used. Any adhering lubricant is therefore discharged to the atmosphere in an oxidised form. Oil adhering to workpiece items is generally removed either by alkaline washing or by solvent washing. In both cases, remaining lubricant is generally distributed between emission to water and chemical waste in the ratio of 1 to 4.

401. Unlike the European situation, a number of neat cutting oils in the UK contain chlorinated additives. Regulatory and environmental protection organisations have expressed concern about the chlorine content of all chemical products because of the potential to create polychlorinated dibenzo-p-dioxins (PCDDs - commonly known as dioxins) when combusted, including the situation when metal swarf, containing chlorinated cutting oil, is re-melted.

402. The chlorinated additives have now been virtually completely substituted in Europe by non-chlorinated EP additives (see Section 2.3.5)

403. Two situations are considered below: those organisations with swarf processing facilities and those without.

8.5.1.1 With swarf processing

404. A typical installation in a large organisation would contain some 50,000 litres of neat oil. Some 2,000 litres of fresh oil per month would be used to top up the system. The complete charge would be replenished every 5 years. A quarter of the oil (12,500 litres) would be sent for external re-processing every quarter. 10% (i.e. 5,000 litres per annum) of the oil would be lost during re-processing. Losses per annum are therefore as in Table 8.3.

Table 8.3 Losses of neat oils with swarf processing

Losses/annum	Emissions to
Misting/evaporation 2%	Air ($F_{mist, air}$)
Overalls 2%	Water ($F_{overalls, water}$)
Leaks 2%	Water/collected for re-use as waste oil ($F_{leaks, water}$ or $F_{leaks, re-user}$)
Internal reprocessing 1%	Water/collected for re-use as waste oil ($F_{int reprocess, water}$ or $F_{int reprocess, re-use}$)
External reprocessing 10%	Re-used as waste oil ($F_{waste, re-use}$)
Dragout-swarf 30%	90% incinerated to air ($F_{waste, incin}$) 10% to landfill ($F_{waste, landfill}$)
Dragout workpiece 3%	1% to water ($F_{dragout, water}$) 2% to chemical waste (solvents/degreasants) ($F_{dragout, treated}$)

Notes: Waste oil for disposal every 5 years is ~30% of total input.
Swarf dragout would show wide variations according to the nature of the operation, i.e. the metal involved in the machining operation (drilling, grinding, boring etc.) which would influence the nature of the swarf and its capacity to retain oil.

8.5.1.2 Without swarf reprocessing

405. Typical addition rates would be some 10% of the charge per week. The complete charge would be replenished every year. (Table 8.4).

Table 8.4 Losses of neat oils without swarf processing

Losses/annum	Emissions to
Misting/evaporation 2%	Air ($F_{mist, air}$)
Overalls 2%	Water ($F_{overalls, water}$)
Leaks 3%	Water/collected for re-use as waste oil ($F_{leaks, water}$ or $F_{leaks, re-user}$)
Dragout-swarf 90%	90% incinerated to air ($F_{waste, incin}$) 10% to landfill ($F_{waste, landfill}$)
Dragout-workpiece 3%	1% to water ($F_{dragout, water}$) 2% to chemical waste (solvents/degreasants) ($F_{dragout, treated}$)

Note: Waste oil for disposal per year would be ~15% of total input.

8.5.2 Emulsifiable and synthetic fluids

8.5.2.1 Conventional soluble oils

406. The same general comments apply as for neat oils. Oil losses by misting/evaporation are higher due to the tendency for steam distillation of the lubricant components at lower temperatures. It is not normally economic to recover oil from swarf except in the largest establishments. Waste emulsion from large machine shops is split before disposal, the aqueous phase and the oil phase being disposed of as waste water and waste oil respectively. Recovered emulsion is not normally recycled, so dragout on swarf is the major exit route for the cutting fluid from the process, except in the cases where more frequent changes of fluid are necessary due to a poor standard of housekeeping and fluid maintenance. It appears that at least 50% of waste emulsion is discharged to drain without any pre-treatment, and this represents a significant environmental loading on the sewage system.

407. Table 8.5 summarises the loss of soluble oils.

Table 8.5 Losses of soluble oils

Losses/annum	**Emissions to**
Misting/evaporation 5%	Air ($F_{mist, air}$)
Overalls 2%	Water ($F_{overalls, water}$)
Leaks 3%	Waste oil/water ($F_{leaks, water}$ or $F_{leaks, re-user}$)
Dragout-swarf 87%	90% incinerated to air ($F_{waste, incin}$) 10% to landfill ($F_{waste, landfill}$)
Dragout-workpiece 3%	Water 1% ($F_{dragout, water}$) Chemical waste (alkaline degreasant) 2% ($F_{dragout, treated}$)

408. Assuming a 10,000 litre holding tank (i.e. 500 litre of oil at 5%), a typical weekly top-up rate would be 1,000 litre of half-strength emulsion (i.e. 25 litre oil) since preferential loss of water takes place during evaporation/misting. The whole system would be replenished at intervals of between 1 and 6 months depending on the ability of the operator to maintain the oil in good condition by proper housekeeping.

8.5.2.2 Semi-synthetic fluids

409. Compared with the conventional soluble oils, the ratios are slightly changed as a result of the longer working life of the oil. The waste to drain is reduced in proportion to the losses by dragout. Losses are as for the conventional soluble oils (Table 8.5) but the working life is generally 12-24 months. A typical holding tank for these fluids would be similar to that for soluble oils, i.e. 10,000 litres.

8.5.2.3 Synthetic fluids

410. Again, the even longer working life further reduces losses to drain compared with those due to dragout. Because of the nature of the product, synthetics are difficult to treat and were often discharged directly to drain after being further diluted with water. However, this is becoming increasingly unacceptable, and the cost of properly treating the waste is offsetting the advantages of these fluids. The soluble components need to be oxidised chemically or biologically to insoluble and non-polluting

substances. However, the low viscosity has enabled ultrafine filtration to be used to prolong the life of synthetic products.

411. Losses are as for conventional soluble oils (Table 8.5) but the working life is generally 18-36 months. Holding tank size is also similar (10,000 litres).

412. In all cases involving disposal of cutting fluid wastes, it should be noted that the fluid is likely to be heavily contaminated with metal fines from the cutting process. The fluid is normally allowed to stand before disposal, whereupon the heavier fines will separate out. However, there will always be a considerable quantity of finer material dispersed in the fluid. If the metal involved in the cutting operation is classified as toxic, then the waste should be classified as notifiable waste, and treated accordingly. Discharge of such waste directly to drain could pose an environmental hazard.

8.6 Waste treatment for metal working fluids

413. This applies largely to emulsifiable fluids and synthetic cutting fluids. It will usually happen at specialist treatment plants, this is the usual pattern in Germany. It can also be carried out at sites using larger quantities of such fluids. It is not normal to treat neat cutting oils on site. If they are no longer suitable for external re-processing, then they would be removed from site by a waste oil carrier. This is discussed in Section 9.

8.6.1 Emulsifiable fluids (water miscible cooling lubricants)

414. In order to process these waste fluids for disposal, the emulsions have to be split to separate the oil and water phases. The emulsion separation process is made up of the following steps:

- Separation of any non-emulsified foreign oils through skimming, possibly with support (for example flotation)
- Separation of hard materials through filtration and/or settling in a settling tank
- Emulsion separation
- Treatment of the separated water, removal of dissolved heavy metals and organic substances (COD), neutralization
- Possibly further treatment of the separated oil phase to reduce the water content

415. Processes used in the treatment of used emulsions include chemical separation processes (organic and inorganic), membrane processes, ultra filtration, reverse osmosis, evaporation processes, electrochemical processes, flotation, coagulation and adsorption.

416. The separated oil phase has a residual water content of ~40%. High quality materials may be reprocessed, while other materials are incinerated. The treated water phase will be discharged to a water treatment plant.

417. For Germany, where a very high proportion of spent emulsifiable fluids is collected, a typical treatment plant has a capacity of 45,000 tonnes of lubricant per year. Around 50% of this is made up of separable emulsions, with other wastes forming the remaining 50%. A daily treatment rate of 200 m^3 of this type of fluid is considered representative.

418. When the emulsions are split, the additives will partition between the oil and water phases. This can be modeled using the Nernst distribution law. The concentration in the water phase after splitting is given by:

$$C_{\text{waste-water}} = C_{\text{add\_in\_lubricant}} \cdot \frac{\left(\text{DILUTION}_{\text{oil\_to\_water}} + 1\right)}{(\text{DILUTION}_{\text{oil\_to\_water}} \cdot K_{\text{ow}} + 1)} \cdot \left(1 - \text{Fadd}_{\text{elim}}\right)$$

The daily volume of the water phase produced is given by:

$$V_{\text{waste-water}} = \frac{V_{\text{lubricant}}}{\text{DILUTION}_{\text{oil\_to\_water}} + 1}$$

Hence the emission of the additive per day is given by $C_{\text{waste-water}}$ x $V_{\text{waste-water}}$, or:

$$\text{Elocal}_{\text{waste-water}} = C_{\text{add\_in\_lubricant}} \cdot V_{\text{lubricant}} \cdot \frac{1}{(\text{DILUTION}_{\text{oil\_to\_water}} \cdot K_{\text{ow}} + 1)} \cdot \left(1 - \text{Fadd}_{\text{elim}}\right) \quad (Eq\,8.1)$$

The symbols used are as follows:

Symbol	**Explanation**	**Unit**	**Default**	**Notes**
$\text{Elocal}_{\text{waste-water}}$	Emission per day	kg/d		
$C_{\text{waste-water}}$	Concentration of additive in water phase after treatment	mg/l		
$C_{\text{add\_in\_lubricant}}$	Concentration of additive in the lubricant as used	kg/m^3		From notifier, industry or Tables 4.7 and 4.9, but see below.
$V_{\text{lubricant}}$	Volume of lubricant (as used) treated in plant per day	m^3/day	200	See this section
$V_{\text{waste-water}}$	Volume of the water phase after treatment	m^3/day		
$\text{DILUTION}_{\text{oil\_to\_water}}$	Volume ratio oil phase:water phase in lubricant as used	-	1:20	From notifier, industry or Table 4.10
Kow	n-octanol-water partition coefficient	-		
$\text{Fadd}_{\text{elim}}$	Fraction of additive removed by physical or chemical processes during treatment	-	0	From notifier or industry

419. The concentration $C_{\text{add\_in\_lubricant}}$ is the concentration of the additive in the lubricant as used. In Tables 2.3 and 2.4, some of the concentrations relate to the concentrated form of the lubricant as supplied, which has to be mixed or diluted with water to produce the lubricant as used. The values in the tables are also in the form of weight percentages and need to be converted into volume concentrations. If the weight percentage of additive is Fadd, then the mass of additive in 1 kg of concentrate is 0.01Fadd kg. The mass of base fluid (assumed to be the rest of the concentrate for simplicity) is (1- 0.01Fadd) kg, and the volume is (1 - 0.01Fadd)/$\text{RHO}_{\text{lubricant}}$ where $\text{RHO}_{\text{lubricant}}$ is the density of the fluid. Assuming the density to be 1 kg/l or 1000 kg/m^3 (again for simplicity), then the concentration of additive in the concentrate in kg/m^3 is:

$$C_{\text{add\_in\_concentrate}} = \frac{10 \cdot \text{Fadd}}{\left(1 - 0.01\text{Fadd}\right)} \quad (Eq\,8.2)$$

420. Where the concentrate is diluted with water before use, the concentration has to be adjusted to account for this dilution. The ratio of concentrate to water is $\text{DILUTION}_{\text{oil\_to\_water}}$, and a value of 1:20 is

suggested where more specific information is not available. Thus the concentration of additive in the lubricant as used is given by:

$$C_{add\_in\_lubricant} = C_{add\_in\_concentrate} \cdot DILUTION_{oil\_to\_water} \qquad (Eq\ 8.3)$$

If the weight fraction used relates to the lubricant as used, then $C_{add\_in\_lubricant} = C_{add\_in\_concentrate}$, or $DILUTION_{oil\_to\_water} = 1$.

8.6.2 Synthetic cutting fluids (aqueous cooling lubricant solutions)

421. As with the emulsifiable fluids, the concentrations of additives in the synthetic fluids on disposal can be considered to be those in the lubricants as prepared for use. Foreign materials introduced during sue can be removed by filters, oil skimmers or decanters. Once this has been done, the solutions are treated by reverse osmosis or evaporation. The solutions often become mixed with emulsions, which makes the dissolved oils difficult to separate from the aqueous phase. This can lead to the water phase containing a high percentage of the leftover oil, and the high COD content makes discharge to receiving waters impossible.

422. A representative volume of this type of fluid to be treated is 40 m^3 per day.

423. The release of additive from the treatment of the solutions is given by:

$$Elocal_{waste\text{-}water} = C_{add\_in\_lubricant} \cdot V_{lubricant} \cdot (1 - Fadd_{elim}) \quad (Eq\ 8.4)$$

424. The symbols used are as follows:

Symbol	**Explanation**	**Unit**	**Default**	**Notes**
$Elocal_{waste\text{-}water}$	Emission per day	kg/d		
$C_{add\ in\ lubricant}$	Concentration of additive in the lubricant as used	kg/m^3		From notifier, industry or Tables 4.11 – 4.13, but see below.
$V_{lubricant}$	Volume of lubricant (as used) treated in plant per day	m^3/day	40	See this section
$Fadd_{elim}$	Fraction of additive removed by physical or chemical processes during treatment	-	0.8	From notifier or industry

425. As for the emulsifiable lubricants, the concentration in the lubricant as used can be calculated from the weight percentage using the equations above.

8.7 Example release calculations

8.7.1 Corrosion inhibitor in semi-synthetic metal working fluid

Total EU usage of additive = 100 tonnes
Concentration of corrosion inhibitor in fluid = 3% (Table 4.11)

426. Local releases are calculated during use at a large metal working plant. From Section 8.5.2.2 a typical holding tank for these fluids would have a capacity of 10,000 litres. To replace losses this tank is replenished at a rate of 10% per week, or 1000 litres (Section 8.2.2). As water is lost preferentially through evaporation, this addition is usually at half strength in terms of the metal-working fluid, hence 500 litres of fluid are added together with 500 litres of water. The addition of this amount of fluid is assumed to balance the losses of base fluid and additive in the areas indicated in Table 8.5 (same losses for semi-synthetics as for soluble oils).

427. In this case, a weekly loss of 500 litres of fluid corresponds to 15 kg of additive (present at 3% and assuming that the density of the fluid is 1 kg/litre). For a 5-day week this is 3 kg/day. This loss is broken down according to the percentages in Table 8.5 as follows:

Loss of corrosion inhibitor to air (misting/evaporation) ($F_{\text{mist, air}}$) = 5% = 0.15 kg/day
Loss of corrosion inhibitor to water (overalls) ($F_{\text{overalls, waste-water}}$) = 2% = 0.06 kg/day
Loss of corrosion inhibitor to water (leaks) ($F_{\text{leaks, waste-water}}$) = 3% = 0.09 kg/day
Loss of corrosion inhibitor to chemical waste (alkaline cleaning of
work pieces) ($F_{\text{dragout, treated}}$) = 2% = 0.06 kg/day
Loss of corrosion inhibitor to water (dragout) ($F_{\text{dragout, waste-water}}$) = 1% = 0.03 kg/day
Loss of corrosion inhibitor on swarf (90% incinerated,
10% to landfill) ($F_{\text{waste, incin}} + F_{\text{waste, landfill}}$) = 87% = 2.61 kg/day

From this the combined release to waste water ($Elocal_{\text{proc, waste-water}}$) is 0.18 kg/day, and to air ($Elocal_{\text{proc, air}}$) is 0.15 kg/day.

428. In addition to these releases during use, the whole of the holding tank will be emptied at intervals of 12-24 months (Section 8.5.2.2). The contents may be treated by splitting the emulsion before external release, but the majority of spent emulsions are expected to be disposed of to drain. The active ingredients in the tank are expected to be present at their designed working concentration. The content of the corrosion inhibitor is therefore 3%, or 300 kg. Hence there will be an intermittent release of 300 kg once every year to two years.

429. On the EU scale, it can be assumed that the annual usage of any additive goes to replace the amount lost in use. To estimate the overall EU releases the distribution of losses in Table 8.5 should be applied to the total EU tonnage of additive used. Here the total tonnage is 100 tonnes; the combined water emissions are 6%, or 6 tonnes, and the air emissions are 5% or 5 tonnes. There are a large number of locations using metal cutting fluids in the EU, so the regional releases can be estimated as 10% of the EU total. Hence $RELEASEreg_{\text{proc, waste-water}}$ is 600 kg/year and $RELEASEreg_{\text{proc, air}}$ is 500 kg/year.

8.7.2 Releases from waste treatment of metal working fluids

8.7.2.1 Corrosion protection in a semi-synthetic emulsifiable lubricant

Weight percentage of additive in concentrate (Fadd)	10% (Table 4.1.2)
Dilution of concentrate in use ($DILUTION_{oil\_to\_water}$)	1:20 (default)
Volume of waste lubricant treated ($V_{lubricant}$)	200 m^3/day (default)
Octanol-water partition coefficient (Kow)	199 (log value 2.3, from substance data)
Elimination by other processes ($Fadd_{elim}$)	0 (default)

From *Eq* 8.2 in Section 8.6.1 the concentration of the additive in the concentrate $C_{add\_in\_concentrate}$ is calculated as 111 kg/m^3. Using the default dilution rate, the concentration in the lubricant as used $C_{add\_in\_lubricant}$ is 5.6 kg/m^3 using *Eq* 8.3.

The resulting emission to waste water ($Elocal_{waste\text{-}water}$) calculated from *Eq 8.1* in Section 8.6.1 is 101 kg/d.

8.7.2.2 Solubiliser in a synthetic cutting fluid (aqueous cooling lubricant)

Weight percentage of additive in concentrate (Fadd)	20% (Table 4.14)
Dilution of concentrate in use ($DILUTION_{oil\_to\_water}$)	1:20 (default)
Volume of waste lubricant treated ($V_{lubricant}$)	200 m^3/day (default)
Elimination by other processes ($Fadd_{elim}$)	0.8 (default)

From *Eq* 8.2 in Section 8.6.1, the concentration of the additive in the concentrate $C_{add\_in\_concentrate}$ is calculated as 250 kg/m^3. Using the default dilution rate, the concentration in the lubricant as used $C_{add\_in\_lubricant}$ is 12.5 kg/m^3 using *Eq* 8.3.

The resulting emission to waste water ($Elocal_{waste\text{-}water}$) calculated from *Eq* 8.4 in Section 8.6.2 is 400 kg/d.

9 RECYCLING OF LUBRICANTS

9.1 Introduction

430. During use, the accumulation of oxidation products, dirt or other contaminants can reduce the quality of the lubricant to such an extent that it is no longer fit for its intended purpose. There are then several options:

- disposal - dumping at landfill, or incineration with or without energy recovery. This includes use as a fuel oil, for example in cement kilns. These processes involve the destruction or containment of the waste lubricant and any additives it may contain, and so there should be no environmental release from them. As noted above, however a significant amount of oil, mainly from DIY car servicing, is illegally disposed of into surface water, drains etc.

- re-use as a fuel oil (e.g. in cement kilns)

- reprocessing/reclaiming - for use in its original application. This may occur on site or externally. It is thought that only simple industrial oils (of known source and composition) are 'laundered' or reprocessed. This involves the recycling of the lubricant as a whole including any chemicals that it still contains. Recycling processes vary enormously in their effects upon additives and their levels in the recycled product. Virtually all of the additives can be lost in this process and are not recoverable from the residues. The activity of the chemical additive can be restored where appropriate by boosting or 'spiking' the level in the final product after recycling. Used oil recycling is practised in some European countries.

- regeneration - re-refining and distillation to a base oil of virgin quality. This involves extensive processing in which all additives and contamination are removed. This is a very expensive process and is only used for heavily contaminated oils containing a variety of undesirable materials - for example automotive crankcase oils.

431. The manufacturing of 1 tonne of mineral base oil by conventionally processing a typical Mid Eastern crude oil atmospheric residue (see Section 2.2.1) requires 1.4 to 1.6 tonnes of fuel oil equivalent (FOE), i.e. feed consumed plus energy. The same calculation made on the basis of waste oil re-refining shows that the production of 1 tonne requires 1.1 to 1.2 tonnes of FOE (Kajdas, 1994). There is clearly an advantage of regeneration over conventional processing. From an energy conservation viewpoint, and also from the need to conserve natural resources, the regeneration of waste oil to manufacture a base oil conserves more energy than reprocessing the waste oil for use as a fuel. Also, the energy required to manufacture re-refined oil from used oil is only one-third of the energy required to refine crude oil to produce virgin base oil (Müller Associates Inc., 1989). However, when the overall environmental burden is taken into account, including, for example, the energy required to collect waste oil from numerous outlets, recycling may not be the best option. It has been suggested that the yield of useful products for re-refined oil is ~ 65% on average, although there are large variations depending upon the quality or contamination level of the feedstock. Additives lost during the recycling process are largely disposed of to landfill, together with the extraction clay or as a concentrated sludge from a distillation process.

432. Only ~1% of crude oil throughput is used in the manufacture of lubricating oils, and of these some 30% are used as automotive crankcase lubricants. When all the losses involved in the recovery process are taken into account only ~0.1% savings of crude oil could be achieved if all automotive crankcase lubricants were manufactured entirely from recycled oil. Nevertheless, reclaiming and reprocessing of waste oil is a large and well-established industry in many countries in the EU and in the US, but not particularly so in the UK. The US in particular has in fact suffered from a recycling overcapacity - some eleven plants closing during the period 1977 to 1987, during which time only one new plant was started up.

433. The profitability of waste oil recycling is somewhat unpredictable, being controlled by three major factors, all of which are far from stable in the longer term. These are the price of crude oil, regulatory and legal requirements, and tax policy as to recycled lubricating oils. The supply and cost of used oil feedstock, the cost of the process and the value of the products are also important factors. The regulatory and taxation requirements currently in force in the UK do not favour the economics of used oil recycling to produce virgin basestocks. In 1985 it was estimated that approximately 2 million tonnes of waste oil was generated in European Community countries (CONCAWE, 1985). Of this approximately 750,000 tonnes were used as fuel, 700,000 tonnes were regenerated and 600,000 tonnes were unaccounted for.

434. The recycling processes themselves vary in terms of the treatment operations. In addition, because of the wide variety of lubricant types involved, each category is considered separately from the recycling viewpoint under the general headings of automotive crankcase lubricants, hydraulic fluids and cutting oils.

435. For certain categories of lubricant, e.g. industrial oils such as hydraulic fluids, the recycling option is well established, and there are a number of companies who operate recycling processes, either as a stand alone specialist operation, or as part of a larger lubricants manufacturing plant.

436. In the automotive crankcase lubricant field, the use of recycled oil has not always found favour with either original equipment manufacturers (OEMs) or customers. This is probably due to the variety of recycling processes, some of which are purely laundering processes and are unsuited to the production of recycled oil of sufficient quality to be incorporated into premium automotive engine oils. Certain of the German OEMs have approved the use of lubricants containing oils that have been recycled by specified processes that ensure the quality of the recycled material.

9.2 Recycling processes

437. Recycling processes are generally described as follows:

Mechanical purification or reclaiming	This process conserves most of the chemical content.
Adsorptive purification or reprocessing	During this process, many additives will be at least partially removed; the additive contents would need to be restored to the original levels before re-use.
Regeneration or re-refining	These processes produce base oils.
Incineration	This process may be used to recover the energy content of the lubricant or simply to destroy it.

9.2.1 Mechanical purification

438. Mechanical purification of lubricants involves processes such as decantation, centrifugation, or filtration. In situations where the lubricant is unsuitable for further use only as a result of particulate contamination, mechanical separation is all that is required to restore the lubricant to a satisfactory condition. Mechanical separation processes are also normally used as an initial cleanup stage prior to a more comprehensive treatment when this is required. Such processes are often carried out on site (see Sections 7.6 and 8.6).

439. Where there is a significant difference in density between the lubricant and contaminant, such as the presence of metal particles in cutting oils, separation by sedimentation is effective in restoring the lubricant to a satisfactory condition. This can be considerably accelerated by heating the oil to 50-80°C to reduce the viscosity. Centrifugation can be regarded as an enhanced sedimentation process, and can be repeated if required to increase the purification effect. The addition of a small amount of water prior to centrifugation can be advantageous in assisting the coagulation of very fine impurities, although this approach cannot be adopted for oils with emulsion-forming properties.

440. Filtration through paper and paper strip filters, pre-coated filters and membrane filters can be used to remove finely dispersed solids or small quantities of sludge materials from large oil volumes.

441. In general, this method of treatment has little effect upon the additive content of the lubricant, regardless of the type of additive present in the lubricant.

9.2.2 Adsorptive purification

442. Oils contaminated with oxidation products, acidity, or of poor colour, which cannot be purified by the mechanical methods described previously, can be rectified by mixing with adsorbents such as natural or activated bleaching clays or activated carbon. Activated clays are effective in reducing both organic and inorganic acidities, whilst carbon is useful for removing colour and oxidation products. In such processes, the oil is normally first subjected to a water removal stage (decantation or centrifugation) before the adsorbent is added at a level of 1-10 % volume at a temperature of 50-80°C. The mixture is stirred for some 30 to 60 minutes before filtration to remove the adsorbent. The filtration normally consists of several stages, typically:

1. A recessed plate filter press to remove the main part of the adsorbents and impurities.

2. A plate and frame filter press to 'polish' the oil by removing very fine particles. In both this process and the previous process the oil is filtered through paper supported on cloth.

3. A cartridge filter, typically 25 micron to ensure absolute cleanliness.

4. A second cartridge to achieve any pre-determined standard of very fine filtration where required, for example, for hydraulic oils.

5. Following the adsorption treatment, the oil is then normally dehydrated under vacuum to remove dissolved water.

443. The overall yield from this process can be as high as 95%, but a disadvantage is that many of the additives present in the oil can be removed partially or completely by the adsorption process, and must be replenished in order to restore the original properties of the lubricant.

9.2.3 Regeneration

444. Regeneration is only used in the case of heavily contaminated and oxidised oils, i.e. used automotive oils. Conventional regeneration is a multi-stage operation and some of the steps are described in more detail below. Around 25 plants in Europe currently produce regenerated base oils using methods which include distillation, acid/clay and propane extraction. Regeneration is not currently practised in the UK.

445. The oldest and most well established process of regeneration is the acid/clay process. This consists of contacting the used oil with concentrated sulphuric acid which sulphonates the undesirable impurities. After separating off the acid, the recovered oil is treated with lime and bleaching clay to remove further impurities. There are significant environmental problems and costs associated with disposal of large quantities of acid sludge, so later developments of this process have concentrated on reducing the amount of acid used. In many areas the acid/clay processes are now being superseded by the newer processes involving hydrogenation, or thin-film distillation under vacuum.

446. As has been described already, most chemical additives are lost during this process, and the scope for recycling chemicals is virtually nil. The only exceptions are those chemicals, e.g. sulphurised fatty acids, chlorinated paraffins, etc., whose distillation characteristics are similar to those of the base oils. When the process of distillation under vacuum is used to regenerate the oil, some carry-over of these chemicals is possible, although normally the overall quantities are insignificant.

447. When distilling lubricants, the residue from such processes contains most of the additives originally present in the lubricant, either unchanged or as their reaction products. This residue is of limited use, and is normally directly incorporated into bitumen products or burnt as fuel oil under controlled conditions. Sometimes, by following up with a further solvent-extraction processing stage such as propane-deasphalting, some bright stock base oil can be recovered from this additive-rich concentrate.

448. There are a number of variations in the regeneration processes, used in various locations around Europe, which are mainly based on the acid/clay process, thin film evaporation/clay contact finishing or thin film evaporation/hydrotreat finishing. Some examples of processes used in Europe are the Meinken process (a modified acid/clay process), the IFP process (solvent extraction followed by acid/clay treatment), the KTI process (vacuum thin film distillation/hydrotreat) and the Recyclon process (sodium treatment/vacuum distillation). Another technique which is used in the USA is molecular vaporisation which aims to avoid excessive heating of the oil.

9.2.4 Incineration

449. There are a number of options for burning the collected used oil (CONCAWE 1996):

Direct burning	no pre-treatment of the used oil, with several methods of energy recovery; eg burning of used oil in cement manufacture, space heaters, or municipal waste and chemical waste reactors.
Mild reprocessingsimple	cleaning process (mainly separation from water and solids) before further use, eg burning after blending into fuel oil, in road stone plants and in power stations.
Severe reprocessing	used oil is transformed into fuels which can be burned with similar emissions to those from burning other fuel oils. The process unit to produce these includes a flash column to remove water, a light vacuum distillation

column to remove light ends and gas oil, and a high vacuum distillation column producing distillates and vacuum residues containing the additives.

9.3 General comments

450. Product recycling in the UK is limited to very few operators. Of these, by far the most significant are Castrol, Lanstar Refineries and Smallman Lubricants. Smaller operators include Chapelsvant, Oil Inventions and some specialised products at Silkolene.

451. The total volume of lubricant currently recycled in the UK is estimated at some 40,000 tonnes/year. Of this total approximately 60% (24,000 tonnes/year) is mineral oil hydraulic fluid, 22% (8,800 tonnes/year) is neat cutting oil, and the remaining 18% (7,200 tonnes/year) is made up of transformer oils, gear oils, heat treatment (quenching) oils, spark erosion fluids, circulatory system oils, etc. Collected used oil is sometimes contaminated with other liquids.

452. Unlike lubricant blending plants, in the UK recycling plants are identified as prescribed processes, and for the purposes of compliance with the Environmental Protection Act, 1990, are registered with HMIP (Her Majesty's Inspectorate of Pollution) as the regulatory authority.

453. The quality of re-refined base oils depends on the used oil feedstock, the process technology employed, the severity of re-refining carried out and the quality control procedures for the products.

454. Chlorine in used oils can pose problems in re-refining. Various halogenated volatile organic compounds such as perchloroethylene and 1,1,1-trichloroethane have been detected in used oil.

9.4 Recycling of automotive crankcase lubricants

455. These products are heavily contaminated during use and are not therefore suitable for re-processing using simple laundering processes such as mechanical purification or adsorptive purification. The disposal options are therefore limited to regeneration or to burning as fuel. The regeneration of automotive used oils by re-refining has not been habitually practised in the UK due to generally unfavourable economics. In times of high oil prices, when the re-refining route becomes a more attractive proposition, the potential for additive recycling is zero since virtually all additives are removed during the re-refining process, and are disposed of as landfill or incorporated into bitumen products.

456. A further complication that arises in the case of the re-processing of automotive crankcase oils is the difficulty of collection. Sump-drainings emanating from car and commercial vehicle-servicing workshops can be bulked, and, since the waste oil has a value, can then be collected in viable quantities by a suitably registered waste disposal contractor. Problems can arise for the re-processor in that the used oil can be contaminated with, for example, battery acid, brake fluid and anti-freeze, chlorine-containing solvents and even vegetable oils from chip frying.

457. Some organisations equipped with suitable facilities burn the used oil in-house to provide heating, although there is some concern of the possibility of adverse environmental or health and safety consequences arising from this practice.

458. The main problem arises with the DIY car owner. It has been estimated (UKPIA/BLF, 1994) that some 40,000-45,000 tonnes/year of used oil comes from such sources in the UK. Since this oil is defined as household waste in the UK under the terms of the Environmental Protection Act (1990), it becomes the responsibility of the local authority to ensure that such used oil is properly collected and disposed of in a suitable manner.

459. In fact, the same report describes that it is estimated that only 4.5% of the waste oil from the DIY sector is collected at local authority facilities. A number of attempts have been made to improve this situation including the provision of oil recovery banks on filling station forecourts, educating the public by the provision of point-of-sale leaflets, provision of free-of-charge under-car waste oil receptacles, environmental labelling of oil packs, etc.

460. To summarise, the most attractive option currently applicable to used automotive crankcase oils in the UK is to incorporate the waste oil into fuel oil after a preliminary cleanup procedure, typically involving a heat-soak, followed by filtering and centrifuging. There are some residual concerns regarding the environmental effects of burning such waste oils that can contain appreciable quantities of some heavy metals, including lead. Subject to some control on metals content, the cement kiln is an attractive option for burning such waste oils. The main advantage of the cement kiln operation is that undesirable contaminants which would otherwise pollute the atmosphere are chemically 'fixed' within the cement and not released.

461. CONCAWE (1996) presented an indication of the amounts of used oil burnt in European countries (Table 9.1). The figures are based on data obtained from Denmark, Finland, France, Germany, Italy, The Netherlands, Norway, Spain and the United Kingdom.

462. In the US, approximately 75% of used oil is reprocessed into industrial fuels and other items, and a further 11% is burned in specific furnaces as space heaters in garages and other related businesses. The other 14% is re-refined in motor oil.

Table 9.1 Indication of amounts of used oil burned in EU countries (CONCAWE 1996)

Burning options	**Amount (kT)**	**%**
Cement kilns	307	42
Waste incinerators	52	7
Garage heaters	40	6
Mixed with fuel oil	213	29
Other	120	16
Total burned	732	

9.5 Recycling of hydraulic fluids

463. In general, industrial oils such as hydraulic fluids are only lightly contaminated, and are normally returned to the re-processor in bulk as a discrete batch. This batch is re-processed in its entirety, treated with extra additive if necessary to regain its original properties, and returned, again in bulk, to the customer, i.e. a 'closed-loop system'. The whole procedure is well regulated and tightly controlled, even more so since the introduction of the UK Waste Disposal Regulations, (see Section 5.2.2.3).

464. Such external recycling of hydraulic fluids is limited to non-aqueous products, i.e. based on mineral oil or phosphate esters. Hydraulic oils are generally treated by the adsorptive process, using activated clay or carbon, generally as a single pass. The additives present in the hydraulic fluid are depleted to differing extents depending upon their polarity, and their consequent susceptibility to removal by adsorption onto the surface of the active ingredient. The overall yield of the process varies between 80 and

95% depending upon the depth of the treatment. This recovery is expressed on a water-free basis, since fluids presented for laundering quite often contain appreciable quantities of water. Most of the balance of the 5-20% of oil not recovered is used for line flushing etc., and would be disposed of as waste oil. Additives removed during reprocessing would be adsorbed onto the activated clay or carbon, which would then be used as landfill. Additives that are present to improve the frictional characteristics of the fluid such as zinc dialkyldithiophosphate (ZDDP) are generally little depleted by activated clay, but more so by activated carbon. If hydrolysis of the ZDDP has occurred, then the additive may precipitate and be largely removed.

465. After a laundering process, typically the re-processed product will be 'spiked' with some 50% of the original ZDDP level, in order to fully restore the characteristics of the product. Viscosity-index improvers and pour-point depressants, although being relatively non-polar, are also depleted to some extent, and limited 'spiking' may be necessary of the re-processed product. Corrosion inhibitors are not generally depleted, and are not boosted in the re-processed product.

466. Phosphate ester fluids are re-processed in a similar fashion, the overall yields being similar to those of the mineral fluids. Additive boosting is not as relevant as for the mineral oil products. The main purpose of laundering such products is to remove the products of hydrolysis, to which certain phosphate ester fluids are particularly susceptible.

9.6 Recycling of cutting oils

467. The external recycling of cutting oils is limited to neat oils based on mineral hydrocarbons. As with hydraulic fluids, such products are relatively lightly contaminated, and are normally returned to the re-processor in bulk or in drums as a discrete batch. This batch is re-processed in its entirety, treated with extra additive if necessary in order to regain its original properties, and returned, again in bulk or drums, to the customer. As with hydraulic fluids, the whole procedure is well regulated and tightly controlled in the UK.

468. Neat cutting oils are generally treated by the adsorptive process, using activated clay or carbon, generally as a single pass, and at a treat level of between 1 and 10%. Any additives present in the cutting fluid are depleted to differing extents depending upon their polarity, and their consequent susceptibility to removal by adsorption onto the surface of the active ingredient. The overall yield of the process varies between 80 and 95% depending upon the depth of the treatment.

469. Cutting fluids vary more in their composition and additive treat than hydraulic fluids, since their characteristics are tailored to meet a variety of cutting operations involving a variety of metals. The most straightforward fluids consist only of mineral oils containing no additives, therefore additive recycling is not appropriate. Fluids designed for somewhat heavier duties, or when cutting soft metals such as aluminium, contain fatty acid additives. Due to the polar nature of these additives, they are partially removed by both activated clay and carbon. The re-processor will often add back typically some 50% of the original level of these additives.

470. Heavy-duty cutting fluids contain extreme-pressure additives such as chlorine or sulphur compounds. The chlorinated additives used consist of chlorinated paraffins, which are relatively non-polar, and are therefore virtually unaffected by the treatment process, regardless of whether activated clay or carbon is used. The sulphurised additives normally consist of sulphurised fats or neat sulphur. These additives are intended for use in those fluids designed for particularly arduous applications. Similarly to the chlorinated additives above, such additives are little affected by the treatment process, and the sulphur contents of the re-processed fluids are little changed, and do not require replenishment following processing.

471. It must be noted that in the case of soluble or synthetic (water-based) cutting fluids, in-house treatment normally takes place, which can be a form of recycling. Also, in large organisations such as motor vehicle manufacturers, in-house re-processing often extends to include the sort of recycling treatment provided by external companies to the smaller organisations.

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Comma Oils & Chemicals Ltd
Ethyl Petroleum Additives Ltd
Exxon Chemical Ltd
Hornett Bros & Co Ltd
Houghton Vaughan plc
Hunting Secon Ltd
International Bioremediation Services Ltd
Industrial Lubricant Manufacturers Association (ILMA)
Lanstar Oil Refineries Ltd
Lubrizol (Great Britain) Ltd
Machine Tool Technical Association (MTTA)
Mobil Oil Company Ltd
Polartech Ltd
Rhein Chemie Business Group
Shell Oils
Silkolene Lubricants plc
Smallman Lubricants Ltd
Technical Committee of Petroleum Additive Manufacturers in Europe (ATC)

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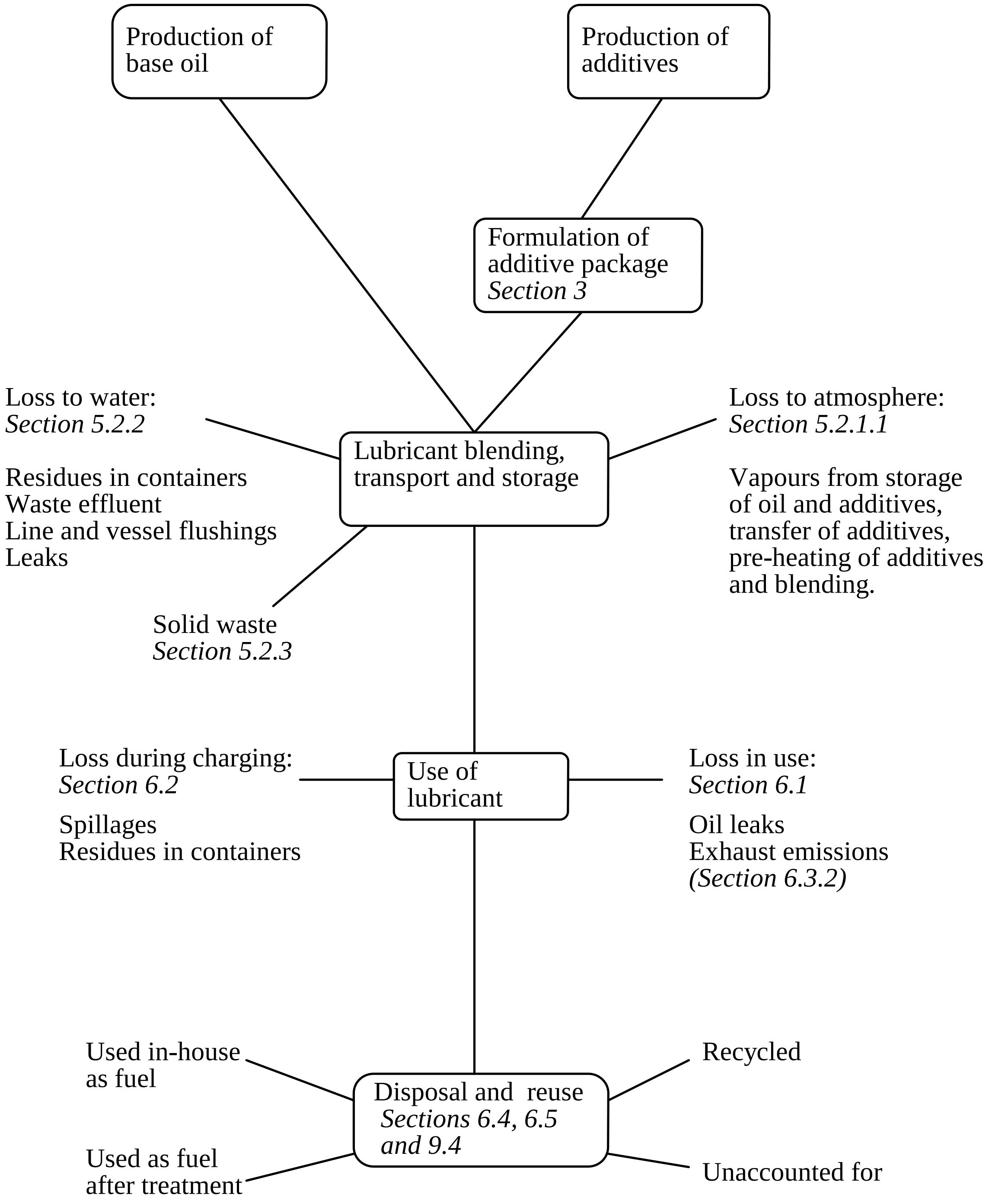
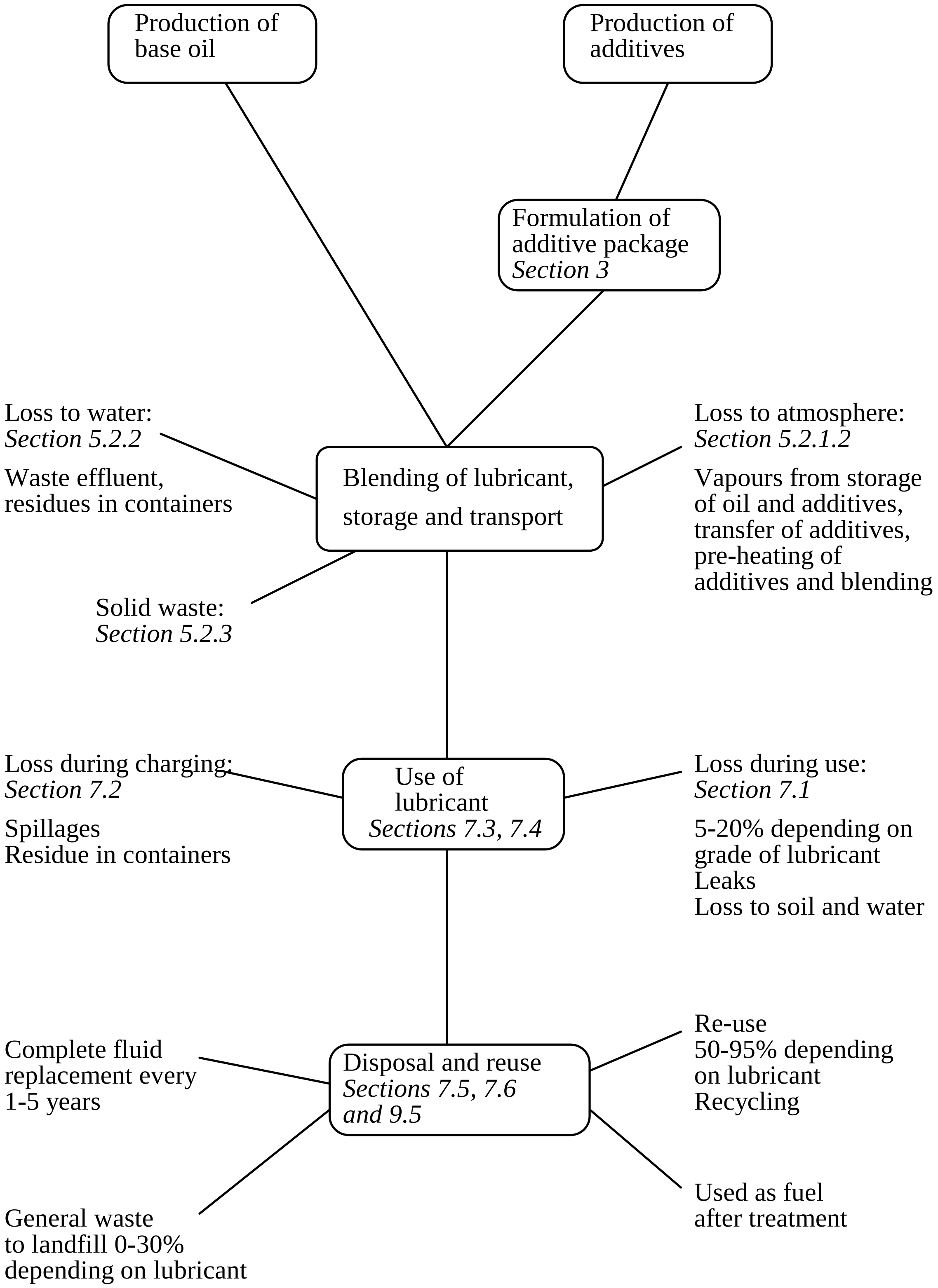
APPENDIX A

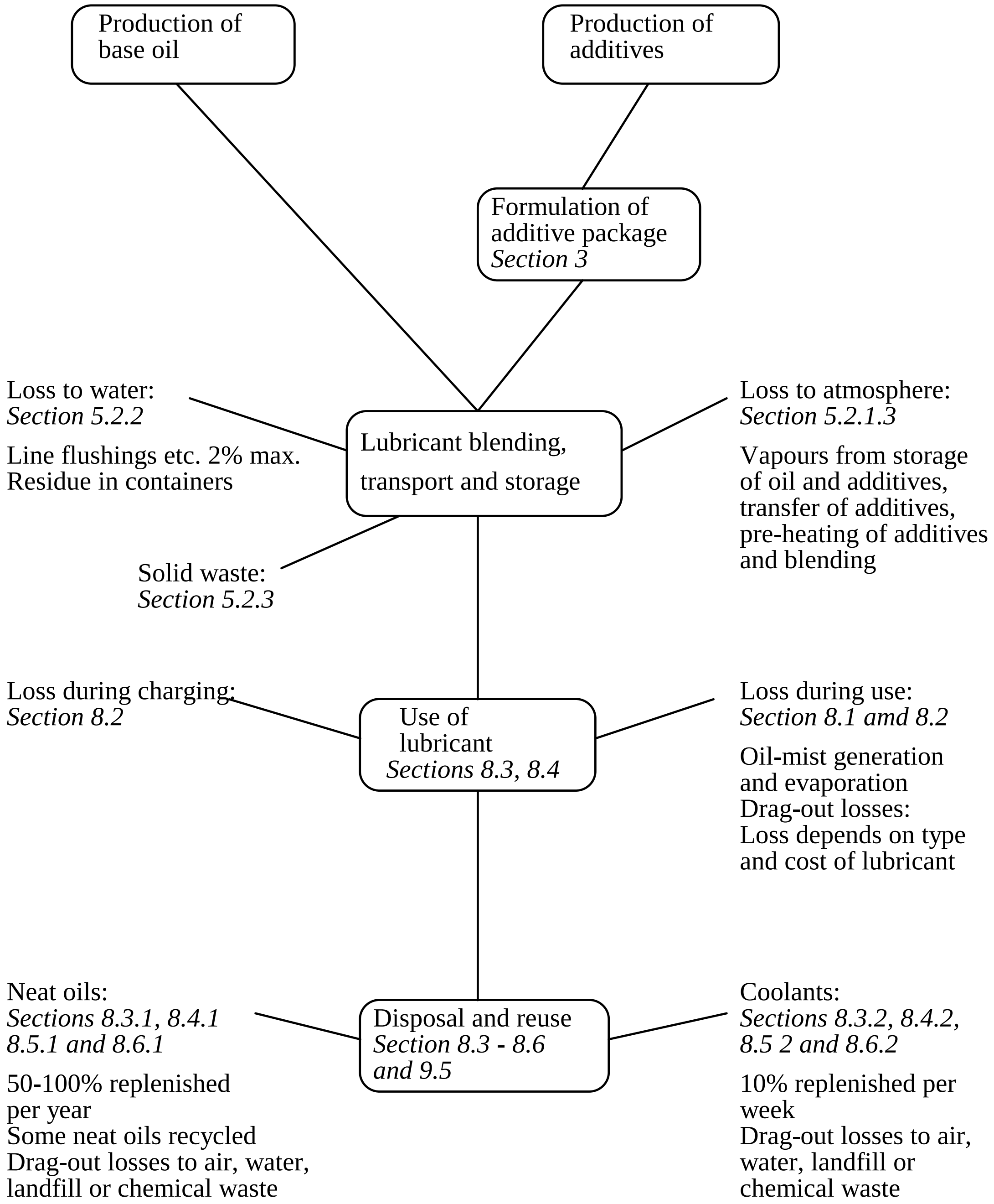
AUTOMOTIVE CRANKCASE LUBRICANT FLOW DIAGRAM



HYDRAULIC FLUIDS FLOW DIAGRAM



METAL WORKING (CUTTING) FLUIDS FLOW DIAGRAM



Appendix B

Glossary

Alkylation - A process in which hydrocarbons with a branched ring structure combine catalytically with an unsaturated hydrocarbon.

API - The American petroleum Institute: an organisation of the North American petroleum industry. API's Committees, made up of member company participants, function by consensus in communicating recommended practices to government officials and other appropriate parties.

ASTM - American Society for Testing Materials. This organisation (along with the IP, see below) is responsible for the issue of many of the standard methods used in the petroleum industry.

ATC - Technical Committee of Petroleum Additive Manufacturers in Europe: all major European additive suppliers are represented.

Flash Point - A term applied to materials that ignite and burn easily. There are a number of variants of standard test procedures, which may influence the results obtained. It is the lowest temperature at which vapours arising from the oil will ignites momentarily (i.e. flash) on application of a flame under specified conditions.

Hydrocracking - A process combining cracking, or pyrolysis, with hydrogenation.

ILMA - The Independent Lubricant Manufacturers Association. An American organisation which is composed of companies not associated with major petroleum companies.

IP - Institute of petroleum. The official British organisation which deals with the petroleum technology and with the standardisation of methods of test for petroleum.

MTA - Metric tonnes per annum.

Pour Point - This is the lowest temperature at which an oil will pour or flow when it is chilled without disturbance under prescribed conditions.

Raffinate - The desired product of the solvent extraction process.

Solvent Extraction - Processes in which solvents are used to dissolve out undesirable components, e.g. the removal of aromatics from kerosene by extraction with liquid sulphur dioxide.

Viscosity Index (often abbreviated to VI) - An arbitrary number used to describe the rate at which the viscosity of a lubricating oil changes with temperature. Oils of high VI exhibit relatively small changes in viscosity with increased in temperature and vice versa.

VT - Viscosity/Temperature, i.e. as in VT characteristics, which are defined under VI above.

Appendix C

Molecular weight and vapour pressures of base oils

a Molecular weights (MW)

The values are derived from a summary of the data in the Kirk-Othmer Encylopedia of Chemical Technology, 3rd Edition, Vol 14 relating to the main types of base oils for automotive crankcase lubricants.

Petroleum lubricants (page 484)

Paraffinic

low viscosity oils	molecular weight	250
very viscous oils	molecular weight	1000
estimated average	molecular weight	625

Synthetic oils

Organic esters of carboxylic acids (page 496)
Dicarboxylic acids from C_6 (adipic) to C_9 (azaleic) or C_{10} (sebacic) acid esterified with C_6 to C_9 branched-chain alcohols.
MWs: adipic acid and C_6-alcohol, 146 and 102 respectively for ‘minimum’
MWs: sebacic acid and C_9-alcohol, 202 and 144 respectively for ‘maximum’.
From these the minimum and maximum molecular weights can be calculated as the MW of the acid plus twice the MW of the alcohol minus 2*18 (water formed by esterification).
Minimum MW: 146 + 2*102 - 2*18 = 314
Maximum MW: 201 + 2*144 - 2*18 = 454
Estimated MW: 400 (average of maximum and minimum is 384).

Hydrocarbons (polyolefins) (page 499)
Chain size of about 20 to more than 100 carbon atoms, formula C_nH_{2n+2}.
MW for C_{20} chain: 282
MW for C_{100} chain: 1402
Estimated MW: 800 (average of minimum and maximum 842)

b Vapour pressures

Approximate vapour pressures for the base oils are calculated from the assumption of a maximum concentration of 1 mg/m^3 in air, also assuming that the base oil can be considered as a single substance and that the ideal gas law applies. The formula used is:

$$C = (MW/22.4) * (p^o_b/101300) * (273/T) * 10^6$$

where

Symbol	Variable	Unit	Value(s) in calculations
C	concentration	mg/m^3	1
MW	molecular weight of oil (from above)		(1) 625; (2) 400; (3) 800
p^o_b	saturated vapour pressure of pure oil	Pa	to be calculated
T	Temperature	K	285

The resulting vapour pressures from these calculations are:

(1)	paraffinic base oils	0.004 Pa
(2)	organic esters	0.006 Pa
(3)	synthetic hydrocarbons	0.003 Pa

Appendix D

Emission scenario for release of crankcase lubricants to roadside soil and water

The release of crankcase oils and oil additives to roads and hence to soil and water at roadsides can be estimated in two steps:

a) Calculation of emission factors for oil losses due to leakage
b) Calculation of the emissions using actual data on vehicle flows and emission factors of different vehicle types.

Emission factors can be calculated by using the ATC estimation of 1% loss of lubricant through leakage during service life and the data on annual mileage and total used oil per car per year from Table 6.1, Chapter 6.2. A density for the lubricant of 0.9 kg/l is assumed to convert the emission factors to a mass basis.

$$Q_{\text{lubricant, road}}\ (\text{kg/km}) = \frac{\text{Used oil per car per year}}{\text{Annual mileage}} * \frac{1}{100} * 0.9$$

The results of this calculation are in Table D1.

Table D1Emission factors for crankcase oils and additives due to leakage

	Passenger cars (petrol)	**Passenger cars (diesel)**	**Commercial heavy duty diesel**
Emission factor $Q_{\text{lubricant, road}}$ (kg/km)	$2.4*10^{-6}$	$3.6*10^{-6}$	$18*10^{-6}$

For the calculation of the emissions data on vehicle flows (VF) should be available. Table D2 gives data on approximate vehicle flows on different road classes.

Table D2Vehicle flows by road class

vehicles/day ($\mathbf{N_{vehicle\_type,\ road\_type}}$)	**road surface (m2/km)** ($\mathbf{AREA_{road\_type}}$)	**road class**
500 - 2000	4000 - 6000	*Minor roads*
10000 - 30000	6000 - 8000	*Major roads*
30000 - 80000	20000	Motorways

The lubricant may be washed from the road surface by rain water. For the current scenario, any partitioning of additives between the rain water and oil is ignored, and it is assumed that the lubricant is removed containing its active level of each additive. Where there is a drainage system beside the road, the runoff may be taken into a waste water system or into surface water. It is also possible for runoff to infiltrate the soil at the edge of the road. Two extreme scenarios will be considered here.

In the first, it is assumed that all of the lubricant lost from vehicles is removed by runoff water and the concentration in this runoff water is estimated. Note that this is not necessarily the concentration in surface water. The annual rainfall is used for this calculation. The calculation needs to be performed for each vehicle type (petrol and diesel passenger cars, commercial diesels) of relevance for the substance of interest.

The percentages of the total vehicle kilometres covered by passenger cars (petrol), passenger cars (diesel) and commercial heavy duty diesel are 79%, 10% and 11% respectively (calculated from the data in Table 6.1, Chapter 6.2). These figures are $F_{vehicle\_type}$.

The concentration of lubricant in the runoff water is given by:

$$C_{road\_runoff} = \frac{Q_{lube,road} \times N_{vehicle\_type,road\_type} \times F_{vehicle\_type}}{\left(DEPTH_{rain} \times 10^{-3} / 365\right) \times AREA_{road\_type}} \times 1000$$

Symbols are explained and summarised below. The equation above calculates the concentration of the whole lubricant; concentrations of additives can be derived using the appropriate concentration in the lubricant (F_{add} from Table 4.1).

For the second scenario, it is assumed that all of the runoff infiltrates a section of soil at the side of the road which has an area of 10% of the road surface. In this case the flux of lubricant into the soil is calculated.

The equation for the flux of lubricant into the soil is:

$$FLUX_{lube,\,soil} = \frac{Q_{lube,road} \times N_{vehicle\_type,road\_type} \times F_{vehicle\_type}}{AREA_{road\_type} \times 0.1}$$

Again, the flux of additive can be obtained using the relevant F_{add} from Table 4.1.

Explanation of symbols:

37 $Q_{lube,\ road}$	**38** = average quantity of lubricant leaked per vehicle in 1 km	**39** [kg.km^{-1}.car^{-1}]	**40** Table D1 or similar statistics
41 $N_{vehicle\_type,\ road\_type}$	**42** = number of vehicles of each type per day on each type of road	**43** [car.d^{-1}]	**44** Table D2 or similar statistics
45 $AREA_{road\_type}$	**46** = area of each road type per km	**47** [m^{2}.km^{-1}]	**48** Table D2 or similar statistics
49 $F_{vehicle\_type}$	**50** = fraction of total vehicle kilometres covered by vehicle type	**51** [-]	**52** Values calculated above, or similar statistics
53 $DEPTH_{rain}$	**54** = annual rainfall depth in mm	**55** [mm]	**56** Default 700 mm, or specific data
57 C_{road_runoff}	**58** = concentration of lubricant in runoff water	**59** [mg.l^{-1}]	**60**
61 $FLUX_{lube,\ soil}$	**62** = flux of lubricant to soil	**63** [kg.m^{2}.d^{-1}]	**64**