

SELECTION OF SYNTHETIC OILS

1. INTRODUCTION

This Data Item will assist in the selection of a liquid lubricant for applications in which a mineral oil is not the most suitable. A mineral oil might be unsuitable where the operating temperature range is too great or where there are special requirements such as low carbonisation or low flammability. The Item is mainly applicable in situations where a continuous lubricant film is maintained between the moving surfaces (for example, hydrodynamic or hydrostatic bearings) but will also be of use for applications involving boundary lubrication. The Item describes the general characteristics of the available synthetic alternatives and provides a comparison between the various types. Only the most important commercially available finished oils, incorporating whatever additives have been found to be appropriate, are considered. Greases, the properties of which depend on the base oil and the thickener, are not considered.

Petroleum or mineral oils are generally complex mixtures consisting mainly of hydrocarbons. In contrast, synthetic oils are usually composed of molecules of similar type with a more limited spread of molecular weights. Among the potential advantages of synthetic oils are extremely wide operating temperature ranges, fire resistance and resistance to oxidation and nuclear radiation. Of course, no single lubricant can combine all potential advantages, but the relative ease with which the performance properties of synthetic lubricants can be controlled in general, means that it is often possible to optimise individual members of a lubricant family to satisfy the requirements of a particular application.

The synthetic lubricants considered in this Item are classified by their basic chemistry (see Table 1.1). The Item consists of two major parts. The first part discusses the main requirements of a lubricant and provides a broad indication of the trade-off between those requirements that is provided by the various classes. The second part of the Item discusses each lubricant class in turn and indicates the properties of typical members.

TABLE 1.1 LUBRICANT CLASSES (IN APPROXIMATE ORDER OF USE)

Class name	Other names or sub-classes
Mineral Oils (for comparison)	Paraffinic Naphthenic
Synthetic Hydrocarbons	Polyalphaolefines (PAO) Polyisobutenes (PIB) Alkylbenzenes
Di-Esters	Dibasic acid esters Aliphatic diesters Sebacate diesters
Polyol Esters	Hindered esters Complex esters Neopentyl polyol esters Neopentyl glycol esters Trimethylolethane esters Trimethylolpropane esters Pentaerythritol esters
Polyglycols	Glycols Polyethers Polyalkylene glycols Polyoxyalkylene glycols Polyethylene glycols Polypropylene glycols
Phosphate Esters	Triaryl phosphates Alkyl aryl phosphates Phosphoric acid esters
Silicones	Polysiloxanes Dimethyl silicones Phenylmethyl silicones Chlorophenyl silicones
Silicate Esters and Disiloxanes	Orthosilicate esters Tetra-aryl silicates Alkyl silicates
Polyphenyl Ethers and C-Ethers	
Perfluoropolyalkyl Ethers (PFPAE) [†]	Perfluoroalkyl ethers (PFAE) Perfluoroalkyl polyethers Perfluoropolyethers (PFPE)

[†] There are a number of different types of perfluoropolyalkyl ether with significantly different properties. The trade names "Krytox", "Fomblin Y", "Fomblin Z" and "Demnum" have been used throughout this Item to distinguish between the types.

2. LUBRICATING OIL REQUIREMENTS

This section discusses the primary requirements of a lubricating oil and provides, where appropriate, a broad comparison between the lubricant classes. Individual properties and characteristics are discussed under the following headings.

- (i) Viscosity Characteristics and Density
- (ii) Lubricant Life
- (iii) Equipment Life
- (iv) Hazards
- (v) Cost

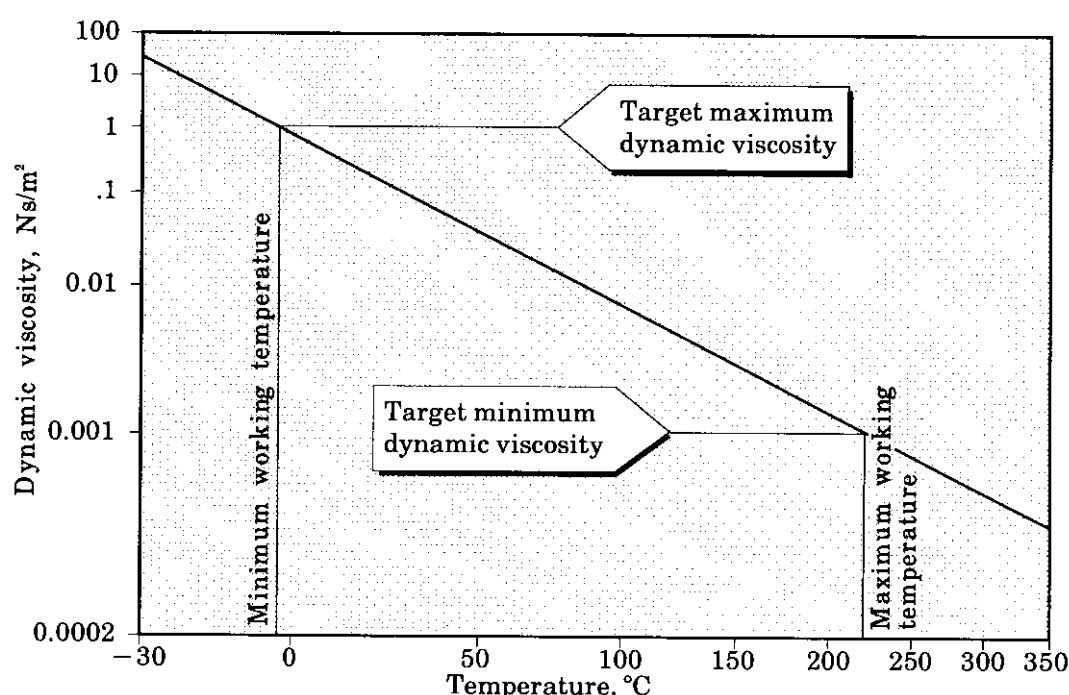
Within any one class of lubricant a considerable range of properties is possible and so it is difficult to characterise the lubricant classes on the basis of individual properties. However, a lubricant is rarely selected on the basis of one all-important requirement and usually a whole host of often-conflicting requirements will need to be considered. Different classes of lubricant often allow different trade-offs to be made thus allowing the most appropriate lubricant class to be identified.

The charts presented in this section are approximate only and are intended to allow a broad comparison of the various classes. To select a particular lubricant the lubricant suppliers should be consulted.

2.1 Viscosity Characteristics and Density

• Viscosity/temperature characteristics

One of the primary requirements of a lubricant is to exhibit a suitable dynamic viscosity over the whole of the working temperature range. The viscosity should not be too high at the lowest expected operating temperature or too low at the highest expected operating temperature. The minimum allowable viscosity is often determined by the requirement to generate sufficiently thick lubricating films in, for example, hydrodynamic bearings (see Reference 1) and rolling bearings (see Reference 2). For the purposes of characterising lubricants, various target values of viscosity can be set. However, values of dynamic viscosity below about 10^{-3} N s/m^2 (1 cP) are usually regarded as inadequate on the basis of lubricant film generation. Similarly, values of dynamic viscosity above about 1 N s/m^2 (1000 cP) can incur pumping problems and excessive start-up power losses.



Sketch 2.1 Definition of temperature limits based on viscosity constraints

Sketch 2.1, which shows the viscosity/temperature characteristics for a typical lubricant within the class of Perfluoropolyalkyl ethers, illustrates that by imposing arbitrary target maximum and minimum viscosity values of 1 N s/m^2 and 10^{-3} N s/m^2 , a minimum and a maximum working temperature can be established for each individual lubricant. Figure 2.1 includes these temperature limits as axes and accordingly, individual lubricants would be represented by single points on the chart. The chart can be used to select the classes of lubricant that are most likely to include a suitable lubricant for a required working temperature range. The envelope for each class encloses data for the available formulations and grades. Within each class of lubricant, a wide range of viscosity grades is often available. However, a lubricant chosen from a class with generally poor viscosity/temperature characteristics, such as the Polyphenyl Ethers, will allow only a narrow working temperature range. On the other hand, a lubricant chosen from a class with generally very flat viscosity/temperature characteristics, such as the Silicones or the Perfluoropolyalkyl ethers, will allow a very wide operating temperature range.

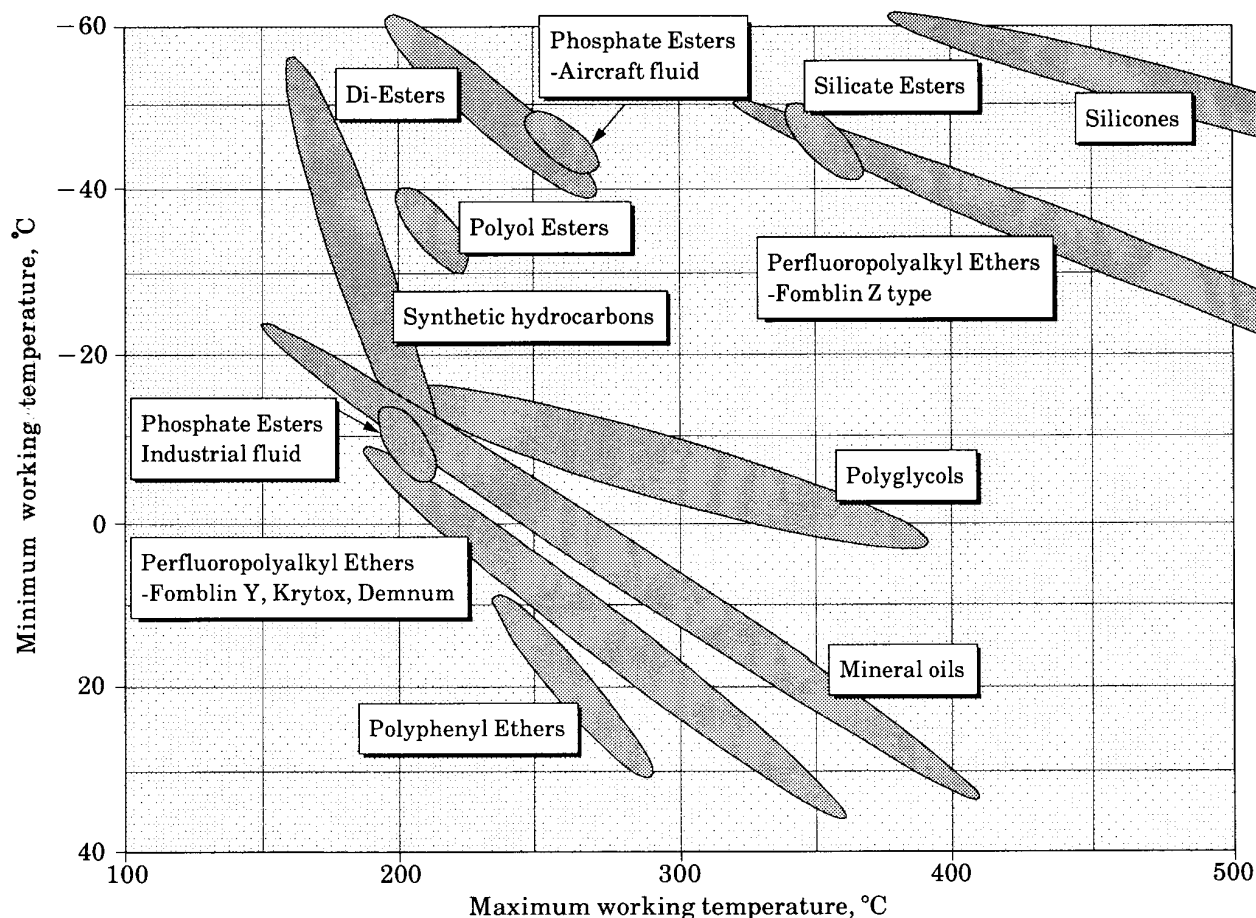


FIGURE 2.1 TEMPERATURE LIMITS BASED ON DYNAMIC VISCOSITY CONSTRAINTS

EXAMPLE:

A lubricant is required for equipment that is to operate in sub-zero temperatures. The specification calls for start-up in ambient temperatures of -20°C . In operation, lubricated surface temperatures of up to 250°C are expected.

The example application calls for a minimum working temperature of -20°C and a maximum working temperature of 250°C . A perfluoropolyalkyl ether, a silicone or a silicate ester would appear to be required although some di-esters or phosphate esters might be suitable. All other lubricant classes (as indicated by the cross-hatched area) are unlikely to include a suitable lubricant.

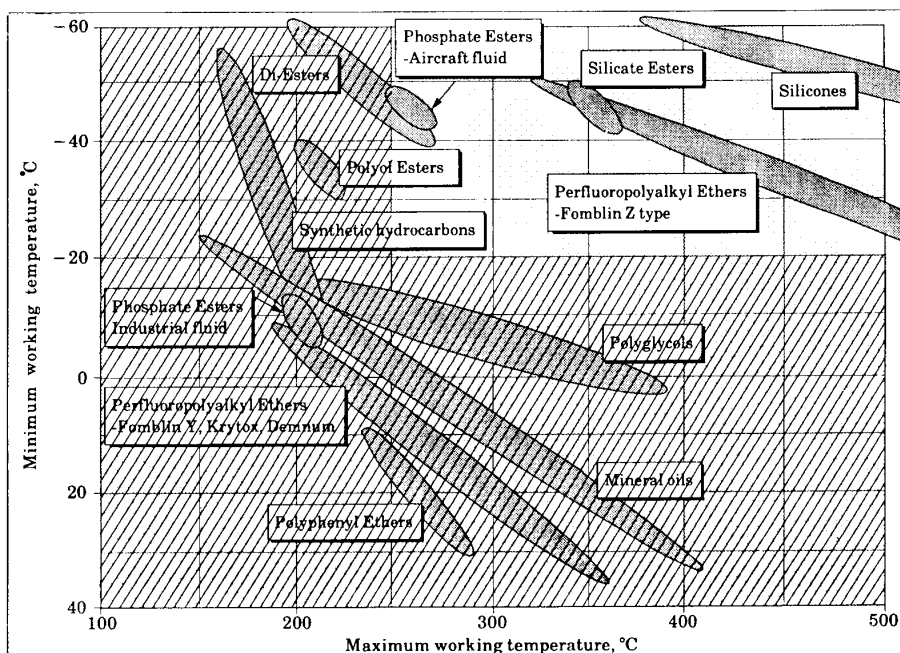


FIGURE 2.1 TEMPERATURE LIMITS BASED ON DYNAMIC VISCOSITY CONSTRAINTS

- **Viscosity/pressure characteristics**

The viscosity of most lubricants increases significantly under pressure. The rate at which the viscosity changes with pressure is indicated by the so-called “pressure exponent of lubricant viscosity”[†] typical values of which are indicated in Figure 2.2. A lubricant with a higher pressure exponent can provide an increase in lubricant film thickness under the elastohydrodynamic lubrication conditions (see References 3 and 4) that occur in gears and rolling bearings. However, in some cases the benefit of a high pressure exponent will be offset by a greater change of viscosity with temperature.

- **Viscosity/shear rate characteristics**

A lubricant is often subjected to high shear rates in bearings and pumps and when forced through small orifices. Some lubricants, particularly silicone oils and those incorporating a viscosity index improver, exhibit non-Newtonian behaviour in which the viscosity decreases at high shear rates. In such cases the effective viscosity of the lubricant in a bearing may be lower than the quoted value measured by a standard test method in which shear rates are low.

Most lubricants suffer little or no permanent reduction in viscosity in use. However, some lubricants, particularly those incorporating a viscosity index improver, suffer a steady and permanent reduction in viscosity when repeatedly subjected to high shear rates. The manufacturers should be consulted if precise control of lubricant viscosity is required.

- **Density**

As detailed in Table 2.2 the density of some of the synthetic oils, especially the perfluoropolyalkyl ethers, is significantly higher than that of the mineral oils. Density may need to be considered when designing systems involving suction lift.

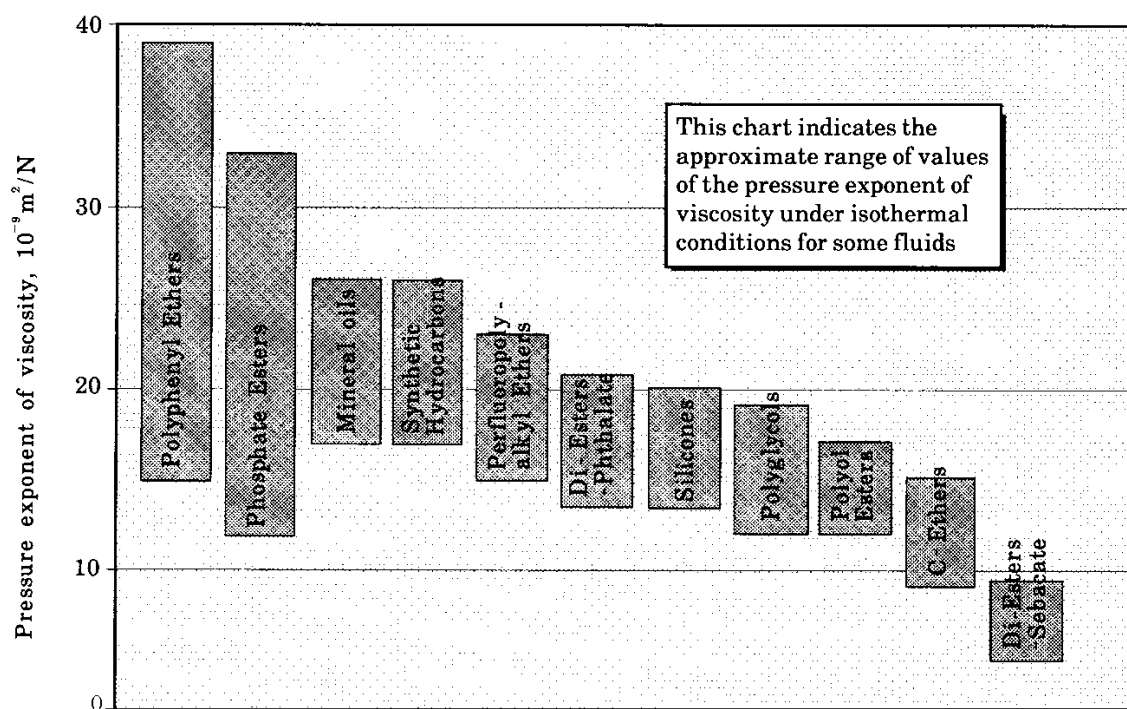


FIGURE 2.2 PRESSURE EXPONENT OF VISCOSITY

[†] The pressure exponent of lubricant viscosity is defined by the expression $\eta = \eta_0 \exp(\alpha p)$ where η is the dynamic viscosity, η_0 is the dynamic viscosity at atmospheric pressure and at operating temperature, α is the pressure exponent of lubricant viscosity and p is the lubricant pressure.

2.2 Lubricant Life

As well as having acceptable viscosity characteristics, a lubricant must have an adequate life under the expected operating cycle. Lubricant life is determined by deterioration and contamination. Thermal decomposition rates and oxidation rates must both be acceptably low. Degradation of the lubricant due to ingress of contaminants such as water can also be significant.

- **Thermal stability and oxidation limits**

Figures 2.3 and 2.4 indicate the approximate thermal stability limits and the oxidation limits for the various classes of lubricants. The rate at which the properties of a lubricant change when maintained in an inert atmosphere at elevated temperatures is indicated by the thermal stability limits. A related parameter, the initial thermal degradation temperature, indicates the temperature at which thermal decomposition, as opposed to other degradation processes already operating, begins to affect lubricant life (see Section 3 for comments on specific lubricants).

In many applications, such as internal combustion engines, turbines and hydraulic equipment, oxygen will be present and the resistance of the lubricant to oxidation is then very important. Lubricant oxidation products are undesirable for several reasons. Insoluble decomposition products (sludge) may clog oil holes, pipelines, filters and other components of the lubrication system. Soluble decomposition products tend to be acidic and may eventually lead to corrosion or pitting of bearing surfaces or form tenacious varnish deposits on parts operating at high temperatures. Table 2.1 summarises the decomposition products of the various classes.

Oxidation limits can only ever be very approximate because oxidation rates are very sensitive to the particular conditions of use. Oxidation is never entirely absent but proceeds very slowly at room temperature. Oxidation rates increase rapidly with temperature and can be catalysed by metals, especially particles of copper and iron. The presence of moisture can also encourage decomposition as can agitation or churning of the lubricant.

Experimentally determined thermal stability and oxidation limits do not always correlate with lubricant performance in, for example, gas turbine engines. In such equipment the lubricant may spend long periods of time at quite modest temperatures but experience comparatively short duration, high temperature conditions at so called "hot-spots". Any decomposition products produced may then accumulate in critical components such as bearings and valves.

- **Hydrolytic stability**

The resistance of a lubricant to degeneration by water can be an important characteristic in its use. Hydrolytic stability is often measured by refluxing a sample of the lubricant with pure water for a length of time and then determining the total acidity of both the water and the lubricant. In general, the ester lubricants are the most susceptible to hydrolysis (see Table 2.2).

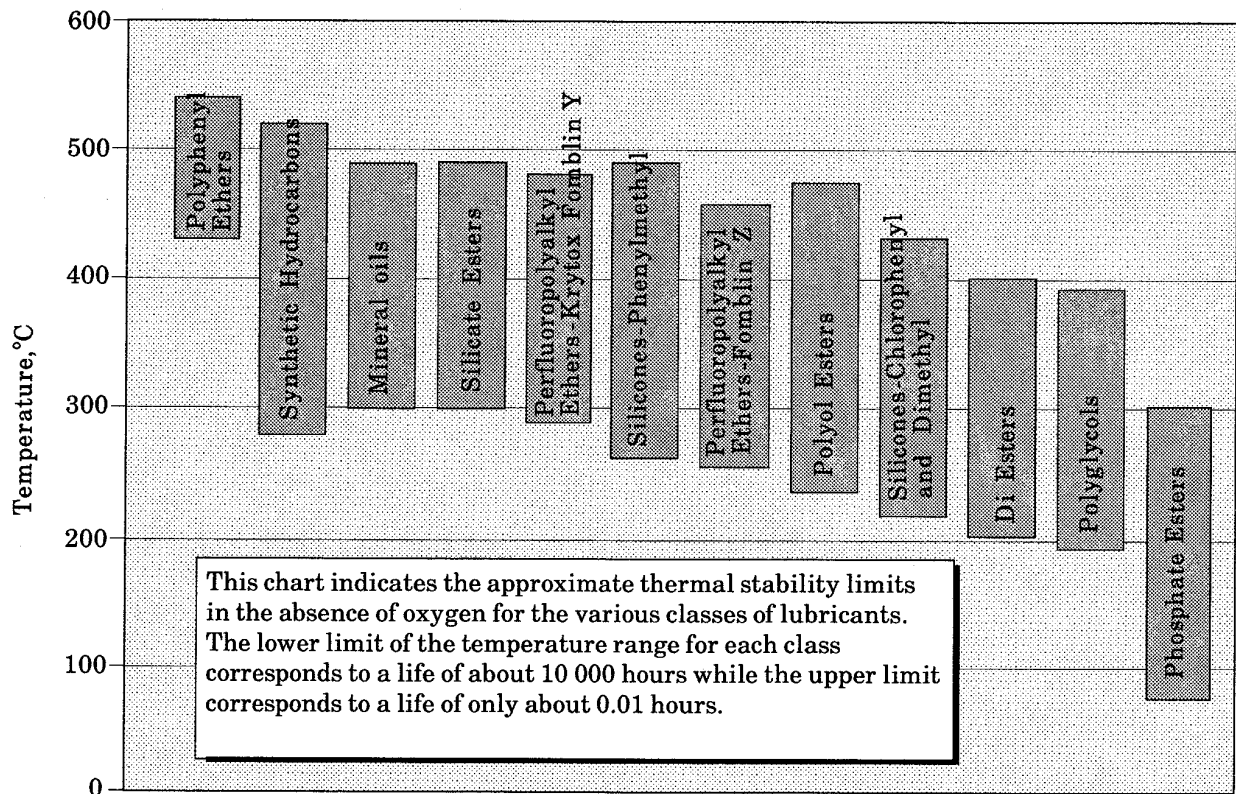


FIGURE 2.3 THERMAL STABILITY LIMITS

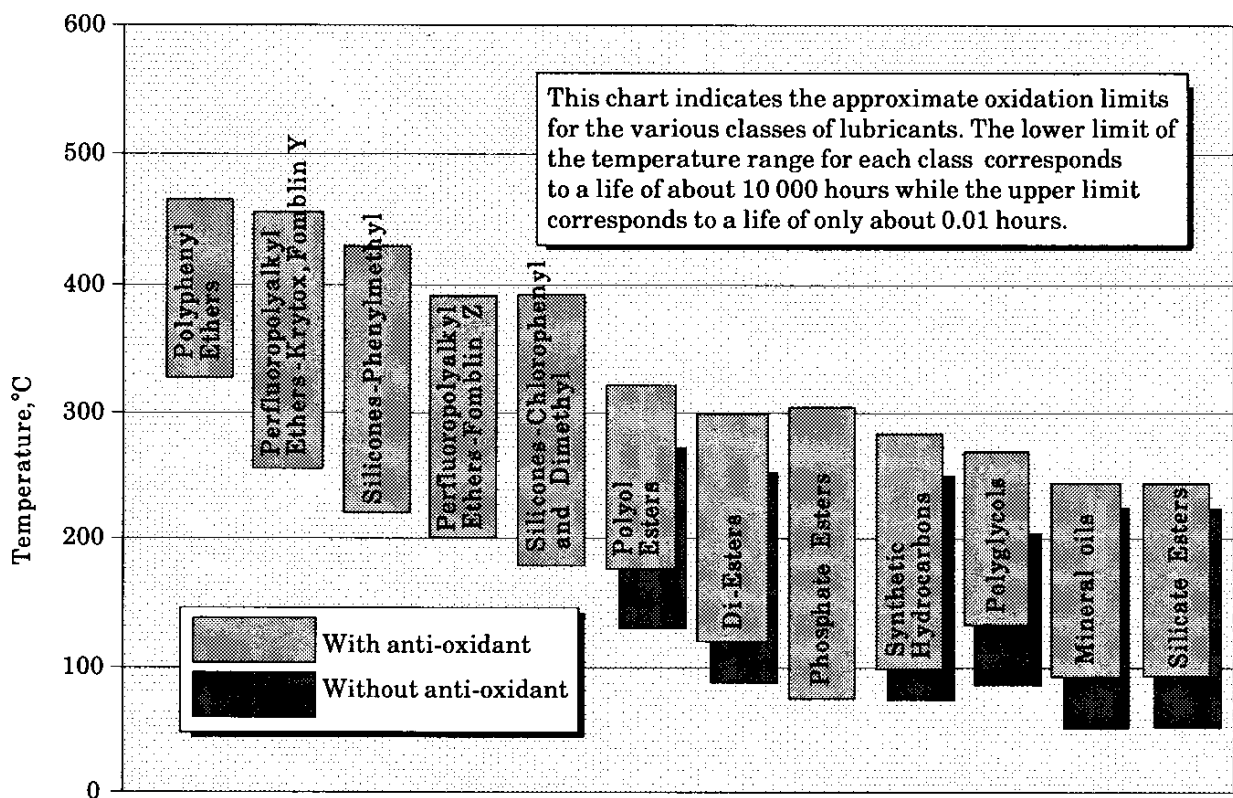


FIGURE 2.4 OXIDATION LIMITS

- **Radiation resistance**

Lubricants for nuclear applications can have special requirements of radiation resistance. However, it is important not to lose sight of the fact that they are also affected by the same degradation processes as lubricants in normal environments and that the life does not only depend on radiation effects.

All mineral and synthetic oils are reasonably stable up to a dosage of 10^7 Rad[†] gamma radiation but at 10^8 Rad appreciable degradation of the lubricant can occur. Deterioration can involve an increase in acidity, evaporation loss, coking tendency, foaming tendency and corrosion of lead, copper and magnesium. Other effects include a decrease in flash point temperature, autogenous ignition temperature and oxidation resistance. Viscosity at low to moderate temperatures tends to be increased by radiation exposure while high temperature viscosity can be reduced. Figure 2.5 indicates the approximate resistance of the various classes of lubricant to gamma ray radiation. Lubricants with good thermal stability also tend to have good radiation resistance and additives can give a 5–10 per cent improvement in resistance.

Note that not all performance parameters are equally affected by radiation and different members of a class are not equally susceptible. Use of a synthetic lubricant in an application involving nuclear radiation requires the study of the various types within a class to determine the effect of radiation on those properties of most importance for the particular application.

2.3 Equipment life

The lubricant must not damage any part of the equipment, such as seals, or cause corrosion of any component surfaces. Indeed, the lubricant is often expected to protect the equipment from rusting and to prevent surface damage when full film lubrication cannot be maintained under heavy loads or at start up.

- **Boundary lubrication**

Lubricants that are able to prevent surface damage when appreciable asperity contact occurs (see Reference 3) are often referred to as “extreme pressure lubricants” or “boundary lubricants”. As with mineral oils, additives are used to improve the boundary lubrication properties but suitable additives do not exist for all types. For example, none of the usual oil-soluble extreme pressure additives is effective in silicones. An indication of the boundary lubrication properties of the various oils is given in Table 2.2.

- **Effect on rubbers and paints**

The lubricant must be compatible with elastomeric materials in, for example, seals. Some synthetic oils require special types if excessive hardening or softening and consequent loss of function is to be avoided (see Table 2.2). Some paints are removed by particular synthetic oils.

- **Corrosion**

Some lubricants may be corrosive to certain types of metals as summarised in Table 2.2. Damage may also occur due to the build-up of corrosive decomposition products (see Table 2.1).

[†] 1 Rad = 100 erg/g.
1 erg/g = 10^{-4} J/kg.

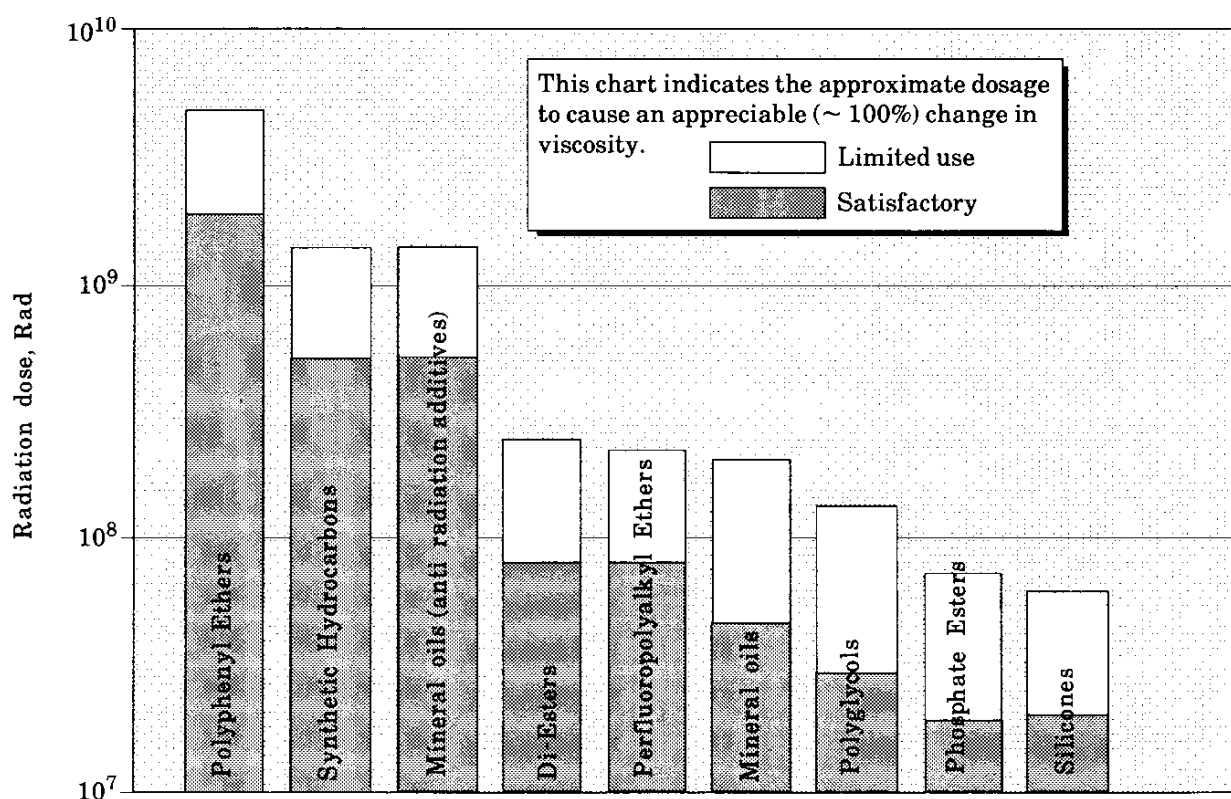


FIGURE 2.5 RESISTANCE TO NUCLEAR RADIATION

TABLE 2.1 THERMAL AND OXIDATION DECOMPOSITION PRODUCTS

Class Name	Decomposition products
Mineral oils	Acidic compounds which may be corrosive. Lacquers, sludges and coke-like deposits can form.
Synthetic Hydrocarbons	Similar to those of mineral oils. Less tendency to form tarry and coke-like deposits (PIB oils produce no deposits).
Di-Esters	Generally similar to those of mineral oils but can produce corrosive acids.
Polyol Esters	Generally similar to those of mineral oils but can produce corrosive acids.
Polyglycols	Volatile low molecular weight decomposition products.
Phosphate Esters	Phosphoric acids which may be corrosive to metals such as copper, whitemetals and aluminium.
Silicones	Gel-like cross-linked polymer. Lacquers and silicon dioxide can form under rubbing conditions.
Silicate Esters and Disiloxanes	Silicon dioxide
Polyphenyl Ethers and C-Ethers	Tendency to produce a sludge under sliding conditions at high temperature in presence of oxygen.
Perfluoropolyalkyl Ethers (PFPAE)	Mainly volatile low molecular weight decomposition products.

2.4 Hazards

The lubricant must not present unacceptable safety hazards such as fire or explosion risk or toxicity.

- **Fire resistance**

The measurement of the fire resistance of lubricants is extremely complex and there is no single test that can be used to evaluate all types. Two approximate indicators of fire resistance are generally quoted. They are the flash point, which indicates the temperature at which the vapour can be ignited by a small flame under standard conditions, and the spontaneous ignition temperature, at which an oil ignites if injected into a hot vessel containing air. Flash point temperatures and spontaneous ignition temperatures are shown in Figure 2.6.

Flash points are closely associated with volatility and in well ventilated applications may have little or no relevance. They may, however, be highly significant with regard to storage and handling of the bulk lubricant. The spontaneous ignition temperature is often regarded as providing a meaningful indication of fire resistance but there are also a number of tests which attempt to simulate practical ignition situations in which a mist or spray of the lubricant is ignited or in which liquid lubricant impinges on to a hot surface. Again, the subject is complex and the temperature at which a mist can be ignited in air depends on the pressure, the concentration of the oil in the air, the size and form of the ignition source and the droplet size. For example, a fine mist of mineral oil in air at atmospheric pressure with a concentration between 4 per cent and 10 per cent by weight will ignite spontaneously at temperatures around 400°C. However, at concentrations approaching 18 per cent, spontaneous ignition can occur at temperatures as low as 270°C. Also, a coarse dispersion of mineral oil in air might require surfaces as hot as 400°C or a powerful flame to catch fire while a fine spray might ignite if it impacts onto a surface at about 250°C.

- **Toxicity**

The toxicity of the various classes of lubricants is indicated in Table 2.2. Direct contact with any synthetic oil should be minimised. However, some types, such as the phosphate esters, require more care than others. Detailed advice on safe handling should be obtained from the supplier.

- **Biodegradability**

The biodegradability of the lubricant is especially important in two-stroke engines used in the open such as outboard motors and drivers for agricultural tools. The relative biodegradability of the various oils is indicated in Table 2.2. The suppliers should be consulted on the safe handling and disposal of their products.

2.5 Cost

The best lubricant for a particular application will be the cheapest that will meet the requirements. Synthetic lubricants, in general, have a higher cost per volume than mineral oils but can often provide an overall cost saving if, for example, lubricant life is extended or maintenance improved. Figure 2.7 provides an approximate indication of the bulk cost of synthetic lubricant oils relative to mineral oils.

A number of other performance parameters might need to be considered when selecting a lubricant. Some of the more obvious ones are included in Table 2.2.

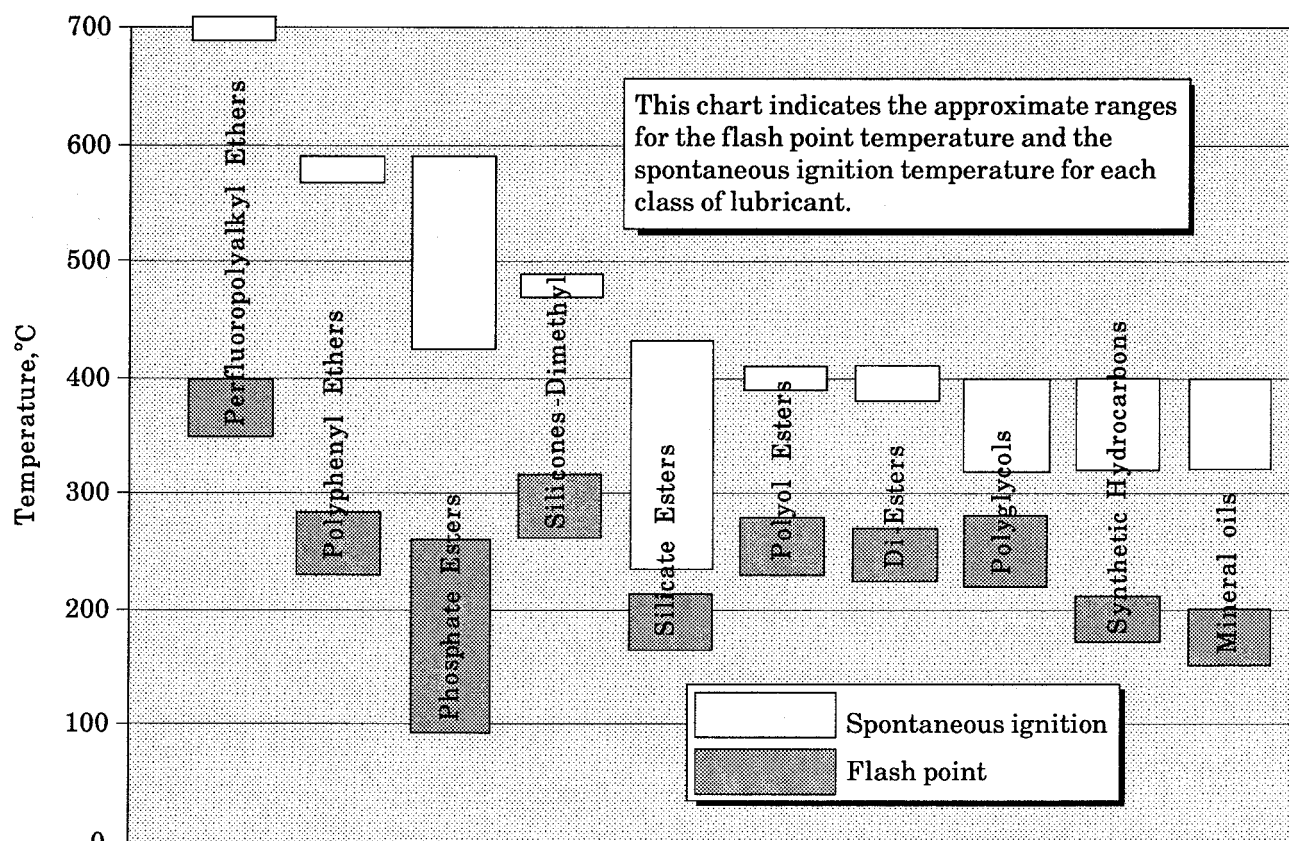


FIGURE 2.6 FLASH POINTS AND SPONTANEOUS IGNITION TEMPERATURES

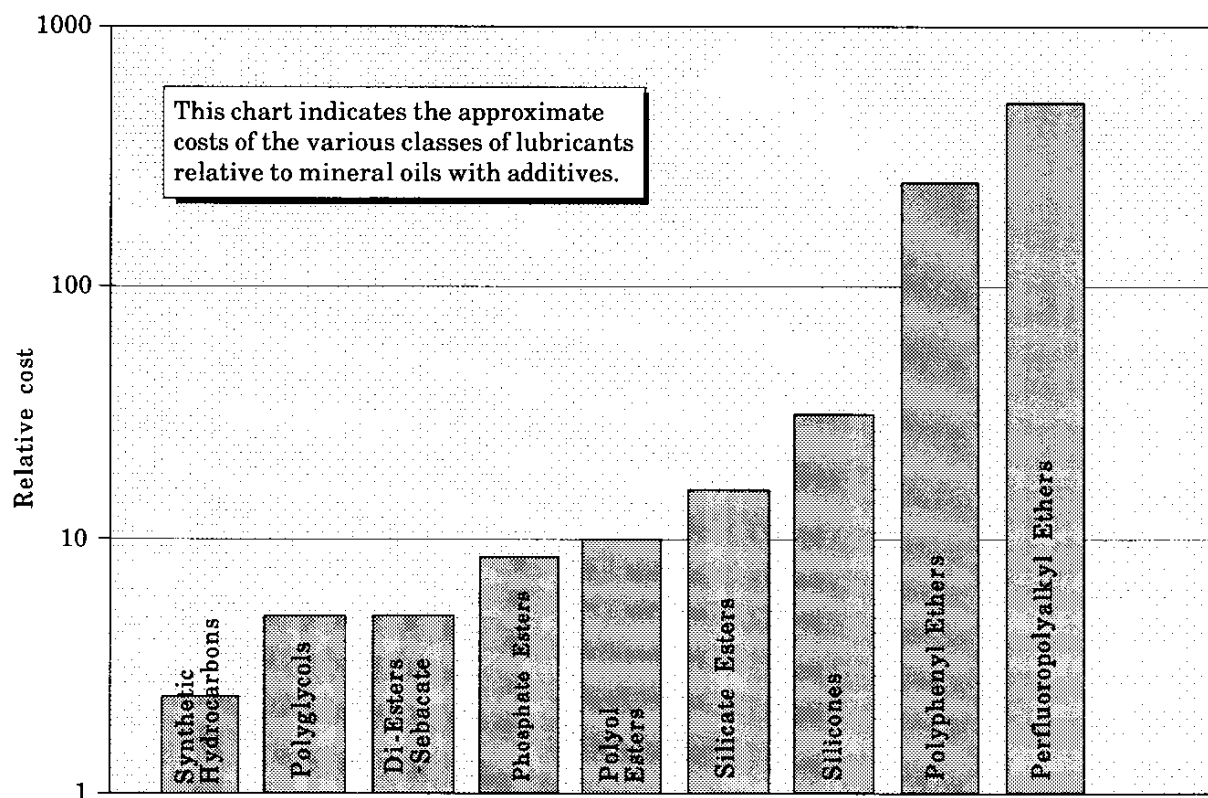


FIGURE 2.7 RELATIVE COST