BASE OIL HANDBOOK
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WHY NAPHTHENIC BASE OILS?

What is better for a specific application, naphthenic or paraffinic oils? There is no hard and fast answer. In some applications naphthenic base oils will be more cost-effective, in others paraffinic oils might have the edge under certain conditions.

This handbook has been compiled to provide a detailed introduction to base oils in general and naphthenic oils in particular.

Naphthenic base oils have a number of distinct advantages over paraffinic oils. They demonstrate greater solvating power than paraffinic oils. This means that additives are easily dissolved, which is of particular interest in formulating metalworking fluids, and that in manufacturing grease, higher yields are possible because less soap is required. Naphthenic base oils also provide better low-temperature performance than paraffinic oils, which makes them ideal for formulating hydraulic fluids and automatic transmission fluids (ATFs).

Not only do Nynas oils offer good solvating power, but they also possess a very favourable environmental profile. This is thanks to a sophisticated refining technique, hydrotreatment, which removes a large part of the polycyclic aromatic content of the naphthenic oil, without destroying its good solvating power.

As a specialty oil company, you'll find our sales technicians well informed about base oils. If you have any questions not covered by this handbook, please do not hesitate to get in touch.

MINERAL BASE OILS

Mineral oils can be divided into two distinct groups: paraffinic and naphthenic oils. Naphthenic crudes are available around the world, with large reserves to be found in Europe, North and South America and Asia. The greater part of the crude used by Nynas comes from Venezuela. At the time of writing (1997), the known reserves of Venezuelan crude oil total 60 billion barrels. Nynas is thus assured supplies for the foreseeable future and beyond.
2. REQUIREMENT FOR BASE OILS

For a base oil, many requirements have to be fulfilled in various applications. Different properties are measured according to a specific method: ASTM, ISO, DIN, GOST etc. A list of corresponding methods is presented in Appendix III.

2.1 VISCOSITY

The viscosity of an oil is important for its cooling and lubricity properties. The lower the viscosity, the better the cooling. An increase in temperature reduces the viscosity. The rate of change in viscosity with temperature can be expressed in terms of viscosity index (VI). A small reduction in viscosity coupled with a large temperature changes indicates a high viscosity index.

Paraffinic oils have a higher VI than naphthenic oils. A high VI is required in certain applications. Automotive lubricants is one example where lubrication is needed at both high and low temperatures. However, for cooling applications, such as metal working or quenching, a low VI is better because of the lower viscosity (better heat transfer) at operating temperatures. Viscosity (kinematic) is measured according to ASTM D 445.

![Figure 1. Viscosity index.](image)

The internationally established unit of kinematic viscosity is the centistoke (cSt), which is equivalent to mm²/s. The cSt unit is used by the International Standards Organisation (ISO) for viscosity classification (see Table 1).
<table>
<thead>
<tr>
<th>ISO Viscosity grade classification</th>
<th>Kinematic viscosity limits, cSt at 40°C</th>
<th>Mid-point kinematic viscosity, cSt at 40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO VG 2</td>
<td>Min. 2.2</td>
<td>Max. 2.2</td>
</tr>
<tr>
<td>ISO VG 3</td>
<td>Min. 3.2</td>
<td>Max. 3.2</td>
</tr>
<tr>
<td>ISO VG 5</td>
<td>Min. 4.6</td>
<td>Max. 4.6</td>
</tr>
<tr>
<td>ISO VG 7</td>
<td>Min. 6.8</td>
<td>Max. 6.8</td>
</tr>
<tr>
<td>ISO VG 10</td>
<td>Min. 9.0</td>
<td>Max. 10.0</td>
</tr>
<tr>
<td>ISO VG 15</td>
<td>Min. 13.5</td>
<td>Max. 15.0</td>
</tr>
<tr>
<td>ISO VG 22</td>
<td>Min. 19.8</td>
<td>Max. 22.0</td>
</tr>
<tr>
<td>ISO VG 32</td>
<td>Min. 28.8</td>
<td>Max. 32.0</td>
</tr>
<tr>
<td>ISO VG 46</td>
<td>Min. 41.4</td>
<td>Max. 46.0</td>
</tr>
<tr>
<td>ISO VG 68</td>
<td>Min. 61.2</td>
<td>Max. 68.0</td>
</tr>
<tr>
<td>ISO VG 100</td>
<td>Min. 90.0</td>
<td>Max. 100</td>
</tr>
<tr>
<td>ISO VG 150</td>
<td>Min. 135.0</td>
<td>Max. 150</td>
</tr>
<tr>
<td>ISO VG 220</td>
<td>Min. 198.0</td>
<td>Max. 220.0</td>
</tr>
<tr>
<td>ISO VG 320</td>
<td>Min. 288.0</td>
<td>Max. 320.0</td>
</tr>
<tr>
<td>ISO VG 460</td>
<td>Min. 414.0</td>
<td>Max. 460.0</td>
</tr>
<tr>
<td>ISO VG 680</td>
<td>Min. 612.0</td>
<td>Max. 680.0</td>
</tr>
<tr>
<td>ISO VG 1000</td>
<td>Min. 900.0</td>
<td>Max. 1000</td>
</tr>
<tr>
<td>ISO VG 1500</td>
<td>Min. 1350.0</td>
<td>Max. 1500</td>
</tr>
</tbody>
</table>

Table 1. ISO Viscosity Grade Classification (ISO 3446).

2.2 VISCOSITY VS BOILING RANGE

An oil is a mixture of many different kinds of molecules, each with its own boiling point. Therefore, an oil will boil over a range of temperatures, hence boiling range.

The higher the boiling range temperatures (i.e. the higher molecular weight), the higher the viscosity. It has been found that the point of 50% distillation in the boiling range relates to the viscosity of an oil.

Paraffinic oils give lower viscosity at a given boiling range, due to the higher mobility of the paraffinic molecules. This means that the boiling range for a paraffinic oil will lie at a higher level than for a naphthenic oil of the same viscosity.

2.3 FLASH POINT

The flash point of an oil is specified for safety reasons, but also because it indicates how volatile the oil is. Light parts of the oil determine the flash point which is extremely sensitive to contaminants from lighter oils, such as gas oil or gasoline. The flash point is reached when the oil releases enough gases to make the gas mixture above the oil ignitable in the presence of an open flame. The PM (Pensky Marten) closed cup method (ASTM D 93) gives the best repeatability. Another method is the COC (Cleveland Open Cup) ASTM D 92, which, generally, gives 5-10°C higher flash point values. This method is often used in the USA and elsewhere for formulated products.
2.4 FLASH POINT VS BOILING RANGE

It is at the low temperature area of the boiling range that flash point is determined. A correlation exists between the 5% point in the boiling range and the flashpoint. The lighter the products, the lower the flashpoint. Thus, two oils with the same viscosity (50% point) may have different flash points depending on the shape of the distillation curve at low temperatures (see Figure 2).

![Distillation curves for two oils with the same viscosity but different flash points.](image)

2.5 LOW TEMPERATURE PROPERTIES

Low temperature properties are important in a cold climate. The N-alkanes in paraffinic oils crystallise upon cooling which impedes the free flow of the oil. A differential scanning calorimeter (DSC) can be used for measuring the amount of N-alkanes. When the cloud point occurs (i.e. the crystallisation point), the oil is no longer a Newtonian fluid, but has become a two-phase system.

Naphthenic oils are virtually free from N-alkanes. This means that no yield stress is needed to start moving the oil at low temperatures, which is important in many applications.

Pour point, the lowest temperature at which an oil flows, is measured according to ASTM D 97.

2.6 VOLATILITY

As mentioned earlier, volatility is related to the flash point. Low volatility is important for high temperature applications, e.g. some metalworking operations, like drawing and stamping and high-temperature greases. A method for measuring the volatility is ASTM D 972. The loss in mass after 22 hours evaporation at a certain temperature (often 107°C) is determined.
2.7 DENSITY

Density increases with the aromatic and naphthenic content. A standard coefficient, 0.00065/°C, can be used in most cases for calculating the density at other temperatures than those already measured. Density is measured according to ASTM D 4052.

2.8 SOLUBILITY

The solubility properties of an oil are important in areas such as grease manufacturing. It is also important for keeping oxidation products in solution and for seal swell.

Viscosity Gravity Constant (VGC) is an indication of solubility. A high VGC value means good ability to dissolve polymers, additives and oxidation products. VGC can be calculated from density and kinematic viscosity (ASTM D 2501).

Aniline point is also a property that indicates the solubility of an oil. It is defined as the lowest temperature at which a mineral oil is completely miscible with an equal volume of aniline (ASTM D 611). The lower the aniline point, the better the solubility.

In the past, low refined oils, such as aromatic oils or distillates, were used where high solubility was needed. Due to health and safety reasons, these products are now banned in most countries. Due to sophisticated refining techniques, Nynas naphthenic oils are label-free, and yet retain low aniline scores i.e. good solubility. Nynas T-grades have the best solubility properties (see Table 2).

<table>
<thead>
<tr>
<th>Oil</th>
<th>VGC</th>
<th>Aniline point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>XHVI</td>
<td>0.763</td>
<td>126</td>
</tr>
<tr>
<td>PAO 4</td>
<td>0.768</td>
<td>120</td>
</tr>
<tr>
<td>VHVI</td>
<td>0.785</td>
<td>110</td>
</tr>
<tr>
<td>SN 150 (Paraf.)</td>
<td>0.818</td>
<td>96</td>
</tr>
<tr>
<td>SR 130 (N ynas)</td>
<td>0.841</td>
<td>95</td>
</tr>
<tr>
<td>T110 (N ynas)</td>
<td>0.856</td>
<td>84</td>
</tr>
<tr>
<td>T22 (N ynas)</td>
<td>0.865</td>
<td>71</td>
</tr>
</tbody>
</table>

Table 2. VGC and aniline points for different types of oils.

XHVI = extra high viscosity index (hydrocracked oil),
PAO = polyalphaolefin, VHVI = very high viscosity index (hydrocracked oil),
SN 150 = solvent neutral 150 (paraffinic oil with 150 SUS viscosity)
2.9 AROMATIC CONTENT

There are two methods commonly used to measure the aromatic content of an oil. One, the IR-method, gives the percentage of aromatic carbons. In the other method, ASTM D 2140, the weight percent of aromatic carbons is calculated from VGC, refractive index and density.

The values for aromatic content for low-aromatic oils will differ between the two methods. ASTM 2140 gives lower values (see Table 3).

<table>
<thead>
<tr>
<th>Test method</th>
<th>T9</th>
<th>N S100</th>
<th>S8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic content (IR-method), %</td>
<td>15</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Aromatic content (ASTM 2140), %</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3. Differences in aromatic content by using the IR-method and ASTM 2140.

2.9.1 Polyaromates and labelling

Measurements of polyaromatic content (PAC) by using methods like IP 346, HPLC and GC yield a very wide variety of results, because they measure different things. It is important to have a clear understanding of what is measured.

Short descriptions of the three methods will follow. More about PAC measurements can be found in the Nynas handbook “Health and safety aspects of naphthenic oil”.

IP 346

IP 346 is the method used for deciding which oils that have to be labelled under EU regulations. The limit for labelling is three per cent by weight.

The method measures the content of substances which are soluble in dimethylsulphoxide (DMSO). DMSO dissolves all polyaromatates, as well as a number of single aromates and naphthenes, especially if they contain a hetero atom. Thus, values obtained by IP 346 are a good deal higher than the true polyaromatic content, especially for naphthenic oils.

HPLC

High performance liquid chromatography (HPLC) is one of the methods that Nynas uses in-house for measuring PAC. It measures the quantity of substances that are more polar than a given marker. The marker used is generally either naphthalene or anthracene.

GC

If Gas Chromatography (GC) is combined with mass spectrophotometry (GC-MS), concentrations of individual polyaromatic substances can be measured. From a scientific point of view, this method is the best for
identifying polyaromatics. But is has been shown that no correlation exists to skin cancer when using the skin painting test on mice. Therefore, it has been decided to use the IP 346 as a marker for carcinogenity. If the amount of extracted compounds is less than 3% according to IP 346 the oil is considered to be non-carcinogenic and is therefore unlabelled.

Other labelling criteria

The American Occupational Safety and Health Administration (OSHA) introduced in 1985 the Hazard Communication Standard (HCS) (29 CFR 1910.1200) for lubricants. This states that raffinates are label-free and considered non-carcinogenic if either the hydrotreating temperature exceeds 800°F (427°C), or the pressure exceeds 800 psi. The Nynas hydrotreated oils are produced at process conditions fulfilling this criteria.

2.10 Oxidation Stability

All oils contain a small amount of air and the presence of oxygen leads to oxidation. As a rule-of-thumb in all chemical reactions (e.g. oxidation), the reaction rate doubles when the temperature is raised 10°C. This means that an increase by 10°C reduces the lifetime of an oil by half. However, some oxidation reactions start only at high temperatures.

Oxidation mechanisms:

1. Creation of a free radical (by heat, UV light or mechanical shear)
   \[ \text{RH} \rightarrow \text{R}^{*} + \text{H}^{*} \]

2. Creation of peroxides by the reaction of the free radical with oxygen.
   \[ \text{R}^{*} + \text{O}_{2} \rightarrow \text{RO}_{2}^{*} \]

3. The peroxide may react and give a new radical, alcohols, ketones, aldehydes and acids.
   \[ \text{RO}_{2}^{*} + \text{RH} \rightarrow \text{ROOH} + \text{R}^{*} \]
   \[ \text{ROOH} \rightarrow \text{R}^{*} + \text{HO}^{*} \]

There are two kinds of anti-oxidants: radical- and peroxide-catchers. The radical-catchers stabilise free radicals by donating a hydrogen atom. Phenols and amines are common radical-catchers. A peroxide-catchers decomposes peroxides into more stable compounds, which thus prevents the formation of additional free radicals.

\[ \text{RO}_{2}^{*} + \text{XH} \rightarrow \text{RO}_{2} \text{H} + \text{X}^{*} \]
Radical catcher (phenol or amine type).

\[ \text{ROOH} + \text{X} \rightarrow \text{ROH} + \text{XO} \]
Peroxide disrupting effect (amine or sulphur type)
White oil, or some other absolutely clean oil, has nothing that inhibits oxidation processes naturally. Other oils contain natural oxidation inhibitors.

Low-refined oils have low oxidation stability. In traditional comparisons between paraffinic and naphthenic oils, solvent-refined paraffinic was compared with low-refined naphthenic oil. This lead to false rumours concerning the inferior oxidation stability for all naphthenic oils. However, Nynas’ severe hydrotreatment methods produce naphthenic oils with very good oxidation stability.

Semi-synthetic oils, such as PAO and VHVI oils without additives, have low oxidation stability. This is because they lack natural inhibitors. A certain amount of an antioxidant is often added to such oils to preserve them during storage. When using these oils in formulations, more antioxidants are used.

Naphthenic oils respond well to antioxidants. One oxidation stability test is the IP280. The amount of oxidation products is measured after the oil has been subjected to certain oxidation conditions.

Nynas oils have been compared with a paraffinic SN 150. All oils had equal quantities of two different oxidation inhibitors added. Table 4 shows that the naphthenic oils produce much less oxidation products than the paraffinic oil. Total acid number is measured according to ASTM D 974.

<table>
<thead>
<tr>
<th></th>
<th>N S30 (Nynas)</th>
<th>T22 (Nynas)</th>
<th>SN 150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile acid, mg KOH/g</td>
<td>0.11</td>
<td>0.04</td>
<td>5.7</td>
</tr>
<tr>
<td>Soluble acid, mg KOH/g</td>
<td>0.43</td>
<td>0.47</td>
<td>2.2</td>
</tr>
<tr>
<td>Sludge, %</td>
<td>0.18</td>
<td>0.28</td>
<td>0.72</td>
</tr>
<tr>
<td>Total oxidation products, %</td>
<td>0.35</td>
<td>0.45</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 4. Results after oxidation.

2.11 CORROSION

The most common method to measure corrosion is ASTM D 130, known as the “copper strip” method. A copper strip is immersed in the oil for a certain time and at a certain temperature. The degree of corrosion is then determined. Other methods include the “silver strip test” and potentiometric titration of mercapto sulphur.
2.12 STEAM EMULSION

Some oils are exposed to water from condensation in the application, e.g. in steam turbine oils. Depending upon the chemical composition of the formulation, a water-in-oil emulsion may form. One way of determining the non-additive oil’s ability to separate from water is to use the “steam emulsion method”, IP19/76(1988). According to this method, the time is measured that it takes for the oil to separate from the emulsion after steam injection. Highly refined naphthenic oils have better water separation properties than other oils (see Table 5).

<table>
<thead>
<tr>
<th>Polyol-ester</th>
<th>XHVI/VHVI (Hydrocracked)</th>
<th>SN 150 (Paraf.)</th>
<th>T22 (Nynas)</th>
<th>NS30 (Nynas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (s)</td>
<td>240</td>
<td>180/540</td>
<td>210</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 5. Steam emulsion method

2.13 NYNAS BASE OILS

Nynas Naphthenics AB has a number of base oils in its product range. They have been carefully developed to meet the requirements of a host of different applications. They cover a range of different viscosities, aromatic content as well as many other properties.

The oils are divided into four main types: T, NS, SR and S grades: the NS and T grades are hydrotreated, while the S grades are both solvent-refined and hydrotreated. SR130 is solvent-refined only.

The T grades have a higher aromatic content ($C_A$) than the other grades and therefore better solubility properties. Still, with a level of DMSO extractable compounds (IP 346) below 3%, they are label-free.
In this handbook, we look at the following applications in which base oils can be used: metalworking fluids, greases, automatic transmission fluids, hydraulic fluids and air compressor oils. Other applications include: shock absorber oils, mould oils, textile oils and quenching oils. Mineral oils of the naphthenic type are also used as base stock for marine lubricating oils due to their solubility properties.

3.1 METALWORKING FLUIDS

Metalworking involves forming metal into desired shapes. It might be a question of material-removing methods (cutting) or plastic-machining methods (e.g. drawing and rolling).

In metalworking procedures we talk about boundary lubrication, where-in the fluid lubricating film is penetrated. The friction is very high and metal-to-metal contact occurs.

Coefficient of friction, $\mu$

![Lubrication regimes](image)

Figure 3. Lubrication regimes

The main purposes of metalworking fluids are to cool, lubricate and reduce corrosion. Cutting fluids have the additional function to remove chips from the cutting zone.
3.1.1 Classification

Metalworking fluids can be divided into different groups: straight mineral oils, emulsions (consisting of oil and water), and water solutions.

Straight oils

Straight oils (also called neat oils) are used when the machine tool itself, needs cutting oil as a lubricant. These oils can also be used when they can be easily filtered and reused.

A typical straight cutting oil contains 80-95% mineral oil, the rest consisting of additives. The viscosity of the base oil is an important factor. Temperature and pressure reach very high levels during metalworking. Therefore, different additives are necessary to give the oil the desired properties: fatty materials and esters influence lubricity; zinc and phosphorous compounds reduce wear; phosphorous and sulphur compounds act as extreme pressure (EP) additives. Long chain polymers can be used as anti-mist improvers.

Emulsions

Emulsions, also known as "soluble oils" or "emulsifiable oils", consist of a mineral oil, emulsifiers, corrosion inhibitors, anti-foamants and water. An oil blended with additives is called a "soluble oil concentrate". They also have EP additives included for extreme pressure demands.

An emulsion is formed when the concentrate is mixed with water. The oil content of an emulsion varies between 2 and 5 volume per cent, or higher when good lubrication is needed in heavy duty cutting operations. The appearance of a coarse emulsion is milky-white, while a fine emulsion is semi-transparent.
So called "semi-synthetic fluids" have a lower mineral oil content (10-30%) than soluble oils. They form transparent micro-emulsions or emulsions of the normal type.

Water solutions

Water solutions (also called “synthetic fluids”) consist of substances dissolved in water. They contain no mineral oils. Typically, they consist of 25% boron complex, 20% corrosion inhibitors, 8% lubricity improvers and other additives. They are transparent in appearance.

3.1.2 Additives

As already stated, metalworking fluids contain a number of additives such as emulsifiers (this is not the case with straight oils), EP additives, corrosion inhibitors and biocides.

Emulsifiers

Emulsifiers are present in emulsions in quantities of approximately 40%. Sodium sulphonate is often used. For “soluble oils”, petroleum sulphonates have been found to improve lubrication and the cleaning of metal parts.

Hydrophilic-lipophilic balance (HLB) is an expression of the relative simultaneous attraction of an emulsifier for water and for oil. An emulsifier consists of a hydrophilic and a lipophilic part. Depending on the relative percentage of hydrophilic to lipophilic groups, emulsifiers assume different HLB values. To produce stable emulsions, two or more emulsifiers with different HLB values are often combined. Naphthenic oils usually give more stable emulsions due to their higher polarity compared to paraffinic oils.

Different oils (naphthenic, paraffinic and esters) demand different HLB values of the emulsifiers. Nynas has performed a series of tests to determine optimal HLB values for emulsifiers in various oil/water

<table>
<thead>
<tr>
<th>Oil</th>
<th>VGC</th>
<th>Viscosity 40°C (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White oil (P-base)</td>
<td>0.800</td>
<td>30</td>
</tr>
<tr>
<td>150 SUS P-base</td>
<td>0.820</td>
<td>30</td>
</tr>
<tr>
<td>Solvent refined N-base</td>
<td>0.836</td>
<td>22</td>
</tr>
<tr>
<td>NS30</td>
<td>0.850</td>
<td>30</td>
</tr>
<tr>
<td>T22</td>
<td>0.865</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 6. Optimal VGC for oil/water emulsions.
emulsions. Five oils with different aromatic contents (see table 6) were tested with polyglycol ethers with HLB values of 9.2, 9.6, 10.5 and 11.8. Viscosity gravity constant (VGC) was used as a measure of the aromatic content of the oils.

The emulsions tested contained 5 ml of oil containing 10, 12, 14 and 16 per cent emulsifier respectively. After 24 hours, the stability of the emulsions was tested by measuring the amount of “cream”, in some cases a layer of oil, above the emulsion. The less “cream”, the more stable the emulsion.

Results showed that the higher the VGC value of an oil, the greater the HLB value of the emulsifier must be if a stable emulsion is to be achieved. Figure 5 shows the correlation found between VGC and HLB value.

A comparison was also made between T22 and 150 SUS base oils regarding the stability of emulsions. A “fine emulsion” concentrate consisting of base oil, emulsifier package (Hostacor BT40) with co-emulsifier (Emulsogen LP) and tall fatty acid was mixed. The result showed that T22 gave a clear and stable concentrate while the one based on P-base 150 SUS separated. When mixed with water, the T22-concentrate gave a semi-transparent stable emulsion, while the 150 SUS concentrate gave a milky-white emulsion.

Similarly, a test was performed with a petroleum sulphonate package plus a co-emulsifier. The amount of emulsifiers were 15 and 18% in three different base oils. After 24 hours, the amount of “cream” was determined as well as any free oil layer present. The results are described in Figure 6.
**EP additives**

Extreme Pressure (EP) additives allow metalworking fluids to be used at higher temperatures. Boundary lubrication is the normal condition in metalworking. The EP additive reacts with the metal surface at higher temperatures which produces salts giving a lower coefficient of friction. EP additives are compounds of sulphur, chlorine or phosphorous. They react to the metal at different temperatures (fig.7) which means that the choice depends on the temperature conditions during processing.

**3.1.3 Base oil requirements**

When designing a metalworking fluid, it is important to choose the right base oil.
Naphthenic oils

To dissolve the large amount of additives, especially in heavy-duty cutting fluids, a naphthenic oil is preferred because it has better solubility properties than a paraffinic oil.

Figure 8 shows the different capacities to dissolve free sulphur added to the oil. Two Nynas oils are compared with a paraffinic 150 SUS.

The load capacity was also tested for the three oils (fig. 9). According to the results, the original sulphur content in the oil does not influence the load capacity. However, with added sulphur, the difference in the load capacity between the different oil increases. Therefore, the solubility of sulphur is a most important property.

For emulsions, a naphthenic oil is preferred, as it is easier to emulsify than a paraffinic. There are emulsifier packages adapted for paraffinic base oils available, but naphthenic-based emulsions are generally the more stable ones.
Also, the low viscosity index of a naphthenic oil is an advantage when a straight oil is to be filtrated at higher temperatures.

3.1.4 General formulations

Different formulations are used for different types of operations, as well as for different metals and alloys. The additives are usually added to a base oil as an "additive package". The amount of additives (packages) varies considerably for different operations. For more information, see guidelines from the additive suppliers. A number of examples of formulations are given below.

Cutting fluids

**Straight oils:**
- Additive package (e.g. Lubrizol 5347 and 5309)
- Base oil (20-30 cSt, 40°C)

**Coarse (opaque) emulsion:**
- Emulsifying package, 15-20% (e.g. Lubrizol 5375)
  (incl. corrosion inhibitors)
- Biocide
- Base oil

**Fine emulsion (semi-synthetic):**
- Emulsifying package, 30-50% (e.g. Lubrizol 5683)
- Biocide
- Base oil

Rolling fluids

**Aluminium alloys:**
- Antioxidant 0.2%
- Fatty alcohol 5%
- Base oil (4-7 cSt, 40°C) balance

**Steel-carbon and steel alloys:**
- Antioxidant 0.3%
- Corrosion inhibitor 0.1%
- Defoaming agent <0.002 ppm
- Base oil (20-30 cSt, 40°C) balance

**Other non-ferrous:**
- Lubricity agent 1%
  (e.g. stearic acid)
- Antioxidant 0.3%
- Corrosion inhibitor 0.1%
- Base oil balance
3.2 GREASES

A lubricating grease is a solid to semi-fluid product, consisting of a fluid lubricant (oil) and a thickening agent. Other ingredients imparting particular properties may be included. The fluid lubricant constitutes the single largest ingredient in a grease.

Figure 10. Grease composition.

3.2.1 Grease types

Greases are usually classified by the type of thickener used, because it is the thickener which has the greatest influence on the final properties of a grease.

Soap greases

A soap thickener is the product of the reaction between a metal or alkali metal hydroxide with a fatty acid. Soap base greases account for about 90% of the greases made. The metal/alkali metals are usually lithium, calcium, sodium or aluminium. Calcium soaps were the first used. They have rather low dropping points (~100°C) while sodium soaps exhibit higher dropping points (~160°C). Lithium soaps which have even higher dropping points (~180°C) were developed during the 1940s. Lithium 12-hydroxy stearate is the most used soap for lubricating greases today.

Complex greases

Complex greases are formed from at least two very different acids and one metal/alkali metal or acids of two different metals. The properties of a complex grease are very different from a conventional grease and usually superior in some important respects, particularly in high temperature properties (i.e. higher dropping point). Common types of complex greases include aluminium, calcium and barium complexes as well as lithium complexes.
Non-soap greases

Finely divided solids act as thickeners and can also be used. Typical materials are treated clay, silica, carbon black, a number of pigments/dyes and several different polymers.

![Figure 11. Types of grease.](image)

### 3.2.2 Grease properties

#### Consistency

Greases are classified according to their consistency (hardness) into NLGI grades determined by measuring the penetration (distance in mm/10) of a standard cone at 25°C. The measurement is usually made after “working” the grease for 60 strokes in a standard grease worker.

<table>
<thead>
<tr>
<th>NLGI grade number</th>
<th>Penetration range (worked 60 str.)</th>
<th>Grade description</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>445-475</td>
<td>semi-fluid</td>
</tr>
<tr>
<td>00</td>
<td>400-430</td>
<td>semi-fluid</td>
</tr>
<tr>
<td>0</td>
<td>355-385</td>
<td>very soft</td>
</tr>
<tr>
<td>1</td>
<td>310-340</td>
<td>very soft</td>
</tr>
<tr>
<td>2</td>
<td>265-295</td>
<td>soft</td>
</tr>
<tr>
<td>3</td>
<td>220-250</td>
<td>almost solid</td>
</tr>
<tr>
<td>4</td>
<td>175-205</td>
<td>hard</td>
</tr>
<tr>
<td>5</td>
<td>130-160</td>
<td>very hard</td>
</tr>
<tr>
<td>6</td>
<td>85-115</td>
<td>soap-like</td>
</tr>
</tbody>
</table>

Table 7. The NLGI grades.
Dropping point

The dropping point is the temperature at which the grease passes from a semi-solid to a liquid state. Working temperatures for greases are, however, normally well below the dropping point.

Bleeding

When oil separates from a grease, bleeding is said to occur. The stability of a grease can be determined by measuring the bleeding tendency. ASTM D 1742 determines the amount of oil likely to bleed out of a grease under pressure. IP 121 or DIN 51817 are used for determination of oil bleed at static conditions (shelf life). When heated, the bleeding increases.

3.2.3 Additives

The oil soluble additives are nearly always of the same types as those used in liquid lubricants - oxidation inhibitors, corrosion inhibitors, anti-wear additives, EP additives etc. The most commonly used EP additives today are different types containing active sulphur as the effective component. Other types of EP additives are so called solid lubricants, such as molybdenum sulphide, graphite and calcium carbonate. Other additives, such as tackiness additives, anti-bleed additives and fillers may also be incorporated.

3.2.4 Manufacture and structure

The essential characteristic of most soaps, is their ability to dissolve in mineral oils at temperatures above their melting point. On cooling, they crystallise out into tiny soap crystallites which aggregate into fibres. These fibres form a three-dimensional network or “tangled mass” that encloses the oil.

Non-soap thickeners require thorough dispersion of the thickener by mechanical means only.

The manufacturing process (for soap greases) can be described as follows:

1. Fatty acids and metal hydroxides are saponified in an autoclave or open kettle, together with a part of the oil.

2. Final heating is carried out in a kettle together with more oil. (In stages 1 and 2, naphthenic oils are used to advantage)

3. The mixture is cooled, partly with the addition of cooling oil.

4. The required additives are added. The consistency is adjusted by adding more oil.

5. To obtain a smooth product, the grease is homogenised. At this stage of the process, the grease is also de-aerated and filtered.
3.2.5 Rheology

The grease matrix is held together by internal binding forces which give the grease a solid character. This rigidity can be referred to as consistency and has traditionally been measured as the penetration value.

Greases can be described as viscoelastic materials. This means that they have both elastic and viscous properties depending on the conditions present. Special viscometers or rheometers are needed to study the viscoelastic properties.

When external shear stresses exceed a certain yield value, \( \sigma_0 \), the grease turns into a flowing liquid. However, the yield value you get is dependent on how you measure it.

![Graph showing shear stress vs. shear rate for grease and oil](image)

**Figure 12 Yield value of a grease.**

**Definition of viscosity: shear stress / shear rate**

An oil is a Newtonian fluid. This means that the viscosity (the slope of the line) does not change at different shear rates. However, the viscosity does, of course, change with temperature and pressure.

A grease is a non-Newtonian fluid. The viscosity is dependent on the shear rates applied to the grease. This is called the apparent viscosity. A grease has a shear-thinning behaviour, but will, at high shear rates, still have a higher viscosity than the incorporated oil component.

This apparent viscosity of a grease above its yield value, determines the flow characteristics of the grease along pipes. Lubricating greases are also thixotropic materials. Thixotropy can be defined as viscosity...
decreasing at constant shear rate. In the case of greases, the internal network structure will break, when the grease is subjected to a force that exceeds the yield point. This makes the grease flow like a fluid. When the force is removed, the structure is rebuilt and the grease will regain its solid to semi-solid property. This happen fast.

3.2.6 Base oils

Petroleum oils are by far the most widely used lubricants in grease.

The oil component in a grease must meet certain requirements regarding:

- solubility
- viscosity/viscosity index
- evaporation loss
- oxidation stability/response to inhibitors
- purity
- environmental and health aspects

Solubility

The most important property of an oil in the manufacture of grease is solubility. It is important that the thickening soaps are properly dissolved in the oil. Various parameters can be used to classify the solvating power of different base oils. The viscosity gravity constant (VGC), aniline point and aromatic content can all be used. The Hildebrandt solubility parameter, which is based on thermodynamic interaction forces between substances, can also be used.
The complex solubility structure of the soap must be balanced against the solubility of the oil. Excessive solubility may disrupt the structure of the soap while excessively low solubility may result in too much bleeding. Paraffinic oils can lead to problems with bleeding, because they demonstrate lower solvating power than naphthenic oils.

A lower amount of soap is required to reach the desired consistency in the manufacturing process when using naphthenic oils. Table 8 shows the difference in soap consumption between naphthenic and paraffinic oils.

A lower amount of soap is required to reach the desired consistency in the manufacturing process when using naphthenic oils. Table 8 shows the difference in soap consumption between naphthenic and paraffinic oils.

<table>
<thead>
<tr>
<th></th>
<th>P-base</th>
<th>Nynas 100 cSt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (15°C)</td>
<td>0.885</td>
<td>0.912</td>
</tr>
<tr>
<td>Viscosity (40°C)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>VG C</td>
<td>0.820</td>
<td>0.860</td>
</tr>
<tr>
<td>Soap quantity (%)</td>
<td>12</td>
<td>9</td>
</tr>
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</table>

Table 8. Soap consumption.

**Viscosity**

In most cases, the viscosity of the oil in a grease is about the same as when the oil alone is used in an application. High speed bearings require relatively low viscosity oils and low speeds need higher viscosity oils. Similarly, for low temperature applications, low viscosity oils are needed. However, in most cases, a grease has to perform over a wider range of conditions than an oil. The choice of base oil viscosity therefore has to be a compromise, with a relatively narrow band being used for most greases (90 to 250 cSt at 40°C).

A high viscosity oil gives good bleeding properties and better load capacity of the oil film. A low viscosity oil gives better heat transfer and low temperature properties.

During manufacture, it may be an advantage that the oil has a low viscosity at blending temperature - a low viscosity index (VI). When a higher viscosity index is needed, naphthenic oils are still often used in blends with paraffinics.
Evaporation loss

The temperature at grease manufacture is quite high. Greases are also often used at high operating temperatures in bearings or gear boxes. Therefore, low evaporation loss is desirable.

ASTM D 972 is a test for determining the volatility of oils. Some of the NYNAS base oils are listed in table 9.

<table>
<thead>
<tr>
<th></th>
<th>Volatility 107°C, 22h, wt%</th>
<th>Flash point, PM °C</th>
<th>Kinematic viscosity (40°C), cSt</th>
</tr>
</thead>
<tbody>
<tr>
<td>T110</td>
<td>0.5</td>
<td>216</td>
<td>110</td>
</tr>
<tr>
<td>SR130</td>
<td>0.4</td>
<td>228</td>
<td>144</td>
</tr>
</tbody>
</table>

Table 9. Evaporation loss.

3.2.7 Tests

There are a number of functional tests that are intended to simulate practical operating conditions for greases in bearings or gearboxes.

Wheel bearing leakage tests measure the amount of grease leaking from a wheel bearing assembly, as well as the tendency to slump in the housing.

Rolling bearing tests have been devised by bearing manufacturers. These measure wear, thermal, mechanical and oxidation stability under practical conditions.

Tests for comparing the EP properties for different greases are the Timken (ring on block) and Four Ball tests. These are used for determining load carrying and anti-wear properties.

3.2.8 Temperature limits

Table 10 shows the recommended working temperature limits for different types of grease (from SKF’s Main Catalogue 1997).
The ability to withstand speed varies between different greases. Therefore, a bearing speed factor, should also be taken into consideration when selecting a grease.

3.3 AUTOMATIC TRANSMISSION FLUIDS

The composition of engine oils, gear oils and automatic transmission fluids (ATFs) differ greatly due to the different lubrication requirements of the equipment in which they are used. Two characteristics set ATFs apart from engine and gear oils: ATFs are formulated to have highly specialised frictional characteristics; and they have much better low temperature fluidity than the other two automotive lubricants.

A very important property is viscosity. At high temperatures, the viscosity must be high enough to prevent leaking seals. At low temperatures, the viscosity must be low enough to permit starting at temperatures down to -40°C. Other important properties are: rubber swell, rust prevention, oxidation stability and foaming tendency.

A refilled ATF must be miscible with the fluid already in service. Thus, the base oils used must be based on molecules that are compatible at all blending proportions and temperatures. This excludes some esters and other oxygenated products.

Similar arguments about low temperature properties etc., are valid for shock absorber oils and hydraulic oils.

3.3.1 Base oils

In general, an automatic transmission fluid consists of 85-90% base oil and 10-15% of a performance additive package. Since the base oil is the

<table>
<thead>
<tr>
<th>Type of grease</th>
<th>Recommended working temperature Min.,°C</th>
<th>Max.,°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium soap</td>
<td>-30</td>
<td>+110</td>
</tr>
<tr>
<td>Lithium complex</td>
<td>-20</td>
<td>+140</td>
</tr>
<tr>
<td>Sodium soap</td>
<td>-30</td>
<td>+80</td>
</tr>
<tr>
<td>Sodium complex</td>
<td>-20</td>
<td>+140</td>
</tr>
<tr>
<td>Calcium soap</td>
<td>-10</td>
<td>+60</td>
</tr>
<tr>
<td>Calcium complex</td>
<td>-20</td>
<td>+130</td>
</tr>
<tr>
<td>Barium complex</td>
<td>-20</td>
<td>+130</td>
</tr>
<tr>
<td>Aluminium complex</td>
<td>-30</td>
<td>+110</td>
</tr>
</tbody>
</table>

Table 10. Working temperatures.
largest component in an ATF, it has a dramatic effect on the performance of the fluid. The base oil, of course, strongly effects viscosity, oxidation, foaming tendencies and flash point. Wax content is the biggest factor in influencing the low-temperature characteristics of base stocks.

Since naphthenic oils have very good low-temperature properties, they are well suited for being a part of ATF formulations. However, the use of naphthenic base oils may require additional VI improver. Naphthenic oil improves seal swell properties considerably. Table 11 shows the changes in pour point, cloud point, viscosity index and seal compatibility index (SCI) for different proportions of paraffinic-base and naphthenic-base oil (Nynas' N S8). Blends with T9 will show similar results.

<table>
<thead>
<tr>
<th>150 SUS P-base, % P-base</th>
<th>100</th>
<th>90</th>
<th>80</th>
<th>70</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS8, %</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Pour point depr., %</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>-27</td>
<td>-30</td>
<td>-33</td>
<td>-33</td>
<td>-45</td>
</tr>
<tr>
<td>Cloud point, °C</td>
<td>-13</td>
<td>-15</td>
<td>-18</td>
<td>-20</td>
<td>-24</td>
</tr>
<tr>
<td>Viscosity index</td>
<td>102</td>
<td>98</td>
<td>90</td>
<td>82</td>
<td>75</td>
</tr>
<tr>
<td>SCI</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 11. Blends of P-base with N-base oils.

The highly refined naphthenic oils of today have much better oxidation stability than the earlier low-refined naphthenic oils.

For highly refined naphthenic oils, an oxidation stability in the same range as synthetics such as PAO (polyalphaolefins) can be achieved. This makes these kind of highly refined base oils suitable for use in automatic transmission fluids, low temperature hydraulic fluids and shock absorber oils.

3.3.2 Specifications

In general, ATF performance is defined by the service-fill specifications of passenger-car and commercial-vehicle transmission manufacturers. These specifications establish both testing procedures and pass/fail criteria for the performance parameters. OEMs (Original Equipment Manufacturers), especially General Motors and the Ford Motor Company, are setting these specifications. Viscosity, flash point, oxidation stability, friction characteristics, wear resistance and seal compatibility are specifications which have to be fulfilled. All ATFs contain red dye to differ from other automotive lubricants.

Since January 1, 1994, General Motors has required the use of fluids certified as meeting its DEXRON®-III specification.
Ford has required the use of fluids meeting the MERCON® specification since 1987. The specification has undergone significant revisions since its original release. Since January 1, 1994, only fluids meeting the latest requirements may display the trademark term. These formulations are identified on the market by an identifying code ("M-number") beginning M 93 or higher. The MERCON® V specification was released on October 15, 1995.

The specifications have evolved as follows:

**Ford**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>MERCON®</td>
<td>1987—1993</td>
</tr>
<tr>
<td>MERCON®(93)</td>
<td>1993—</td>
</tr>
<tr>
<td>MERCON® V</td>
<td>1996—</td>
</tr>
</tbody>
</table>

**General Motors**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEXRON®-IID</td>
<td>1973—1992</td>
</tr>
<tr>
<td>DEXRON®-IIE</td>
<td>1993—1994</td>
</tr>
<tr>
<td>DEXRON®-III</td>
<td>1994</td>
</tr>
</tbody>
</table>

The DEXRON® and MERCON® specifications presently in service (1997) regarding viscosity:

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Viscosity requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEXRON®-III</td>
<td>Kinematic visc. at 100°C to be reported 6.8 cSt min. 6.8 cSt min.</td>
</tr>
<tr>
<td></td>
<td>Brookfield at -40°C, max. 20000 cP 20000 cP 13000 cP</td>
</tr>
</tbody>
</table>

The new versions of the specifications demand better low temperature properties and oxidation stability.

### 3.3.3 Hydrotreated oils

The oxidative sensitive aromatic and olefinic molecules are saturated during the hydrotreating process. When comparing hydrotreated and conventional mineral oils, with both containing the same additive system, the conventional refined oils will not meet the more severe oxidation requirements that will soon supersede those of DEXRON®-III and MERCON®.

When paraffinic mineral oils are subjected to de-waxing, good low temperature properties are produced. However, Nynas oils are based on a wax-free crude which means that they have superior low temperature properties from the outset.
3.4 HYDRAULIC FLUIDS

Hydraulic fluids are used in many areas in industry. A hydraulic system consists of several parts, e.g.: reservoir, pump, filters and seals.

Important demands for a hydraulic fluid are:
- good seal compatibility
- oxidation stability
- compatibility with metals in the system
- anti-wear properties
- good low temperature properties when used in cold climate
- good shear stability
- non-toxicity

Mineral oils are widely used as a base for hydraulic fluids. A mineral base oil is blended with suitable additives to achieve good properties. Suitable additive packages including oxidation inhibitors, corrosion inhibitors, anti-wear additives, VI-improvers and foam inhibitors are available. Examples of additive packages for hydraulic fluids are: IRGALUBE® ML 3010A (Ciba) for normal grade antiwear fluids and IRGALUBE® ML 605A (Ciba) for high EP fluids.

In hydraulic fluids, naphthenic oils are mostly seen as “additives”. An addition of up to 20 per cent addition can be used to improve some properties, such as seal swell. See section 3.3.1 in the chapter about automatic transmission fluids. For low temperature applications, pure naphthenic oils with VI-improvers are useful.

3.5 AIR COMPRESSOR OILS

Oils in air compressors are subjected to very difficult conditions. High temperatures and the presence of air and condensates are not the ideal environment for a lubricating oil.

3.5.1 Compressor types

Compressors can be divided into two basic types: positive-displacement and dynamic. In positive-displacement machines, air is confined within a closed space and the pressure is increased by reducing the volume of space. The positive-displacement compressors can be further divided into rotary and reciprocating machines.

In dynamic compressors, rotating elements are used to accelerate the air. The velocity is converted into static pressure rise.
3.5.2 Required oil properties

In dynamic compressors, lubricants are not used in the compression space. Thus, the air will be oil-free. But in positive-displacement units, air comes into contact with the lubricant.

The requirements of a lubricating oil will of course depend on the type of compressor used but, in general, properties such as good oxidation stability, resistance to forming carbon deposits and good water separation are essential.

Low temperature properties

Good low temperature properties of the oil are very important during cold start-ups. If the viscosity is too high at start-up problems may occur for rotary-vane, rotary-screw and reciprocating machines.

If viscosity is high when a compressor is started up, the cooling will be inefficient. For screw compressors, this may lead to a rapid temperature increase which can be dangerous. Also, excessively high viscosity will work against the movement of the compressor parts which can lead to mechanical damage. Some parts may also be completely unprotected by lubricating oil. Naphthenic oils, with their excellent low temperature properties, are clearly preferable to paraffinic oils in this respect.

Air release

Air becomes entrained in a lubricating fluid in a compressor. The rate at which air is released from the oil is dependent on both temperature and viscosity (the higher the temperature and the lower the viscosity, the higher the rate of release). Additives cannot be used to enhance this property.

3.5.3 Carbon deposits

The main cause of compressor fires and explosions is the build-up of carbon deposits in the air spaces of compressors. Failures in cooling can lead to these dangerous conditions. These risks are reduced by using oils with good oxidation stability at high temperatures.


4. BASE OIL SELECTION

Recommended base oils for different applications

<table>
<thead>
<tr>
<th>Application</th>
<th>T9</th>
<th>T22</th>
<th>T110</th>
<th>T400</th>
<th>NS3</th>
<th>NS8</th>
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<tbody>
<tr>
<td>Cutting fluid*</td>
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<table>
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<td>•</td>
<td></td>
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</tr>
</tbody>
</table>

* fluids for turning, milling, sawing, drilling, honing, broaching, reaming, threading, grinding and lapping.
5. HANDLING

During refining a number of analyses are used to control the process so that the finished product possesses the correct properties. When the oil is ready to leave the refinery, it has exactly the right, specified, properties which must not be allowed to change thereafter.

Ships are normally only used for transportation from a refinery to a depot, before the oil is delivered to the end customer. Deliveries by road tankers are the most common method of transportation to the customer.

Care has to be taken when filling and transporting the oil. It is important to avoid both contamination and conditions that may damage the oil. For instance, contamination by light products will influence the volatility properties of the oil. High storage temperatures and exposure to light may also affect the oil's properties.

White oils have to be handled with particular care due to sensitive parameters such as colour and UV absorption, which have to remain within the FDA limits.

5.1 INSTRUCTIONS, ROUTINES AND QUALITY ASSURANCE

All handling actions and routines are documented to guide our personnel and sub-contractors as well as our customers.

The instructions are a part of our quality system, and their development, distribution, implementation and effectiveness all meet the requirements of ISO 9001, to which Nynas has been officially certified since 1991.
6. HEALTH AND SAFETY

The environmental effects of industrial products are a topic of growing concern on the part of the authorities and, not least, among our customers. The Nynas Petroleum group, to which Nynas Naphthenics AB belongs, has long taken part in the environmental work within the oil industry organisation CONCAWE and the European chemical industry's CEFIC.

All Nynas Naphthenics products are label-free. Within the company, we aim to maintain a high degree of environmental awareness and to act accordingly.

6.1 SAFETY DATA SHEET (SDS)

All purchases from Nynas are accompanied by a Safety Data Sheet (SDS), indicating the properties and effects of the product regarding safety, health and the environment.

6.2 OILS AND LOCAL EFFECTS

Light oils are widely supposed to be more irritating to the skin than heavier oils. Nynas have commissioned an independent institute to test different base oils - naphthenic and paraffinic, light and heavier, to establish their dermatological properties.

The results show that neither naphthenic nor paraffinic oils can be classed as primarily skin irritant. The majority are classed as “slightly irritant”, while some are classed as “non-irritant”. Naphthenic and paraffinic oils demonstrate similar properties.

6.3 OILS AND LONG-TERM EFFECTS

Because mineral oils contain a very large number of chemical substances, assessments of different injury risks have to be based on the whole oil, not on each of the individual constituent chemical substances. Examined in this way, a highly refined naphthenic oil is neither mutagenic, carcinogenic nor teratogenic (impairing fertility or causing injury to the unborn child). This is because, after extreme refining, very little remains of the substances which are known to be mutagenic and carcinogenic, namely the polyaromatics.

There are several ways of analysing polyaromatic content PAC (see 2.9.1). IP 346 is the method used for determining whether an oil has to be labelled or not. Labelling becomes obligatory at three per cent and above.
6.4 LIFE-CYCLE ANALYSIS

In order to assess the environmental impact of a product, it is necessary to perform a life-cycle analysis (LCA). This serves to identify all potential sources of environmental impact: from sourcing and transport of the raw material, through production and distribution, to use and final destruction.

A life-cycle analysis examines the environmental impact of a system throughout its entire life-time. Note that the reference is to a system performing a certain function, not to a product.

A life-cycle analysis should involve some kind of comparison between two systems, or parts of systems, if it is to be meaningful. The different environmental impacts can then be evaluated, given different numerical values and the two totals for all the environmental impacts of the two systems could then be compared. However, there is not yet any universally accepted standard for evaluating impact on the environment.

Nynas have not yet decided in favour of any particular evaluation method but have in the case of transformer oils used the Swedish EPS system. Here, the environmental impact is calculated in terms of Environmental Load Units (ELUs).

More information about health and safety issues can be found in the Nynas booklet “Health and safety aspects of naphthenic oil”.
The basic hydrocarbon structures in a mineral oil are paraffins, naphthenes, aromates and polyaromates.

Paraffinic structures can either be straight or branched chains. Waxes are straight type N-alkanes. At cloud point, the waxes begin to crystallise, which leads to a two-phase system. Oils which are to be used in cold climates, must have the wax content reduced.

Paraffinic structures provide inferior solubility of water and oxidation products, which may lead to precipitated sludge in the oil system. The advantage with paraffinic oils however is their high viscosity index.

Naphthenic structures are also called cycloalkanes. They have excellent low temperature properties and better solubility than N-alkanes. The ring structure can have five, six or seven carbons - six being the predominant number.

Aromatic molecules are ring structures with alternating double bonds. They are totally different from paraffinic and naphthenic molecules, chemically and physically. Nearly all the sulphur and nitrogen in an oil are present in its aromatic structures. Aromates can be present both as monoaromates and polyaromates. Polyaromates have several aromatic rings directly adjacent to each other.

A typical “oil molecule” is illustrated in fig.2. One way of characterising oils is by carbon-type analysis, of which there are several methods. One of these measures the amount of carbons bonded to aromatic or paraffinic structures by using an IR (infra-red) technique.
Atoms in the oil molecule which are not carbons (or hydrogen) are called heteroatoms. These atoms consist of nitrogen, sulphur and oxygen.

Molecules containing nitrogen can be either basic (e.g. quinoline, pyridines) or non-basic (e.g. carbazole, pyrroles). Base oils contain relatively small amounts of nitrogen compounds, but they have an important effect on the character of an oil. They can act in different ways, as:
- oxidation initiators
- oxidation inhibitors
- passivators of copper

The molecules containing sulphur can have both positive and negative effects on oil properties. Some types of sulphur compounds cause corrosion with copper and silver, but also inhibit oxidation processes by destroying peroxides. Examples of sulphur compounds in mineral oil are thiophenes, carbazoles and sulphides. An intermediate oxidation product can be mercapto sulphur. This can mean that slightly oxidised base oils may have a corrosive effect on copper.

The oxygen content is low in fresh base oils. Used oils have higher levels due to oxidation, e.g. acids, ketones and phenols. As stated earlier (2.10), phenols may act as radical destroying inhibitors.
A typical feedstock for the production of base oils has the following composition:

<table>
<thead>
<tr>
<th>Type</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-alkane, wt%</td>
<td>0.05-15</td>
</tr>
<tr>
<td>C_A, % (IR-method)</td>
<td>4-25</td>
</tr>
<tr>
<td>C_P, % (IR-method)</td>
<td>42-66</td>
</tr>
<tr>
<td>C_N, % (IR-method)</td>
<td>to 100%</td>
</tr>
<tr>
<td>PA C, % (H PLC-method)</td>
<td>&gt;2</td>
</tr>
<tr>
<td>Sulphur, wt% (X-ray method)</td>
<td>1-2</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>70-600</td>
</tr>
<tr>
<td>Oxygen, acid number</td>
<td>0.05-2</td>
</tr>
</tbody>
</table>

Table 1. Feedstock (distillate) composition.
APPENDIX II
- REFINING TECHNIQUES

A refining process is a tool for changing the properties of an oil. Refining processes can be divided into two sub-groups: physical and chemical. Where full refining is referred to, it usually entails a combination of the two methods.

Crude oil is divided into light or heavy, paraffinic or naphthenic. Only about 1% of all products from crude oils are used as lubes, insulating oils included. For most refineries, the lube sector is a minor part of their operations.

DISTILLATION

The first step in a “refining train” is always distillation. A “physical” process, the crude oil is fractionated into different boiling point ranges.

Figure 1. End products from crude oil (other than Nynas).

An important advantage with naphthenic oil refineries is that they are dedicated to lubes and are able to produce oils of many types and qualities. Paraffinic refineries are more limited in this respect, since they are generally fuel-dedicated.
Bitumen emerges from the bottom of the distillation tower and various fractions from the side of the fractionating tower. To prevent thermal cracking of the molecules, distillation is often performed under vacuum conditions. However, distillation can be carried out at normal pressure if the boiling point is below 350°C.

Different crude oils yield different amounts of products from the distillation process.

![Figure 3. Typical composition of different crude oils.]

**REFINING OF DISTILLATES**

The next step in refining after distillation consists of two main methods: solvent-extraction and hydrogenation.

**Solvent refining**

![Figure 4. Solvent refining.]
Dewaxing

Paraffinic crudes need to be dewaxed while naphthenic crudes do not. This is because naphthenic crudes are virtually free from waxes.

In dewaxing the oil is blended with a solvent with which it is miscible. The mixture is cooled, the N-alkanes will crystallise and can then be filtrated off. The solvent is subsequently removed by distillation.

Extraction

Extraction is one of the oldest methods of removing unstable molecules from a distillate. The oil is mixed with a solvent (SO₂ or furfural) that forms a separate phase. Aromatic and hetero-aromatic molecules will to some extent dissolve in the solvent phase and can be removed. Due to the equilibrium between the two phases, the amount of aromatics in the raffinate phase lies between 5 and 11%. After the extraction step, a mild hydrogenation is usually performed.

Hydrogenation

Dewaxing and extraction are based on physical methods. Hydrogenation is a chemical conversion of undesirable and environmentally dangerous molecules into harmless compounds.

![Distillation and Hydrogenation Diagram](image)

Figure 5. Hydrogenation.

In hydrogenation, polar, aromatic and hetero-aromatic compounds are adsorbed on to a catalyst surface. The active surface of the catalyst is up to 200 m²/g. Here, the molecules are made to react in the presence of hydrogen.

At low severity - i.e. low pressure, low temperature and high space velocity - only sulphur, oxygen and nitrogen will be removed, forming H₂S, H₂O and NH₃.

By increasing the severity, the aromatic rings become increasingly saturated and, to a certain extent, opened. Since the polyaromatics are the most reactive compounds, the major part of the aromatic compounds remaining in the oil will consist of stable monoaromatics.
The hydrotreatment process is an environment-friendly process which converts undesirable polyaromatic molecules into useful compounds. The result is a high yield of products and little waste products. The H₂S from the process is, for example, converted into pure sulphur in a Claus unit and then sold commercially.

Other refining methods

There are other ways to produce lubricating oils, such as hydrocracking or wax isomerisation. These methods involve large changes in the chemical structure of the raw material.

Hydrocracking

If the oil is hydrogenated even more than in the severe hydrotreating process, the naphthenic molecules are opened. This results in the so-called unconventional, or semi-synthetic base oils known as VHVI (very high viscosity index) and XHVI (extra high viscosity index) stocks. The main application for these oils is in automotive lubricants.

Wax isomerisation

Here, starting with a waxy feedstock, straight chain molecules are converted into branched ones. This process yields products with a high viscosity index and good low temperature properties.
### APPENDIX III

Some corresponding methods

<table>
<thead>
<tr>
<th>Name</th>
<th>ASTM</th>
<th>DIN</th>
<th>ISO</th>
<th>IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>D 4052</td>
<td>ISO 12185</td>
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</tr>
<tr>
<td>Viscosity</td>
<td>D 445</td>
<td>ISO 3104</td>
<td>IP 71/1/95</td>
<td></td>
</tr>
<tr>
<td>Flash point, PM</td>
<td>D 93</td>
<td>DIN 51758</td>
<td>ISO 2719</td>
<td>IP 34/88</td>
</tr>
<tr>
<td>Flash point, C O C</td>
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<td>DIN 51376</td>
<td>ISO 2592</td>
<td>IP 36/84 (89)</td>
</tr>
<tr>
<td>Pour point</td>
<td>D 97</td>
<td>DIN 51597</td>
<td>ISO 3016</td>
<td>IP 15/95</td>
</tr>
<tr>
<td>Sulphur</td>
<td>D 2622</td>
<td>DIN 51400 T6</td>
<td></td>
<td></td>
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<tr>
<td>Colour</td>
<td>D 1500</td>
<td>DIN 51578</td>
<td>ISO 2049</td>
<td>IP 196/91</td>
</tr>
<tr>
<td>Total Acid Number</td>
<td>D 974</td>
<td>DIN 51558 T1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbon type analysis</td>
<td>D 2140</td>
<td>DIN 51378</td>
<td>ISO 2977</td>
<td>IP 2/91</td>
</tr>
<tr>
<td>Aniline point</td>
<td>D 611</td>
<td>DIN 51775/DIN 51787</td>
<td>IS 2160</td>
<td>IP 154/95</td>
</tr>
<tr>
<td>DMSO extractable compounds</td>
<td>D 130</td>
<td>DIN 51759/DIN 51811</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper strip</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Bleeding at static conditions (shelf life)</td>
<td></td>
<td>DIN 51817</td>
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<td>IP 121</td>
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</tbody>
</table>

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Responsible Care

Nynas is a signatory to the international Responsible Care programme of the CEFIC (European Chemical Industry Federation).

The programme is the chemical industry’s commitment to continuous improvement in all aspects of health, safety and environmental protection. Responsible Care is a voluntary initiative, fundamental to the industry’s present and future performance and a key to regaining public confidence and maintaining acceptability.

The signatories pledge that their companies will make health, safety and environmental performance an integral part of overall business policy on all levels within their organizations.