THE RE-REFINING OF USED LUBRICATING OILS

The lubricating oils used by vehicle engines have to be replaced at least every 20 000 km. This oil used to be dumped, but now most of it is re-refined and reused. This is done in a three step process, in which water, solids, lighter oils, dissolved metals, degraded additives etc. are removed.

Step 1 - Dehydration
The oil is boiled in a closed container to remove the water that has been mixed into it.

Step 2 - Diesel stripping
The dehydrated oil is then fed continuously into a vacuum distillation plant for fractionation. Lighter oils boil off first and are removed, followed by the lubricating oil itself. Other heavier components do not boil in the conditions used.

Step 3 - Lube oil distillation and condensation
A liquid extraction process then removes any aromatic components from the oil.

By this stage, the oil is identical to refined virgin oil. It is then tested, appropriate additives are added and the oil is ready to be reused.

INTRODUCTION

Re-refined lubricants have been produced in New Zealand for over 50 years. However, their acceptance as a high quality lubricant has been a gradual process, largely because of the scepticism of the public that the product can be re-refined to its original condition. In New Zealand Dominion Oil rerefines about 7 million litres per year, while an older acid clay method is used at Turua near Thames to treat 0.5 - 1 milion litres per year.

Most of the sceptics regard the process as some sort of simple filtration. In fact, the re-refining process used at Dominion Oil is a highly sophisticated operation using the most modern plant available in the world today. The process used is in many ways similar to that used to refine crude petroleum. Consideration of the composition and refining of crude will give a better understanding of the re-refining process and highlight the similarities.

OIL CHEMISTRY

Petroleum products are essentially composed of hydrocarbons, i.e. compounds containing exclusively carbon and hydrogen. The simplest hydrocarbon molecule is methane, CH_4. This basic molecule is the main constituent of natural gas. It can be extended with the addition of more carbon and hydrogen atoms, usually forming into longer chains. Four carbon atoms in a chain forms butane, one of the main constituents of LPG. The atoms may also form side chains off the main chain, or form into ring structures such as the benzene ring. Lubricating oils are just extensions of these basic hydrocarbon structures, containing from 20 to 70 carbon atoms per molecule, often in an extremely complex arrangement of straight chains, side chains and five and six membered ring structures.

The lubricating oil molecules can be divided into three broad groupings:

Paraffinic: Predominantly straight chains, tend to be waxy, have a high pour point and good viscosity/temperature stability.

Naphthenic: Straight chains with a high proportion of five and to a lesser extent six membered ring structures. Tend to have a low pour point. For this reason they are used as refrigeration oils. They are highly carcinogenic and are little used in engine oil. Dominion Oil treats used refrigerator oils separately from the main plant. As refrigerator oils do not come in contact with products of combustion they are much cleaner than engine oils.

Aromatic: Straight chains with six membered ring benzene structures.

In practise, no sharp distinction exists between these various groupings as many lubricating oil molecules are a combination, to varying degrees, of the different types of hydrocarbons.

The main point to bear in mind is that these molecules are extremely stable. Lubricating oil molecules never wear out - all that happens is that the additives in the oil wear out or deplete and need replacing.

THE COMPOSITION OF CRUDE PETROLEUM

Crude petroleum is formed by the bacterial decomposition of plant and animal remains deposited around 100 million years ago. When pumped from the ground it can be black, brown or colourless, and is often a mixture of solids, liquids and gases. The Taranaki fields, for example, are predominantly gaseous, and are the source of New Zealand's supplies of CNG and LPG. Taranaki crude contains no lube oil.

The composition of crudes from different sources varies tremendously, but a typical make-up is as follows:

Gases	5%
Gasoline	35%
Kerosine	10%
Diesel	20%
Lube oil	2%
Tar, Bitumen	28%

THE REFINING OF CRUDE PETROLEUM

Crude petroleum is initially refined by a process known as fractional distillation. This process basically consists of progressively heating the crude to drive off the various fractions as vapours. Some of the crude is already in gaseous form, but as it is further heated the most volatile fractions (i.e. gasoline) will begin to boil off. As further heat is applied the kerosine will begin to distill off.

The lubricating oil fraction is very stable and involatile. To heat the lubricating oil to the temperature required for distillation will actually decompose the oil, so the diesel and lube oil fractionation is carried out under vacuum to reduce the effective boiling point of these

products. An oil which will normally boil at 500°C will boil at 300°C under the very high vacuum used. Boiling ranges are as follows:

Gasoline	40 - 190°C
Kerosine	190 - 260°C
Diesel	260 - 330°C
Lube oil	330 - 400°C under vacuum

The very heavy components of the crude (i.e. tars) will not distill even under a vacuum and remain as bottoms or residue.

The lubricating oil fraction must then be further refined before being suitable for use. The oil is dewaxed by cooling; asphalts, aromatics and resins are removed by solvent extraction and coloured molecules are removed by hydrotreating, or treatment with activated earths. The base oil molecular type (i.e. paraffinic, naphthenic) must then be blended to provide the desired properties of colour, oxidation stability, viscosity characteristics and additive response. Only then can the additives be blended into the base oils to produce the high quality lubricants available today.

USED OIL AND ITS COMPOSITION

A lubricating oil becomes unfit for further use for two main reasons: accumulation of contaminants in the oil and chemical changes in the oil. The main contaminants are listed below.

Combustion products

Water. Fuel burns to CO_2 and H_2O. For every litre of fuel burnt, a litre of water is created. This normally passes out through the exhaust when the engine is hot, but when cold it can run down and collect in the oil. This leads to sludge formation and rust.

Soot and carbon. These make the oil go black. They form as the result of incomplete combustion, especially during warm-up with a rich mixture.

Lead. Tetraethyl lead, which used to be used as an anti-knock agent in petrol, passes into the oil. A typical used engine oil may have contained up to 2% lead, but today any lead comes from bearing wear and is likely to be in the 2 - 12 ppm range.

Fuel. Unburnt gasoline or diesel can pass into the lubricant, again especially during start-up.

Abrasives

Road dust. This passes into the engine through the air-cleaner. Composed of small particles of silicates.

Wear metals. Iron, copper and aluminium released due to normal engine wear.

Chemical products

Oxidation products. Some of the oil molecules, at elevated temperatures, will oxidise to form complex and corrosive organic acids.

Depleted additive remnants.

THE RE-REFINING OF USED OIL

The re-refiner's job is to remove all the aforementioned contaminants and restore the oil to its original condition. The important point to note is that the technology used by Dominion Oil is virtually identical to that used to refine crude petroleum, the difference being that the level of contamination in used oil is much lower that that in crude oil.

Used oil is uplifted from centralised collection points at places such as service stations, workshops, recycling depots and factory sites. The collector is contracted to the Used Oil Monitoring Group, whose members include BP, Dominion Oil Refining, Caltex, Castrol, Shell, Milburn Cement and the Department of the Environment. Milburn Cement administer the Group, whilst the Department of the Environment represent the Government. Milburn Cement also combust any used oil that cannot be recycled, using it as an alternative to coal. The oil is burned at temperatures of approximately 1400^{o}C, ensuring complete combustion. At this temperature dioxins are not formed as they may be at lower temperatures. This method has been endorsed by the Department of the Environment as the preferred alternative to re-refining.

Step 1 - Dehydration

The oil is stored to allow water and solids to separate out from the oil, then the oil is heated to 120^{o}C in a closed vessel to boil off any emulsified water and some of the fuel diluents.

Step 2 - Diesel stripping

The dehydrated oil is then fed continuously into a vacuum distillation plant for fractionation in exactly the same fashion as crude petroleum. The fractions obtained are as follows:

1. *Light fuel and diesel*. Dominion Oil produces enough diesel from the used oil feedstock to run all the burners and boilers, giving total self-sufficiency in fuel.

2. *Lubricating oil.* The bulk of the feedstock will distill off in the plant to produce a lubricating oil fraction.

3. *Residue.* The non-distillable part of the feedstock. This contains all the carbon, wear metals, degraded additives and most of the lead and oxidation products. This residue is successfully used as bitumen extender for roading.

Step 3 - Lube oil distillation and condensation

The lubricating oil fractions are then passed through an extraction tower in the presence of *N*-methylpyrolidone (NMP). The NMP is an aromatic selective solvent which, in addition to removing some colour and odour, is able to extract all unwanted aromatic contaminants present in the paraffinic lubricating oil fraction, subsequent to fractional distillation. This is important as polycyclic aromatics are very carcinogenic. This process is commonly used in virgin oil refineries, but Dominion Oil Refining is the only manufacturer of re-refined oil to use it.

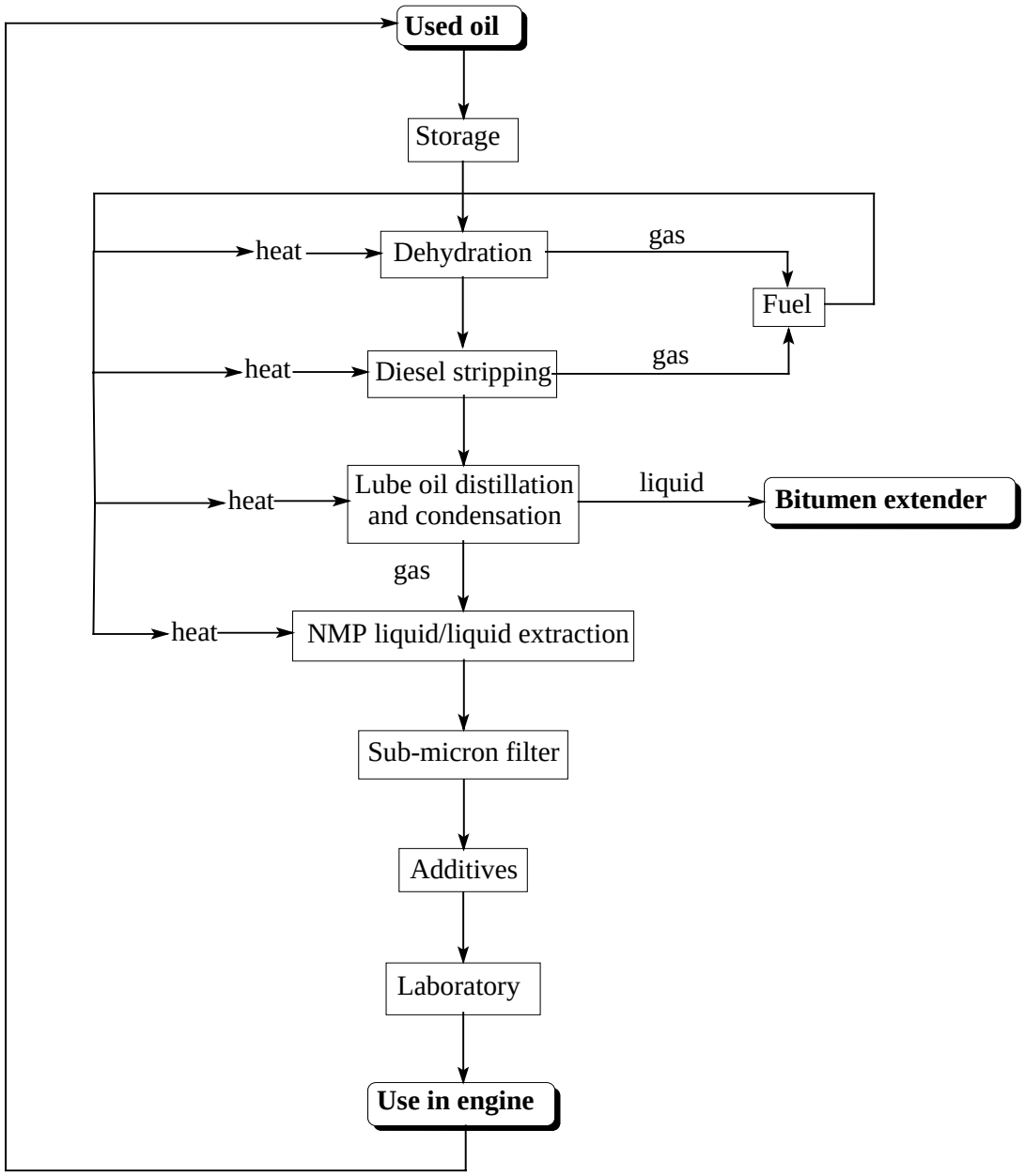

Figure 1 - Schematic of the Dominion Oil Refining Co. Ltd. process

The oil is then passed through a filter press followed by a polishing filter to remove particles larger than one micron diameter.

The base oil thus produced is chemically and physically indistinguishable from virgin base oils.

ADDITIVES AND WHAT THEY DO

Pure mineral oil has good lubricating properties, but it is the additives in the oil that give it its characteristics and enhance its lubricating properties to enable it to meet modern requirements. It is primarily advances in additive technology that have enabled today's 12 months or 20 000 km oil change periods. Thirty years ago oil changes were recommended every 500 miles (800 km). However small Japanese diesels cars still need about 5000 km oil chenges. The base oil is now really only a carrying medium for the additive package.

The base oil produced by Dominion Oil is mainly trucked to BP in Freemans Bay in Auckland where blending occurs.

Further and more detailed information on this process is to be found in "Used Oil. a Renewable Resource and an Environmental Pollutant" by David Layzell,

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