WEAR CHECK® AFRICA
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BASE STOCKS AND ADDITIVES — HOW OILS ARE FORMULATED

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There are tens of thousands of different lubricants on the market, from simple hydraulic fluids to very sophisticated synthetic oils formulated for high performance engines. Think of the technology that is required to lubricate a formula one racing car; after the race the team is more likely to change the engine than the oil!

So, how are oils designed? What physical and chemical properties are required so that each individual oil can do the job that it is supposed to?

Although oils may be required to do many different jobs in many different environments and in a wide range of machinery, they all consist of two fundamental components – a base stock and an additive package.

BASE STOCK

Let's look at the base stocks first. A base stock is usually a variety of chemically related compounds which often consist of hydrocarbons. Hydrocarbons are chains of chemicals that contain a backbone of carbon atoms with hydrogen atoms attached. The length of this backbone can vary and it is this length that determines the viscosity of the base stock. The viscosity of an oil can be defined as the oil's resistance to flow under the force of gravity at a specified temperature. This property is known as the kinematic viscosity and determines how 'thick' or 'thin' the oil is. This is an oil's most important physical property.

Image 1: Viscosity being measured with a viscometer

Up until the nineties, base stocks were either classed as mineral or synthetic. Mineral oils were the result of refining crude oil taken from below the earth's surface to produce a base stock suitable for blending into a finished product. Synthetic base stocks were quite similar but instead of refining crude oil, these were chemically designed in a laboratory to have just the right properties desired by the oil company. It is possible to refine a mineral oil to remove most of the undesirable characteristics but not all of them. Synthetic oils are tailor-made for a specific job. The downside of synthetic lubricants is that they are a lot more expensive than mineral oils.

A court case between Castrol and

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THROUGH OIL ANALYSIS

Mobil in the late nineteen nineties changed the landscape with regards to the meaning of the terms 'mineral' and 'synthetic'. These days the term synthetic is more of a marketing term rather than a scientific definition. Today, base stocks are defined by the American Petroleum Institute and fall into one of five scientifically defined groups. These are simply known as API groups I, II, III, IV or V.

Groups I and II are what were traditionally known as mineral oils and groups IV and V as synthetic. Group III base stocks are mineral in origin but are considered part of the synthetic family. The chart below shows the physical characteristics of each API group.

API Group	Sulphur	Viscosity Index	% Paraffins
I	> 300 ppm	80 - 120	< 90 %
II	< 300 ppm	80 - 120	> 90 %
III	< 300 ppm	> 120	> 90 %
IV	Poly alpha olefins (PAOs)		
V	Anything not covered by groups I - IV		

Chart 1: API base stock groups

Group I base stocks are manufactured by solvent extraction, solvent or catalytic dewaxing and hydrofinishing. These base stocks are the least refined and are usually a mixture of hydrocarbons with little uniformity. They have relatively high sulphur contents and relatively low viscosity indices and percentage paraffin make-up. Group I stocks are found in the market place but tend to be used in less demanding applications.

Group II oils are manufactured by a hydrocracking process with solvent or catalytic dewaxing. This produces a more refined base stock with a lower sulphur content and a higher percentage of paraffins which means the oil is more highly saturated (has fewer double bonds). This results in a base stock with better natural antioxidant properties. Most automotive oils in South Africa are manufactured from Group II stocks.

Group III oils are severely hydrocracked and hydrotreated in the refining process to produce a very pure base stock with low sulphur content, a high degree of saturation (paraffin content) and a naturally high viscosity index. These base stocks have a high resistance to oxidation and are stable over a wide range of operating temperature. They are used to produce high performance lubricants.

Group IV oils consist of a family of compounds known as Poly Alpha Olefins or PAOs. These are also sometimes known as SHCs or Synthesised Hydro-Carbons. These base stocks are created in the laboratory so are very pure but they are chemically very similar to very highly refined stocks derived from crude oil.

Group V base oils consist of all the synthetic base stocks not covered under group IV such as poly alkyl-glycols and esters. These are exotic, synthetic base stocks with very specific properties to do very specific jobs.

Base stocks are sometimes produced from a blend of more than one API group and if groups III or IV are used with groups I or II, then the blend can result in a product that is termed a part or semi synthetic.

ADDITIVES

Once the base stock has been refined or manufactured to the required degree of purity and blended so that it has the desired viscometric properties, it is time to introduce the additive package into the mix in order to produce a lubricant to do a specific job. Some high performance engine oils may have as much as 30% make-up of an additive package. On the other hand, some gear oils may only have 1 or 2% additive content whilst very pure hydraulic fluids may be made up of over 99% base stocks with very little additive; it just depends on what job the oil is expected to do.

There are many additives that impart a variety of properties to a lubricant. Often these are sold as finished additive packages which may have half a dozen different additives, all in the correct concentration that can be blended into the base stock in one go in order to produce the desired product. However, we will treat each additive on its own by looking at the name of the additive, how it functions, what types of oil you would find such chemicals in and, for the sake of completeness, the names of typical chemicals involved.

This is a list of additives we will be looking at.

Anti-wear	Reduces friction thereby reducing wear
Extreme Pressure agent	Prevents scoring and seizure
Corrosion inhibitor	Prevents rusting, particularly during storage
Detergent	Keeps surfaces free of deposits
Dispersant	Keeps deposits in suspension
Friction modifier	Alters the frictional properties of the oil
Pour point depressant	Permits oil to flow at low temperatures
Seal swell agent	Prevents seals from leaking
Viscosity index improver	Ensures viscosity stability over a wide temperature range
Anti-foamant	Reduces foaming
Tackiness agents	Enables oil to stick to metal surfaces
Dyes	Colours the oil for identification and marketing purposes
Anti-oxidant	Retards oxidation of the oil
Demulsifiers	Enables the oil to shed water easily
Emulsifiers	Allows water to mix with fire retardant lubricants
Fungicides	Kills microbes living in the oil
Solid additives	Particulate extreme pressure agents
Metal deactivator	Inhibits the catalytic oxidation of the oil by some metals

Chart 2: Typical additives found in finished lubricants

Let us now take a more detailed look at these additives, their purpose, function, chemistry and applicability.

Anti-foamants

The additive reduces the surface tension of the oil/air interface to speed up the collapse of foam.

Typical compound: Poly methyl siloxane (which explains why silicon is often found in new oils). These molecules are quite big and have the potential to be filtered from the oil. They can also give erroneously high readings on optical particle counters.

Application: Most engine, gear and hydraulic oils because foaming is a danger in all applications.

Antioxidants

The additive works by decomposing peroxides and terminating free radical reactions, both of which are precursors to the oxidation process. They also reduce the reactivity of oxygen (oxygen is very reactive) with the base stock of the oil.

Typical compounds: Organic phosphates, hindered phenols, aromatic amines and sulphurised phenols. ZDDP (zinc-dithio-di-phosphate) is perhaps the best known of all the additives. It was developed after the 2nd world war as an anti-wear agent and was found also to be an effective antioxidant. It is still in use today as the chemists have been unable to find anything cheaper or more effective.

Application: Most engine and some hydraulic oils employ these additives.

Anti-wear and EP (Extreme Pressure) agents

These additives reduce friction and wear and prevent scoring and seizure. They react chemically with metal surfaces to form films of new compounds (metal sulphides and phosphides for example) that have lower shear strength than the naked metal. This, in turn, prevents metal-to-metal contact.

Typical compounds: ZDDP, organic phosphates, organic sulphates, sulphurised fats and oils, sulphides and disulphides.

Application: Engine and hydraulic oils usually have anti-wear agents and EP additives are found in gear oils.

Bactericides, fungicides and algaecides

These additives inhibit the growth of microbes in oils and fuels. Organisms such as anaerobic bacteria live in oils and particularly fuels. They do not need air to respire as long as water is present and the oil or fuel provides a source of nourishment. The bugs live in the oil/water interface and can form acids and block filters.

Typical compounds: Organo-phosphorus poisons.

Application: These additives are more often applied to fuel where there is bulk storage rather than lubricants.

Rust and corrosion inhibitors

These additives prevent corrosion and rusting of metal parts in contact with the lubricant. They are polar compounds that are preferentially adsorbed onto the metal surface providing a protective film whilst neutralising acids at the same time.

Typical compounds: ZDDP, metal phenolates, basic metal sulphontes, fatty acids and amines. This is where the calcium and magnesium come from in a spectrometric analysis of oil.

Application: These additives are found in engine and gear oils and particularly shipping (preservative) lubricants.

Demulsifiers

Demulsifiers insure the ready separation of water from the oil and retard the formation of emulsions. They cause the breakdown of the oil/water interface and allow the coalescence of water droplets that can settle out by gravity.

Typical compounds: Organic soaps and soaps of fatty acids. Organic polymers can also be used. These compounds are actually the same chemicals that are used to form stable emulsions but in much lower quantities. The chemistry is not straightforward however. Note that oils containing ZDDP have a tendency to form stable emulsions, hence the 'mayonnaise' found in engine oils when they get wet.

Application: Most engine, gear and hydraulic oils have them.

Detergents

Detergents, as the name suggests, keep surfaces free of deposits and clean up surfaces that do have deposits. These additives chemically react with sludge and varnish precursors, neutralise them, then keep them in suspension or soluble in the oil.

Typical compounds: Organo-metallic compounds of barium, sodium and, more commonly, calcium and magnesium, usually phenolates, phosphates and sulphonates.

Application: They are generally only found in engine oils and some compressor oils.

Dispersants

Dispersants keep insoluble contaminants dispersed in the lubricant and prevent them from coating metal surfaces. The contaminants (soot and sludge being the most common ones) are bonded by polar compounds to the dispersant molecule, which prevents them from agglomerating, and are kept in suspension in the oil due to the solubility of the dispersant in the oil (much the way ordinary soap works). Larger particles that get suspended in the oil can be filtered out.

Typical compounds: Polymeric alkyl-phosphates and alkyl-succinimides.

Application: They are usually only found in engine oils.

Dyes

Dyes help identify products in complex hydraulic systems and aid in the identification of the source of leaks. Dyes are also used as marketing tools such as red automatic transmission fluids and other speciality products.

Typical compounds: Aromatic dyes.

Application: They are found in hydraulic oils, ATFs and speciality products but most commonly they are used to identify different fuel grades. Note that not all ATFs are red, some are straw coloured or even water white. Also note that not all red oils are ATFs; there is a range of speciality synthetic products that are all dyed red.

Image 2: Some oil additives

Emulsifiers

Emulsifiers do exactly the opposite job that demulsifiers do in shedding water; they allow stable oil/water emulsions to form and retard the coalescence of water droplets. Interestingly, these are the same chemicals that are used for demulsifiers, just in greater quantities.

Typical compounds: Organic soaps such as alkyl succinate salts and soaps of fatty acids (anionic), quaternary ammonium salts (cationic) and alkenyl succinimides (non-ionic).

Application: They are usually only found in fire retardant fluids.

Friction modifiers

Friction modifiers alter the coefficient of friction between the oil and interacting surfaces. They are surface active compounds that can be preferentially adsorbed onto the surfaces of machine componentry such as clutch packs and discs.

Typical compounds: Organic fatty acids and amines, lard oil and high molecular weight organic phosphoric acid esters.

Application: They are usually only found in gear oils and transmission fluids.

Metal deactivators

These additives reduce the catalytic effect of metals (iron and copper) on the oxidation rate of the oil. They form inactive films on metal surfaces by reacting with the underlying metal to form metallic complexes. There is a phenomenon known as additive stripping - these chemicals are not fussy about which metal surfaces they react with and, if there is a lot of fine wear debris at the bottom of the sump, then this is where the additives will end up.

Typical compounds: Organic complexes of nitrogen and sulphur, amines, sulphides and phosphates.

Application: Most oils contain metal deactivators.

Pour point depressants

Pour point depressants (PPDs) allow the oil (and fuels) to flow at low temperatures. Fluidity can be hampered by the formation of wax crystals, which all paraffinic oils will contain when the temperature drops below freezing. PPDs do not stop the crystals from forming but they are surface active compounds that stop them from agglomerating and sticking together.

Typical compounds: Alkylated naphthenes, phenolic polymers and poly-methacrylates. Naphthenic oils used in the lubrication of refrigeration compressors have a naturally low pour point.

Application: They are found in nearly all oils and fuels.

Seal swell agents

These additives swell elastomeric seals to prevent leakage and insure a tight fit. They react with seal materials and cause them to increase in size.

Typical compounds: Organic phosphates and aromatic hydrocarbons.

Application: Engine and gear oils contain seal swell agents but they are most important for hydraulic fluids.

Solid additives

Solid additives reduce friction and increase load carrying ability in heavily loaded (and slow moving) components such as dragline gearboxes. They function by having very low coefficients of friction which reduce overall friction experienced between metal surfaces. They also have good load bearing characteristics.

Typical compounds: The two most common compounds are graphite and molybdenum disulphide (an oil additive that has been around for nearly 100 years).

Application: These additives are generally only found in gear oils.

Tackiness agents

Tackiness agents enable oils to 'stick' to metal surfaces in splash lubricated applications. These are polar compounds that form bi-molecular layers on metal surfaces through adsorption.

Typical compounds: They are typically fatty acids.

Application: They are only found in gear oils.

Viscosity index improvers

Viscosity index improvers (VII's) reduce the rate of change of viscosity with changes in temperature. They are long chain organic polymers that remain tightly curled up when temperatures are low. When the oil is heated up they expand and uncoil which counteracts the tendency of oils to thin out with increasing temperature.

Typical compounds: Polymers and co-polymers of methacrylates, butadienes, olefins and styrenes.

Application: They are used for any oils that require multigrade properties.

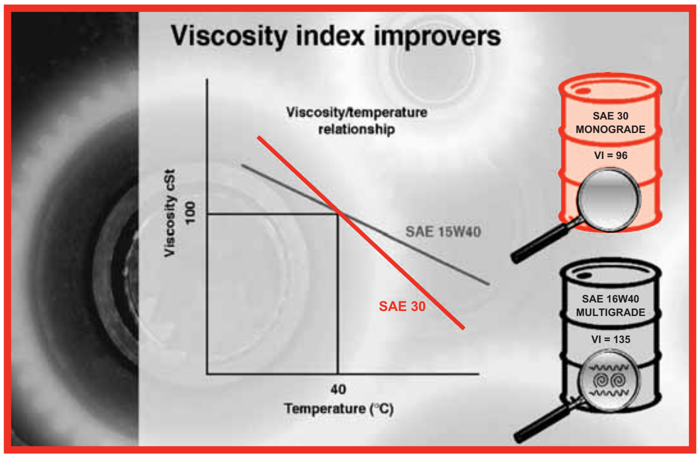

Image 3: How VI improvers affect the viscosity temperature relationship

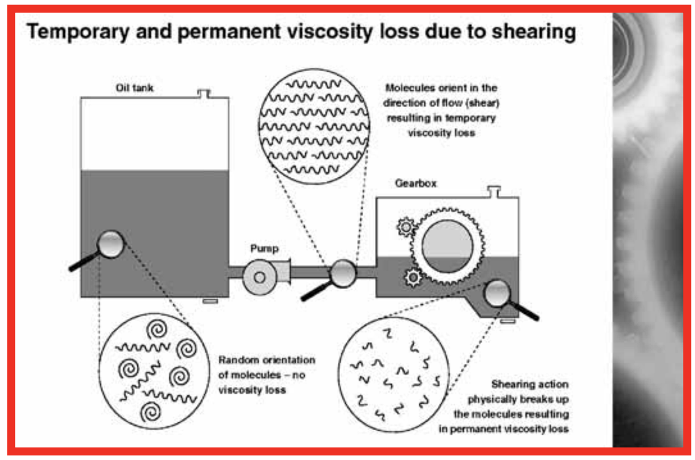

Image 4: Temporary and permanent viscosity loss

The addition of a VII to an oil is what turns a monograde oil into a multigrade oil with the obvious benefits of greater viscosity stability over a wide range of temperatures. However, in mineral oils, this effect is achieved by the addition of additives that are not physically stable. They can physically break down under shearing action found in transmission clutch packs. This results in a permanent loss of viscosity which is why multigrade oils are not recommended for transmissions. This loss of viscosity is permanent but a temporary loss can occur when oil molecules align themselves to the direction of flow of the lubricant.

API Group III oils have high viscosity indices due to their naturally high percentage of paraffins in the base stocks and shearing is not a problem with these oils. The same applies to Group IV oils which are pure compounds and are designed to have a high viscosity index.

The following chart shows the relationship between the base stock and the various additives.

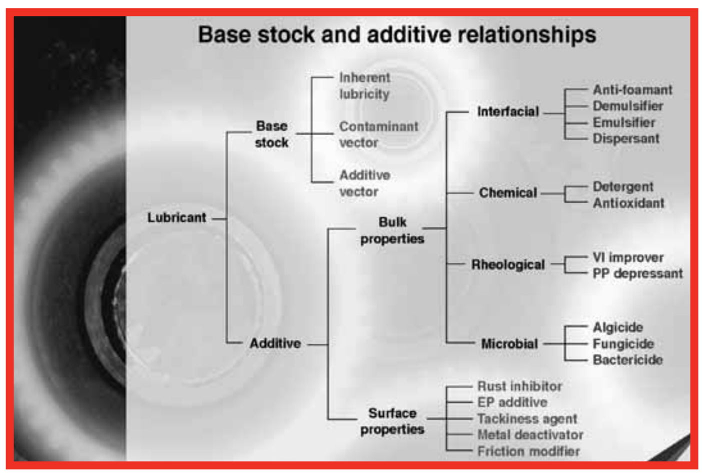

Image 5: Base stock and additive relationships

Finally, when using lubricants it is important to remember the five rights of oils: the right product, in the right place, at the right time and in the right quantity but, most importantly, with the right attitude.

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