LUBRICANTS AND LUBRICATION

15th March 2017

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INTRODUCTION

• The property of reducing friction is known as Lubricity.

• A **lubricant** is a substance introduced to reduce the friction between surfaces in mutual contact.

• Ultimately reduces the heat generated when the surfaces move against each other.

• It may also have the function of transmitting forces, transporting foreign particles, or heating or cooling the surfaces.

• The science of friction, lubrication and wear is called tribology.

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LUBRICANTS

- Lubricating oil is a mixture of base oil, viscosity index improvers and additives.
- BASE OIL+VISCOSITY MODIFIER+ADDITVES-----> LUBRICANT (75 - 80%) (5 - 13%) (6 - 10%)
- Base oil can be mineral, synthetic or a mixture of these.
- Additive system dispersants, detergents, antioxidants, antiwear agents, antifoam, corrosion inhibitors, etc.
- Viscosity modifier polymer added to reduce the change in viscosity with temperature.
- The relative amounts of these components are dependent upon the application, the viscosity grade and the regional performance demand.



PERFORMANCE OF LUBRICANTS

Function	Performance
Wear	 There are two broad types of mechanical wear: Two-body wear – where primary engine components come in contact with each other. It can be controlled by the addition of antiwear additives such as ZDDP.
	• Three-body wear – when a foreign body, e.g. swarf, soot or another solid contaminant, enters the interface between two primary engine components. It is additionally controlled by addition dispersants and detergents .
	• Oxidation of the lubricant leads to viscosity increase and consequent issues of pumpability, fuel economy and ultimately oil starvation.
Oxidation	• Oxidation products also include organic acids which can cause corrosion and deposits around the engine but particularly in the cooler parts of the engine.
	 Antioxidants such as phenols and amines are used to control oil oxidation, and the antiwear agent ZDDP also acts as a powerful antioxidant.
	Acids are produced by oxidation as well as by fuel combustion.
Acid	• Sulphur levels are decreasing in the developed world to enable after-treatment devices to function properly.
neutralization	• This reduction is also reducing the formation of sulphurous acids which affect both engine and environment.
	• In the developing world, lubricants very high fuel sulphur levels of the order of >3000ppm sulphur.
	• Acid neutralization is enhanced by addition of basicity in the form of overbased detergents and, to a lesser degree, by dispersants .

Function		Performance
Black Sludge	•	Black sludge is a soft grease-like deposit around the engine, including the sump and valve-deck.
	•	It's formation results from complex interactions between lubricant, fuel and combustion by-products and is heavily influenced by engine design, climate, drive cycle, oil drain interval and local fuel quality.
	•	If the sludge blocks the oil pickup pipe, then the resulting oil starvation causes catastrophic damage to the engine.
	•	Black sludge protection is provided primarily by dispersants and, to a lesser extent, antioxidants.
	•	In comparison with black sludge, these are high-temperature deposits formed in the ring grooves and on the piston crown, skirts, lands and under crown.
Piston	•	This is particularly true for modern diesel engines where high combustion temperatures mean that deposits form on the piston.
Deposits	•	Piston deposit formation is strongly influenced by the type of base oil used and also by the selection and content of viscosity modifier .
	•	Detergent and dispersant selection also have significant effects on reducing the formation of piston deposits
Soot	•	Soot particles formed during the diesel combustion process can cause three-body wear in the engine.
Dispersion	•	Soot is suspended in the oil by dispersants , which minimizes the effect of soot on wear.

Function		Performance
Soot	•	Lubricants with high levels of soot, e.g. more than 3% by mass, can show dramatic increases in viscosity.
Induced Viscosity	•	Oil formulations must control this viscosity increase and maintain its function in the engine when it contains soot.
Control	•	Soot-induced viscosity control is influenced by dispersant type.
	•	Different geographical regions have different market requirements.
Regional Performance	•	European oils tend to be for longer drain applications, up to 30,000 miles between oil drains,
Demand	•	Whereas North American market lubricants tend to be changed every 3000–10,000 miles.
	•	Additionally, differences between 'developed' and 'developing' markets have an effect on the required lubricant performance and hence the formulation and the lubricant drain interval.

VISCOSITY OF LUBRICANTS

- Viscosity is the most important property for any lubricants.
- Viscosity is a quantitative measure of a fluid's flow resistance.
- Absolute/dynamic viscosity, measures the force required to move a square-centimeter plate parallel to a reference surface at a speed one centimeter per second at a distance of one centimeter. Units are expressed as dyne*sec/cm² or Poise (P) or centiPoise (cP).
- **Kinematic viscosity** measures the time required for a fluid to flow through a tube under the force of gravity and has the units m²/sec.
- Mathematically, Kinematic Viscosity also the same as absolute viscosity divided by the fluid density. Kinematic viscosity is expressed as Stokes (one centistoke = 1cSt=10⁻⁶ m²/sec).



IMPORTANCE OF MONITORING VISCOSITY

- Most components surfaces are separated by a lubrication film thickness of 10 micron or less.
- For high pressure systems, such as hydraulics or high speed turbochargers, to maintain the correct oil viscosity is even more critical.
- Any significant change of oil viscosity, either a reduction or increment, may damage lubrication film stability and effectiveness.



EFFECTS FOR CHANGES IN VISCOSITY

	Reduction in Viscosity	Increase in Viscosity		
•	Loss of oil film resulting in excessive wear	•	Excessive heat generation results in oil oxidation which increases the sludge and varnishes build-up	
•	Increased mechanical friction causing excessive energy consumption and heat generation	•	Gaseous cavitation due to in adequate oil flow to pumps and bearings.	
•	Increased sensitivity to particle contamination due to reduced oil film thickness	•	Lubrication starvation due to lack of flow	
•	Oil film failure at high temperatures, high loads during start-ups.	•	Excess energy consumption to overcome fluid friction	
		•	Poor entrainment and demulsibility	
		•	Poor cold start up pumpability	

The end results of above effects are:

Shorter oil lifespan
Shorter components lifecycle
Increased oil consumption,
Higher power consumption and
Reduced machine reliability

ROOT CAUSES FOR VISCOSITY CHANGES

Reduction in Viscosity	Increase in Viscosity
Thermal cracking of oil molecules	Oxidation
• Shear thinning of VI improvers (for multigrade engine oil)	Water (emulsion)
Fuel dilution	Formation of carbon and oxides insoluble
Cross mixing with lower viscosity oil	• Soot
	Anti freeze (glycol)
	Cross mixing with higher viscosity oil.

HOW TO SET VISCOSITY LIMITS

- The first step is to set a baseline value as a reference.
- This value is based on actual viscosity measurement of new fresh oil and not from the lubricant product sheet.
- Industrial oil (hydraulic, turbine, compressor, gear etc.) should be based on kinematic viscosity @ 40°C, whilst for engine oil, kinematic viscosity @ 100°C should be used.
- The upper limits and lower limits for inservice oil should be based on this value.

Limits	Crankcase oil	Industrial oil	Severe environment Industrial oil
Critical (Upper)	+20%	+10%	+7%
Caution (Upper)	+10%	+5%	+4%
Caution (Lower)	-5%	-5%	-5%
Critical (Lower)	-10%	+10%	-10%

Note: Severe environment oils are at a higher risk of thermal and oxidative degradation.

PROPERTIES OF LUBRICANT

- The Properties of Lubrication:
 - Reducing wear and friction between the rotating and stationary components
 - Absorbing shock
 - Dampening noise
 - Carrying heat generated by friction within the bearing
 - Removing heat transmitted down the shaft from the process end of the machine
 - Minimizing corrosion
 - Keeping contaminates away from the bearing components or Flushing contaminants away from bearings

BASE OIL

- Mineral oils are refined from crude oils.
- Crude oils are a mixture of different types of hydrocarbons (e.g., paraffins, napthenes, aromatics, etc.) with molecules of different molecular weights.
- Refining removes impurities and sorts hydrocarbons by weight.
- For a given viscosity grade molecular weight varies considerably, so that the properties are an 'average' of the component fractions.





BASE OIL CLASSIFICATIONS

Base oil	Туре	Characteristics	Advantage	Disadvantage
Group I		Solvent Refined	Cheap	Not resistant to oxidation and thermal breakdown
droup i	Mineral		Excellent Solubility	Viscosity Index 80 – 100
Group II		Hydro-cracked	Cheap	Less Resistant to oxidation and thermal breakdown
			Excellent Solubility	Viscosity Index 100 – 120
			Better Oxidation and thermal Solubility	
		Hydrocracked at higher temperature	Good Oxidation and Thermal Stability	
Group III	Mineral (svnthetic)	and pressure) and ISO Dewaxed	Excellent solubility	More Expensive when compared to Group I & II.
			High Viscosity Index	

Base oil	Туре	Characteristics	Advantage	Disadvantage
Group IV		Poly Alpha Olefins	Good oxidation and thermal stability	50% More expensive than Group I
			Low Pour Point	May shrink seals
I			Higher Viscosity Index	Poor additive solubility
		Dibasic acid esters	Good oxidation and thermal stability	150% More expensive than Group I
Group V	Synthetic		Low Pour Point	Reacts with water
			Higher Viscosity Index	May swell seals
				May remove paints
		Polyalkylene glycol	Good oxidation and thermal stability	150% More expensive than Group I
			Viscosity Index 160 – 280	Not compatible with other oils
				May Remove Paints
		Polyol Esters	Good oxidation and thermal stability	150% More expensive than Group I
			Low Pour Point	Not compatible with other oils
			Viscosity Index 130 - 190	May Remove Paints and swell seals

VISCOSITY MODIFIERS

- Viscosity Index Improvers are chain like **POLYMERS** whose solubility depends on:
 - Chain length
 - Structure and
 - Chemical Composition
- In lower temperatures, VIIs shrinks and become inert, whereas at higher temperature they expands and entangles with oil molecules to provide high temperature viscosity as per the desired range suggested by <u>SAE</u> <u>J300</u>.
- VII are used in multi-grade oils. Under high shear, these polymers can align and cause a temporary decrease in viscosity –a phenomenon known as "shear thinning"
- If the polymers break, a permanent reduction in high-temperature viscosity occurs.

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• Polymers in the range 10000 – 250000 Molecular weight are preferably used.

• Drop in viscosity reduces the film forming ability at high temperature.

- Viscosity loss can be temporary or permanent:
 - If the viscosity bounces back to the original viscosity when the stress are removed is called as temporary viscosity loss.
 - This type of loss is due to reversible deformation / recoiling of the polymer

• Viscosity loss depends on the shear stability.

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PARAMETERS NEED TO BE ASSESSED BEFORE SELECTION OF VISCOSITY INDEX IMPROVERS

- <u>Poly dispersity Index</u> (PDI).
 - Also known as Heterogeneity Index
 - Ratio of M_w / M_n

PDI	Polymerization method
Close to 1	Anionic Polymerization
1.5 – 2.0	Step Growth Polymerization
2 – 5	Radical Polymerization
Above 5	Co-ordination catalyst



MOLECULAR WEIGHT DISTRIBUTION

- Higher Molecular weight Polymer, generally loose viscosity at higher rate under shear than low molecular weight.
- Lubricants thickened with low molecular weight are more likely to maintained the desired viscosity range.
- Molecular weight **CL** Thickening power.
- Molecular weight **CL**

Shear stability Index







• Thermal and oxidative instability depends on the Molecular weight distribution.

 Viscosity Index Improver/POLYMERS under goes a variety of Thermal and Mechanical Degradation as mentioned below:

Mechanical	Thermal
Molecular weight sensitive	Indiscriminate
Break near middle of molecule	Random break along chain
Self Limiting	Complete degradation Possible
Insensitive to chemistry	Dependent on chemistry

POLYMER STRUCTURE

- Oxidation is a chemical process.
- It is driven either by **oxygen** or by any source of **free radicals**.
- If a polymer back bone is attacked it either forms polymeric carbon or oxygen radicals.
- For example:
 - Styrene containing polymers on oxidation form Formaldehyde and Benzaldehyde.
 - PP, PE and butadiene or isoprene containing polymers also form Formaldehyde and Acetaldehyde.
- For PMAs, OCPs and HSDs in oil no degradation in oil was observed at **170°C**, in **absence** of **OXYGEN**.
- In **absence** of **OXYGEN** PMAs lost a little viscosity, while OCPs underwent a severe degradation.
- At **260°C** all the systems degraded.
- Degradation of PMAs VII is dominated by thermal effects where others are dominated by oxidative effects.

Carbon Atom Center	Carbon – Hydrogen bond strength kJ/mol
Primary	419.0 ± 4.0
Secondary	401.3 ± 2.0
Tertiary	390.2 ± 20
Benzylic	353.1 ± 6.3
Allylic	345.2 ± 5.4

SHEAR STABILITY INDEX

- Shear Stability is a property of **Polymers**, which results in to permanent viscosity loss.
- Polymer undergoes physical breakage which cannot be reversed when the shear is removed. In other word the bond energies exceeds and the polymer breaks into smaller fragments.
- Consequently, the oil's viscosity is permanently reduced.
- **Base oil** and **Additives** will not suffers permanent viscosity loss.
- Moreover, different polymers have different shear stability characteristics, depending on the molecular weight and chemical nature.

- Higher molecular weight VIIs have a greater propensity for polymer coil breakage.
- SSI is the percentage of the polymer-controlled viscosity which is lost as a result of shear degradation. ^{3/15/2017}

SCHEMATIC OF MECHANICAL POLYMER

- Mechanical degradation process is self-limiting, for at some point whatever the application, a molecular weight is reached where the energy concentration during coil distortion is insufficient to break further bonds, referred to as the limiting molecular weight.
- It should be noted, however smallest molecule produced during shearing, it will be slightly greater than half of the limiting molecular weight and still have a finite probability of breaking.
- Example: An oil is formulated with base oil of viscosity 5 cSt and a VII is used to increase its viscosity to 15 cSt. The VII's viscosity contribution is therefore 10 cSt. During the shear test, the oil's viscosity falls to 12 cSt. It has permanently lost 3 cSt of viscosity. The VII polymer's Shear Stability Index is therefore 3 cSt (loss) divided by 10 cSt (VII contribution), or 30% SSI.



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• Shear stability performance is generally expressed as the shear stability index, or SSI, defined as in Equation:

$$SSI = \frac{(\eta_i - \eta_f)}{(\eta_i - \eta_o)} \times 100$$

• Overall viscosity loss= $\frac{(\eta_i - \eta_f)}{\eta_i} \times 100$

Where:

- η_i is the initial formulated oil viscosity,
- η_f is the sheared oil viscosity, and
- η_o is the viscosity of the base oil including all additives except the VI improver.
- Kinetics of the degradation process:

 $dB_i/dt = k(P_i - P_c)n_i$

Where:

- dB_i/d_t is the rate of bond breakage of polymers with a degree of polymerization,
- Pi, Pc is the limiting degree of polymerization for bond breakage,
- n_i is the number of molecules of size P, and
- k is a rate constant which is mainly a function of the shearing device but which may also be related to solvent and temperature.

PETROLENE 6104-P

- Good Viscosity Index Improver.
- Efficient Thicker.
- OCPs
- Available in 4 6mm white pellet, have high surface per unit volume.
- Easily dissolvable in virgin base oils as well as recycle.
- Free flowing and non dust product
- Advantages:
 - Can be solubilized at a faster.
 - Handling losses are avoided.s
 - Easily transferrable and ready to use.
 - Ease of operation

PETROLENE 6104

Olefin Copolymers / OCP (Viscosity Index Improver)



COMPARISON SYUDY

Dosage: 10% (9% Liquid VII) in base oil

Parameters	PETROLENE 6104-P	MAXXLENE - 3070	ESPRENE 141
Kinematic Viscosity at 40°C, cSt	139.6	140.5	138.8
Kinematic Viscosity at 100°C, cSt	18.11	18.00	17.84
Viscosity Index	145	143	143
Pour point °C	-6	-3	0
Pour Point with 0.3% Petrolene PLPPD – 618	-24	-21	-12

PETROLENE - VISCOSITY INDEX IMPROVERS

Parameters	Test Methods	Petrolene 6104P	Maxxlene 3070	Petrolene VI – 400(plus)	Petrolene VX – 9	Petrolene VP - 039	Petrolene VP - 130
Appearance	Visual	Free Flowing Pellets	Free Flowing Pellets	Amber	Amber	Amber	Amber
Physical state	Visual	Solid	Solid	Flow-able Liquid	Flow-able Liquid	Flow-able Liquid	Flow-able Liquid
Color	ASTM D-1500	White	White	2 - 3	2 - 3	2 - 3	2 – 2.5
Viscosity at 40°C	ASTM D-445	38886	23390	16690	17680	78120	853.9
Viscosity at 100°C	ASTM D-445	1750	1338	2625	1163	4373	114.2
Viscosity Index	ASTM D-2270	275 (8%)	282 (10%)	448	288	350	236
Pour point °C	ASTM D-97	-27	-21	-6	-6	-3	-15
Flash Point °C	ASTM D-93	220 - 230	210 - 220	220	210 - 220	210 - 220	200 - 210
Density kg/m ³	ASTM D-4025	488 - 510	520 - 540	930 - 950	930 - 950	930 - 950	900 - 920

Advantages:

- 1) Cost Saving in terms of Power, Time, Man Power costing
- 2) Ease of Handling
- 3) Handling losses avoided
- 4) Easily pumpability
- 5) Good compatibility with other additives
- 6) Better and ease of Mixing.
- 7) Easily solubalization in Virgin as well recycle oils

PETROLENE - ADDITIVES

• Oils, by themselves, are unable to provide all the characteristics required by modern machinery.

• Carefully blended additive packages improve viscosity index and friction, and reduce wear, oxidation, and corrosion.

• Too high a proportion of one additive may interfere with the benefit of others, or degrade lubrication effectiveness.

DEVELOPMENT OF ADDITIVES



Additives	Year
Pour Point Depressant	1932
ZDDP	1940
Detergents	1940s
Dispersants	1950s
Polymeric Viscosity Modifiers	1950s
Ashless Dispersants	1960s
Inhibitors	1970s
Friction modifiers	1970s
Ashless antiwear	1990s

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ADDITIVES THEIR ROLES & FUNCTION

Additives	What It Does	How it Works	Typical Compounds
Anti-wear	• Minimize wear caused by metal to metal contact during condition of mild boundary lubrication.	• Additive reacts chemically and form a film on metal surfaces under normal operating conditions.	ZDDPs, tri-cresyl phosphate, Organic Phosphate, Chlorine and Sulphur compounds
Anti-oxidant	 Inhibits varnish and sludge formation. Reduces viscosity increases resulting from oil oxidation Reduces formation of corrosive acids. 	• Slows the rate of reaction with oxygen by interrupting of chain reactions or by decomposing reactive peroxides.	ZDDPs, Hindered Phenol, Bis-Phenol, Amines, Phenothiazine etc.
Corrosion Inhibitor	• Prevents corrosive attack on non-ferrous metallic surface.	• Forms a film on non-ferrous metallic parts thus protecting them from attack of contaminants in oil.	ZDDPs and Molybdenum based compounds
Detergent	 Prevents oxidation product (gums) which have formed in the oil from sticking to the metal parts. Neutralizes acidic contaminants. 	 Chemically reacts with oxidation products (gums) so that they remains soluble in the oil and do not stick to the metal surfaces. Metal base reacts with acids 	Ca / Mg / Na / Ba TBN
Dispersant	• Keeps oxidation products separated and suspended in the oil, retards formation of sludge and reduces soot related viscosity.	• Additive adsorbs on surface of gum particles or soot and inhibits agglomerations.	PIBSA Ashless Dispersant
Extreme pressure Agents	• Prevents welding and subsequent wear or seizure on contacting metal parts under extreme or shock load conditions.	 Additive combines chemically with surface to form a surface films. Reaction usually occur at high temperature, which results when asperities collide. 	ZDDPs, tri-cresyl phosphate, Organic Phosphate, Chlorine and Sulphur compounds.

Additives		What It Does		How it Works	Typical Compounds
Foam Inhibitor	•	Prevents formation of stable foam	•	Promotes combination of small bubbles into large bubbles which in turn collapse more easily.	Silicone Polymers
Friction Modifier	•	Alters co-efficient of friction	•	Forms an easily shearable film on metal surface	Long chain Polar compounds (Amides, Phosphates, Phosphites, Acids etc.) Molybdenum based compounds.
Metal Deactivator	•	Reduces the catalytic effect of metals on oxidation rate	•	Forms and inactive film on metal surfaces by combining with metallic ions.	ZDDPs, Metal Phenates, Organic Nitrogen Compounds
Rust Inhibitor	•	Prevents rusting of Ferrous (iron or steel) Machine parts.	•	Forms a film on non-ferrous parts thus protecting them from water and other destructive materials.	High Base Additives, sulphonates, phosphonates, amines, organic acids or esters
Pour Point Depressants	•	Lowers the pour point and enables the lubricants to flow at low temperature	•	Changes the size and shape of wax crystals	Low molecular weight methacrylate Polymers
Viscosity Modifiers	•	Reduces the rate of change of viscosity with temperature and makes possible formation of multi-grade oils.	•	Polymers uncoils as temperature rises, thus increasing their effective size and viscosity.	OCPs, PIBs, PAMAs etc

ANTI-OXIDANTS

- Two types of antioxidants are used, either separately or in combination, to improve the oxidation stability of finished lubricants:
 - Radical acceptors or scavengers Low temperature oxidation i.e. up to 150°C
 - Peroxide decomposers High temperature application

• Radical acceptors in combination with peroxide decomposers, have a good synergistic effect may markedly improve the overall oxidation stability.

OXIDATION REACTION MECHANISM

Without Antioxidants

 $RH \rightarrow R\bullet + H\bullet$ ------(i) Initiation

 $R \bullet + O_2 \rightarrow ROO \bullet$ ------(ii) Propagation

ROO• + RH→**ROOH** + **R**• -----(iii)

ROO• + ROO• \rightarrow Inactive product, Termination

 $R \bullet + ROO \bullet \rightarrow ROOR$ ------(iv)

 $R \bullet + R \bullet \rightarrow RR$ ------(v)

Chain branching occurs via:

ROOH→RO• + OH• -----(vi)

2R00H→R0• + R00• + H₂0 -----(vii)

With Anti-Oxidants

 $RH \rightarrow R \bullet + H \bullet$ ------(i) Initiation

 $R \bullet + O_2 \rightarrow ROO \bullet$ ------(ii) Propagation

ROO• + AH + RH→ROOH + A• + RH -----(iii)

AH is the Anti-oxidant

A• is anti-oxidant radicals which is incapable for abstraction of Hydrogen from the RH i.e. oil

ROO• is peroxy Radicals

Termination of chain reaction/Formation of stable inactive compounds.

$ROO \rightarrow + A \rightarrow ROOA$

 $A \bullet + A \bullet \rightarrow 2A$

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FREE RADICAL ACCEPTORS

- Phenols, aromatic amines and compounds which form phenol and amines by their decomposition.
- Phenols may either contain one ring with one or more functional groups, or a multiplicity of rings condensed or linked by bridges.
- Common low temperature antioxidants
- Also called as Scavengers.
- Substituent as Alkyl, Aryl and Alkaryl, in para or ortho positions in phenol ring, increase the electron-donor character of the inhibitor.
- Electron-acceptor substituents (-CI, -NO2, -COOH, etc.) have a negative effect on inhibition

TYPES OF FREE RADICAL ACCEPTORS

Free Radical Acceptors	Compounds	Typical Compounds
Sterically-hindered	• Alkyl Phenols	OH tBu tBu tBu tBu tBu tBu tBu tBu
phenolic rings		 Advantage of Methyl groups in positions 2 and 4 and tert-butyl groups in positions 2 and 6: Stabilize the transition radicals by inductive, hyper-conjugative and steric effects, Increase the solubility of phenols in hydrocarbons, and Protect them from the direct influence of ovvgen
Bis - PHENOL	 2,2'-methylene-bis- phenol, 4,4'-methylene-bis- phenol, Thio-bis-phenols and Dithio-bis-phenols 	 The activity of bis-phenols, which are analogues of hindered monohydroxy phenols, is higher than would result from the doubled hydroxyls. The molar concentrations of bis-phenols required to achieve the same effect is therefore less than half that for alkyl phenols. Much lower volatility. They have a greater tendency to form oxidation sludges, which increases in the order methylene-bis-phenols

Free Radical Acceptors	Compounds	Typical Compounds
	 Primary, Secondary and Tertiary Aromatic amines Cyclic amines Amino-phenolic 	 Secondary Amines are more often used as they acts as a radical acceptor as well as moderate peroxide decomposers: 4,4 - dioctyldiphenyl amine Phenyl -1-naphthylamine Phenyl -2-naphthylamine
Amines		• Tertiary Amines: Me $N \rightarrow CH_2 \rightarrow N$ Me
		 Cyclic Amines: P CH₃ They Possess anti-ozone properties.
		• Amino-phenolic: OH t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu t-Bu
		CH ₂ N(CH ₃) ₂

PEROXIDE DECOMPOSERS

- Rate of formation and disappearance of Peroxy radicals (ROO.) is faster as compared to the reactivity of the Radical Acceptors as a result of which they are ineffective.
- Peroxide decomposers have higher reactivity rates as compared to radical acceptor.
- Peroxide decomposers are also called as high temperature anti-oxidants or oxidation retarders.
- They act by decomposing hydroperoxides and peroxides immediately they have been formed during the propagation phase of the oxidation chain reaction.
- Propagation stage is eliminated and the reaction terminates in stable products after initiation.
- Compounds with Sulphur and Phosphorus or both are common type of Peroxide decomposers.

TYPES OF PEROXIDE DECOMPOSERS

Peroxide Decomposers	Compounds	Typical Compounds
Sulphur Contained	Simple aromatic sulphides and disulphides.Sulphur-containing	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
	 alkylphenols and aromatic amines Aromatic thiols and their derivatives 	$(CH_3)_2C OH \qquad HO \qquad C(CH_3)_2$ $(CH_3)_2C CH_3 CH_3 C(CH_3)_2$
Sulphur – Nitrogen	Phenothiazine	R - O - NH - O - R = R - O - R - R - O - R - R - O - R - R -
Contained	Dithiocarbamates	$\begin{bmatrix} R_2 NC - S \\ S \end{bmatrix}_n^n $ Where M - Zn, Cd, Pb, Ni, Ba, Mg, Co, As, Bi, Sb, Se and Mo.
Phosphorus Contained	 Trialkylphopshites Triarylphosphites and Trialkarylphosphites, 	$\mathbf{O} = \mathbf{P} \left\{ \begin{array}{c} \mathbf{OR} \\ \mathbf{OR} \\ \mathbf{OR} \end{array} \right\}$ Phosphites show very marked anti-corrosion properties, but they are insufficiently stable in the presence of moisture. They are used in plastics more often than in oils.

Peroxide Decomposers	Compounds	Typical Compounds
Sulphur – Phosphorus Contained	 Simple sulphur-containing alkyl phosphonates. Complex esters of phosphoric acid and big (alled all an appl) discluding big (alled all an appl). 	$RS - CH_2 - P \int_{OR'}^{OR'} OR' RO S S OR OR OR OR' RO S - M - S OR $
	 and bis-(alkyl phenol)-disulphides or polysulphides. Most widely used types are the 0,0'- dialkyl-, diaryl- or alkylaryl dithiophosphates (DDP) of metals 	$\begin{bmatrix} \mathbf{A} \\ \mathbf{R} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{P}} \begin{bmatrix} \mathbf{O} \\ \mathbf{O} \\ \mathbf{O} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{O}} \begin{bmatrix} \mathbf{O} \\ \mathbf{O} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{O}} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{O} - \mathbf{O}} \begin{bmatrix} \mathbf{O} \\ \mathbf{O} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{O}} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{O} - \mathbf{O} - \mathbf{O} - \mathbf{O} - \mathbf{O} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{O} \end{bmatrix}_{2}^{\mathbf{O} - \mathbf{O} - \mathbf{O}$

ANTIOXIDANT USAGE BASED ON TEMPERATURE

Types of Anti-oxidants	Recommended Temperature
Sterically Hindered Phenols	Below 125°C
Amines Selenides	Up to 150°C
Phenothiazine	Up to 175°C
1-2% of Phenyl-1-Naphthylamine in combination of C – or N – substituted diphenyl amines	Up to 200°C
Polyalkylated phenols, poly hydroxylated biphenyl, hydroxylated benzophenones, C- & N- alkylated phenothiazine, phenothiazines carboxylic acids and silicon based compounds like 5-ethyl-10,10-diphenylazasilazene (I) & borax derivatives such as 10-hydroxyl-9,10 borax azophenthrene.	Up to 260°C
Polyaromatics like: Fluoroanthrene, 1,1-dinaphthyl-1,2-benzathrene	Up to 285°C

TYPES OF DDPs

- Zn is the most frequently used metal in DDP, but other metals can be used.
- Na and K DDP are water-soluble, promote the formation of emulsions and are corrosive. This property excludes them from practical use.
- Ca and Ba DDP impart detergency and dispersancy.
- Ba and Ni DDP also act as anti-corrosion agents.
- Ni DDP improves the stability of hydrocracked oils against light.
- The Fe derivatives do not have anti-oxidant properties.
- Pb DDP increases the strength of the lubricating film.
- Sb and Bi DDP's are effective high-pressure additives and also have good anti-wear properties, but their thermal stabilities are lower than those of ZDDP's.
- Molybdenum dithiophosphates are used as friction modifiers. Salts of some organic amines, such as guanidine, are effective antioxidants.



- The dominance ZnDDPs as additives for lubricating oils is due to their multifunctional performance.
- Not only do they act as antioxidants, but they also improve the wear inhibition of the lubricant and protect metals against corrosion.
- ZnDDPs are mainly used to formulate anti-wear hydraulic fluids and engine oils
- Zinc Dialkyl- and Diaryl dithiophosphate are used in many lubricating oils as anti-wear agents.
- They have been used since the 1930s and today are the dominant anti-wear agent.
- ZnDDP is used in motor oils, hydraulic pumps, gear boxes, transmissions and metal machining.
- Usually ZnDDP constitutes about 1% of these oils,

FUNCTIONING TO ZDDP

- It functions by creating a protective layer on metallic surfaces at elevated pressures and temperatures.
- Anti-wear agents functioning in this way are usually called EP additives "extreme pressure".

- The characteristic of substances of this type is that at a certain given pressure and temperature they disintegrate and, with their functional groups (sulphur and/or phosphorus) react with the iron in the metal.
- These inorganic iron sulphides and/or iron phosphides which are formed provide extremely strong layers on the metallic surfaces, added to which, they give a lower coefficient of friction.

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MECHANISM OF ZDDPS AS ANTIOXIDANTS



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CORRECT ZDDPS

• Zn : P ratio should be 105% to 110%.

• pH should be between 4.5 to 5.0, pH should not fall below 4.0.

• Zn : P ratio increases the thermal stability.

Elements	Zinc Dialkyl Dithio Phosphate	Zinc Diaryl Dithio Phosphate
% Zinc	9	3.6
% Phosphorus	8.5	3.3
% Sulphur	17	7

STRUCTURE-ACTIVITIES DEPENDENCE OF ZDDPS

- Under service conditions, ZDDPs undergo various chemical transformations and after 2,000–3,000km they cannot be detected.
- However, 35% of the degraded ZDDP products containing P–O–C bonds remain after 10,000km and the antioxidant and anti-wear performance of the lubricant is still satisfactory.
- Thus the antioxidant acidity up to 2,000–3,000km is dominated by ZDDPs and is subsequently governed by products resulting from their thermal cleavage.



DISPERSANTS & DETERGENTS

- Ability to suspend the undesirable products formed either by Thermal or Oxidative degradation is an important property.
- Detergent are over based and have good neutralizing power but poor suspension properties, where are Dispersants are neutral or low in basicity but has good suspension properties.
- Controlling these deposits and wear is the main function of Dispersant-Detergents.
- They keep sludge, carbon and other deposits derived from partial oxidation of the fuel suspended in the oil.
- Detergents and Dispersants together make up of about 50 60% of the lubricant additives.

• Oxidation Inhibitors, Detergents and Dispersants makes up the general class of additive called as stabilizers and deposit control agents.

- Oxidation Inhibitors intercept the oxidation, whereas dispersant and detergents performs the suspending part.
- Detergents are metal salts of organic acid, associated with excess base (carbonates).
- Dispersants are metal free and are of higher in molecular weights as compared to detergents.



• Detergents have been used in engine oil applications since the 1940s

 Neutral metal salts of long-chain organic acids, typically alkyl aromatic sulphonates, used in engine lubricants to reduce the formation of carbonaceous deposits on the hot surfaces of engine parts such as piston ring grooves etc.

• Due to their cleaning ability and chemical similarity to aqueous detergents, those used in laundry soaps, these lubricant additives came to be known as 'detergents'.

- Performance depends upon:
 - Types of detergent soap (sulphonates, Phenates, carboxylates)
 - Molecular configuration of the Hydrocarbon portion
 - Molecular weight of the detergent soap

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- Detergents functions as:
 - Corrosion Protection
 - Deposit prevention
 - Neutralize Acidic Contaminants
- Calcium or Magnesium or Barium or Sodium are Metals (M) used in Detergents.
- $(RSO_3)_a M_b (OH)_c (CO_3)_d$
- Mathematical expressions:
 - Metal Ratio = $\frac{2b}{a}$ (Metal ratio is basically varies from 1 30)
 - TBN (mg KOH / gm) = $\frac{56100 * (2b a)}{Sample weight}$
 - Percent Soap = $\frac{weight [(RSO_3)a Ca]}{Sample weight} \times 100$

- **Total Base Number** (TBN) is a measurement of basicity expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of oil sample (mg KOH/g).
- TBN is an important measurement in petroleum products, and the value varies depending on its application.
- TBN generally ranges from 6–80 mg KOH/g in modern lubricants:
 - 07 10 mg KOH/g for general automotive use
 - **10 15** mg KOH/g for diesel operations.
 - **15 80** mg KOH/g for Marine Engines.
- TBN value **below 3** indicates the need for change of oil.
- Two of the following parameters must be specified to define an over-based sulphonates:
 - Total Base Number
 - Percent Metal (Ca or Mg)
 - Percent Sulphur
 - Metal Ratio
 - Percent of neutral detergent soap



- The first dispersant additive was first introduced in 1950s, with an aim to keep the engine clean.
- Degradation or oxidized product of fuel and lubricants such as soot, sludge, varnish, lacquers, resin have low lubricants solubility and deposits on the surface.
- Separation of these materials depends on the particle size. Small particles are easily suspended in oil as compared to larger ones.
- Small particle agglomerates to form bigger particles prior to deposition.
- Dispersants interferes the agglomeration process via two mechanism:
 - Steric stabilization
 - Electrostatic stabilization.
- Dispersants consist of a polar group usually oxygen and nitrogen based and a large non polar group.
- The polar group associates with the polar particles whereas the non polar group keeps such particles in the suspension.

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- Absence of dispersant results in:
 - Viscosity Thickening
 - Wear and filter plugging
 - Frequent oil change

• Increase in oil's viscosity, causes poor lubricant circulation and film formation, which results in wear and catastrophic failure.

• Due to high molecular weight Dispersants are more effective as compared to Detergents.

SOOT

- Diesel Engines.
- Incomplete oxidation of the fuel during ignition.
- Particles tend to be granular and abrasive in nature and cause wear to the metal surfaces of engine components.
- Soot builds up, leading to problems of oil thickening

SLUDGE

- Gasoline Engines.
- Thermal oxidation of oil and the blow by gases from the combustion chamber containing partially burned fuel.
- Generally finer in nature than soot

- Flocculate in hotter parts of the engine or in the colder regions by the co-action of water
- Varnishes and lacquers form if these oxidized products condense on hot surfaces of the engine.
- Lacquer is water soluble whereas varnish is acetone soluble.
- Lacquer usually occurs on piston skirts, on cylinder walls and in combustion chambers.
- Varnish occurs in valve lifters, piston rings, piston skirts, valve covers.

COMPARATIVE STUDY FOR DIFFERENT DOSAGES OF DISPERSANT

With 1.0% Dispersant the particle size is 1364 nm With 2.3% Dispersant the particle size is 460 nm

With 5.0% Dispersant the particle size is 201 nm





Poor Dispersancy

Improved Dispersancy



Agglomeration of Sludge particle with different dosages of Dispersant

DIFFERENCE BETWEEN DISPERSANT AND DETERGENTS

Dispersants

- Metal Free.
- Will not form ASH on combustion.
- Little or no acid neutralizing ability.
- Ester dispersant have no basicity where as low basicity in case of imide or amide dispersants.
- Weak bases.
- Avoids agglomeration of particles and helps in the suspension in the oil.
- 4 15times high molecular weight than detergents.
- TBN Value is lower

Detergents

- Contains metal such as Mg, Ca, Na and Ba.
- Will lead to ASH formation on combustion.
- Good acid neutralizing ability.
- Highly basic in nature, contain reserve metal bases as metal hydroxides or metal carbonates.
- Strong bases to neutralize combustion and oxidation derived inorganic & organic acid.
- No as such properties.
- Low molecular weight.
- TBN value is 4 15times higher.

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- The Primary function of a lubricant is to create a film between moving mechanical parts to reduce friction and wear.
- It also acts as a coolant, suppresses harmful deposit formation and controls corrosion/oxidation.
- Since the base oil alone would struggle to meet these challenging demands, performance-enhancing additives in tailor-made formulations are added to the lubricant formulation.
- These packages can includes a proper combination of antioxidant, antiwear, corrosion inhibiter, viscosity modifier, detergent and dispersant components.
- Not only DI-PACKAGES improve overall efficiency in the engine, but they also extend the lifetime of the lubricant.

DNA OF DI-PACKAGES

Elements	Indicates the presence of
Zinc (Zn)	Anti-wear, Anti-corrosion and Anti-oxidants
Phosphorus (P)	Anti-wear, Anti-corrosion and Anti-oxidants
Sulphur (S)	Anti-wear, Anti-corrosion and Anti-oxidants
Calcium (Ca),Magnesium (Mg), Barium (Ba), Sodium (Na)	Ash forming Detergents
Nitrogen (N)	Succinimide type ashless dispersant or other compounds of amino or amido type
Molybdenum (Mo)	Friction Modifier Agent
Boron (B)	Dispersant
Chlorine (Cl)	High Pressure Anti-wear Agents
Lead (Pb)	High Pressure Anti-wear Agents
Silicon (Si)	Anti-foaming Agents

NEED OF DEVELOPED LUBRICANTS

- Good Fuel Economy.
- Modernization of Engines.
- Environmental Issues.
- Long Drain Intervals More than 50% of the used oil is going as waste.
- Improved oxidation and Thermal stability.
- Reduced sludge formation (better filterability).
- Less internal friction (energy conservation).
- Good hydrolytic stability.

WHY DO WE NEED DEVELOPED LUBRICANTS

- High levels of fuel sulphur lead to higher levels of sulphurous acids in the combustion products which lead to faster depletion of the lubricant's acid neutralizing properties.
- Fuel quality around the world is improving but not at the same rate or to the same levels.
- These differences must be taken into account when specifying appropriate lubricant formulations in different regions.
- Poor base fuel quality has a detrimental impact on engine deposits and oxidation control.
- Fuel contamination gives a variety of problems, dependent upon the nature of the impurity, ranging from contamination by water to tar fractions

API STANDARDS

Set Standards for Both: Gasoline and Diesel Engines.

API Grades for Gasoline Engines			
Grade	Introduction Year		
SJ	2001		
SL	2004		
SM	2010		
SN	2011		

API Grades for Diesel Engines	
Grade	Introduction Year
CH-4	1998
CI – 4	2002
CJ – 4	2010
CK – 4 and FA - 4	2017

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IMPACT OF STANDARDS

Vehicle Engineering and Lubricant Additive Development. Higher performance, with reduced lubricant quantity for gasoline passenger cars 1992 Factor Model Year 1949 1972 2005 2005/1949 Power (kW) 25 74 96 120 4.8 21 37 45 2.85 Power Density (kW/L) 60 3.7 3.5 3.5 Oil fill (L) 3.0 0.5 Oil Consumption (L/1000km) 0.25 0.1 0.1 5 Oil Change Interval (km) 1500 5000 15000 30000 20 Oil Flush at oil change Yes No No No Total oil used after 30000km (L) 87.0 29.8 10 6.5 13.4 12 Average Fuel Consumption 10 7 7 (L/100 km)Engine Durability (1000km) <100 175 250 250

FUTURE DEVELOPMENTS

- Ashless Additives and DI-Packages.
- Cost competitive products to satisfy the customer needs
- DI-Packages to support the latest API grades.
- To reduce the pollution and emission to maintain a safe environment.
- To increase the fuel economy and the reliability of the Engine.

THANK YOU



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