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**Properties of Petroleum Products
Part (3)**

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Products From Crude Oil

The list of products from petroleum is endless. Crude oil contains a wide range of hydrocarbons and other compounds containing sulfur, nitrogen, etc. In the refinery, petroleum is distilled into various fractions. Depending on the desired final products, these fractions are further processed and then blended to yield a wide variety of products.

Typical final products are:

- gases for chemical synthesis and fuel, liquefied gases
- aviation and automotive gasoline
- aviation (jet) and lighting kerosene
- diesel fuel
- distillate and residual fuel oils
- lubricating oil base grades
- paraffin oils and waxes

Many of the common processes in the refinery are intended to increase the yield of blending feedstocks for gasoline. As such, most modern fuels are represented by fuel fractions compounded from the products of many different processes.

Typical modern refinery processes for gasoline components include:

- Catalytic cracking
- Hydrocracking
- Isomerization
- Reforming
- Alkylation

Gas From Petroleum

Gas from petroleum is classified under several names like natural gas, associated gas, dissolved gas, casing head gas and off gas from refinery.

1. Natural gas

Its name indicates that it is readily available in nature, almost as a finished product. It contains mainly varying proportions of methane. It may be accompanied by other dry gas

2. Associated gas

This is obtained for oil reservoirs and this exists as a separate gas cap over liquid phase. Though the gas mainly consists of methane and to some extent ethane and propane, the proportions vary depending upon the reservoir conditions. When the gas phase is taken out, it may still contain some liquid hydrocarbons mainly of volatile range like butane and pentane, which when condensed are termed as natural gas liquids (NGL)

3. Dissolved gas

Gas may be present in the liquid hydrocarbons mainly in the dissolved state depending upon the formation pressure. When the pressure is decreased, this dissolved gas comes out of the oil. Gas production upto 10% crude produced is not uncommon with the oil reservoirs.

It is fair to strip off such dissolved gas before crude is transported to long distances by means of pipe lines or tankers. The remaining dissolved gas is first to come out of the distillation column because of higher temperature than the surroundings.

4. Casing Head gas

Gas that has escaped through oil well Christmas trees is termed as casing head gas. It is also more or less similar to natural gas but contains less % of methane and high percentage of ethane and propane than natural gas. It is a by-product of oil production

5. Refinery off gas

In a refinery, gas is formed in cracking and reforming operations due to the thermal degradation of liquid hydrocarbons. During stabilization of wild gasolines or processed gasolines, the gases are vented. Thus the gas is mainly a mixture of saturates and unsaturated and quantity is also not assessable. This forms a major source of heat energy for refinery, as well as feed stock for petrochemicals. In fact, without any exclusion, all these gases can be utilized for petrochemical industries.

All the gases contain impurities like CO_2 , mercaptans, H_2S , water vapour, suspended impurities etc. First three paraffins are gases at room temperature. Mixture of methane and ethane is called dry gas, while propane-butane mixture is called wet gas. Where petrochemical industries are not instituted dry gas would find its use mainly in the refinery fuel system. Wet gas is usually liquefied and sold for commercial purposes. Butane is

diverted to gasoline streams as a blending component, as butane has more commercial value when blended with gasoline.

6. Liquefied petroleum gas (LPG)

The gas that is vented from refinery distillation units, is processed and conveniently stored after liquefaction. For domestic heating purposes, it is supplied in small cylinders (15 kg or 12 kg), while for industries tanker supplies are called in. This gas is known as liquefied petroleum gas as it is stored in vapor liquid mixture. Ease of handling, smokelessness, good and steady heating rates are some key points, that made this fuel a popular kitchen aid to the housewife of modern times. Rising demands of this fuel in domestic and industrial circles are met by the refinery by installing processing units.

Different types of mixtures resulting from propane-butane blends are sold as LPG; - In fact propane itself can be utilized for this purpose and hence the dearth of availability of butane does not deter the manufacturers.

Most important property of this fuel mixture is vapour pressure. These fuels are graded according to vapour pressure and temperature at which 90% or 95% is evaporated. LPG is produced in many grades as listed below :

1. Predominantly butanes
2. Butane—propane mixtures, mainly butanes
3. Butane—propane mixture (equal volumes)
4. Less butane—propane mixture
5. Butane—propane mixture (more propane)
6. Predominantly propane

Gasoline

In the late 19th century, the most suitable fuels for automobile use were coal tar distillates and the lighter fractions from the distillation of crude oil. During the early 20th Century, the oil companies were producing gasoline as a simple distillate from petroleum. On the other hand, automotive engines became vastly improved and these required a more suitable fuel. Typical gasoline products in the 1920s had octane numbers (ratings) in the range 40-60. Tetraethyl lead was often used to enhance the octane number.

Because sulfur in gasoline inhibited the octane-enhancing effect of the alkyl lead, there was a restriction on the sulfur content of thermally cracked refinery streams for gasoline. By the 1930s, it was determined that larger hydrocarbon molecules had major adverse effects on the octane number of the gasoline, and specifications consistent with the desired properties were developed.

The increase in the compression ratios of cars started in the 1950s. The consequence was that such car engines required fuels with higher octane numbers. Thus, octane number, lead levels, and vapour pressure increased whereas sulfur and olefin contents decreased. Some new refining processes (such as hydrocracking), designed to provide hydrocarbon components with good lead response and octane number, were introduced. Minor improvements were made to gasoline formulations to improve yields and octane number until the 1970s, when unleaded fuels were introduced to protect the catalysts that were also being introduced for environmental reasons. From 1970 until 1990, there was a slow but progressive change in the gasoline produced. Lead was being phased out. Lead levels decreased, octane number initially decreased as well, but vapor pressures continued to increase while sulfur and olefins remained constant. The aromatic content increased. In 1990, the US Clean Air Act started to force the implementation of major compositional changes in gasoline. This resulted in the plummeting of the vapor pressure and the increase in the oxygenate levels. These changes will continue into the 21st century as a way to minimize the polluting effect of the use of gasoline as fuel in automobile engines.

The move to unleaded fuels continues worldwide. However, several countries have increased the aromatics content (by up to 50%) to replace alkyl lead. These highly aromatic gasolines can lead to damage of elastomers and increased levels of toxic aromatic emissions if is used without catalysts.

Gasoline as a fuel is composed of a mixture of various hydrocarbons, which can be burnt to form water (H_2O) and CO_2 . If combustion is not complete, carbon monoxide (CO) is also formed.

The following main groups of hydrocarbons are contained in gasoline:

- saturated hydrocarbons or alkanes
- unsaturated hydrocarbons or olefins
- naphthene or cyclic hydrocarbons
- aromatics
- oxygenates
- other hetero-atom compounds

Gasoline contains over five hundred types of hydrocarbons that have between 3 to 12 carbon atoms in their structure. Gasoline has a boiling range from 30 to 180°C at atmospheric pressure. The boiling range is narrowing as the initial boiling point is increasing, and the final boiling point is decreasing. Both these changes are for environmental reasons.

Saturated hydrocarbons have the following major properties;

- Are thermally and chemically stable, it is the major component of leaded gasolines.
- Tend to burn in air with a clean flame.

The octane number depends on branching and number of carbon atoms. Generally octane number is low for n-alkanes and high for the iso-alkanes (isooctane is assigned the octane number of 100).

The cyclic hydrocarbons all have the positive properties of the alkanes with regard to thermal and chemical stability as well as good environmental properties. In addition, they have a higher octane number in comparison to alkanes.

Alkenes or unsaturated hydrocarbons have the following major properties:

- Are chemically unstable.
- Tend to be reactive and toxic, but have high octane numbers.

Arenes or aromatics are characterized as follows:

- Gradually being reduced to less than 20% in the US.
- Tend to be more toxic than other hydrocarbons, but have the highest octane ratings.
- Some countries are increasing the aromatic content (up to 50% in some super unleaded fuels) to replace the alkyl lead octane enhancing additive.

Polynuclear aromatics are high boiling compounds, and are only present in small amounts in gasoline. The simplest and least toxic polynuclear arene, naphthalene, is present in only trace amounts in traditional gasoline, and in even lower levels in reformulated gasoline. The larger multi-ringed polynuclear arenes are highly toxic, and are not present in gasoline.

Oxygenates contain oxygen that does not contribute to the energy content, but because of their structure, provides a reasonable antiknock value. Thus, they are good substitutes for aromatics. They also reduce the tendencies of the formation of toxic gases. Most oxygenates used in gasoline are either alcohols or ethers that contain 2 to 6 carbon atoms per molecule. Alcohols have been used in gasoline since the 1930s whereas ether (such as methyl tertiary butyl ether (MTBE)) was first used in commercial gasoline in Italy in 1973 and in the US in 1979.

Oxygenates can be produced from fossil fuels or from biomass. MTBE is produced by reaction of methanol with iso-butylene in the liquid phase over an acidic ion-exchanger resin catalyst at 100°C. MTBE production has increased at the rate of 10 to 20% per year.

Oxygenates are added to gasoline to reduce emissions. However, they can only be effective if the hydrocarbon fractions are modified to utilize the oxygenate's octane number and volatility properties. If the hydrocarbon fraction is not correctly modified, oxygenates can even increase smog-forming and toxic emissions both of which are undesirable. It should also be noted that oxygenates do not necessarily reduce all toxins.

Initially, oxygenates were added to hydrocarbon fractions that were just slightly modified unleaded gasoline fractions. These were known as "oxygenated" gasolines. Since 1995, the hydrocarbon fraction has been significantly modified resulting in "reformulated gasoline".

Oxygenates added to gasoline function in two ways. First, they have a high blending octane number, and so can replace high octane aromatics in the fuel. These aromatics are responsible for disproportionate amounts of CO and hydrocarbons emissions during combustion. Oxygenates cause engines without sophisticated engine management systems to move to the lean side of stoichiometry, thus reducing emissions of CO (2% oxygen can reduce CO by 16%) and hydrocarbons (2% oxygen can reduce hydrocarbons emissions by 10%). Other researchers have observed that similar reductions occur when oxygenates are added to reformulated gasoline and used on older and newer vehicles. They have also shown that, unfortunately, NO levels may increase, as may some regulated toxins.

On the other hand, on vehicles with engine management systems, the fuel volume will be increased to bring the stoichiometric combustion to the preferred optimum setting. It is to be noted that oxygen in the fuel cannot contribute energy. Consequently, the fuel has less energy content. Thus, for the same efficiency and power output, more fuel has to be burned. Therefore, the slight improvements in combustion efficiency that oxygenates provide on some engines usually do not completely compensate for the energy loss due to the presence of oxygen.

There are some other properties of oxygenates that have to be considered if they are to be used as fuels. These relate particularly to (i) their ability to form very volatile azeotropes that cause the fuel's vapor pressure to increase, (ii) the chemical nature of the emissions, and (iii) their tendency to separate into a separate water-oxygenate phase when water is present. These problems are solved more successfully in the reformulated gasoline than in the original oxygenated gasoline.

The main characteristics of gasoline are:

- Vapor pressure and distillation classes. There are six different classes according to location and/or season. As gasoline is distilled, the temperatures at which various fractions are evaporated are recorded. Specifications define the temperatures at which various percentages of the fuel are evaporated. Distillation limits include maximum temperatures at

which 10% is evaporated (50-70°C), 50% is evaporated (110-121°C), 90% is evaporated (185-190°C), and the final boiling point (225°C). A minimum temperature for 50% evaporated (77°C), and a maximum amount of residue (2%) after distillation. Vapor pressure limits for each class (54, 62, 69, 79, 93, 103 kPa, respectively) are also specified.

- Vapor lock protection classes. There are five classes for vapor lock protection. This classification depends on location and/or season. The limit for each class is a maximum vapor-liquid ratio of 20 at one of the specified testing temperatures of 41, 47, 51, 56, or 60°C.
- Antiknock index. Limits are not specified, but changes in engine requirements according season and location are discussed.
- Lead content
- Copper strip corrosion. This determines the ability to tarnish clean copper, indicating the presence of any corrosive sulfur compounds.
- Maximum sulfur content. Sulfur adversely affects catalysts and fuel hydrocarbon lead response. Sulfur may also be emitted as polluting sulfur oxides.
- Maximum solvent washed gum limits the amount of gums present in fuel at the time of testing to 5 mg/100 mLs. The results do not correlate well with actual engine deposits caused by fuel vaporization.
- Minimum oxidation stability. This ensures that the fuel remains chemically stable, and does not form additional gums during periods in the distribution systems (can be up to 3-6 months). The test is conducted by heating the sample with oxygen inside a pressure vessel. The time required for a significant oxygen uptake is measured to indicate minimum oxygen stability.
- Water tolerance. This is the highest temperature that causes phase separation of oxygenated fuels, the limits vary according to location and month.

An understanding of the reasons for detonation makes it obvious that there are two ways to improve the octane number of gasoline. It is possible to change the composition of gasoline. However, this is a difficult and expensive method. It is also possible to add additives that destroy peroxides. However, any "knock" caused by the fuel will rapidly mechanically destroy the engine. The problem is to identify economic additives which could be added to gasoline to prevent knock effects. Originally, iodine was the best antiknock additive available, but was not a practical gasoline additive, and was used as the benchmark. Later, tetra ethyl lead was added to the gasoline to improve the octane number.

Tetra ethyl lead (C_2H_5)₄Pb is an organometallic compound, which is well soluble in hydrocarbons in the gasoline. At the temperatures of 200-250°C, this substance is cracked to lead and four ethyl radicals C_2H_5 . All the compounds formed prevent the formation of explosive compounds in gasoline, or promote their fast destruction. However, the application of pure tetra ethyl lead was impossible. The formed lead deposits as a residue on

the walls of the cylinder, and further makes the working of the engine impossible. This is why, in practice, tetra ethyl lead is mixed with various alkyl-halogens. At high temperature, alkyl- halogens are cracked and react with lead to form volatile salts, which leave the engine together with the exhaust gases.

Adding tetra ethyl lead appeared to be quite an effective method to improve antidetonating properties of gasoline. The additive added in a very small amount in gasoline allows the increase of the octane number by about 5-10 units. Unfortunately however, lead and tetra ethyl lead are very poisonous substances. If contacted with the skin, they can filter into the blood. The lead compounds formed in engines falls on the ground and near vegetation. This can produce tragic consequences for the ecology.

The alkyl leads rapidly became the most cost-effective method of enhancing octane. Up until the late 1960s, alkyl leads were added to gasoline in increasing concentrations to improve octane number. However, in later years, the use of tetra ethyl lead was not encouraged. Presently in most countries of the world, the use of tetra ethyl lead as an additive to gasoline is prohibited by law.

However, the need for gasoline with high octane number is ever increasing. The next possible way to improve the octane number of gasoline is to mix it with other compounds having high octane numbers.

In the table above is shown that oxygenates have very high octane number (over 100). It is known that in the US, the so-called gasohol, a mixture of gasoline and alcohol, was used. In Europe syntin was produced from CO_2 and hydrogen. The product of this process includes a mixture of different types of alcohol.

However, the most effective and ecologically sound additive to gasoline nowadays is methyl tetra butyl ether ($(\text{CH}_3)_3\text{COCH}_3$). This additive is well known as MTBE. The octane number of MTBE is 135. The use of methyl tetra butyl ether as the additive fortunately solved a problem that resulted from using alcohols as the additive. In contrast to alcohols, MTBE is not soluble in water. It is known that water in different amounts can be found in industrial reservoirs. Even gasoline contains small traces of water. All alcohols are well soluble in water such that alcohol can stay in water at the bottom of the reservoir during storage. MTBE is insoluble in water and so this problem does not arise. Another problem with alcohol is that light alcohols (for example methanol) have a much lower heat of combustion than gasoline. It means that the need of fuel in tanks of the cars should be increased. MTBE has approximately the same fuel characteristics as gasoline. Moreover the presence of oxygen in its structure essentially improves the combustion process of gasoline in cylinders and reduces the contents of products of incomplete combustion in the exhaust gas.

There is only one disadvantage of using MTBE. There is a shortage in the production of MTBE in comparison to the need for high quality fuel for modern cars. One more method

to improve the antidetonating properties of gasoline was introduced in the 1970s. In this method, the properties of gasoline were not changed. Instead the working mechanism of the engine was changed. It was introduced to make the engine capable of working with two different gasolines. Because the highest danger of detonation in engine occurs only during the forced working regime, it is rational to use two different gasolines in one engine: the high quality gasoline for the forced regime of the engine and the gasoline with low octane number for the stable working regime. It was shown that normally the engine works about 20% of the general working time in forced regime. This means that by using two tanks in a car, one can save up to 80% of the high quality gasoline by partly using low quality fuel. However, this method did not become popular and therefore did not result in industrial production of cars with dual tanks.

It is useful to mention additional properties of gasoline of importance:

- **Volatility.** This affects evaporative emissions and derivability. It is a property that is changed with location and season. For example, fuel for mid-summer Arizona would be difficult to use in mid-winter Alaska. For this reason, the US is divided into zones, according to altitude and seasonal temperatures. The fuel volatility is adjusted accordingly. Incorrect fuel may result in difficult starting in cold weather, carburetor icing, vapor lock in hot weather, and crankcase oil dilution. Volatility is controlled by distillation and vapor pressure specifications. The higher boiling fractions of the gasoline have significant effects on the emission levels of undesirable compounds (hydrocarbons and oxygen containing compounds), and a reduction of 40°C in the end boiling point will reduce the levels of benzene, butadiene, formaldehyde and acetaldehyde by 25%, and will also reduce hydrocarbons emissions.
- **Combustion Characteristics.** Gasoline contains a wide variety of hydrocarbons. Thus, the only significant variable that characterizes different gasoline grades is the octane number. Most other properties are similar. There are only slight differences in combustion temperatures (most are around 2000°C in isobaric adiabatic combustion). It should also be noted that the actual temperature in the combustion chamber is also determined by other factors, such as load and engine design. The addition of oxygenates changes the pre-flame reaction pathways and also reduces the energy content of the fuel. The level of oxygen in the fuel is regulated according to regional air quality standards.
 - **Stability.** Motor gasoline may be stored up to six months. As such, they must not form gums during storage. Gums formed may precipitate. Gums are formed due to oxidation and polymerization reactions involving unsaturated hydrocarbons. Antioxidants and metal deactivators are added to prevent gum formation due to these reactions.
 - **Corrosiveness.** Sulfur in the fuel facilitates corrosion. The combustion of sulfur containing fuels results in the formation of corrosive gases that attack the engine, the exhaust as well as the environment. Sulfur also adversely affects the alkyl lead octane

response. Furthermore, it adversely affects the exhaust catalysts. However, the monolithic catalysts usually recover when the sulfur content of the fuel is reduced. In this case, sulfur is considered to be an inhibitor rather than a catalyst poison. The copper strip corrosion test and the sulfur content specification are used to ensure fuel quality. The copper strip test measures the active sulfur whereas the sulfur content reports the total sulfur present.

It has to be noted, that aviation gasoline is required to be an all hydrocarbon product. Its components must be chemicals that contain only carbon and hydrogen atoms. The use of oxygenated or other oxygen containing compounds, such as alcohols or ethers, is not allowed. Only a few select additives are permitted and their use is strictly controlled and limited. The primary ingredient in aviation gasoline is isooctane.

Naphtha

These fractions are highly volatile and fall in the boiling range of motor spirits. These are mostly used as solvents in paints perfumery and other industries. Solvent grades are produced by distilling wide cut naphtha into small boiling range cuts. Naphtha are not suitable for combustion, because of the rapid flame propagation, resulting in explosions. Cuts boiling below 80°C do not have any aromatics, hence their solvent power is also less. Such fractions are sent for cracking operation. 80-120°C fraction is reformed to improve octane number and this goes as a blend into straight run gasolines.

General requirements of solvent naphthas are

1. Almost water white in color
2. Non-corrosive nature
3. High stability
4. High solvent power (Kauri Butanol test ASTM D1133)
5. Low boiling point
6. Low acidity

Suspended impurities are removed by filtration. Solvent power is determined by Kauri Butanol number. The volume of solvent that causes a standard Kauri Butanol gum in butyl alcohol to become a 10 point type illegible when viewed through this solution. Another method of estimation of solvent power is by Aniline point. Harvey Mills relationship for KBN is given by

$$\text{KBN} = 99.6 - 0.806 G - 0.09912 A + 0.0755 (340 - B \times 0.56)$$
 (For less than 50) where G = Sp. Gravity, A = Aniline point °C B = Mid boiling temperature °C

Jet Fuel (Kerosene)

Kerosene is a hydrocarbon fraction that typically boils between 170-270°C (for narrow kerosene fraction or Jet A), 100-250°C (for wide kerosene fraction or JP-4), or 170-315°C (for heavy kerosene, Russian standards). It contains about 20% aromatics. However, the aromatic content is usually reduced for high quality lighting kerosene, as the aromatics reduce the smoke point. The other constituents include 20 to 60% aliphatic compounds, 20 to 60% naphthenes and up to 1% unsaturated compounds. The major use for kerosene today is as aviation turbine jet fuels. Special properties are required for this application, including high flash point for safe refueling (38°C for Jet A), low freezing point for high altitude flying (-47°C for Jet A), and good water separation characteristics.

The quantity and quality of kerosene vary with the type of crude oil; some crude oils yield excellent kerosene, but others produce kerosene that requires substantial refining and hydrotreatment. Kerosene is a very stable product, and additives are not required to improve the quality. Apart from the removal of excessive quantities of aromatics, kerosene fractions may need only hydrotreatment if hydrogen sulfide is present. The kerosene fraction from shale oil is like the gasoline fraction, which generally contains high amounts of nitrogen and oxygen. However, hydrotreatment will remove most of the nitrogen, but catalyst degeneration can be quite severe.

Jet fuels must burn cleanly and remain fluid and free from wax particles at the low temperatures experienced in high-altitude flight. The conventional freeze-point specification for commercial jet fuel is -50°C. The fuel must also be free of any suspended water particles that might cause blockage of the fuel system with ice particles. Special-purpose military jet fuels have even more stringent specifications.

The quality of this fuel varies widely. This is why there is no universal jet fuel. Instead, there are very many different types of jet fuels. The main types for North America and Russia are:

- Jet-A: This is a narrow cut kerosene product. This is the standard commercial and general jet fuel available in the United States. It usually contains no additives but anti-icing chemicals may be added.
- Jet-A 1: This is identical to Jet-A with the exception of its freezing point. It is used outside of the US and is the fuel of choice for long haul flights where the fuel temperature may fall to near the freezing point. It often contains a static dissipater additive.
- Jet-B: This is a wide cut kerosene with lighter gasoline type naphtha components. It is used widely in Canada. It contains a static dissipater and has a very low flash point;

- JP-4: This is a military designation for a fuel like Jet-B but contains a full additive package including corrosion inhibitor, anti-icing and static dissipater.
- JP-5: This is another military fuel. It has a higher flash point than JP-4 and was designed for use by the US Navy on board aircraft carriers. It contains anti-ice and corrosion inhibitors.
- JP-8: This is like Jet-A1 with a full additive package.
- T-5: This is a Russian heavy jet fuel without any additives and had been used for civil aviation. It has not been used any more since 1971.
- RT: This is a Russian hydrotreated jet fuel with antioxidation additive ionol;
- T6: This is a Russian thermo-stabilized jet fuel made from the east sulfuric petroleum with antioxidation additive ionol.
- T7: This is the same as the RT jet fuel without any additives.
- T8W: This is a Russian hydrotreated jet fuel without any additives.

Diesel

Diesel fuel is derived from petroleum. Diesel, gasoline and jet fuel are different cuts from the refining of petroleum. The difference is that diesel contains heavier hydrocarbons with a higher boiling point than gasoline and jet fuel. The term diesel fuel is therefore generic; it refers to any fuel mixture developed to run a diesel-powered vehicle, i.e. engines with compression ignition engines.

Diesel is a hydrocarbon fraction that typically boils between 250-380°C. Diesel engines use the cetane (n-hexadecane) rating to assess ignition delay. Normal alkanes have a high cetane rating, (n-C₁₆=100) representing short ignition delays. On the other hand, aromatics (alpha-methylnaphthalene = 0) and isoalkanes have low ratings representing long ignition delays. Because of the size of the hydrocarbons, the low temperature flow properties control the composition of diesel. Consequently, additives are usually added to prevent filter blocking in cooler temperatures. There are usually summer and winter diesel grades. Environmental legislation is reducing the amount of aromatics and sulfur permitted in diesel. Their emission as well as those of small particulates are considered as possible carcinogens and are also known to cause other adverse health effects.

Cetane number is one of the most widely known quality characteristics of diesel fuel. It is important to not confuse cetane number with cetane index.

The fuel in a diesel engine is ignited by the high-temperature and high- pressure air created in the cylinder as the piston nears the end of the compression stroke. In contrast, fuel in gasoline engines is ignited by a spark plug.

Cetane number is therefore a measure of the power with which diesel fuel is ignited during the compression stroke. The number is determined using a specified laboratory test engine. Cetane index is calculated using an equation involving the density and the distillation curve of the fuel. Consequently cetane index cannot be increased and improved by cetane improving additives because the equation does not account for the type and amount of cetane-improving additive in the fuel. However, cetane index can be modified through changes in the density or distillation curve of the fuel.

The time between the beginning of fuel injection and the start of combustion is called “ignition delay”. As stated earlier, higher cetane number fuels result in shorter ignition delays, providing improved combustion, lower combustion noise, easier cold starting, faster warm-up, less smoke, and in many engines, reduction of emissions.

In most diesel engines, the ignition delay is shorter than the duration of injection. Under these circumstances, the total combustion period can be divided into the following four stages:

- Ignition delay
- Rapid pressure rise

- Constant pressure or controlled pressure rise
- Burning on the expansion stroke

Rapid pressure rise results from the large number of ignition points and the accumulation of fuel during the ignition delay period. Following this stage, the rate of combustion can be controlled to a much greater degree by controlling the injection rate since the fuel is being injected into the flame. Because the rapid pressure rise represents uncontrolled and inefficient combustion, it is necessary to limit the ignition delay to a minimum. This limitation can be accomplished mechanically by the selection of a spray pattern configuration properly tailored to the combustion chamber.

The nature of the fuel is also an important factor in reducing ignition delay. Physical characteristics such as viscosity, density, and medium boiling point are influencing parameters. Hydrocarbon composition is also important as it affects both the physical and combustion characteristics of the fuel. Ignition delay characteristics of diesel fuel are of primary importance since they directly influence the interval of uncontrolled combustion during the injection and, as such, the overall engine performance.

The next important parameter of diesel fuel is stability or storage stability. As fuel ages, it can become unstable and form insoluble particulates that accumulate and eventually end up on the fuel filter. For the most part, instability involves the chemical conversion of precursors to compounds of higher molecular weight with limited fuel solubility. The precursors are certain nitrogen and/or sulfur containing compounds, organic acids, and reactive olefins. The conversion process often involves oxidation of the precursors. Certain dissolved metals, especially copper, contribute by functioning as oxidation catalysts. Fuel solvency also plays a role because the development of insoluble compounds is always a function of both the presence of higher molecular weight compounds and the capacity of the fuel to dissolve them. Diesel fuel is increasingly used as a coolant for high-pressure fuel injection systems in which the fuel can be thermally stressed. Sometimes, this can cause the fuel to degrade and form insoluble materials that can restrict fuel flow through filters and injection systems. Three tests are routinely used to evaluate fuel stability in the USA. These are ASTM D 2274, the Octet F21-90, and the Octel F21-180. ASTM D 2274 is an accelerated oxidation stability test. Oxygen is bubbled through a fuel sample for 16 hours, after which the fuel is filtered to collect any insoluble materials. Fuels that have insoluble materials of less than 15 mg/liter are considered to be stable.

Both Octel tests are thermal stability tests. The difference between the two is the length of time the fuel is thermally stressed. A sample is subjected to a 150°C bath for either 90 or 180 minutes, filtered to collect insoluble materials, and measured by light reflectance.

ASTM has developed the 180-minute test as a standard because it works better than the 90-minute test.

The storage stability is very important for bio-stability as well, especially for states with a warm climate. Microorganisms in diesel fuel have increasingly become a concern for fuel users. Prevention is important in fuel storage facilities. These bugs grow wherever water comes into contact with fuel, feeding at the interface, but living in the water.

The best way to prevent the problem is to keep water out of the fuel system. This is, however, practically impossible. The storage tanks cannot always keep the fuel from the humidity from the air.

In order to make diesel work most efficiently in engines year round, the low temperature properties of seasonal diesels are adjusted throughout the year according to historical temperature data of the region where the fuel is used. Generally all the diesel fuels can be divided into two groups:

- diesel fuel for summer season
- diesel fuel for winter season

For this classification of diesel fuel, the low temperature properties of the fuel are especially important. At low temperatures, wax crystals can be formed in the diesel fuel. These wax crystals can collect on and plug fuel filters in a vehicle's fuel system causing the engine to stumble or stall. The temperature at which this occurs is called the low temperature operability limit of the fuel and vehicle. Both the fuel system design and the fuel properties are important factors in determining this minimum temperature for acceptable operation.

The next quality parameter of diesel fuel is the ability to keep the fuel injector clean. The fuel injector is the heart of a diesel engine. These precision components meter fuel to a high degree of accuracy. Correct engine behavior depends on the injector functioning properly.

Proper injector functioning is essential for optimum performance. As such, it is beneficial to keep the nozzles operating at their optimum. Buildup of carbon on the injector can disrupt the spray pattern of the fuel being injected into the cylinder. This can lead to incomplete combustion, which, in turn, can cause increased emission and high fuel utilization.

Many various additives are used to improve the quality of diesel fuel. These additives are used for a variety of purposes that can be classified into four major categories:

- Engine performance
- Fuel handling
- Fuel stability
- Contaminant control

The engine performance additives improve engine performance. Different members of this class are used to improve engine performance in different time frames. Any benefit that is provided by a cetane number improver is immediate, whereas that provided by detergent additives or lubricity additives is typically seen over the long term.

Cetane number improvers or diesel ignition improvers reduce combustion noise and smoke. The magnitude of the benefit varies among engine designs and operating modes, ranging from no effect to readily perceptible improvement.

2-Ethylhexyl nitrate (EHN) is the most widely used cetane number improver. It is also sometimes called, “octyl nitrate”. EHN is thermally unstable and decomposes rapidly at the high temperatures in the combustion chamber. The products of decomposition help initiate fuel combustion and, thus, shorten the ignition delay period as compared with that of the fuel without the additive.

The increase in cetane number from a given concentration of EHN varies from one fuel to another. It is greater for a fuel whose natural cetane number is already relatively high. The incremental increase gets smaller as more EHN is added. Thus, there is little benefit to exceed a certain concentration. EHN typically is used in the concentration range of 0.05 to 0.4 mass % and this may yield a 3 to 8 cetane number benefit. A disadvantage of EHN is that it decreases the thermal stability of the fuels.

Other alkyl nitrates as well as ether nitrates and some nitroso compounds, have also been found to be effective cetane number improvers. However, they are not currently used commercially. Di-tertiary butyl peroxide has recently been introduced as a commercial cetane number improver.

Injector cleanliness additives and crankcase lubricant can form deposits in the nozzle area of injectors. The extent of deposit formation varies with engine design, fuel composition, lubricant composition, and operating conditions. Excessive deposits upset the injector spray patterns and these hinder the fuel-air mixing process. In some engines, this leads to increased emissions and fuel utilization. Ashless polymeric detergent additives can clean the fuel injector from deposits.

These additives are composed of a polar group that bonds to deposits and deposit precursors and a non-polar group that dissolves in the fuel. Thus, the additive can redissolve deposits that already have formed and reduce the opportunity for deposit precursors to form deposits.

Lubricity additives are used to compensate for the poor lubricity of severely hydrotreated diesel fuels. They contain a polar group that is attracted to metal surfaces, causing the additive to form a thin surface film. The film acts as a boundary lubricant when two metal surfaces come in contact. Two additive chemicals, fatty acids and esters, are typically used for this purpose.

Smoke suppressants are combustion catalysts. This class of additives is usually composed of organometallic compounds. Adding these compounds to fuel can reduce the emissions of pollutants that result from incomplete combustion. Smoke suppressants that are based on organometallic compounds of iron, cerium, platinum are in common use.

The following additives belong to the fuel handling additives:

- Antifoam additives prevent formation of foam. Diesel fuels tend to be prone to foam formation when they are pumped into the tanks. Most antifoam additives are organosilicone compounds and are typically used at very low concentrations (about 10 ppm).
- De-icing additives prevent ice formation from the free water in diesel fuel. If free water in diesel freezes, the resulting ice crystals can plug fuel lines and filters. Low molecular weight alcohols or glycols can be added to diesel fuel to prevent ice formation. The alcohols/glycols preferentially dissolve in the free water, giving the resulting mixture a lower freezing point than that of pure water.
- Low temperature operability additives lower a diesel fuel's pour point and improve its cold flow properties. Most of these additives are polymers that interact with the wax crystals that form in diesel fuel when it is cooled below the pour point. The added polymers mitigate the adverse effect of wax crystal formation on fuel flow by modifying their size, shape, and degree of agglomeration. The polymer-wax interactions are fairly specific. As such, a particular additive generally will not perform equally well in all fuels. Unfortunately, the best additive for a particular fuel cannot be predicted; it must be determined experimentally.
- Drag reducing additives are used by pipeline companies to increase the volume of product they deliver. These high molecular weight polymers reduce turbulence in fluids flowing in a pipeline. This can increase the maximum flow rate by up to 40%. When the additive modified product passes through a pump, the additive is broken into smaller molecules that have no effect on product performance in engines.
- Fuel stability additives prevent the formation of gums that can lead to injector deposits or particulates that can plug fuel filters and the fuel injection system. The need for a stability additive varies widely from one fuel to another. Stability additives typically work by blocking one step in a multi-step reaction pathway of gum formation. Because of the complex chemistry involved, an additive that is effective in one fuel may not work as well in another. If a fuel needs to be stabilized, it should be tested to select an effective additive and treatment rate. The best results are obtained when the additive is added immediately after the fuel is manufactured.
- Antioxidants prevent the oxidation of the fuel. Antioxidants work by interrupting the chain in free radical chain reaction by blocking the free radicals. Phenylated diamines are the most commonly used antioxidants.
- Stabilizers prevent acid-base reactions in the diesel fuel. Basic amines are usually used as stabilizers. They react with weakly acidic compounds with the formation of products that remain dissolved in the fuel and do not react further.

- Metal deactivators prevent the catalytic influence of the metals on reactions that can lead to its instability in diesel fuel. They are typically used in concentrations of up to 15 ppm.
- Dispersants disperse the formed insoluble products in diesel fuel, preventing them from clustering into aggregates large enough to plug fuel filters or injectors. Dispersants are typically used in concentrations of up to 100 ppm.
- Biocides prevent the growth of bio-organisms. The best choice is an additive that dissolves in both the fuel and the water such that it can attack the microbes in both phases. Biocides are typically used in concentrations of up to 600 ppm. A biocide may not work if a heavy biofilm has accumulated on the surface of the tank or other equipment, because then it does not reach the organisms living deep within the film.
- Demulsifiers aid in the separation of fuel from water. Normally, hydrocarbons and water separate rapidly and cleanly. But if the fuel contains polar compounds that behave like surfactants and if free water is present, the fuel and water can form a stable emulsion. Any operation that subjects the mixture to high shear forces, like pumping the fuel, can stabilize the emulsion. Demulsifiers are surfactants which can destabilize the emulsions and allow the fuel and water phases to separate. Demulsifiers are used in concentrations of up to 30 ppm.
- Corrosion inhibitors prevent the oxidation of the metal pieces in diesel engines. Since most petroleum pipes and tanks are made of steel, the most common corrosion is the formation of rust in the presence of water. The fuel is thus contaminated with rust particles, and these can plug fuel filters as well as increase fuel pump and injector wear. Corrosion inhibitors attach to metal surfaces and form a film that prevents attack by corrosive agents. They typically are used in concentrations of up to 15 ppm.
- Modern diesel fuel can be produced from sources other than petroleum. Recently, attention has been focused on biodiesel. This is a cleaner-burning fuel made from natural and renewable sources such as vegetable oils. Just like petroleum diesel, biodiesel can operate in combustion-ignition engines. Essentially no engine modifications are required, and also biodiesel maintains the payload capacity and range of diesel.

The use of biodiesel in a petroleum diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and formation of particulate matter, i.e. in reduction of emission of pollutants. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle and testing methods. The use of biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in biodiesel enables more complete combustion to CO_2) and eliminates sulfate fraction (as there is no sulfur in the fuel), while the soluble and hydrocarbon fraction

stay the same or are increased. Therefore, biodiesel works well with new technologies such as catalysts (which reduce the soluble fraction of diesel particulate but not the solid carbon fraction), particulate traps, and exhaust gas recirculation (leads potentially to longer engine life due to less carbon).

Biodiesel has physical properties that are very similar to those of petroleum diesel. As mentioned earlier, emission properties, however, are better for biodiesel than for petroleum diesel.

Biodiesel is produced by a process called “trans-esterification”. Vegetable oil or animal fat is first filtered, then pre-processed with alkali to remove free fatty acids. It is then mixed with an alcohol and a catalyst. The oil's triglycerides react to form esters and glycerol, which are then separated from each other and purified.

Much of the current interest in biodiesel production comes from vegetable oil sources such as soybean (in the USA), canola oil (in Canada) and rapeseed oil (in Europe) because the vegetable oil producers are faced with excess production capacity, product surpluses, and declining prices.

Waste animal fats and used frying oils (known as 'Fellow grease') are also potential feedstocks. These are cheaper than soybean oil and are being considered as a way to reduce feedstock costs.

Residual Fuel

Many marine vessels, power plants, commercial buildings and industrial facilities use residual fuels or combinations of residual and distillate fuels for heating and processing. The two most critical specifications of residual fuels are viscosity and low sulfur content for environmental control.

Furnace oil is one kind of residual fuel. These are blended with other suitable gas oil fractions in order to achieve the viscosity required for convenient handling. As a residue product, fuel oil is the only refined product of significant quantity that commands a market price lower than the cost of crude oil.

Because the sulfur contained in crude oil is concentrated in the residue material, residual fuel sulfur levels naturally vary from less than 1 to over 6%. The sulfur level is not a critical factor for the combustion process as long as the flue gases do not impinge on cool surfaces. However, residual fuels may contain large quantities of heavy metals such as nickel and vanadium; these produce ash upon burning and can foul the burner systems. Such contaminants are not easily removed and usually lead to lower market prices for fuel oils with high metal contents.

In order to reduce air pollution, most industrialized countries have restricted the sulfur content of residual fuel. Such regulations have led to the design and construction of residual desulfurization units or cokers in modern refineries to produce fuels that meet these restrictions.

The standardized properties of residual fuels are:

- Density at 15°C ranging from 0.975 to 1.01 g/cm³.
- Kinematic viscosity at 100°C ranging from 10 to 55 mm²/s.

The viscosity of an oil is a measure of its resistance to flow. Over the years different units have been used for viscosity (Engler Degrees, Saybolt Universal Seconds, Saybolt Furol Seconds and Redwood No. 1 Seconds). Nowadays, a majority of residual fuels are traded internationally on the basis of viscosity' measured in centistokes (one centistoke = 1 mm²/sec). The value for viscosity should be given together with the temperature at which it is determined. Accepted temperatures for viscosity determination of residual fuels are 40°C for distillate fuels and 100°C for vacuum residues. If a fuel contains an appreciable amount of water, testing for viscosity determination at 100°C is impossible. In this case, viscosity is determined at a lower temperature (usually 80-90°C). It is then recalculated to obtain viscosity at 100°C. Due to the variability of the composition of residual fuels, calculations for viscosity at another temperature from that measured at one temperature may not be accurate. Therefore, such calculated results should be treated with caution. The viscosity result is used first to ensure that the fuel is correctly heated in storage and made ready for pumping. The maximum viscosity for efficient pumping is considered to be around 600 cSt. However, lower viscosity should be maintained if long pipelines are installed.

- Flash point has to be over 60°C for residual fuels. The flash point is considered to be a useful indicator of the fire hazard associated with the storage of residual fuels. The flash point is determined by using the Pensky Martens closed cup tester. It should be remembered that results can be affected if the fuel sample contains a significant amount of water. There is one difficulty encountered by laboratories, which are requested to carry out a wide range of tests on one sample of residual fuel, including flash point. To ensure that a fuel sample is fully homogeneous, it should be heated for a period of time and shaken or preferably homogenized before it is split to perform individual tests. This preheating and homogenization may release some of the vapors from the sample thereby affecting the flash point result.
- Pour point varies from 0 to 45°C depending on the kind of fuel. Pour point is defined as the lowest temperature at which an oil will continue to flow when it is cooled under prescribed standardized conditions. If fuels are held at temperatures below their pour points, wax will begin to crystallize. This wax causes blocking of the filters and can deposit on heat exchangers. Generally, high viscosity fuels need to be heated well above the pour point to achieve the desired pumping viscosity. However, these fuels should be stored at a temperature of around 10°C above the pour point if wax deposition is to be avoided. Some waxy residual fuels have pour points between 40 and 45°C. Carbon residue varies from 10 to 22% depending on the residual fuel. The carbon residue provides information on the coke or carbonaceous deposits which result from combustion of the fuel. Fuels which are rich in carbon prove more difficult to burn fully, resulting in increased deposits in the combustion and exhaust spaces. Fuels produced from thermal cracking residues show a higher carbon/hydrogen ratio and, hence, high percentage carbon residue. Carbon residue can only be an indicator of potential deposit-forming tendency of the fuel. Thus, operating experience with different fuels at different engine loadings and conditions should be recorded to determine individual engine tolerance levels to high carbon fuels.
- Ash ranges from 0.1 to 0.2%. The ash content of a fuel is a measure of the amount of inorganic noncombustible material it contains. Some of the ash-forming constituents occur naturally in crude oil; others are present as a result of refining or contamination during storage or distribution. For instance, it could be due to the presence of compounds of the following elements: vanadium, sodium, calcium, magnesium, zinc, lead, iron, nickel.
- Water content varies from 0.5 to 1%. Water is introduced into residual fuels by poor storage. The standards allow water up to a maximum of 1% in residual fuels. However, the majority of fuel deliveries have water contents below 0.5%. The problems with high water levels in fuel can be complex and include sludging of fuel

tanks, filter blockage, corrosion of fuel injection equipment, exhaust valve corrosion, etc.

- Sulfur ranges from 3.5 to 5%. The main problem resulting from the use of high sulfur fuels is corrosion. During the combustion process, sulfur dioxide (SO_2) and sulfur trioxide (SO_3) are produced. Depending upon engine conditions such as excess air, temperature and pressures, these gases will convert to sulfurous acid (H_2SO_3) and sulfuric acid (H_2SO_4), to some extent. These acids are formed when the gases exist below their dew points. For the formation of sulfurous acid, the favorable temperature should range between 50 and 60°C whereas for sulfuric acid, it should range between 110 and 150°C. These acids cause corrosion in the low temperature zones of engines and boilers. Hence, their effect is often referred to as "cold end corrosion".
- Vanadium content ranges from 150 to 600 mg/kg. The vanadium content of fuels from different countries varies considerably and is directly related to the crude oil source. Problems associated with high vanadium have been addressed under ash, sodium and sulfur. These problems are largely overcome by good engine design, and correct fuel treatment. To prevent these problems additives are widely used.

Lubricating Oils And Lubricants

Lubricants are of multiple importance in the forging process. They serve as the cooling agent of the forging parts, support the filing of parts and prevent the fusion of work piece and tool. The main functions of lubricating oils and lubricants are:

- Reducing friction. Putting lubricating oil between moving metal surfaces decreases friction. This results in energy conservation and significantly less wear.
- Reducing wear. Lubricating oils reduce mechanical wear (caused by abrasion and erosion) and chemical wear (corrosion caused by combustion acids and water). Wear is influenced by various factors which can be divided into the fields of tool, rough part, forming machine, lubricant and actual contact area. Possible ways to reduce wear lie in the increase of annealing durability as well as in the hardness of the surface, for example through nit riding, and application of mostly ceramic wear resistant layers on the tool surface. Also, massive wear reduction can be achieved by lowering the tool temperature.
- Cooling. Lubricating oil cools the mechanical components by helping to remove heat and decreasing the amount of heat produced (by reducing friction).
- Ensuring leak tightness. Lubricants ensure leak tightness between the mechanical components such as the cylinder and the piston, improving compression and producing better engine performance.
- Removing impurities. Lubricants keep engine components clean by preventing the formation of deposits and suspended impurities (dust, combustion residue, engine wear particles) that then build up on the oil filter.

Properties differ from one lubricant to another. However, the one component that lubricants have in common is that they are composed of a main ingredient called the lubricating base. The lubricating base may be petroleum derived or synthetic. The lubricating base accounts for 75 to 85% of the lubricant. There are three different classes of lubricating bases that are used in modern oil industry:

- Mineral bases are manufactured from petroleum that has undergone a variety of complex separation processes. They are the most commonly used for both automotive and industrial applications.
- Synthetic bases or synthetics are products created by the chemical reaction of several ingredients. Two main classes are used for lubricants: esters and synthetic hydrocarbons (in particular polyalphaolefins manufactured from ethylene). These products have excellent physical properties and exceptional thermal stability.
- Semi-synthetic oils are obtained from mixing both types of bases (generally 70 to 80% of mineral oil and 20 to 30% of synthetic oil).

The development of modern lubricants and their correct use are especially important as these have substantial economic consequence on the use of these devices. Optimally chosen lubricant brings saving of energy needed for machine work, conserves the parts of these devices, reduces wear and tear, reduces the maintenance time and shortens the overhaul

intervals, which can take away millions of dollars from industry. The characteristics of lubricants are improved by special substances called additives. In the current industrialized society, the use of lubricants without these enhanced characteristics is no longer conceivable. Lubricating oil additives are synthetic active substances, which are added to the basic oils in order to give the products the desired characteristics or properties. This is why, additives are the next main compounds of the oils (15 to 25%).

The following main classes of additives are available:

- Viscosity index improvers. These make the oil a sufficiently low viscous fluid when cold (to facilitate starting) by lowering the pour point to between -45 and -45°C (depending on the oil), and to viscous fluid when hot (to prevent the contact between moving mechanical components). This class of additives are polymers which are introduced into a lubricating base to produce a relative greater increase in viscosity when hot than when cold.
- Antiwear additives. These reinforce the antiwear action of the lubricant. The main family of antiwear additives are alkyl-zinc dithiophosphates and numerous phosphorus derivatives.
- Antioxidants. These eliminate or slow down lubricant oxidation, increasing the time between oil changes through improved resistance to high temperatures. Dithiophosphates that are used as antiwear additives are also excellent antioxidants. Other chemical families such as substituted phenols and aromatic amines are also used.
- Detergents. These prevent the formation of deposits and varnish on the hottest areas of the engines (such as ring grooves). Calcium or magnesium metal salts from main chemical families such as alkylaryl-sulfonate, alkylphenate and alkylsalicylate are used as detergents.
 - Dispersing agents. These maintain in suspension all the solid impurities formed during engine operation. The solid impurities include unburned residue, gums, sludge, diesel soot, deposits cleaned by detergents. Usually polar compounds from the alkenylsuccinimides, succinic esters or their derivatives are used as dispersing additives.
 - Alkalinity additives. Those that neutralize combustion acid residue from fuels are made primarily for diesel engines. The main compounds of this class of additives are phenols and salicylates (which are natural alkaline), and sulfonates. In the case of sulfonates, their neutralizing property can be reinforced by adding basic salts such as carbonates or hydroxides.
 - Corrosion inhibitors. These prevent the corrosion of ferrous metals under the combined effects of water, atmospheric oxygen and a number of oxides formed during combustion. Mainly alkaline or alkaline-earth sulfonates, neutral or alkaline (Na, Mg, Ca) salts, fatty acids or amines, alkenylsuccinic acids and their derivatives are used as corrosion inhibitors.

- Antifreeze agents. These enable lubricating oils to retain good fluidity at low temperatures (from -15 to -45°C). The main classes of this type of additive are
- polymethacrylates, maleate-styrene copolymers, naphthalene waxes and vinylacetate-fumarate polyesters.
- • Foaming inhibitors. Oil foaming can be caused by the presence of other additives. For example, detergent additives act in the same way as soap in water; they clean the engine, but tend to foam. Foaming can also be caused by lubricating system design for which the major aim is to facilitate air-oil mixing. Such designs can cause turbulence during lubricant flow as well as formation of bubbles in the oil. Very small amounts of silicon oil or alkyl acrylates can be used as an antifoaming additive.
- • Extreme-pressure additives. These reduce friction torques and, as a result, conserve energy and protect the surfaces from heavy loads. The most common classes of these additives are organometallic derivatives of molybdenum and some compounds derived from fatty acids, phosphorus-sulfur molecules, borates, etc.

It can be seen that the main functions of additives are to improve the lubricating properties of the lubricant and to make the lubricant as stable against adverse effects such as oxidation, corrosion, etc. It is important to know the mechanisms of the various effects that each additive is trying to inhibit in order to make the right choice of the additive or mixture of various additives to select. The most important function of all lubricants is to lubricate the surfaces in order to prevent friction between them.

One more important requirement for lubricating oils, which can be improved by adding additives, is the ability to keep their properties for a long time. One of the most important additives used to improve this ability of oils is antioxidants.

Oxidation is a radical chain reaction promoted by alkyl and peroxide radicals. This means that it is necessary to add radical acceptors to the oil to prevent its oxidation. It is possible to classify most of the modern antioxidants in six groups:

1. Antioxidants, which prevent oxidation by reaction with peroxide radicals. Such additives often contain aromatic compounds in their structure with relatively weak O-H and N-H bonds. Examples of such compounds are phenols, naphthols, aromatic amines, aminephenols, and diamines. This type of additive has strong reducing properties and reacts quickly with peroxide radicals.
2. Antioxidants which prevent oxidation by reaction with alkyl radicals. The additives react quickly with alkyl radicals. Examples of such additives are hynones, iminehynones, methylhynones, stable nitrogen oxide radicals, and molecular iodine. Alkyl radicals react quickly with oxygen. This is why antioxidants of this type are effective under conditions of oils with low concentration of oxygen.
3. Antioxidants which destroy hydroperoxides. This type of additive reacts quickly with hydroperoxides without free radical formation. The following substances are good

examples of such additives: sulphide, phosphite, arsenate and so on, and also thiophosphate and carbonates of various metals, and various complexes.

4. Antioxidants which deactivate the surface of metals. Some compounds of metals with variable valency react with hydroperoxides with the formation of free radicals, which strongly promotes oxidation. This type of catalytic oxidation can be prevented by adding a "complex former", which forms with a metal complex that is rendered inactive to hydroperoxide. Examples include diamines, hydroacids and other compounds that form strong complexes with metals.

5. Antioxidants with repeated action. During the oxidation of some classes of substances such as alcohols and aliphatic amines, peroxide radicals are formed, which have both oxidizing and reducing functions. In such systems, additives that prevent oxidation are regenerated again in the reducing reaction. This involves a catalytic breakage of the chain in the radical chain reaction. The number of chain breakages depends on the reaction ratio of additive regeneration and its consumption in the reversible reaction. Examples are aromatic amines, nitrogen oxide compounds, compounds of metals with variable valency, etc.

6. Antioxidants with combined function. Some additives prevent oxidation by simultaneous reactions with many compounds that promote oxidation. For example, it can react with both alkyl and with peroxide radicals (anthracene, methylhynon), or can destroy hydroperoxides and break off the reaction chain with RCA radicals (carbomate and thiophosphate of metals). Such compounds are referred to as antioxidants with combined function. The parallel reactions can occur with the same group in one additive. For example, R- and ROy radicals react with the double bond of methylhynon. Frequently, two or more functional groups exist in one molecule, each of which is responsible for an appropriate reaction. For example, phenolsulphide reacts with hydroperoxide with the sulfide group and with RCA with the phenol group. In a different type of reaction, it can take part in the initial reaction with antioxidant and products of its transformation. Often the mixtures of additives have combined function. For example, adding phenol and sulphide to the oil first prevents oxidation by breaking the reaction chain with ROy radical, and second reduces the reaction rate for branching reactions by destroying the hydroperoxide. Synergy may be obtained if two antioxidants strengthen the action of each other. Also, it is possible for the action of two or more antioxidants to be additive. However, if the action of a mixture is less than the sum of the actions of each antioxidants, antagonism results.

In the last type of antioxidants we learn that an important property of antioxidants is synergy. It is to be understood that by synergy one can mix antioxidants each with a weak action against oxidation and obtain a strong antioxidant action as a combination. That may sound strange but this effect really occurs during the preparing of many industrial additives. This is why it is especially important to understand the nature of synergetic effects in order

to be able to use the maximum possible potential of additives. How to obtain synergistic effects can be classified in three groups:

1. One antioxidant breaks the reaction chain and the second reduces the ratio of initiation by destroying ROOH groups or by deactivating the catalyst that promotes the formation of the ROOH.
2. Two initial substances (antioxidants or not) react with each other and form an effective antioxidant.
3. The transformation products of antioxidants strengthen the antioxidant function.

The main properties of lubricants and lubricating oils are determined by carrying out the following specific tests:

- Oxidation tests. The combined effects of ambient oxygen and temperature affect lubricant aging; this phenomenon is known as oxidation. In laboratory oxidation tests, temperatures are selected in accordance with those encountered during equipment operation.
- Corrosion tests. One of the lubricant's main functions is protection against corrosion. Accordingly, the reactions between the lubricant and various metal surfaces need to be determined and, where appropriate, modified.
- Chemical compatibility tests. These tests are used to determine the behavior of various materials when they are in contact with oil. For example, specific tests are conducted to ensure the compatibility of a lubricant with seals.
- Storage stability tests. Some lubricant combinations are formed by the association of products that are not fully miscible in oil. In this case, the final stability that represents changes during storage needs to be verified.
- Dispersion tests. The purpose of these tests is to determine the ability of an oil to maintain in suspension solids that are likely to form during operation. For example, combustion engines produce carbon residues, some of which are found in the oil. The latter must be able to maintain the soot in suspension and prevent deposits that could result in fouling or even clogging.
- Shear tests. These tests determine how well lubricants withstand mechanical loads that can cause the molecules of some components to break up.
- Pressure tests. There is currently no device available that can directly measure the ability of an oil film to withstand pressure. Various properties (film strength, high pressure, extreme pressure) can only be assessed using bench tests in the laboratory to determine their effects on other oil properties, the same types of tests are carried out for greases as for oils, using special devices: four-ball machine, Timken, etc.
 - Laboratory tests are supplemented by bench tests on machines very similar to real ones and which operate under controlled conditions.
 - Engine tests are designed to determine the behavior of oils on either gasoline or diesel engines. Each test is performed in such a way as to highlight one or more

lubricant properties. No single engine test is available that enables all properties to be tested simultaneously.

- Bench tests are carried out either on standard automotive multi-cylinder engines or on single-cylinder engines.
- Gear tests check the internal cohesion and pressure withstanding properties of lubricants on real gears. Various methods are used depending on the type of gear and test conditions.

Bitumen

Bitumen is the residual product obtained from crude distillation unit. It is essentially solid at room temperature and has got very high viscosity. Asphalt is usually a mixture of bitumen in oil, containing much mineral matter. Bitumen natural deposits are also available; famous Trinidad pitch lake is such a deposit. Bitumen obtained from the distillation column is poor in qualities. This has necessitated air blowing of bitumen to obtain suitable grades. Most of the bitumen is used in highway constructions, waterproofing and coatings works.

Bitumen is specified by the following two tests

- (a) Softening Point
- (b) Penetration index.

These two tests do not describe the properties of bitumen completely. Other tests like viscosity, volatility, durability, ductility are necessary for obvious reasons. Outlines of these tests and significance are mentioned below :

2.3.10.1 Softening Point (ASTM D 1398 1P.198 Ball & Ring test)

Bitumen being amorphous does not melt sharply. The softening point is found out by the Ball & Ring Test. Bitumen is first melted and casted into discs of two numbers in standard rings. A steel ball weighing (3.5 ± 0.05) gms (dia 9.53 mm.) is kept on each casted disc of bitumen. The whole stand carrying these two discs with ball is immersed in a water or glycol bath. As the heating proceeds, softening occurs. The temperature at which the sample detaches from the die and falls; indicates its softening point. The two samples from such rings are supposed to fall within a difference of 5 seconds. Higher the softening point, the better is consistency of bitumen. (See Fig. 2.24).

2.3.10.2 Penetration Index

The hardness or penetration quality of bitumen is assessed by this test (IP 49/72).

A standard needle is allowed to penetrate under a load of 100 gms, through a sample kept at 25°C for 5 sec. Distance travelled under those conditions indicates the consistency of sample. The distance (easily) travelled would naturally depend upon its load, and softening point. More penetration index naturally impairs the surface applications, where hardness is sole criteria.

2.3.10.3 Ductility (D 113)

Bitumen must possess good ductility, when it is used in surface application. The ductility is measured by a ductilometer.

ductility is a measure of the capacity of bitumen to elongate or stretch. This test is carried out by pulling a test piece of bitumen of standard dimensions at a uniform rate (5 mm/min) keeping sample at 25°C. Higher capacity for elongation indicates that the sample is having high ductility.

Other tests like viscosity, boiling point, ash content are desirable. Suitable solvents are added to solubilise the bitumen and then applied over the surface, when the solvent evaporates a fine layer of bitumen appears. These cutback bitumens after full curing period must possess the same properties as the bitumen from which they are made.

Indian specifications of bitumen are given below :