Properties of Petroleum Fuels Lectures Notes, First Semester Lecture: Luma H.

2018-2019

BITUMEN

Bitumen is

- a black or brown highly viscous liquid or semisolid material that is present in most crude oils and in some natural deposits.
- Bitumen is a complex mixture of organic compounds containing up to 150 carbon atoms, mainly

 aromatic, naphthenic, and aliphatic.
- Bitumen may also contain
 - small amounts of organic acids, bases, heterocyclic compounds nitrogen, oxygen, and sulfur.
 - Some metals arc also found in bitumen.
- Bitumen may typically contain
 - 83 to 86 percent carbon.
 - 9 to 10 percent hydrogen.
 - 1 to 5 percent sulfur,
 - less than 1 percent each of nitrogen and oxygen, and minor amounts of metals such as vanadium and nickel.
- Bitumen is
 - useful anywhere where waterproofing, insulation, or chemical resistance problems are encountered.
- Bitumen is
 - used in the lining of water reservoirs, canals, and the upstream side of large dams to prevent water seepage and erosion.
- Bitumen is
 - used in diverse industries such as cable jointing compound, cold sticker compound for sticking, roofing felt over metallic surfaces, timber, battery scaling compound, for making printing inks, in automobiles for undercoating, as a base for paint and lacquers, manufacture of floor covering, and a wide variety of waterproofing and damp-proofing applications.
- Bitumen or asphalt refer to the same product.

BITUMEN COMPOSITION

- Bitumen is
 - a thermoplastic material:
 - It softens when heated and hardens on cooling.
 - Within a certain temperature range, bitumen is viscoelastic.
 - It exhibits the mechanical characteristics of viscous flow and elastic deformation.
- Bitumen can be considered a colloidal solution in which asphaltenes are held in suspension in a mixture of oil and resins.

Typical composition is as follows:

- Constituent Wt % (percentage of weight)
- Saturates + aromatics 50-60
- Resins 25
- Asphaltenes 20
- Saturates and aromatics are the fraction with the lowest molecular weight, ranging from 300 to 2000.
- The hydrogen-to-carbon ratio of this fraction is much higher than those of asphaltenes or resins.
- This fraction acts as the dispersion medium for asphaltenes.

Asphaltenes

- The asphaltene molecule1 has a core of saturated condensed aromatic rings and an aliphatic side chain.
- Heteroatoms (0. N. S. Ni. V. and others) have been found in rings.
- The asphaltene molecule is typically composed of 10 or more fused aromatic and naphthenic rings with a significant number of alkyl side chains.
- The molecular weight of asphaltene is in the range of 2000 to 5000. The higher the asphaltene percentage, the harder the bitumen.
- Asphaltene constitutes from 5 to 25 wt % of bitumen.
- When heated, at a low cracking temperature of 750°F.
- thermal cracking with coke formation occurs rapidly.

Resins

- Resins are composed of heterogeneous polar compounds with a small percentage of oxygen, nitrogen. sulfur, and metals.
- The molecular weight is typically 800 to 2000.
- Resins constitute approximately 15 to 25 percent of the weight of asphalt.
- Resins are aromatic groups with high polarity.
- Resins have a higher hydrogen-to-carbon ratio compared to those of asphaltenes.
- Resins can be considered as low molecular weight asphaltenes.

Aromatic Oils

- Aromatic oils consist mainly of carbon, hydrogen, and sulfur with a minor amount of nitrogen and sulfur.
- with a molecular weight of 500 to 900.
- These oils constitute 45 to 60 percent of the weight of bitumen.
- These compounds have mainly aromatic ring or naphthenic-aromatic nuclei with a side chain.

Saturated Oils

- Saturated oils consist mainly of long chain saturated hydrocarbons with some branched chain compoundscyclic paraffins.
- Molecular weight is in the range of 500 to 1000.
- Saturated oils constitute 5 to 20 percent of the weight of bitumen.

BITUMEN FOR PAVEMENT

- For making paving bitumen, the cut point between heavy distillate and vacuum residue is adjusted to give a residuum of the required viscosity and penetration for use in road paving.
- Both the yield and quality of paving bitumen varies widely, ranging from a few percentage points to as high as 70 percent.
- Some crude oils, generally known as bitumen crudes, yield high-quality paving bitumen simply by distillation, whereas in the ease of many other crude oils, either the quality of bitumen produced is unsatisfactory or the bitumen yield is too low to be economical.
- Not all crude oils are suitable for making good road bitumen.
- If crude oil has a high wax content, its viscosity temperature characteristics may not be suitable for making road paving asphalts.
- Vacuum residue may have a high penetration and too a low viscosity at 275°F.
- For example. Arab light crude has a moderately high wax and gives vacuum residue, which has poor low-temperature properties.

TYPES OF BITUMEN

Apart from straight run bitumen, the following other types of bitumen are produced and used in the industry:

- Cutback bitumen
- Bitumen emulsion
- Polymer-modified bitumen
- Oxidized or blown bitumen

Cutback Bitumen

- Cutbacks do not require heating before spreading on the pavement.
- Cutbacks are used in many applications because the solvent reduces asphalt viscosity for use at a lower temperature.
- Cutbacks are used in road applications for priming road surfaces because they can penetrate and bind the surface layers and thus create waterproofing.
- Other road building uses are tack coats, fog seals, and slurry seals in roads and highways.

Bitumen Emulsions

- Emulsified bitumen is simply a suspension of small bitumen cement globules in water assisted by an emulsifying agent such as soap.
- Bitumen emulsions can be used in almost any application where cutback bitumens are used.
- The advantage of bitumen emulsions includes the ability to handle asphalt with minimal or no heating and the absence of significant reduction of cutter in the binder.
- Standard grades of emulsions contain approximately 60 percent bitumen by weight and 40 percent water.
- Bitumen may contain additives such as petroleum cutters and polymers.
- Disadvantages are their slow initial curing rates and higher cost.
- Emulsions effectively reduce asphalt viscosity for use at lower temperatures.
- Bitumen emulsions are used for various applications.
- For road building, emulsions are used for tack coats, fog seals, slurry seals, and bituminous surface treatment.

Bitumen Binder Modifiers

- Some bitumen binders require modifications to meet specifications.
- Modifiers can increase bitumen binder stiffness at normal service temperature while decreasing its stiffness at low temperatures to improve resistance to thermal cracking.

• There are many bitumen binder modifiers available, and the selection is done with the following objectives in mind:

- Lower viscosity at high temperature associated with construction.
- Higher viscosity at high temperature to reduce rutting and shoving.
- Lower stiffness and faster relaxation to reduce thermal cracking.
- Increased adhesion between the asphalt binder and the aggregate in the presence of moisture. This is achieved by an anti-stripping additive (0.5 percent by weight).

Polymer-Modified Bitumen

Polymer-modified bitumens are penetration-grade binders used in roads, airfields, and other high- stress applications such as road intersections with heavy traffic density and busy highways with heavy truck movement.

Examples of this type of polymers are as follows:

- Styrene-butadiene-styrene (SBS)
- Styrene-isoprene-styrene (SIS)
- Styrene-butadiene

INDUSTRIAL USES OF BITUMEN

- Roofing ,There are two basic types of bitumen roofs: a built up roof and a prepared roof.
- Built-Up Roofing.

STORAGE AND HANDLING OF BITUMEN

• Bitumen is stored and maintained at elevated temperature during production and transportation to the end user.

• When handled properly, bitumen can be reheated or maintained at elevated temperatures without any adverse effect on its properties.

Bitumen Storage Tank Heating Systems

• Direct-Fired Heating.

- In this method of heating, oil or gas is burned in a burner inside a tube and hot exhaust gases are circulated through a coil immersed in bitumen.

- Cooled exhaust gases are next vented to the atmosphere through a high stack.
- The heat input and temperature increase in tank is regulated by controlling the fuel input to the burner.
- this method suitable only for small bitumen tanks or for mobile bitumen tanks.

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PETROLEUM COKE

- Petroleum coke is a black carbonaceous solid material produced as a by-product of delayed coking or fluid coking units in refineries.
- There is a large world market for petroleum coke as fuel because of its
 - high calorific value,
 - low ash.
 - and discount pricing relative to coal.
- The largest single nonfuel use of petroleum coke is in the manufacture of
 - carbon anodes for the aluminum smelling industry which accounts for almost 80 percent of all petroleum coke produced.
 - Other important uses of petroleum coke are in the manufacture of graphite anodes for electric arc furnaces (used in steel plants, phosphoric acid, and calcium carbide manufacture) and in titanium dioxide (TiO,) manufacture. Each end use requires a different quality of petroleum coke.
 - Both physical and chemical characteristics of petroleum coke determine its suitability for a specific use.

Coking is a thermal cracking process used in refineries to maximize residuum conversion to distillates and thus minimize low-value fuel oil production.

- Petroleum coke is a by-product of coker units.
 - If the coke produced has high sulfur and metals, it is sold as fuel for power generation or cement plants.
 - If the by-product coke is of a low sulfur and low metal content, it can be further upgraded in value by the coke calcining process.

MANUFACTURING PROCESSES

- Raw petroleum coke is a by-product of coking units of refineries.
- There are two coking processes:
 - the fluid coking process and
 - the delayed coking process.

Due to their lower capital cost, most of the coker units built in refineries use the delayed coking process.

Also the properties of the coke produced in the fluid coker units are much inferior to that produced in delayed coker units

- For these reasons, most of the petroleum coke produced in the refineries is from delayed coker units.
- Coking is a noncatalylic thermal cracking process based on the concept of carbon rejection.
- The heaviest hydrogen-deficient portion of feed (asphaltenes, resins, etc.) are rejected as coke, which contain essentially all the feed metals and ash and a substantial portion of feed sulfur and nitrogen.

PETROLEUM COKE TYPES

Different physical forms of coke are produced in the delayed coker:

- Sponge coke
- Needle coke
- Shot cokeSponge Coke
 - Sponge coke is dull black with an amorphous appearance.
 - It is produced from vacuum resids of low to moderate asphaltene concentration.
 - Straight run vacuum residues tends to produce a large percentage of isotropic or amorphous cokes.
 - These are visibly very porous and are called "sponge coke."
 - Petroleum coke with a high sulfur and high metal content that is not suitable for anode making is used as a fuel in various applications and known as "fuel grade."
 - Its use is frequently limited by its high sulfur content, which restricts its use in power generation.

PROPERTIES OF CALCINED COKE

Density

- The real density (RD) of raw green coke, 1.3 to 1.4 g/cc, is measured on -200 mesh particles using a helium pyknometer.
- After calcinations, anode grade coke density increased from 2.05 to 2.08 g/cm3.
- Calcined needle coke for graphite electrodes can reach an RD of 2.13 g/cm3.

Electrical Resistivity

- The electrical resistivity of calcined coke decreases with increasing calcination temperatures.
- Petroleum coke actually changes from an insulating material to an electrical conductor upon calcination.

Mercury Apparent Density

- The Hg (mercury) apparent density (AD) is a measure of the porosity and density of calcined coke.
- Anisotropic needle-type coke produces a higher AD upon calcining than isotropic sponge coke or shot coke.
- Calcination above 2280°F decreases AD for all coke types with the exception of low-sulfur cokes.
- Low-sulfur coke decreases in AD only beyond 2460°F.
- AD decreases very rapidly in high- sulfur cokes with the onset of desulfurization.

Vibrated Bulk Density

- Vibrated bulk density (VBD) of calcined petroleum coke is of great importance for the aluminum industry.
- VBD is measured on screened particle fraction.

HardgroveGrindability Index

- The HGI (HardgroveGrindability Index) is a measure of the hardness of coke and can be measured on both raw/green coke and calcined coke.
- The property is most useful for green coke and is important for fuel-grade cokes that need to be crushed before burning in a power plant.

Air and Carbon Dioxide Reactivity

• Reactivities of calcined coke in air at two different heat-up rates and in carbon dioxide (C02) are determined to provide information as to how an anode will behave in a smelting pot.

Shot Coke Content

- Shot coke cannot be used for making anodes in the aluminum smelting industry.
- Shot coke balls are made of two layers of materials with different CTE values. These small balls (2 to 4 mm in diameter) fracture at the interface of the layers when calcined, due to the difference in their CTEs.

Screen Sizing

- Aluminum smelters require strict specifications on the amount of different size fractions of the calcined coke.
- To make carbon anodes, calcined coke is first screened in the calciner plant to separate out different size fractions.

Chemical Properties

- Volatile Matter.
- Volatile matter (VM) is a weight loss on heating of coke. The test is done on a 60-mesh sample.
- The coke is placed in a covered platinum crucible and heated to 1740°F at a controlled rate in a furnace.
- The weight loss of the sample as the percentage of feed is the volatile matter of the coke.
- Typically the VM of green coke is between 8.5 and 12.5 percent by weight.
- This is reduced to approximately 0.4 percent after calcining at 1650 to 1830°F.
- The VM of the raw coke is correlated with the VBD.
- Some VM is burned during calcinations, which accounts for some of the calcining yield loss.

- Hydrogen Content.
- Hydrogen content is determined by combustion in oxygen.
- This property provides a measure of the calcination of the product.
- During calcination, most of the hydrogen is evolved before a temperature of 1800°F is reached.
- Moisture and Ash.
 - Moisture is determined by oven drying.
 - Ash is determined by muffle furnace ashing of the coke sample.
 - Calcined coke must be dry to avoid problems with screening and the fabrication of carbon anodes.
 - The ash content of the calcined coke is in the range of 0.1 to 0.3 percent by weight.

Sulfur and Metals (V, Si, Fe, Ca. Na).

- In aluminum smelting, any excess metal in the coke migrates to the aluminum metal because coke is consumed during the process.
- Some grades of aluminum metal require very low values of certain metals depending on the end use of aluminum.
- Sulfur and some metals also affect the air and CO, reactivity of calcined coke.
- The concentration of metal in coke increases upon calcining due to the loss of volatile matter, sulfur, hydrogen, nitrogen, and moisture.

USES OF PETROLEUM COKE

Carbon Anodes

- Aluminum reduction cell in modem smelters use two types of carbon anodes.
- Carbon anodes must be dense, strong, electrically conductive, and of high carbon purity.
- Anode properties depend on the quality of the calcined petroleum coke and the pitch used for binding anodes.
- The uniformity of the coke is important to permit suitable anode fabrication.

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CARBON BLACK

- Carbon black products are direct descendants of earlier "lamp blacks," a black pigment produced and used by various civilizations to create rock paintings more than 3000 years ago.
- For a long time, black pigment was obtained by charring organic materials such as wood or bone or collecting soot from burning oils in wick lamps.
- These early blacks were not very pure and differed greatly in their chemical composition from present-day carbon blacks, which are almost pure carbon.

The main use of carbon black in

- the rubber industry is as a reinforcement and filler.
- The addition of carbon black to rubber improves the wear resistance of tires and other properties.
- The stability against UV radiation is also enhanced because black pigment hinders light.
- The content of carbon black is the reason why so many rubber products are black.
- Carbon black in rubbers and plastics not only makes the substance black, but it also make them UV stable and heat conducting: taking heat away from the tread and thus producing less static.
- Practically all rubber products where tensile and abrasion wear properties are important use carbon black as a reinforcing material. Rubber such as styrene butadiene rubber (SBR) may be blended with up to 50 percent by weight (wt %) of carbon black to improve its tensile strength and wear resistance.

MANUFACTURING PROCESSES

Today, a variety of processes are used to produce carbon black.

 Most processes involve partial combustion in a restricted supply of air or thermal decomposition of hydrocarbons such as oil or natural gas.

 The characteristics of carbon blacks produced vary, depending more on manufacturing process employed and less on feedstock.

- Therefore carbon blacks are classified by their manufacturing methods.

Major processes used to manufacture carbon blacks are as follows:

- Channel process
- Gas black process
- Thermal black process)
- Acetylene black process
- Lamp black process
- Furnace black process

Furnace black process

- is the most important one for the production of carbon black and allows production of nearly all types of carbon blacks required for rubber, plastics, paint, and pigment manufacture.

– Lamp and gas blacks are important alternatives to furnace blacks.

- These processes yield carbon blacks having properties that partially overlap with those obtainable from furnace black process

- The acetylene black process produces high-conductivity carbon blacks specifically for the dry cell industry.

CHANNEL BLACK PROCESS

- The channel process for carbon black manufacture uses natural gas as raw material.

 A large numbers of small flames fed by natural gas from ceramic burners impinge on the underside of a water-cooled steel channel, depositing a layer of carbon black that is periodically removed by scrapping devices.

- These iron channels, which moved slowly back and forth over the flames, have since lent their name to this manufacturing process.

 The deposited carbon black is scrapped off into a funnel-shaped trough and transferred by screw conveyers to storage silos.

- The yield of carbon black was only 5 percent.
- The channel process produced carbon black with a particle size of 10 to 30 nm.

- It was possible to vary carbon black particle size by altering the distance of the burner tip from the channel and changing the natural gas and air flow rates.

- The channel process produced several grades of fine carbon blacks that had maximum color and were fully reinforcing in rubber.

GAS BLACK PROCESS

- the gas black process uses vaporized oil instead of natural gas as a feedstock.
- Coal tar distillates arc the preferred feedstock.
- These oils arc heated in a vaporizer, and the resultant vapors arc carried by a hydrogen-rich gas to the burner.
- The hydrogen-rich gas is called producer gas (CO + H,).
- The flame is allowed to impinge on water-cooled rollers.
- Most of the carbon black formed is deposited on rollers, and the remainder is collected in filters.
- Both the streams arc combined and processed further into pellets for export.
- The process of charging carrier gas with vaporized oil provides a means of controlling particle size or specific surface area.
- Carbon black particle size is in the range of 10 to 30 nm.
- In this process, natural gas is thermally decomposed into carbon and hydrogen at elevated temperatures of 2500 to 3000°F in a cyclic operation.
- The reaction is conducted in a checker brick furnace.

- In the make cycle, natural gas feed is passed through the heated refractory brickwork in a furnace.
- Because the thermal black process is carried out at comparatively lower temperature and long residence times, thermal black differs from other carbon blacks:
- carbon black particles grow slowly to very large sizes: 200 to 500 nm.

ACETYLENE BLACK PROCESS

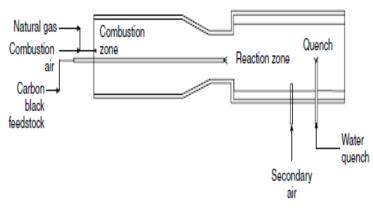
- Acetylene black is also used as an additive to antistatic and electrically conductive rubbers and plastic materials.
- Acetylene black is produced by the continuous thermal decomposition of acetylene gas in the absence of oxygen.
- The reactor is heated initially by burning acetylene to a temperature of 1112°F.
- The air flow is stopped when the required reactor temperature is reached while acetylene flow continues.
- Acetylene rapidly decomposes into carbon and hydrogen.

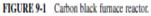
LAMP BLACK PROCESS

- Currently, lamp black is used as black pigment in printing inks, crayons, shoe polishes, carbon paper, ceramics, and cements.
- Lamp black is a deep black pigment consisting of amorphous carbon in a fine state of division.
- It is obtained by the imperfect combustion of highly carbonaceous substances such as resins, resinous wood, fatty oils and fats, paraffin oils, and coal tar oils are burned with an insufficient supply of air.
- A considerable part of carbon may be deposited in the form of soot.
- This soot, however, is not pure carbon but retains variable proportions of tarry products of imperfect combustion.
- Today, lamp blacks are prepared by the imperfect combustion of coal lar distillates.
- They are generally of large particle size (110 to 120 nm) and display a high degree of structure.
- Lamp black possesses little reinforcing ability in rubber.

FURNACE BLACK PROCESS

- Most carbon black production throughout the world is now from furnace black.
- The furnace black process allows for the production of nearly all the types of carbon blacks required for rubber, plastics, paints, inks, and so on.





CARBON BLACK PROPERTIES

The most important properties of carbon blacks are as follows:

- Particle size
- Structure
- Surface activity

These properties have a large effect on some important physical properties of carbon blacks for use in rubber, pigments, and plastics.

Particle Size

• The typical carbon black particle size ranges from 8 nm for furnace blacks to 300 nm for thermal blacks.

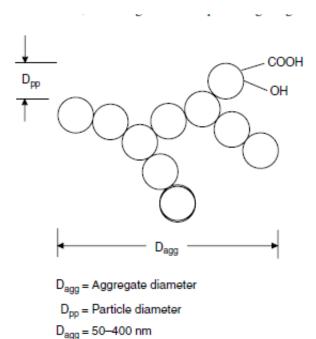
• In rubber processing, finer particles increase reinforcement and abrasion resistance and improve tensile strength.

• Surface area is used by the industry to define carbon black fineness.

Structures

- During the manufacture of carbon black, primary carbon particles fuse to form aggregates .
- The shape and degree of aggregate branching is referred to as structure.

- Increasing the structure typically increases the modulus, hardness, electrical conductivity, and compound viscosity.
- Generally, an increase in structure size improves dispersibility but lowers blackness.
- Carbon black with large structure shows excellent electric conductivity. DBPA absorption is a measure of structure, with a high number representing a higher structure.





Surface Activity

• All carbon blacks have chemisorbed oxygen complexes (carboxylic, quinonic. lactonic. or phenolic groups) on their surfaces to varying degrees depending on the condition of manufacture.

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• These surface groups are called volatile content and expressed as weight loss in percent after heating a dried sample of carbon black.

Porosity

- Porosity is the fundamental property of carbon black that can be controlled during the manufacturing process.
- Increasing the porosity reduces the density of the aggregate.
- This allows increased carbon black loading, which in turn leads to increased modulus and electrical conductivity for a fixed loading.

CARBON BLACK

APPLICATION AND USES

- Carbon black is the predominant reinforcing filler used in rubber compounds.
- A typical passenger car or truck tire may contain approximately 30 percent by weight carbon black.
- The improvement in rubber properties is a function of the physical and chemical properties of carbon black.
- The most important physical and chemical properties of carbon black that affect rubber properties are
 - aggregate size,
 - shape (structure),
 - particle size,
 - surface activity,
 - and porosity.
- The physical form of carbon black (beads or powder) can affect its handling and mixing characteristics and thus rubber properties.
- The ultimate degree of dispersion is also a function of the mixing procedure and equipment used.

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LUBE BASE STOCKS

- Lubricants are required in machines to reduce friction and wear between moving parts.
- Lubricant base stocks make up a large portion of finished lubricants, from about 75 to 80 percent in automotive engine oils to 90 percent or more in some industrial oils.
- Thus, base stocks contribute significantly to the finished product properties.
- Base stock has a major impact on the viscosity, volatility, low temperature fluidity, solvency for additives and contaminants.
- Petroleum lubricating base stocks are made of a higher boiling portion of crude oil that remains after the removal of lighter hydrocarbons.
- Starting material for their manufacture is usually atmospheric residue boiling above 650°F.
- Careful selection of a base stock is key to formulating a quality finished lubricant.
- Base stock properties are related to base stock composition.
- Base stocks contain three types of hydrocarbon: paraffins, naphthenes. and aromatics.
- In the paraffin group,
- isoparaffins are the preferred type because they exhibit excellent oxidation stability. low volatility, and good viscosity characteristics.
- Normal paraffins, however, are not a desirable component because of their poor cold flow properties such as pour point, cold filter plug point (CFPP).
- Aromatics are good for the solvency of additives and contaminants but generally have poor oxidation stability and high volatility.
- Naphthenes also have good low temperature fluidity and oxidation stability.
- Sulfur and nitrogen are often present in combination with hydrocarbons in a base stock, particularly the aromatics.

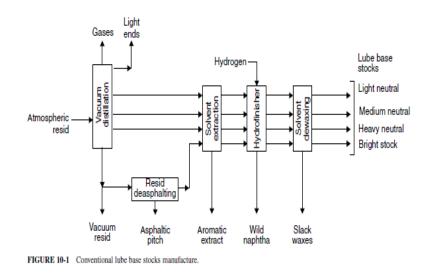
The manufacture of lube base stocks from crude oil involves a series of steps aimed at the removal of certain undesirable components resulting in a base oil that meets the performance requirements of lubricating oils.

- There are two basic routes for making lube base stocks:
- the conventional process, consisting of
- solvent extraction,
- solvent dewaxing, and
- hydrofinishing, and
- the hydroprocessing route, consisting of
- lube hydrocracking,
- hydrodewaxing, and
- deephydrotreating.
- The hydrotreating route produces higher viscosity index (VI) lubes with superior quality but cannot produce high-viscosity lube base stocks.

CONVENTIONAL PROCESS

The conventional lube base stock manufacturing process consists of the following steps:

- Vacuum distillation of atmospheric resid to yield several distillate cuts and vacuum resid
- Propane deasphalting of vacuum residuum to yield bright stock and asphaltic pitch
- Solvent extraction of vacuum distillates and bright stock to remove aromatics and improve the viscosity index of lubricating oil base stock
- Solvent dewaxing of distillate cuts to yield slack wax and various lube cuts, which improves the cold flow properties such as pour point and cloud point of the lube base stock
- Hydrofinishing or clay treatment to improve color, oxidation stability, and thermal stability of lubricating oils



CLASSIFICATION OF LUBRICATING OILS

Lubricating oils and greases can be classified in many ways;

- by viscosity grades,
- by their additives package, or
- by their producers' brand names.
- The most popular classification of lubes is according to their usage:
 - Engine oils (petrol and diesel engines, aircraft, marine engines)
 - Turbine oils
 - Gear oils
 - Compressor (refrigeration, air) oils
 - Quench oils used in metalworking
 - Cutting oils (in metal cutting)
 - Insulating oils used in transformer and circuit breakers
 - Hydraulic oils

• CLASSIFICATION BY VISCOSITY

Classification according to viscosity has been done by these professional societies and organizations:

- SAE (Society of Automotive Engineers. USA)
- API (American Petroleum Institute)
- AGMA (American Gear Manufacturers Association)
- NLGI (National Lubricating Grease Institute)

CLASSIFICATION BY ADDITIVE TYPES

Lube oils may be classified by additive type as follows:

- Inhibited or RO (rust and oxidation inhibitor containing additives)
- Anti-wear (AW) containing lube oils
- Lubes with extreme pressure (EP) additives
- Compounded oils: containing 3 to 10 percent fatty or synthetic fatty oils
- Residual compounds

AUTOMOTIVE ENGINE OILS

- Viscosity is considered the most important single property of lubricating oils.
- Automotive crankcase and gear oils used in gasoline and diesel engine lubrication.
- The viscosity classification takes into account the temperature at which the oils are to be used.
- The SAE viscosity rating was based on average time

SAE viscosity Temperature conditions grade for use, °F		Recommendations for use			
5W-30	<0	Provide excellent fuel economy and low-temperature performance.			
10W-30	>0	Most frequently recommended viscosity grade for most automobile engines, including high- performance multivalve engines and turbocharged engines.			
10W-40	<0	For greater protection against engine wear and oil breakdown from oxidation.			
20W-50	>20	Maximum protection for high-performance, high r/min racing engines.			
30	>40	For high temperatures and heavy loads, such as driving in the desert or towing a trailer at high speeds for long periods.			

TABLE 11-3 Optimum Motor Oil Grades

AUTOMOTIVE OIL ADDITIVES

- Viscosity index improvers
- Detergents
- Dispersants
- Anti-wear/Extreme pressure additives
- Friction modifiers
- Antioxidants/Corrosion inhibitors
- Rust and corrosion control additives
- Anti-foam agents

ENGINE OIL FORMULATION

- In an engine oil.
 - o the base oil components may be 75 to 85 percent of the total formulated lube,
 - o and the remaining 15 to 25 percent may be different types of additives.
- Viscosity modifiers and detergent inhibitors are the most prominent additives.
- Other additives used in lube formulation are dispersants. AW/EP agents, oxidation inhibitors, antifoamants. rust inhibitors, and demulsifiers.
- Base oils of a required viscosity are obtained by blending different base stocks such as neutrals and bright stocks.
- The additives are added to the base oil to enhance its performance when used in various types of engines.
- The most important properties of a lubricating oil are its viscosity and alkali reserve (base number, or BN).
- In addition, many other properties of the oil affect the performance of the engine.
- Fuel quality significantly affects the kind of lubricating oil to be used.
- For example, for a low-sulfur fuel such as natural gas.
 - o little sulfur dioxide is formed during combustion.
 - In this case a lubricating oil with a low BN. 4 to 7. may be OK.
- In case the fuel contains high sulfur. 0.5 to 5 percent,
 - o a higher alkali reserve is required to prevent corrosion damage.
- For fuels containing 2 percent or more sulfur,
- The high water content can be reduced by efficient centrifuging, which can extend the life of lubricating oil.

TABLE 11-6	Typical Properties of Commercial Motor O	ils
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	1	2	3	4	5
SAE grade 20W-50					
Viscosity index	122	119	155	121	130
Flash point, °F	440	419	430	432	450
Pour point, °F	-15	-13	-25	-11	-15
Sulfated ash, Wt %	0.85	0.7	0.9	0.74	1
Zinc, Wt %	0.12	0.11	0.15	0.12	0.15
SAE grade 15W-40					
Viscosity index	134	136	135	146	140
Flash point, °F	415	421	399	410	420
Pour point, °F	-15	-27	-11	-25	-10
Sulfated ash, Wt %	1.3	1	0.9	1	0.99
Zinc, Wt %	0.14		0.14	0.13	0.13
SAE grade 15W-30					
Viscosity index	140	150	133	155	130
Flash point, °F	415	401	400	405	410
Pour point, °F	-33	-26	-31	-35	-26
Sulfated ash, Wt %	0.85	0.96	0.85	1	1.2
Zinc, Wt %	0.12	0.11	0.13	0.15	0.2

TABLE 11-5 Commercial Lubricating Oil Characteristics

SAE viscosity grade		15W-40	10W-30
API service classification	Diesel	CH-4, CG-4, CF-4, CF-2, CF	CG-4, CF-4, CF
	Gasoline	SJ	SH
API gravity		27.9	28.9
Specific gravity		0.8877	0.8822
Flash point	°C	218	210
Pour point	°C	-33	-33
Viscosity at °C			
-15	cP	3000	
-20	cP		2840
-25	cP	25,000	
-30	cP		19,500
40	cSt	120.7	73
100	cSt	15.5	11.0
High-temperature/high-shear viscosity	cP, 150°C	4.4	3.4
Viscosity index		134	141
Zinc	Wt %	0.142	0.142
Nitrogen	Wt %	0.124	0.113
Sulfate ash	Wt %	1.4	1.4
TBN	mg KOH/g	12.2	11.8

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SYNTHETIC LUBRICANTS

• Synthetic lubricants were developed more than 50 years ago and became widely used in jet engines.

• Lower than $-120^{\circ}F$ operating temperatures, 60.000 r/min shaft speed, and $500^{\circ}F$ + exhaust temperatures proved too much for conventional lubes.

• Synthetic lubes were created specifically for these harsh operating conditions, and at present every jet engine in the world uses synthetic lubricants.

• A synthetic lubricant base stock is a product made from a chemical reaction of two or more simple chemical compounds.

• These base stocks are manufactured to meet specific physical and chemical characteristics not found in petroleum lubricant base stocks.

- This base stock is then used to formulate lubricants by the addition of performance additives.
- Some of the most common synthetic lubricants are as follows:
 - Polymerized alpha olefins, olefin polymers, olefin oligomers
 - Dibasic acid esters
 - Polyols esters
 - Polyalkaylene glycol ethers
 - Phosphate esters
 - Alkylated benzenes, a synthetic hydrocarbon
 - Silicons

• Their viscosity indexes and flash points are higher, however, and their pour points are considerably lower.

The following performance features are claimed for synthetic lubricants over mineral oil lubes:

- Engine cleanliness
- Improved fuel economy
- Lower oil consumption
- Good low temperature (cold starting) fluidity
 - Outstanding performance in extended oil drain intervals
 - Superior high-temperature oxidation resistance
 - Excellent wear protection

The main disadvantage of synthetics is that they are

- inherently more expensive than mineral oil and
- available in limited supply.
- This limits their use only to specialty oils and greases that command a premium price.
- Esters suffer the further disadvantage of

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TURBINE OILS

- Turbine oil is a high-quality circulating oil used in
 - steam turbines and
 - many other industrial applications.
- It is essentially a bearing lubricant, and as such it must be able to lubricate
 - the bearing/gears and
 - protect these machine parts against wear.
 - Also turbine oil acts as a heat transfer medium and keeps bearing temperatures below 150 to 180°F.
- The function of the turbine and the type of service dictates the viscosity of turbine oil.
- Turbine may be
 - a direct drive,
 - geared turbine,
 - or hydraulic turbine.
- Industrial and marine power generation turbines are generally horizontal turbines.
- Hydraulic (water) turbines are generally vertical units.
- Gas turbines, similar to aircraft turbines, are often used in naval or other high-speed vessels.
- In general, steam turbine oils generally meet the requirements of industrial gas turbine systems.
- The major difference between steam and gas turbine workings is
 - that in gas turbines, oil works in a dry atmosphere,
 - whereas in steam turbines, oil works in the presence of steam.
 - Higher temperatures are encountered in gas turbines.
- Typical oil temperature at full load may exceed 390°F.

- The viscosity of turbine oils ranges from
 - 20 to 450 cSt at I04°F
- Viscosity is largely determined by any associated transmission gearing, as in the case of steam turbines. Turbine oils protect critical system components from rust and corrosion.
- The oil must have good water separation characteristics to minimize the formation of emulsions.
- Turbine oils are formulated from
 - high-quality paraffinic base oils and
 - fortified with additives that provide oxidation resistance and minimize the formation of sludge and varnish deposits.
 - A foam inhibitor additive is generally included in the formulation to prevent excessive foam buildup, which interferes with lubrication.

BASE OILS

Turbine oils are formulated from highly refined paraffinic base oils with a high viscosity index (VI). the following advantages:

- Lesser antioxidant requirement
- Longer life
- Possible design and operation of machine at higher temperature
- Less carbon and varnish deposits
- Improved low-temperature fluidity
- More efficient water and foam separation

turbine oils must have more than 85 percent saturates, aromatics below 15 percent, and sulfur less than 0.4 percent by weight

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LUBRICATING GREASES

- Lithium soap greases were first introduced in the 1950s.
- Today, lithium soap greases are the most widely used greases.
- The primary function of a grease, like any other oil lubricant, is to reduce friction between moving metal surfaces such as those found in gears and bearings.
- Many applications are encountered where it is more practical and economical to lubricate the moving surface with grease rather than with lubricating oil.
- Because grease does not flow readily,
 - it is used where extended lubrication is required and
 - where oil would not be retained.
- Lubricating grease is preferable under extreme operating conditions, such as
 - high temperature,
 - extreme pressures,
 - low speeds,
 - shock loading and
 - bearings that operate intermittently or reversing.
- GREASE COMPOSITION

GREASE COMI OSITION

Grease consists of three main constituents:

- Base oil
- Thickening agent
- Performance additives

Grease consists of a thickening agent dispersed in a lubricating oil.

Performance-enhancing additives are added to impart such additional properties as

- antiaging,
- rust prevention,
- anti-wear,
- and extreme pressure resistance.

The lubricating oil may be petroleum based or synthetic oil.

The lubricating oil is commonly a mineral oil from paraffinic, naphthenic, or aromatic base crude oils.

Synthetic oils are usually used for grease formulation in extreme temperature conditions.

- Other components of grease include unreacted fat. fatty acids, alkali, unsaponifiable matter (including glycerol and fatly alcohols), rosin or wood grease, and water.
- Additives used in grease are antioxidants, rust and corrosion inhibitors, color stabilizers, water repellants and viscosity index improvers.

BASE OIL

- Lubricating oil is the largest component in a grease formulation: typically 80 to 95 percent of total grease mass.
 - The lubricating oil used in grease formulation may be a natural mineral oil or a synthetic oil such as diester oil. silicon oil. fluorocarbon oil.
 - For petroleum oils in general, naphthenic oils are a better choice than paraffinic oils because of their better solubility characteristics for metallic soaps and additives.
- The property of any grease is determined by the properties of the base oil.
- Greases with a low-viscosity base oil are best suited for low-temperature and high-speed applications, whereas greases made from a high-viscosity base oil are best suited for heavy loads.

GREASE THICKENERS

- The thickener may play as important a role as oil in lubrication. Thickener constitutes 5 to 20 percent of total grease mass.
- The thickener in grease may be
 - metallic soap,
 - clay, or
 - organic compounds.

ADDITIVES

- Additives may constitute 0 to 15 percent of the total grease mass. Additives used in lubricating greases are similar to those used in lubricating oils with a few exceptions.
- Various additives are added to greases to enhance the various properties desired in the finished grease.
- These are
 - antioxidants.
 - anti-wear,
 - and anticorrosion additives,
 - lackifiers. and dyes.

GREASE MANUFACTURE

- Grease can be made either in a batch or in a continuous process.
- The batch process is the most common manufacturing method.
- The first step involved in soap-based grease making is the saponification of fatty acid with an alkali to produce a metallic soap.
- This soap acts as a thickener for the grease.
- This step however is not required for making clay-based greases.

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WAXES

- The chemical composition of waxes is complex, but normal alkanes are always present in high proportions, and molecular weight profiles tend to be wide.
- The main commercial source of wax is crude oil, but not all crude oils when processed produce wax.
- Wax is also produced from lignite, plants, and animals.
- Even insects produce a material sold commercially as wax.

PARAFFIN WAXES

- The three general categories of petroleum waxes obtained from lube oil refining are
 - paraffin,
 - microcrystalline waxes,
 - and petrolatum.
- Paraffin waxes are derived from light lubricating oil distillate processing.
- Paraffin waxes contain predominantly straight chain hydrocarbons with an average chain length of 20 to 30 carbon atoms.
- Paraffin waxes are characterized by a clearly defined crystal structure and have the tendency to be hard and brittle.
- The melting point of paraffin wax falls between 120 and I60°F.
- Wax properties are determined by molecular weight, chemical composition, and oil content.
- Paraffin waxes have the following general properties:
 - Nonreactive
 - Nontoxic
 - Good water barrier
 - Clean burning fuel
 - Colorless

The properties of wax that can be measured and controlled are as follows:

- Melting point
- Hardness
- Oil content
- Viscosity
- Color
- Odor and taste
- However, these physical properties alone do not completely define the suitability of wax for a particular application.
- The important functional properties of wax are translucency or opaqueness, solid appearance (dry. waxy, mottled, or shiny), and flexibility.
- It is the combination of physical and functional properties that ultimately determines whether a particular wax is suitable for a given application.
- Fully refined paraffin waxes are hard, brittle, white, and odorless materials with less than 0.5 percent oil.
- They have good gloss properties and a melting point between 115 and 155°F.
- It is a softer material with a color varying between white and yellow.

PROPERTIES

- The properties of petroleum wax depend on its hydrocarbon composition and degree of refining.
- Some important properties of petroleum waxes are described next (Table 16-7).

Property		Paraffin wax	
Average mol wt		350-420	
Carbon atoms/molecule		20-36	
Flash point	COC, °F	399.2	
Melting point	°F	115-155	
Needle penetration	77°F	11-15	
Oil content	Wt %	0.5	
Refractive index	210°F	1.43-1.433	
Viscosity	cSt, @ 210°F	4.2-7.4	

TABLE 16-7	Typical	Properties	of	Paraffin	Waxes
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- Melting Point
 - The melting point is the temperature at which wax liquefies when heated or reverts back to a solid state when cooled. Paraffin waxes have a sharp melting point.
- Oil Content
 - The oil content of paraffin wax is reduced during the refining process. All petroleum waxes contain oil.
 - Oil in paraffin wax adversely affects the gloss, hardness, strength, and color.
- Taste, Odor, and Color
 - Taste, odor, and color depend on the degree of refining. Food-grade petroleum waxes are white with little or no odor or taste. The color of highly refined paraffin wax is reported as the Saybolt color.

TEST METHODS

- Melting Point
 - Selection of a proper melting point method depends on the characteristics of the wax. Open or closed capillary tubes are used to measure the melting point of many natural waxes.
- Oil Content
 - The production of petroleum wax involves the removal of oil. The oil content of wax is thus an indication of the quality of the wax.
- Viscosity
- Viscosity is an important test for mineral and synthetic waxes. ASTM D 88 is used to measure the time in seconds required for a specified quantity of wax at a specified temperature to flow by gravity through an orifice of specified dimensions. This viscosity is expressed in Saybolt Universal Seconds (SUS).
- Acid Number
 - Acid number (ASTM D 1386) is the milligrams of potassium hydroxide necessary to neutralize 1 g of wax. It indicates the free carboxylic acid present. The test is widely used for vegetable, insect wax. and synthetic waxes containing carboxylic acid groups.

- Saponification Number
 - The saponification number (ASTM D 1387) is the milligrams of potassium hydroxide that react with 1 g of wax at an elevated temperature and indicates the amount of free carboxylic acid plus any ester materials that may be saponified. Both acid number and saponification number are generally provided to give an indication of the free carboxylic acid and ester content of vegetable and insect waxes and synthetic waxes containing carboxylic acids and/or esters.

Wax Applications

- Waxes are used as a feedstock for many products and for a wide range of applications:
 - candle making,
 - coatings
 - foods
 - cosmetics
 - adhesives
 - inks
 - casting
 - crayons
 - polishes
 - chewing gums.