

CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1 Chlorinated paraffins

2.1.1 Introduction [2,10]

Chlorinated paraffins are the collective name given to industrial products prepared by chlorination of C_{10} - C_{30} paraffins and containing 20-70 % chlorine. Chlorinated paraffins with the general molecular formula $C_xH_{(2x-y+2)}Cl_y$ have been manufactured on a commercial basis for over 50 years. The early products were based on paraffin wax feedstocks and were used as fire retardants and plasticizers in surface coatings and textile treatments and as extreme pressure antiwear additive in lubricants. The development of chlorinated paraffins into new and emerging technologies was constrained principally because of the limitations of grades based on paraffin wax and the lack of suitable alternative feedstocks to meet the demands of the new potential markets.

In the early 1960s the petroleum industry employing molecular sieve technology made available a low cost and plentiful supply of normal paraffin fractions of very high purity. This enabled chlorinated paraffin manufacturers to exploit new applications with a range of products specifically designed to meet the technical and commercial requirements.

The principal feedstocks used today are the normal paraffin fractions C_{10} - C_{13} , C_{12} - C_{14} , C_{14} - C_{17} and C_{18} - C_{20} together with paraffin wax fractions of C_{24} - C_{30} , precise compositions may vary depending on petroleum oil source. Chlorination extent generally varies from 30 to 70 % by weight. The choice of paraffinic feedstock and chlorine content is dependent on the application.

2.1.2 Manufacture [2]

Chlorinated paraffins are manufactured by passing pure chlorine gas into a liquid paraffin at a temperature at which the viscosity of the paraffin is sufficiently low to permit free evolution of the hydrogen chloride and solution of the chlorine, and at which decomposition of the chlorinated paraffin is not extensive. Chlorine feed rates and reaction temperature differ slightly among the different producers. Temperatures are usually kept between 80 and 100 °C. At these temperatures chlorination occurs exothermically and cooling is necessary to maintain the temperature at around 100 °C. Elevated temperatures must be avoided to prevent violent reactions, which may cause dark or black products.

Visible light is especially effective in initiating the reaction at relatively low temperatures. Later on, when the reaction has started, the light source may be reduced in intensity or eliminated. The presence of such chlorination catalysts as metal chlorides can promote decomposition of the chlorinated paraffins with subsequent darkening of the product. The reaction is terminated by stopping the flow of chloride when desired degree of chlorination has been achieved. This is estimated by density, viscosity, or refractive index measurements. The reaction is then purged with air or nitrogen to remove excess chloride and hydrochloric acid gas. Small quantities of a

storage stabilizer, typically epoxidized vegetable oil, may be mixed in at this stage or later in a blending vessel. Manufacture of resinous chlorinated paraffins (70 %chlorine content) requires the use of a solvent during the chlorination step. Additional steps of solvent stripping and grinding the product are necessary.

Both batch and continuous processes are known for the preparation of chlorinated paraffins on an industrial scale. Batch processes are preferred, however, because of the large variety of special products synthesized. An apparatus for preparation of chlorinated paraffins in laboratory is shown in figure 2.1 and a typical system employed in commercial production is shown in the figure 2.2

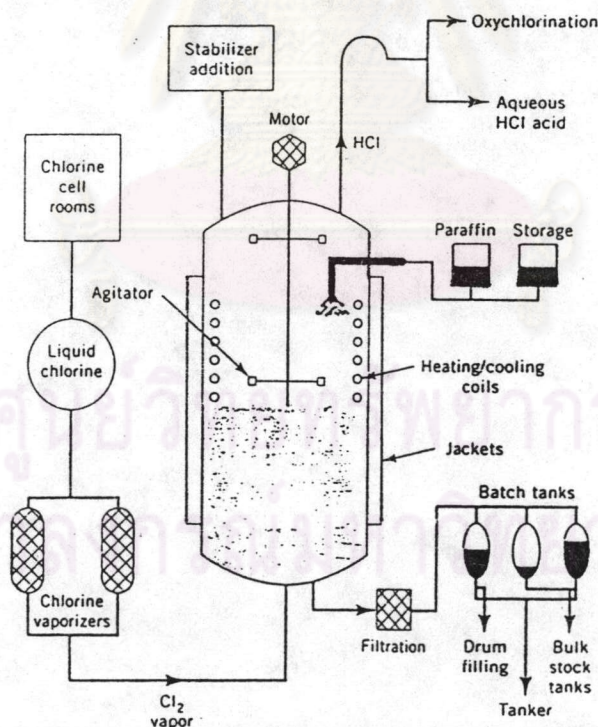


Figure. 2.1 Chlorinated paraffins preparation in laboratory

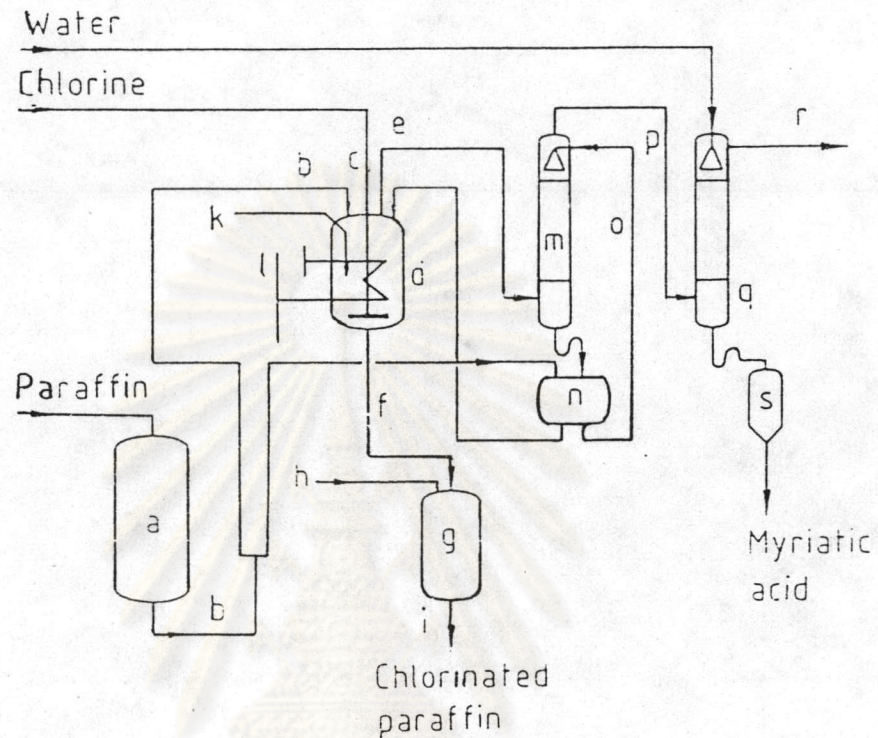


Figure 2.2 The commercial production of chlorinated paraffins

- a) Paraffin tank ; b) Paraffin input ; c) Chlorine input ; d) Reactor
- e) Effluent gas ; f) Chlorinated paraffins, unstabilized outlet ;
- g) Addition of stabilizing agents ; h) stabilizing input ;
- i) Chlorinated paraffins, stabilized, outlet, k) Light sources ;
- l) Cooling and heating circuit ; m) Chlorine removal from effluent gas n) Partially chlorinated paraffins ; o) Paraffin circuit ;
- p) Effluent gas, chlorine free outlet ; q) Absorption of hydrogen chloride ; r) Inert gas, outlet ; s) Activated charcoal

In general terms for each ton of chlorinated paraffins produced, approximately one-half ton of hydrochloric acid is generated. Thus materials of construction must be resistant to acid attack. Reactor vessels were traditionally lined with lead or ceramics but glass-lined mild steel is now preferred. Ancillary equipment such as stirrers, pumps, valves and pipelines should be of corrosion and acid resistant material. Good housekeeping is vital as minute traces of metal chlorides entering the process can cause dehydrochlorination leading to discoloration of the chlorinated paraffins.

In order to operate an economically viable chlorinated paraffin business, it is essential to have a profitable outlet for the surplus hydrochloric acid, either through direct sales into the market, or preferably via an oxychlorination unit in an integrated vinyl chloride/chlorinated solvent unit, while still maintaining the option of direct sales.

2.1.3 Research Works

The first systematic study on chlorinated paraffins were made by P.A. Bolly [3] in 1856-1858. Because of the increase in viscosity with chlorine content, Bolly was unable to prepare chlorinated paraffins containing more than 61% chlorine. In 1910, Bohringer patented a process for chlorinating the higher paraffins in carbon tetrachloride thus overcoming the difficulty experienced by Bolly. Knowledge of the chemical nature of the lower chlorinated paraffins was advanced by the work of Asinger in 1942 and of the effect of manufacturing conditions on the properties of chlorinated paraffins by the researches of Girelli and Siniramed in 1949 [4].

Girelli and Siniramed studied the effect of chlorine flow rate and temperature on the yields and properties of the chlorinated paraffins, found that, with a paraffin of mp 48 °C and average molecular weight 370, a maximum rate of chlorine absorption was reached at 100 °C, and that the color of the product became darker with increasing temperature. They conclude from their experiment that the optimum chlorine flow rate and temperature for the particular paraffin they were using 28 liters Cl₂/(hr)(kg paraffin) and 80 °C, respectively. Variation of these two conditions, using the same paraffinic material, resulted in the products of different color and viscosity. Color and viscosity are also affected by variation of mixing and heat transfer conditions during chlorination.

In some chlorinated paraffins production processes, a solvent is used, eg, carbon tetrachloride and hexachlorobutadiene. Chlorination has been carried out with the solvent under reflux. Several patented variants of the chlorination process use different temperatures for progressive stage of chlorination. A Diamond Alkali Co. [5] produced liquid chlorinated paraffins by contacting a molten paraffinic substance with chlorine, which comprised the steps of contacting a molten body of said substance with gaseous chlorine at a chlorination temperature of below about 90 °C, maintaining this temperature until up to about 33 % of the desired chlorination has been obtained, and continuing chlorination at a temperature below 100 °C, until the desired amount of chlorine has reacted. By the process of this study, it is found that liquid chlorinated paraffins can be prepared possessing improved uniform light color characteristics and good heat stability.

Imhausen Werke [11] produced solid chlorinated paraffins from a mixture of high molecular paraffin hydrocarbons containing more than 20 carbon atoms. He found that it was advantage to add inorganic and/or organic nitrogen compounds such as ammonium chloride, urea or amines, before and/or during chlorination, in order to prevent the product from darkening.

In Japanese process [6], chlorination is begun at 70 °C and progressively raised to 150 °C, over a period of 24 hrs. This latter process employs calcium oleate or benzoate as a catalyst. The use of normal pentane to extract a 60 % chlorine content paraffin from the crude chlorination product has been described, with the pentane being subsequently removed from the extracted product by a stream of air at 40 °C or in vacuo.

2.1.4 Physical and Chemical Properties

By virtue of the nature of the paraffinic feedstocks readily available, commercial chlorinated paraffins are mixtures rather than single substances. The degree of chlorination is a matter of judgement by the manufacturers on the basis of their perception of market requirements; as a result, chlorine contents may vary from one manufacturer to another. However, customers purchasing requirements often demand equivalent products from different suppliers and hence similar products are widely available.

The physical and chemical properties of chlorinated paraffins are determined by the carbon chain length of the paraffin and the chlorine content. This is most readily seen with respect to viscosity and volatility as shown in figure 2.3 and 2.4, respectively.

The chlorinated paraffins are homogeneous, neutral, colorless or pale yellow liquids. Color, however, is not a constant characteristic; although most of the commercial products are in the yellow range, the precise color density and tint is dependent on manufacturing and subsequent storage conditions. The color of most of the chlorinated paraffin is permanently increased upon prolonged heating, because of the action of the liberated hydrogen chloride.

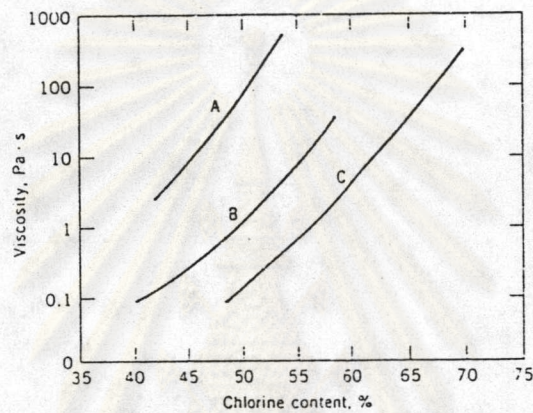


Figure 2.3 Viscosity of chlorinated paraffins at 25 °C.*

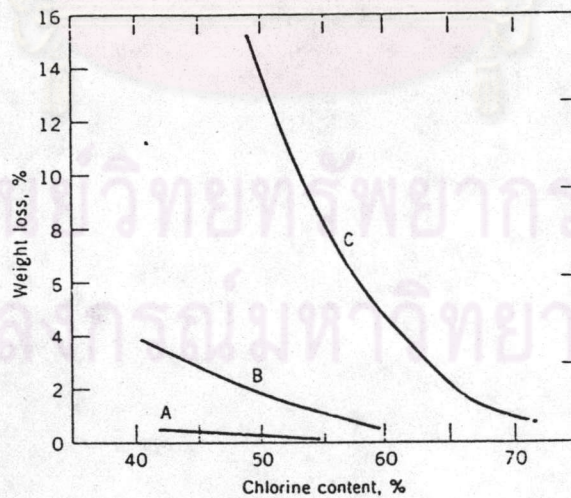


Figure 2.4 Volatility of chlorinated paraffins at 180 °C after four hours*

*Paraffin feedstock : A, wax ; B, C₁₄-C₁₇ ; C, C₁₀-C₁₃

Chlorinated paraffins vary in their physical form from free flowing mobile liquids to highly viscous glassy materials. Physical properties of some commercially available chlorinated paraffins are listed in table. 2.1.

Paraffin carbon chain length	Chlorine contents %w/w	Viscosity mPa.s (=cP)	Density g/ml	Refractive index
C10 - C13	50	80	1.19	1.493
	56	800	1.30	1.508
	60	3500	1.36	1.516
	65	30,000	1.44	1.525
	70	800	1.50	1.537
C14 - C17	40	70	1.10	1.488
	45	200	1.16	1.498
	52	1600	1.25	1.508
	58	40,000	1.36	1.522
C18 - C20	47	1700	1.21	1.506
	50	18,000	1.27	1.512
Wax (C>20)	42	2500	1.16	1.506
	48	28,000	1.26	1.516
	70	-	1.63	-

Table 2.1 Physical properties of selected commercial chlorinated paraffins

A key properties associated with chlorinated paraffins, particularly the high chlorine grades, is nonflammability, which has led to their use as fire retardant additives and plasticizers in a wide range of polymeric materials. The fire retardant properties are considerably enhanced by the inclusion of antimony trioxide.

None of the chlorinated paraffins are soluble in water or the lower alcohols. Most of them readily form emulsions with water in the presence of a suitable emulsifying agent. Those with chlorine contents greater than about 40 % are soluble in mineral and lubricating oils, benzene, the industrial chlorinated solvent, ether, ketones, esters, cyclohexanol, castor oil and linseed oil. They are compatible with natural rubber, chlorinated rubber, synthetic rubber, polyester resins and many alkyd resins as well as with such common plasticizing compounds as dioctyl or dibutyl phthalate and tricresyl phosphate.

Chlorinated paraffins are relatively inert and exhibit excellent resistance to chemical attack and hydrolytically stable. Although, considered to possess good thermal stability, chlorinated paraffins, if held at high temperatures for prolonged periods, first darken in color and then release detectable quantities of hydrochloric acid. Manufacturers often quote a thermal stability index which is a measure of the quantity of hydrochloric acid released expressed as a percentage by weight after heating the product for four hours at 175 °C. Degradation of chlorinated paraffins can also be accelerated at elevated temperatures in the presence of iron, zinc and dehydrochlorination catalysts. The thermal stability of chlorinated paraffins can be improved by the inclusion of epoxidized compounds which typically are epoxy esters, antioxidants of the hindered phenol-type and metal soaps.

2.1.5 Applications

Chlorinated paraffins are versatile materials and are used in widely differing applications.

2.1.5.1 Direct utilizations

(1) Plasticizers in PVC

Various types of chlorinated paraffins have been widely used as secondary plasticizers in the production of PVC. The best combination of good plasticizing effects, sufficient compatibility, and suitable viscosity is obtained with products containing about 50 % chlorine and based on C₁₄-C₁₇ paraffins. By raising the chlorine content, compatibility and viscosity can be increased, but the plasticizing effect decreases.

By selection of those chlorinated paraffins specifically developed for the PVC industry to match the properties of primary plasticizers, reduction in cost can be achieved without significant change in properties. However, certain aspects can be improved by the inclusion of chlorinated paraffins such as flame resistance, chemical and water resistance, low temperature performance and the viscosity aging stability in plastisols.

(2) Flame Retardants in Rubbers, Textiles, and Plastics

Certain type of chlorinated paraffins have been widely studied as potentially efficacious flame inhibiting additives. This is particularly true of C₁₀-C₁₃ paraffins so treated as to have a chlorine content as high as 70-71 %. Such materials are especially effective when combined with antimony or

phosphorus containing synergists. The solid 70 % chlorine product is the preferred choice in most polymeric systems, but the liquid grades are widely used in rubbers, polyurethane and textile treatments.

(3) Metal-Working Lubricants

A range of chlorinated paraffins are used as components of straight and emulsifiable metal-working lubricants as well as gear oils for industrial and automotive applications. In heavy-duty industrial gears, hypoid gears, metal cutting and allied operations where high pressures and rubbing action are encountered, hydrodynamic lubrication cannot be maintained. In order to maintain lubrication under such conditions, extreme pressure or antiwear additives must be added to the lubricant. Such additives contain one or more of the elements of chlorine, sulfur or phosphorus. Chlorinated paraffins are cost-effective extreme pressure additives and are either used alone or in combination with additives containing sulfur and/or phosphorus according to the application. High chlorine content lubricants are used for severe metal-forming operations such as deep drawing and stamping. The selection of chlorinated paraffin and the level of additives to a lubricating oil depends on the type of application and the severity of the operation.

(4) Paints and Varnishes

Chlorinated paraffins have become widely used components in the formulation of special varnishes and paints, including road marking paints, outdoor paints and marine paints. Important characteristics include desirable plasticizing effects, resistance to hydrolysis, inflammability, resistance to most chemicals, low volatility and outstanding compatibility with typical resins.

Additives have also been reported which increase the resistance of varnishes containing chlorinated paraffins to the effects of ultraviolet light.

(5) Water-Repellent and Rot-Prevention Agent

Chlorinated paraffins having a chlorine content of 60-70 % have been shown to be suitable water-repellent and rot-preventing impregnants for textiles, especially those intended for use as sailcloths, tarpaulins and tents. Appropriate emulsified products or mixtures containing organic solvents are available.

(6) Adhesives and Sealants

Various grades of chlorinated paraffins are used as nonvolatile inert fire retardant plasticizers and modifying resins in adhesives and sealants. They find wide application in polysulfide, polyurethane, acrylic and butyl sealants for use in building and construction. The low volatility high chlorine types are also employed in sealants for double- and triple-glazed windows.

(7) Carbonless Copies

Chlorinated paraffins and modified types are used as solvents in carbonless copying paper production based on the encapsulation of a solution of reactive dyes. Chlorinated paraffins fulfill the technical requirements for a solvent including excellent solvency for the dyes; they do not react with the dyes nor encapsulation material, are miscible with water, and have low volatility and low odor.

2.1.5.2 Conversion to other products [1]

(1) Semi-synthetic Lubricants

Valuable semi-synthetic lubricants, especially motor lubricating oils and machine oils, can be obtained from chlorinated paraffins. In general, chlorinated paraffins can be converted into a synthetic lubricating material in two way.

1. Chlorinated paraffins can be caused to react with aromatic hydrocarbons such as toluene, xylene, etc., with anhydrous aluminum chloride in a Friedel- Crafts alkylation process, one or more alkyl groups entering the aromatic nucleus according to the process conditions.

2. Chlorinated paraffins are converted directly to lubricating materials by self-condensation by means of anhydrous aluminum chloride.

These methods for the manufacture of synthetic lubricating oils are necessary to follow with hydrogenating the aromatic or unsaturation using nickle, platinum or palladium on alumina as a catalyst. The viscosity-temperature behavior will be improved.

(2) Detergents and Textile Auxiliaries

There are two routes leading to synthetic detergents and textile auxiliaries. The reaction of the chlorination products of the higher paraffins with phenol to give alkylphenols and their conversion by oxyethylation to alkylphenol polyglycol ethers. These products are soluble in water and exhibit

outstanding surface-active and detergent properties because of the long alkyl residue.

Another suitable method for the preparation of water-soluble materials with long alkyl residues and, therefore, useful detergent properties, readily and with good yields, consists in alkylating aromatic hydrocarbons with products of the direct chlorination of higher paraffinic hydrocarbons or the petroleum fractions boiling in the corresponding temperature range by means of aluminum chloride in a Friedel-Crafts reaction. The resulting compounds become soluble in water after subsequent sulphonation of the aromatic nucleus.

(3) Further Possible Conversions

Further possibilities of converting the chlorination products of higher paraffinic hydrocarbons into valuable raw materials and auxiliaries by chemical reactions consist in the partial replacement of chlorine by hydroxyl, amino, alkoxyl and mercapto groups, etc. Here considerable quantities of olefins are also produced so that, taking the paraffin unconverted during chlorination into consideration, a very complex mixture of different materials is produced. These mixtures can be used successfully in the textile and leather industries.

In chlorinated paraffins containing four or more chlorine atoms, by gentle treatment with alkali only part of the chlorine present in the starting material may be replaced by hydroxyl groups and the rest of the chlorine can then be exchanged with other functional groups. This procedure yields products in the form of more or less viscous, faintly colored oils which find application, because of their special properties, either directly as lubricating and greasing agents or as important and essential constituents of emulsions in the textile and leather industries.

The treatment of chlorinated paraffins with alcoholic caustic soda gives mixtures of alcohols, olefins and ethers with unchanged chlorinated and non-chlorinated paraffin which are very suitable as leather greases.

By treating highly chlorinated paraffins with alcoholic ammonia in an autoclave at 150°C or with sodium hydrogen sulphide, compounds containing nitrogen or sulfur are obtained which are either substantially free from chlorine or contain the residual chlorine in a very stable form (vinyl chloride) and can be used for a very wide range of technical purposes.

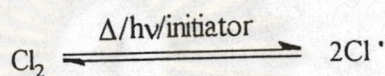
2.2 Reactions and Mechanisms [12]

2.2.1 Substitution Chlorination.[12]

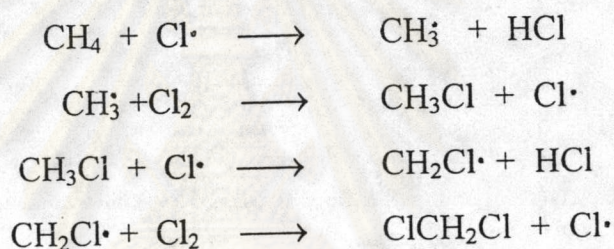
The substitution of chlorine for hydrogen atoms in a hydrocarbon is an important commercial chlorination process. Chlorine free radicals used for the substitution reaction are obtained by either thermal, photochemical, or chemical means. The thermal method requires temperatures of at least 250°C to initiate decomposition of the diatomic chlorine molecules into chlorine radicals. The large reaction exotherm demands close temperature control by cooling or dilution, although adiabatic reactors with an appropriate diluent are commonly used in industrial processes. Thermal chlorination is inexpensive and less sensitive to inhibition than the photochemical process. Mercury arc lamps are the usual source of ultraviolet light for photochemical processes furnishing wavelengths from 300-500 nm.

Chemical initiation generates organic radicals, usually by decomposition of azo or peroxide compounds, to form radicals which then react with chlorine to initiate the radical-chain chlorination reaction. The reaction proceeds by a radical-chain mechanism, as shown in equation 1 through 8.

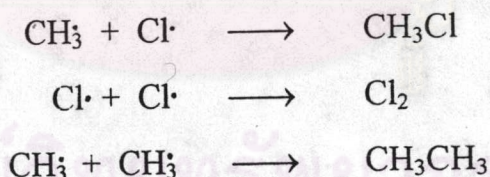
Chain initiation



Chain propagation



Chain termination

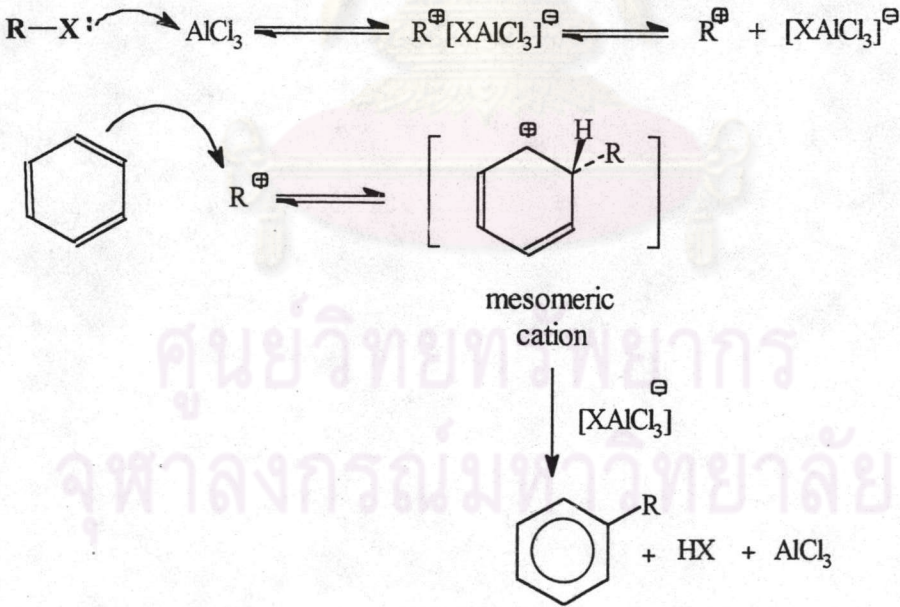


Chlorine atoms obtained from the association of chlorine molecules by thermal, photochemical or chemically initiated processes react with methane molecule to form hydrogen chloride and a methyl free radical. The methyl radical reacts with an undissociated chlorine molecule to give methyl chloride and a new chlorine radical necessary to continue the reaction. Other more highly chlorinated products are formed in a similar manner. Chain termination may proceed by way of several of the examples cited in equations 6, 7, and 8.

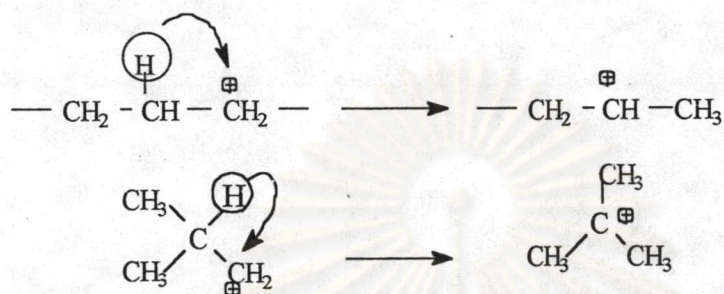
The initial radical producing catalytic process is inhibited by oxygen to an extent that only a few ppm of oxygen can drastically decrease the reaction rate. In some commercial processes, small amounts of air are deliberately added to inhibit chlorination beyond the monochloro stage.

2.2.2 Friedel-Crafts Alkylation [13,14]

An alkyl halide reacts with an aromatic hydrocarbon in the presence of lewis acid catalysts such as a aluminum chloride (AlCl₃) or ferric chloride (FeCl₃), alkyl halide was found to alkylate aromatic. The mechanism of the reaction is generally considered to proceed by way of carbocations which attack the aromatic nucleus :



In many cases the alkyl group may undergo extensive skeletal rearrangement under the reaction conditions employed, to form a more stable secondary or tertiary carbocation.



The chlorination products of the paraffinic hydrocarbons take part readily and smoothly in the Friedel-Crafts reaction with aromatic hydrocarbons and in the dehydrochlorination reaction to form olefins. The first reaction can take place in two ways, both of which lead to the desired product, so that such reactions are always successful. On the one hand, a normal Friedel-Crafts reaction can take place, in which the alkyl halide behaves in the usual manner. On the other hand, dehydrochlorination can take place with the formation of an olefin. However, in the presence of hydrogen chloride and anhydrous aluminum chloride the olefin also alkylates the aromatic hydrocarbon very smoothly. The conversion of the saturated aliphatic hydrocarbons through the chlorination products into well-defined materials by double decomposition is, under present conditions, only applied to those molecular sizes for which pure monochlorides can easily be prepared. The difference in the boiling point of the initial hydrocarbon and monochloride must be as possible. This method is used even in those cases where, in the further processing chlorides, the olefin arising in considerable amounts as unavoidable by-products can easily be separated and used in a technically valuable manner. This type of olefin formation can then be considered as chlorinating dehydrogenation.

2.2.3 Hydrogenation [15]

The hydrogenation of petroleum and its fractions comprises a wide assortment of reactions involving all the components present in the complex mixture. The hydrogenation reactions shown in figure 2.5 are typical of those undergo by hydrocarbon components of straight run or cracked in some commercial applications.

The extent of any specific reaction varies over a wide range depending on the time, temperature, and hydrogen pressure utilized. Potentially, given the proper catalytic environment, hydrogen will react in some manner with each of the hydrocarbon constituents of petroleum at almost any temperature and pressure. Normally, for commercial operation, temperature is limited to a mixture of about 532 °C and pressure to a maximum of about 10,000 psig.

2.3 Crude oil

2.3.1 Appearance and Composition [16-19]

Crude oil is an extremely complex mixture of organic chemicals ranging in size from simple gaseous molecules, such as methane, to very high molecular weight asphaltic components. In fact, its composition can vary not only with the location and age of the oil field but also with the depth of the individual well. Common colors are green, brown and black and occasionally almost white or straw color. Specific gravity can range from 0.73 to 1.02. Viscosity varies widely, from about 0.7 centipoise to more than 42,000 centipoise.

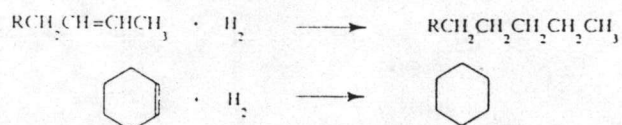
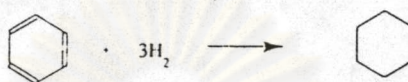
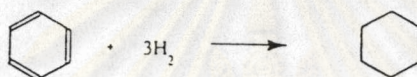
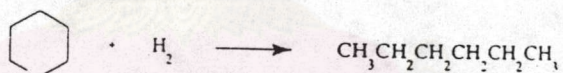
Saturation Olefinic bonds*Saturation* Aromatic bonds*Saturation* : Aromatic bonds*Hydrocracking* Dealkylation*Hydrocracking* : Ring open*Hydroisomerization* : Paraffins and naphthenes

Figure 2.5 Typical hydrogenation reactions

The composition of crude oil can be classified into a few broad categories.

2.3.1.1 Hydrocarbons

Hydrocarbons predominate in all crude oils and can be further subdivided into:

- Alkanes (Paraffinic hydrocarbons) These have saturated linear or branched chain structures. Their stability to oxidation or chemical change is very good.

- Alkenes (Olefinic hydrocarbons) These are unsaturated molecules , but they are comparatively rare in crude oil. Certain refining processes , however , do produce large amounts of alkanes by cracking or dehydrogenation.

- Alicyclics (Naphthenic hydrocarbons) These are saturated cyclic structures base on five- and six-membered rings. They are extremely stable compounds.

- Aromatics These are cyclic structures with conjugated double bonds , based on the six- membered benzene ring.

Example of these types are shown in figure 2.6

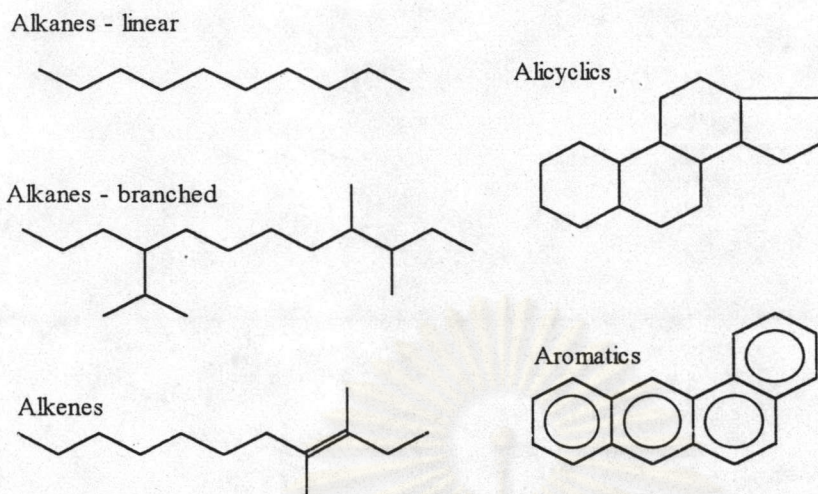


Figure 2.6 Example of hydrocarbons

2.3.1.2 Non-hydrocarbons

Crude oil also contains varying amounts of compounds of sulfur, nitrogen, oxygen, varying metals such as vanadium, nickel, water and salts. All of these materials can cause problems in refining or in subsequent product applications. Their reduction or removal increases refining cost appreciably.

2.3.2 Types of crude oil

Crude oil is commonly classified according to the residue from their distillation, this depending on their relative contents of three basic hydrocarbons : paraffins, naphthenes and aromatics. About 85 % of all crude oils fall into the following three classifications :

(1) Asphalt-base, containing very little paraffin wax and a residue primarily asphaltic (predominantly condensed aromatics). Sulfur, oxygen, and nitrogen contents are often relatively high. Light and intermediate fractions

have high percentages of naphthenes. These crude oils are particularly suitable for making high quality gasoline, machine lubricating oils and asphalt.

(2) Paraffin-base, containing little or no asphaltic materials, are good sources of paraffin wax, quality motor lube oils, and high grade kerosine. they usually have lower nonhydrocarbon content than do the asphalt-base crudes.

(3) Mixed-base, containing considerable amounts of both wax and asphalt. virtually all products can be obtained, although at lower yields than from the other two classes.

Because of the variations in hydrocarbon fractions in different crude oils, there are several differences in general properties, as indicated in table 2.2

Property	Paraffin base	Asphalt base
API gravity	High	Low
Naphtha content	High	Low
Naphtha octane number	Low	High
Naphtha odor	Sweet	Sour
Kerosine smoking tendency	Low	High
Diese-fuel knocking tendency	Low	High
Lube oil pour point	High	Low
Lube oil content	High	Low
Lube oil viscosity index	High	Low

Table 2.2 General properties of crude oils

2.3.3 Refining [19]

A petroleum refinery is an organized and coordinated arrangement of manufacturing processes designed to provide both physical and chemical change of crude petroleum into salable products with the qualities required and in the volumes demanded by the market. The crude distillation unit is shown in figure 2.7

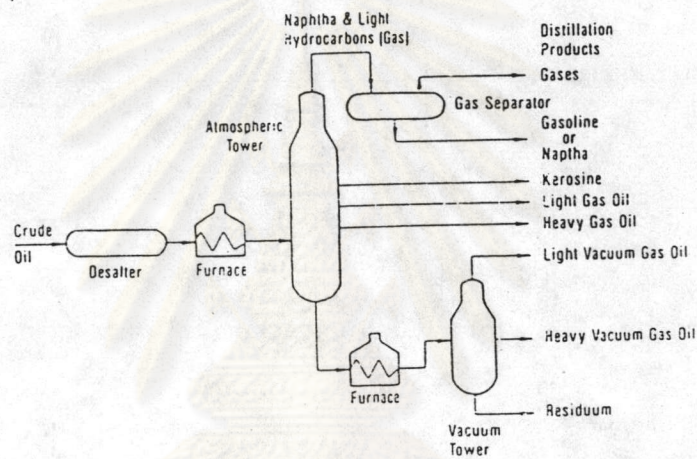


Figure 2.7 Crude oil distillation unit

The first step in the refinery of petroleum is usually a desalting operation to remove inorganic salt suspended as minute crystals or dissolved in entrained water. These salts break down during processing to form acids that severely corrode refinery equipment, plug heat exchanger and other equipment, and poison catalysts used in subsequent processes. Therefore, the crude is mixed with additional water to dissolve the salts and the resultant brine is removed by settling.

After desalting, the crude is pumped through a tubular furnace where it is heated and partially vaporized. The refinery usually consists of connected lengths of pipe heated externally by gas or oil burners. The mixture of hot liquid and vapor from the furnace enters a fractionating column. This is a device that operates at a slightly above atmospheric pressure and separates groups of hydrocarbon according to their boiling ranges. The fractionating column works because there is a graduation in temperature from bottom to top so that, as the vapors rise toward the cooler upper portion, the higher boiling components condense first. As the vapor stream moves up the column, lower boiling vapors are progressively condensed. Trays are inserted at various levels. Naphtha, an industry term for raw gasoline that requires further processing, and light hydrocarbons are carried over the top of the column as vapor and are condensed to liquid by cooling. Kerosine, diesel fuel, home heating fuels, and heavy oils (called gas oils) are withdrawn as side cuts from the successively lower and hotter levels of the tower.

A heavy black, atmospheric residuum is drawn from the bottom of the column. Because the tendency of residuum to decompose at temperatures about $371\text{ }^{\circ}\text{C}$ (700°F), heavier (higher boiling) oils such as lubricating oils must be distilled off in a separate vacuum fractionating tower. The greatly reduced pressure in the tower markedly lowers the boiling points of the desired hydrocarbons compounds. Bottom materials from the vacuum tower are for asphalt, or are further processed to make other products. The fraction separated by crude distillation are sometimes referred to as " straight run " products. The character of their hydrocarbon constituents is not changed by distillation.

2.3.4 Fang Oil Refinery [8,9]

Fang oil refinery, located at Fang district in Chaing Mai, has been in operation under the supervision of the Defence Energy Department (DED), Ministry of Defence. All of crude supplies come from the nearby Fang basin area. The refined products from Fang are mainly supplied to the military, government agencies and state enterprises operating under the Ministry of Defence. Part of the production is distributed to local consumers who have long been customers of the refinery.

Up to 1500 barrels of local crude oil can be refined at Fang Oil Refinery per day. The refinery products are consisting of

- straight run oil	6 %
- diesel	26 %
- light distillate	17 %
- heavy distillate	14 %
- heavy fuel oil	37 %

The process consists of several operation units including topping distillation unit, vacuum distillation unit, gasoline trading unit, gasoline blending unit, power unit and facilities unit.

Once crude oil from Mae Soon Huang is shipped to Fang Oil Refinery, the water will be separated in the separation unit where treat-o-lite is used as a demulsifier. After that, the crude is pumped through preheat exchanger and its temperature raise to about 120 °C by exchanging with hot oil from vacuum tower. It is then further heated to 340 °C in atmospheric heating and charged to atmospheric fractionators. The liquid withdrawn from this tower will contain straight run oil, kerosine and diesel. Reduced crude from the

bottom of the atmospheric tower is sent to vacuum heater and its temperature raise to 350 °C and is then charged to a vacuum tower where it is separated into light distillate, heavy distillate, and heavy fuel oil.

2.4 Lubricating Base Oil

2.4.1 Sources [18-24]

There are essential two sources from which the base lubricant fluids are obtained. These are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties which are suitable for lubricant purposes.

Different crude oil contain different proportions of these classes of organic components and they also vary in the boiling range distribution of their components. The main factors affecting crude selection for manufacture of base oils are :

- Content of material of suitable boiling range for lubricant
- Yield of base oil after manufacturing processes
- Base oil product properties , physical and chemical

Crude oil assay data will reveal the potential content of lubricant boiling material. The manufacturing process at a base oil refinery consists of a series of steps to separate the desirable lube components from the bulk of the crude oil. Their briefly aims are as follows :

Distillation This step removes both the components of too low boiling point and too high boiling point, leaving the lubricantboiling range distillates.

Aromatics removing This step leaves an oil that is high in saturated hydrocarbons and improves VI and stability.

Dewaxing This step removes wax and controls the low temperature properties of the base oil.

Finishing This step removes traces of polar components and improves the color and stability of the oil

The yield of base oil after the application of these processes depends on the amount of desirable components in the lube boiling range. Lube distillates made from different crudes can have radically different properties.

2.4.2 Composition

The petroleum fraction used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating base oil fraction is complex mixtures consisting of paraffinic, cycloparaffinic (naphthenic) and aromatic compounds, together with heterocyclic compounds containing sulfur and nitrogen atoms (e.g. of thionaphthene, of indole, of quinoline and carbazoles) and various oxygen compounds including naphthenic acids which account for most of the chemically bond oxygen in petroleum fractions.

The molecules in the lubricating base oil fraction consists essentially of one long carbon atom chain to one or both ends of which a ring system or short branch may be attached. Monocycloalkanes and monoaromatics usually have several short (e.g. methyl) branches on the ring. Most of the compounds are paraffin-naphthenes with cycloparaffinic ring attached to paraffinic chain. Aromatic compounds usually have cycloparaffinic ring attach to them along with long paraffinic chains. Polyaromatics usually have all their rings in a single condensed nucleus which also might have short branches attached.

Polycyclic saturates may have all the rings in a single condensed system or two or more ring system may be separated by alkyl chains. Aromatic compounds may also be in form of biphenyls and their derivatives. Thus the lubricating base oil is composed primarily of five characteristics classes :

- paraffin naphthenes
- condensed naphthenes
- aromatic naphthenes
- naphthalenes
- multiring aromatics

2.4.3 Properties

2.4.3.1 Physical properties

Specific gravity

Specific gravity is the ratio of the mass of a volume of the substance at the standard temperature to the mass of the same volume of water at the same temperature. The standard temperature for specific gravity is 15.6/15.6 °C (60/60 °F). In the petroleum industry the API gravity scale is almost universally used as the measure of the density of a petroleum product. API gravity is an arbitrary scale calibrated in degree and related to specific gravity by

$$\text{API gravity (degree)} = \frac{141.5}{\text{sp. gr. } 15.6/15.6 \text{ } ^\circ\text{C}} - 131.5$$

The API gravity value increases as the specific gravity decreases. Since both density and gravity change with temperature, determinations are

made at a controlled temperature and then corrected to a standard temperature by using special table.

Viscosity

Viscosity is the most significant property of a lubricating oil. It is generally the most important controlling property for manufacture and for selection to meet a particular application.

Viscosity is a measure of resistance to flow. It decreases with increasing temperature and increases with large increasing temperature. There are two measures of viscosity : kinematic and absolute , kinematic viscosity is the more common and is measured by the time for an oil at a specified temperature to flow through a capillary tube. Test temperature are usually 40 and 100 °C for centistokes unit.

Viscosity index

The viscosity index is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increased, all lubricating oils film thin out or have lower viscosity. Likewise, oils become thicker or more viscous as the temperature reduces. The higher the viscosity index, the smaller its change in viscosity for a given change in temperature. The viscosity index of an oil is calculated from viscosities determined at two temperatures by means of tables polished by ASTM. Table based on viscosities determined at both 100 and 212 °F , and 40 and 100 °C are suitable.

Pour point

Most oil contains some dissolved wax and, as an oil is chilled, this wax begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets in the structure. When this wax crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test.

The pour point is the lowest temperature at which the oil will just flow under specified test condition and is roughly equivalent to the tendency of an oil to cease flowing from a gravity-fed system or container. Since the size and shape of the containers, the head of oil, and the physical structure of the solidified oil all influence the tendency of the oil to flow, the pour point of the oil is, and not an exact measure of, the temperature at which flow ceases under the service conditions of a specific system. The importance of the pour point is limited to applications where low temperature are likely to influence oil flow.

Color

The color of lubricating oil is normally no indication of its lubricating properties. It is, however, a guide to the presence of contaminants or to the degree of deterioration in storage. It is also an indication of the intensity of refining. Color varies from partially clear or transparent to opaque or black. It is measured in a standard glass container by comparing the color of the transmitted light with that transmitted by a series of numbered glass standard, and the best match noted. The test is used for manufacturing control purposes, and is important since the color is readily observed by the customer.

Flash point

The flash point test gives an indication of the presence of volatile components in an oil and is the temperature to which the oil must be heated under specified test conditions to give off sufficient vapor to form a flammable mixture with air.

Normally, these test are used to determine the storage and operating temperatures and the type of storage that will produce the possibility of a fire. Flash point is also useful in evaluating used oils. A drop in flash point indicates contamination by dilution of motor oils with unburned fuel. An increase indicates evaporation of the oil. These tests of lubricating oils are determined by the open-cup method, usually call Cleveland Open Cup and abbreviated COC.

2.4.3.2 Chemical properties

Oxidation stability [25]

Degradation of lubricants by oxidative mechanisms is potentially a very serious problem. Although the formulated lubricant may have many desirable properties when new, oxidation can lead to adramatic loss of performance in service by reactions such as :

- corrosion due to formation of organic acids
- formation of polymers leading to sludge and resins
- viscosity change
- loss of electrical resistivity

Resistance to oxidation is important in the performance of a lubricant. A variety of different stability tests has been devised to measure resistance to oxidation under different conditions which correlate with different service uses of lubricants.

The sulfur content of base oils is often regarded as a useful indicator of natural oxidation resistance. This is because many naturally occurring organosulfur compounds in crude oil are moderately effective in destroying organic peroxide intermediates and breaking the oxidation chain mechanism. However, the effectiveness of these natural inhibitors is usually rather inferior to synthesised additives which can be much more specific in their action.

The thermogravimetric balance (TG) is the one of the recent technique developed to evaluate thermal behavior of different chemical compounds. Its useful in evaluating the effect of temperature on the weight loss of the compounds. Applying the procedure to the different chemical structure base oils has been taken into consideration.

Loss in weight for most of the tested samples was found to be negligible up to the temperature of 300 °C. Higher than 300 °C, the sample weight begins a rapid and continuous loss. Such a weight loss is typical to what occurs in tested samples in the absence of oxygen, i.e. due to thermal decomposition only. But, in the presence of oxygen, a reaction of decompose sample with oxygen is observed at temperature around 350 °C or higher which leads to retard decreaseing in weight loss. These temperatures can be named oxidation points. At higher temperatures than these oxidation points, weight loss was rapid and continuous again until the completed resin remains nearly constant with further increase in temperature. The oxidation points can be used as an indication for base oil thermooxidation stability.

Oxidative compounds can be defined as the weight of oxygenated compounds in milligrams which remains the pan of balance at the oxidation point. Higher than that point, the oxidative compounds start to carbonize and finally evaporate completely as CO_2 .

2.4.4 Properties and Structure Relationship [26]

Hydrocarbon structures are relative to the performance of lubricating oil. Paraffins, naphthenes, and aromatics of the same molecular weight have markedly different physical and chemical characteristics. Physical characteristics will affect the viscometrics of the lubricant, and the chemical stability of each class to oxidation and degradation while in use is also very important. The properties of some typical hydrocarbon structures are shown in table 2.3.

Paraffins have relatively low density and viscosity for their molecular weight and boiling point. They have good viscosity/temperature characteristics (i.e. they show relatively little change in viscosity with change in temperature) compared to cyclic hydrocarbons. However, there are significant differences between isomers as the degree of branching of the paraffin chain increases.

The straight chain paraffins in the lubricant boiling range have good viscosity/temperature characteristics but their high melting point causes them to crystallize out of solution as wax. In contrast, highly branched paraffins are not waxy but have less good viscosity/temperature characteristics. There is a compromise region in which acceptable viscosity index and acceptable low temperature properties are achieved simultaneously.



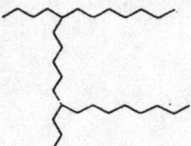
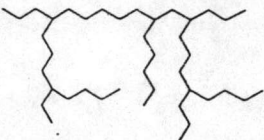
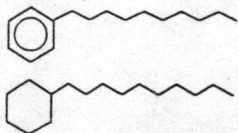
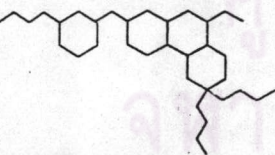
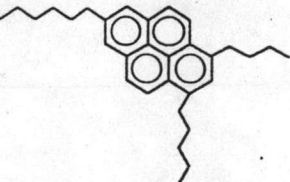
Structures	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin 	Very high	High	Good	Nil
Isoparaffin with linear chain 	High	Medium	Good	Medium
Isoparaffin with isomerized chains 	High	Low	Good	High
Highly substituted isoparaffin 	Medium	Low	Good	Medium
Single ring with long aliphatic chain 	High	Low	Good	High
Polycondensed naphthenes 	Low	Low	Medium	Nil
Polycondensed aromatics 	Very low (< 0)	Low	Weak	Nil

Table 2.3 Lubricating oil properties of some typical hydrocarbon structure

In general, paraffins also have good viscosity/pressure characteristics, are reasonable resistant to oxidation and have particularly good response to oxidation inhibitors.

Naphthenic paraffins have rather higher density and viscosity for their molecular weight compared to the paraffins. An advantage which naphthene have over the paraffins is that they tend to have low melting points and so do not contribute to wax. However, one disadvantage is that naphthenes have inferior viscosity/temperature characteristics. Single ring naphthenes with long alkyl side chains, however, share many properties with branched paraffins and can in fact be highly-desirable components for lubricant base oils. Naphthenes tend to have better solvency power for additives than pure paraffins but their stability to oxidative processes is inferior.

Aromatics have densities and viscosities which are still higher. Viscosity/temperature characteristics are in general rather poor but melting points are low. Although they have the best solvency power of additives, their stability to oxidation is poor. As for naphthenes, single ring aromatics with long side chains (alkylbenzene) may have very desirable base oil components.

2.4.5 The Basic Function of Lubricant

The reduction of friction

Simple stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, there by preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of a lubricating oil is its viscosity. It is factor in the formation of lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumption. It determines that machine may be started under varying temperature conditions , particularly at cold temperature. For any given piece of equipment satisfactory results are obtained only with the use of and oil of proper viscosity under the operated condition.

The basic concept of viscosity is shown in figure 2.8 where a plate is being drawn at uniform speed over a film of oil. The oil adheres to both the moving surface and the stationary surface. Oil in contact with the moving surface travels at the same velocity (U) as that on surface, while oil at contact with the stationary surface is at zero velocity.

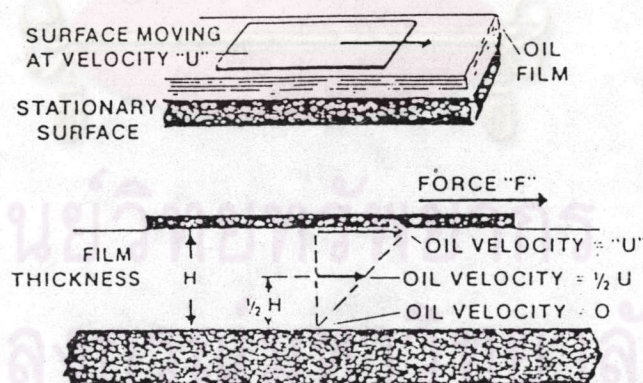


Figure 2.8 Concept of dynamic viscosity

In between, the oil film may be visualized as made up of many layers, each being drawn by the layer above it at a fraction of velocity "U" that is proportional to its distance above the stationary plate (Figure 2.9 - Lower view). A force (F) must be applied to the moving plate to overcome the friction between the fluid layers. Since the friction is the result of viscosity, the force is proportional to viscosity.

Heat removal

Another important function of a lubricant is to act as a coolant, removing heat generated either by friction or other sources such as via combustion process or transfer by contacting with substances at a higher temperature. In performing this function, it is important that the lubricant remain in a relatively unchanged condition. Changes in thermal and oxidation stability which affect its ability to reach the areas involved will materially decrease its efficiency in this respect.

Containment of Contaminants

The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. Among these contaminants are water, acidic combustion products, particulate matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.