

Lubricating Oil Additives

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1. Introduction

1.1 Lubrication (Rizvi, 2009)

The principle of supporting a sliding load on a friction reducing film is known as lubrication (Ludema, 1996). The substance of which the film is composed is a lubricant, and to apply it is to lubricate. These are not new concepts, nor, in their essence, particularly involved ones. Farmers lubricated the axles of their ox carts with animal fat centuries ago. But modern machinery has become many times more complicated since the days of the ox cart, and the demands placed upon the lubricant have become proportionally more exacting. Though the basic principle still prevails the prevention of metal-to-metal contact by means of an intervening layer of fluid or fluid-like material.

1.2 Lubricants (Rizvi, 2009; Ludema, 1996; and Leslie, 2003)

All liquids will provide lubrication of a sort, but some do it a great deal better than others. The difference between one lubricating material and another is often the difference between successful operation of a machine and failure.

Modern equipment must be lubricated in order to prolong its lifetime. A lubricant performs a number of critical functions. These include lubrication, cooling, cleaning and suspending, and protecting metal surfaces against corrosive damage. Lubricant comprises a base fluid and an additive package. The primary function of the base fluid is to lubricate and act as a carrier of additives. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. The examples of already-existing properties include viscosity, viscosity index, pour point, and oxidation resistance. The examples of new properties include cleaning and suspending ability, antiwear performance, and corrosion control.

Engine oil at the dawn of the automotive era was not highly specialized or standardized, and exceedingly frequent oil changes were required.

Engine oil lubricants make up nearly one half of the lubricant market and therefore attract a lot of interest. The principal function of the engine oil lubricant is to extend the life of moving parts operating under many different conditions of speed, temperature, and pressure. At low temperatures the lubricant is expected to flow sufficiently in order that moving parts are not starved of oil. At higher temperatures they are expected to keep the

moving parts apart to minimize wear. The lubricant does this by reducing friction and removing heat from moving parts. Contaminants pose an additional problem, as they accumulate in the engine during operation. The contaminants may be wear debris, sludges, soot particles, acids, or peroxides. An important function of the lubricant is to prevent these contaminants from doing any damage.

The lube oil base stock is the building block with respect to which appropriate additives are selected and properly blended to achieve a delicate balance in performance characteristics of the finished lubricant. Various base stock manufacturing processes can all produce base stocks with the necessary characteristics to formulate finished lubricants with the desirable performance levels. The key to achieving the highest levels of performance in finished lubricants is in the understanding of the interactions of base stocks and additives and matching those to requirements of machinery and operating conditions to which they can be subjected.

1.3 Additives

Additives, (Rizvi, 2009, Ludema, 1996, and Leslie, 2003), are chemical compounds added to lubricating oils to impart specific properties to the finished oils. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life. Additives, in improving the performance characteristics of lubricating oils, have aided significantly in the development of improved prime movers and industrial machinery.

Modern passenger car engines, automatic transmissions, hypoid gears, railroad and marine diesel engines, high speed gas and steam turbines, and industrial processing machinery, as well as many other types of equipment, would have been greatly retarded in their development were it not for additives and the performance benefits they provide.

Additives for lubricating oils were used first during the 1920s, and their use has since increased tremendously. Today, practically all types of lubricating oil contain at least one additive, and some oils contain additives of several different types. The amount of additive used varies from a few hundredths of a percent to 30% or more.

Over a period of many years, oil additives were identified that solved a variety of engine problems: corrosion inhibition, ability to keep particles such as soot dispersed, ability to prohibit acidic combustion products from plating out as varnish on engine surfaces, and ability to minimize wear by laying down a chemical film on heavily loaded surfaces. In addition, engine oil became specialized so that requirements for diesel engine oils began to diverge from requirements for gasoline engines, since enhanced dispersive capability was needed to keep soot from clumping in the oil of diesel engines.

The more commonly used additives are discussed in the following sections. Although some are multifunctional, as in the case of certain viscosity index improvers that also function as pour point depressants or dispersants or antiwear agents that also function as oxidation inhibitors, they are discussed in terms of their primary function only.

1.3.1 Friction Modifiers (FM) (Ludema, 1996)

These are additives that usually reduce friction (Battez et al., 2010 & Mel'nikov, 1997). The mechanism of their performance is similar to that of the rust and corrosion inhibitors in that they form durable low resistance lubricant films via adsorption on surfaces and via association with the oil, Figure (1.1).

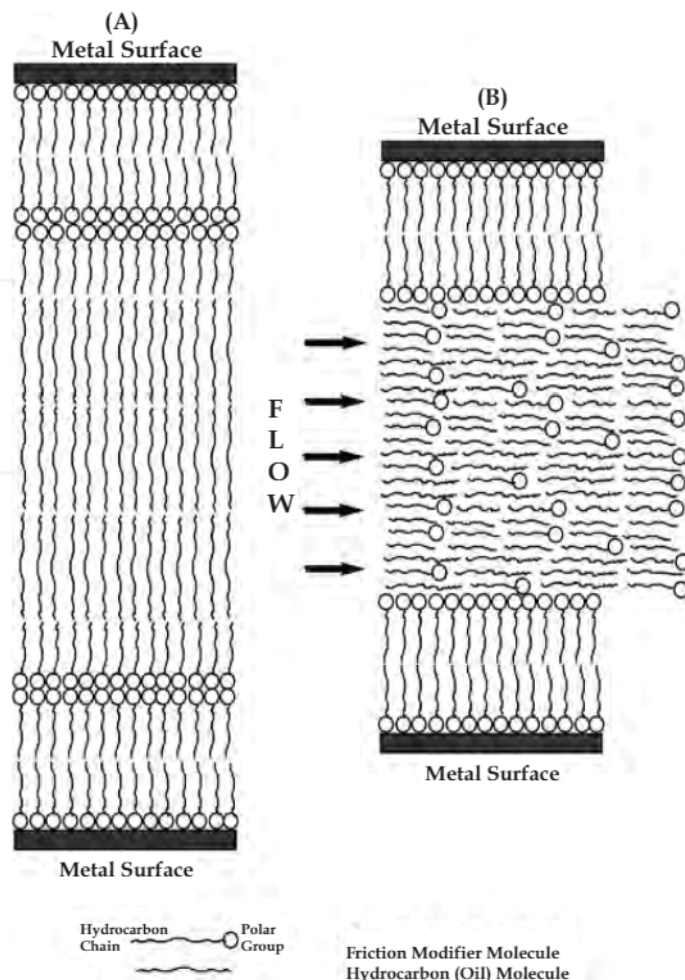


Fig. 1.1 Adsorption of friction modifiers on metal (A) Steady state (B) Under shear

Common materials that are used for this purpose include long-chain fatty acids, their derivatives, and the molybdenum compounds. In addition to reducing friction, the friction modifiers also reduce wear, especially at low temperatures where the anti-wear agents are inactive, and they improve fuel efficiency.

1.3.2 Anti-wear agents (A.W.) and extreme-pressure (E.P.) additives

Anti-wear (AW) (Rizvi, 2009, Ludema, 1996, Leslie, 2003, and Masabumi, 2008), agents have a lower activation temperature than the extreme-pressure (EP) agents. The latter are also referred to as anti-seize and anti-scuffing additives. Organosulfur and organo-phosphorus compounds, Figure (1.2), such as organic polysulfides, phosphates, dithiophosphates, and dithiocarbamates are the most commonly used AW and EP, Rizvi, 2009, Ludema, 1996, Leslie, 2003, agents.

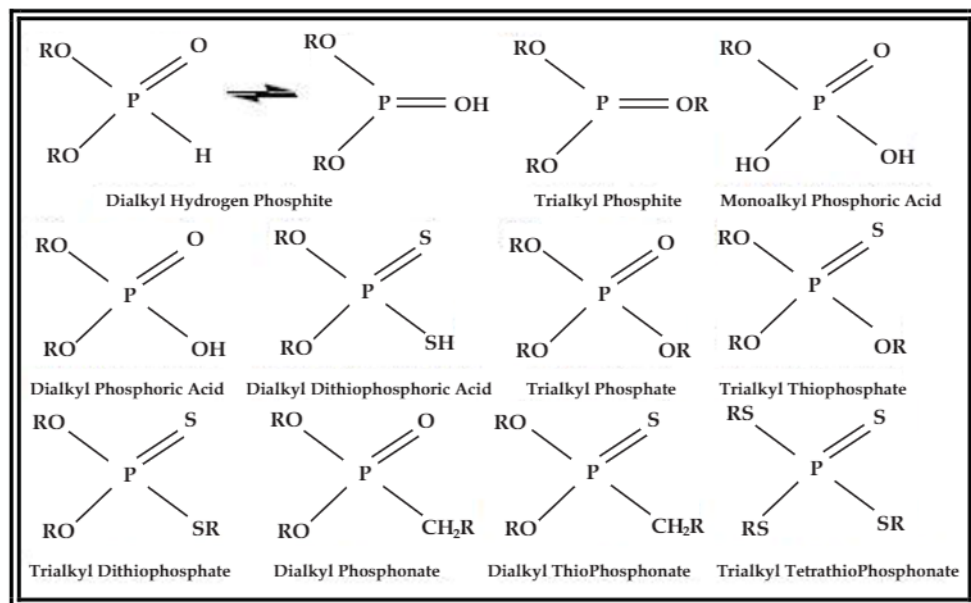
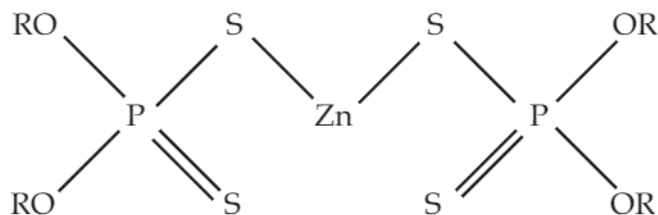


Fig. 1.2 Common phosphorus derivatives used as antiwear agents / extreme-pressure

As the power of engines has risen, the need for additives to prevent wear has become more important. Initially engines were lightly loaded and could withstand the loading on the bearings and valve train. Corrosive protection of bearing metals was one of the early requirements for engine oils. Fortunately, the additives used to protect bearings usually had mild antiwear properties. These antiwear agents were compounds such as lead salts of long-chain carboxylic acids and were often used in combination with sulfur-containing materials. Oil-soluble sulfur-phosphorous and chlorinated compounds also worked well as antiwear agents. However, the most important advance in antiwear chemistry was made during the 1930s and 1940s with the discovery of zinc dialkyldithiophosphates (ZDDP) (Masabumi, et. al., 2008). These compounds were initially used to prevent bearing corrosion but were later found to have exceptional antioxidant and antiwear properties. The antioxidant mechanism of the ZDDP was the key to its ability to reduce bearing corrosion. Since the ZDDP suppresses the formation of peroxides, it prevents the corrosion of Cu/Pb bearings by organic acids. Antiwear and extreme-pressure additives function by thermally decomposing to yield compounds that react with the metal surface. These surface-active compounds form a thin layer that preferentially shears under boundary lubrication conditions.

After the discovery of ZDDP, Figure (1.3) it rapidly became the most widespread antiwear additive used in lubricants. As a result, many interesting studies have been undertaken on ZDDP with many mechanisms proposed for the antiwear and antioxidant action (Masabumi, et. al., 2008).

Extreme pressure additives form extremely durable protective films by thermo-chemically reacting with the metal surfaces. This film can withstand extreme temperatures and mechanical pressures and minimizes direct contact between surfaces, thereby protecting them from scoring and seizing.



The R group may be alkyl or aryl

Fig. 1.3 Zinc dithiophosphate as antiwear additives / extreme pressure

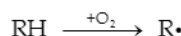
1.3.3 Antioxidant additives (AO)

One of the most important aspects of lubricating oils is that the oxidation stability be maximized. Exposure of hydrocarbons to oxygen and heat will accelerate the oxidation process. The internal combustion engine is an excellent chemical reactor for catalyzing the process of oxidation. Also, the engine's metal parts, such as copper and iron, act as effective oxidation catalysts. Thus, engine oils are probably more susceptible to oxidation than any other lubricant application.

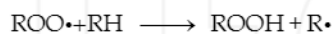
Oxidation mechanism of lubricating oils

The lubricating oils consist of hydrocarbons with ($C_{20} - C_{70}$) carbon atoms. At higher temperature these hydrocarbons are oxidized to form fatty acids, fatty alcohols, fatty aldehydes and ketones, fatty esters and fatty peroxides as shown in the following mechanism, Figure (1.4). All these compounds form the solid asphaltic materials. For this reason, the addition of antioxidants is necessary to all lubricating oils to prevent the formation of such compounds.

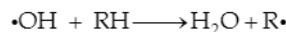
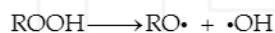
Initiation



Chain propagation



Chain branching



Termination



Fig. 1.4 Oxidation mechanism of lubricating oils

Inhibition effects of antioxidants on lubricating oil oxidations

It is known that high temperature, high pressure, high friction, and high metal concentration in motors, lead to oxidation of lubricating oil it is necessary to improve oil stabilities against oxidation. Oxidation generally increase oil viscosity and results in formation of the following compounds:

- Resins, which are oxygen-containing compounds, soluble in oil and can, lead to lacquer formation.
- Lacquers, slightly colored, relatively plastic, and can form deposits on various engine parts (particularly on piston skirts).
- Insoluble asphaltic compounds, when associated in the oil with combustion residues and condensed water from sludge.
- Acidic compounds and hydroperoxides, which may promote corrosion, particularly of hard alloy bearings.

Thus, addition of antioxidant additives to lubricating oils prevents the formation of all resins, lacquers and acidic compounds.

There is no relationship between the two rates of increasing the viscosity and acidity in the oxidation process. The rate of viscosity increased in direct proportion with the rate of decomposition of an organic peroxides. By studying the antioxidant additives mechanism in turbine aviation oils; it was shown that these antioxidants reacted with oxygenic free radical compounds to form the antioxidant N - oxide derivatives and thus decrease the quantity acids, alcohols, esters in the media. However, any lubricating oil exposed to air and heat will eventually oxidize. Antioxidants are the key additive that protects the lubricant from oxidative degradation, allowing the fluid to meet the demanding requirements for use in engines and industrial applications.

Antioxidant additives mechanism

To define the oxidation stability for lubricating oils, it is necessary to check the rate of acidity and viscosity increase with oxidation time during the oxidation process. Lubricating oils are susceptible to degradation by oxygen. The oil oxidation (Rizvi, 2009, Ludema, 1996, and Leslie, 2003) process is the major cause of oil thickening. This manifests itself as sludge and varnish formation on engine parts, leading to increased engine wear, poor lubrication, and reduced fuel economy. Antioxidants are essential additives incorporated into lubricant formulations to minimize and delay the onset of lubricant oxidative degradation.

The rate of acidity and viscosity was increased (in the oxidation process for oils) due to the continuous repetition of the oxidation process, where a chain reaction occurs. The oxidation process can be considered to progress in the following manner:



Decomposition of the hydroperoxide molecule caused by the so-called branching reaction leads to the formation of oxygen bearing compounds. Their oxidation products form high - molecular - weight -oil -insoluble polymers that settle as deposit causing an increase of oil viscosity. Decomposition of the hydroperoxide as follow:



During oxidation process, in a median period oil viscosity is increased although its acidity is remaining constant because there are alcohol's of unsaturated hydrocarbons, produced from decomposition of hydroperoxides process, so it neutralizes the effect of acidity formed from another oxygen bearing compound such as: aldehydes, ketones and acids.

The proceeding lubricant degradation mechanism makes clear several possible counter measures to control lubricant degradation. Blocking the energy source is one path but is effective only for lubricants used in low-shear and temperature situations. However, more practical for most lubricant applications are the trapping of catalytic impurities and the destruction of hydrocarbon radicals, alkyl peroxy radicals, and hydroperoxides. This can be achieved through the use of radical scavengers, peroxide decomposers, and metal deactivators.

The radical scavengers are known as *primary antioxidants*. They donate hydrogen atoms that react with alkyl radicals and/or alkyl peroxy radicals, interrupting the radical chain mechanism of the auto-oxidation process. The primary antioxidant then becomes a stable radical, the alkyl radical becomes a hydrocarbon, and the alkyl peroxy radical becomes an alkyl hydroperoxide. Hindered phenolics and aromatic amines are the two chemical classes of primary antioxidants for lubricants. The transfer of a hydrogen from the oxygen or nitrogen atom to the radical forms quinones or quinine imines that do not maintain the radical chain mechanism.

The peroxide decomposers are known as *secondary antioxidants* (Rizvi, 2009, Ludema, 1996, and Leslie, 2003). Sulfur and/or phosphorus compounds reduce the alkyl hydroperoxides in the radical chain to alcohols while being oxidized in a sacrificial manner. Zinc dialkyldithiophosphate, phosphites, and thio-ethers are examples of different chemical classes of secondary antioxidants.

There are two types of metal deactivators: chelating agents and film forming agents. The chelating agents will form a stable complex with metal ions, reducing the catalytic activity of the metal ions. Thus, the deactivators can show an antioxidant effect. Film-forming agents act two ways. First, they coat the metal surface, thus preventing metal ions from entering the oil. Second, they minimize corrosive attack of the metal surface by physically restricting access of the corrosive species to the metal surface.

Several effective antioxidants classes have been developed over the years and have seen use in engine oils, automatic transmission fluids, gear oils, turbine oils, compressor oils, greases, hydraulic fluids, and metal-working fluids. The main classes of oil-soluble organic and organo-metallic antioxidants are the following types:

1. Sulfur compounds
2. Phosphorus compounds
3. Sulfur-phosphorus compounds
4. Aromatic amine compounds
5. Hindered phenolic compounds
6. Organo-alkaline earth salt compounds
7. Organo-zinc compounds
8. Organo-copper compounds
9. Organo-molybdenum compounds

1.3.4 Anti-foam (A.F.) agents

The foaming of lubricants, (Rizvi, 2009, Ludema, 1996, and Leslie, 2003), is a very undesirable effect that can cause enhanced oxidation by the intensive mixture with air,

cavitation damage as well as insufficient oil transport in circulation systems that can even lead to lack of lubrication. Beside negative mechanical influences the foaming tendency depends very much on the lubricant itself and is influenced by the surface tension of the base oil and especially by the presence of surface-active substances such as detergents, corrosion inhibitors and other ionic compounds.

In many applications, there may be considerable tendency to agitate the oil and cause foaming, while in other cases even small amounts of foam can be extremely troublesome. In these cases, a defoamant may be added to the oil. It is thought that the defoamant droplets attach themselves to the air bubbles and can either spread or form unstable bridges between bubbles, which then coalesce into larger bubbles, which in turn rise more readily to the surface of the foam layer where they collapse, thus releasing the air.

1.3.5 Rust and corrosion inhibitors

Rust inhibitors, (Rizvi, 2009, Ludema, 1996, and Leslie, 2003), are usually compounds having a high polar attraction toward metal surfaces. By physical or chemical interaction at the metal surface, they form a tenacious, continuous film that prevents water from reaching the metal surface. Typical materials used for this purpose are amine succinates and alkaline earth sulfonates.

Rust inhibitors can be used in most types of lubricating oil, but the selection must be made carefully to avoid problems such as corrosion of nonferrous metals or the formation of troublesome emulsions with water. Because rust inhibitors are adsorbed on metal surfaces, an oil can be depleted of rust inhibitor in time.

A number of kinds of corrosion can occur in systems served by lubricating oils. Probably the two most important types are corrosion by organic acids that develop in the oil itself and corrosion by contaminants that are picked up and carried by the oil.

Corrosion by organic acids can occur, for example, in the bearing inserts used in internal combustion engines. Some of the metals used in these inserts, such as the lead in copper-lead or lead-bronze, are readily attacked by organic acids in oil. The corrosion inhibitors form a protective film on the bearing surfaces that prevents the corrosive materials from reaching or attacking the metal. The film may be either adsorbed on the metal or chemically bonded to it. It has been found that the inclusion of highly alkaline materials in the oil will help to neutralize these strong acids as they are formed, greatly reducing this corrosion and corrosive wear.

1.3.6 Detergent and dispersant (D / D) additives

Modern equipment must be lubricated in order to prolong its lifetime. One of the most critical properties of the automotive lubricants, especially engine oils, is their ability to suspend undesirable products from thermal and oxidative degradation of the lubricant. Such products form when the byproducts of fuel combustion, such as hydroperoxides and free radicals, go past piston rings into the lubricant and, being reactive species, initiate lubricant oxidation. The resulting oxidation products are thermally labile and decompose to highly polar materials with a tendency to separate from the bulk lubricant and form surface deposits and clog small openings.

Oxidation inhibitors, detergents (Rizvi, 2009, Ludema, 1996, Leslie, 2003, and Ming et. al., 2009), and dispersants (Alun, 2010) make up the general class of additives called *stabilizers and deposit control agents*. These additives are designed to control deposit formation, either by inhibiting the oxidative breakdown of the lubricant or by suspending the harmful

products already formed in the bulk lubricant. Oxidation inhibitors intercept the oxidation mechanism, and dispersants and detergents perform the suspending part (Kyunghyun, 2010). Detergents are metal salts of organic acids that frequently contain associated excess base, usually in the form of carbonate. Dispersants are metal-free and are of higher molecular weights than detergents. The two types of additives work in conjunction with each other.

The final products of combustion and lubricant decomposition include organic and inorganic acids, aldehydes, ketones, and other oxygenated materials. The acids have the propensity to attack metal surfaces and cause corrosive wear. Detergents, especially basic detergents, contain reserve base that will neutralize the acids to form salts. While this decreases the corrosive tendency of the acids, the solubility of the salts in the bulk lubricant is still low. The organic portion of the detergent, commonly called “soap”, has the ability to associate with the salts to keep them suspended in the bulk lubricant. However, in this regard, detergents are not as effective as dispersants because of their lower molecular weight. The soap in detergents and the dispersants also have the ability to suspend non-acidic oxygenated products, such as alcohols, aldehydes, and resinous oxygenates. The mechanism by which this occurs is depicted in Figure (1.5).

Dispersants and detergents together make up the bulk, about 45–50%, of the total volume of the lubricant additives manufactured. This is a consequence of their major use in engine oils, transmission fluids, and tractor hydraulic fluids, all of which are high-volume lubricants.

As mentioned, detergents neutralize oxidation-derived acids as well as help suspend polar oxidation products in the bulk lubricant. Because of this, these additives control rust, corrosion, and resinous buildup in the engine. Like most additives detergents contain a surface-active polar functionality and an oleophilic hydrocarbon group, with an appropriate number of carbon atoms to ensure good oil solubility. Sulfonate, phenate, and carboxylate are the common polar groups present in detergent molecules. However, additives containing salicylate and thiophosphonate functional groups are also sometimes used, Figure (1.6).

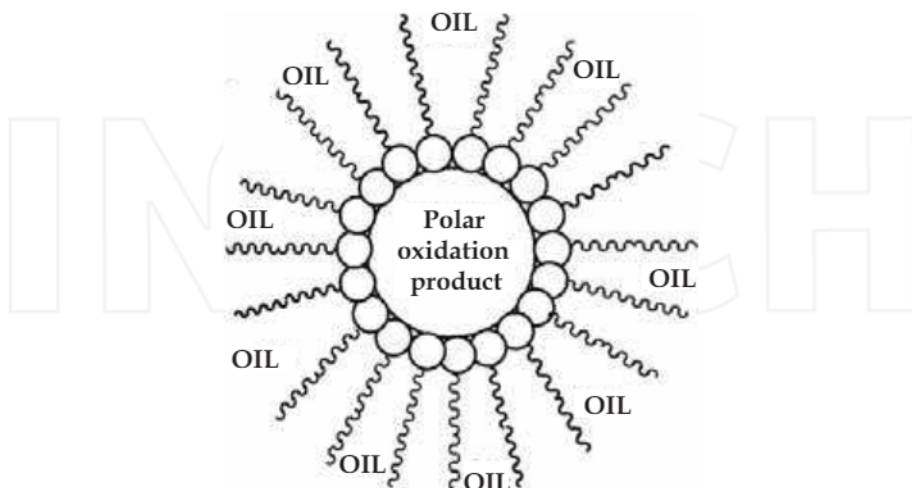


Fig. 1.5 Oil Suspension of polar oxidation products

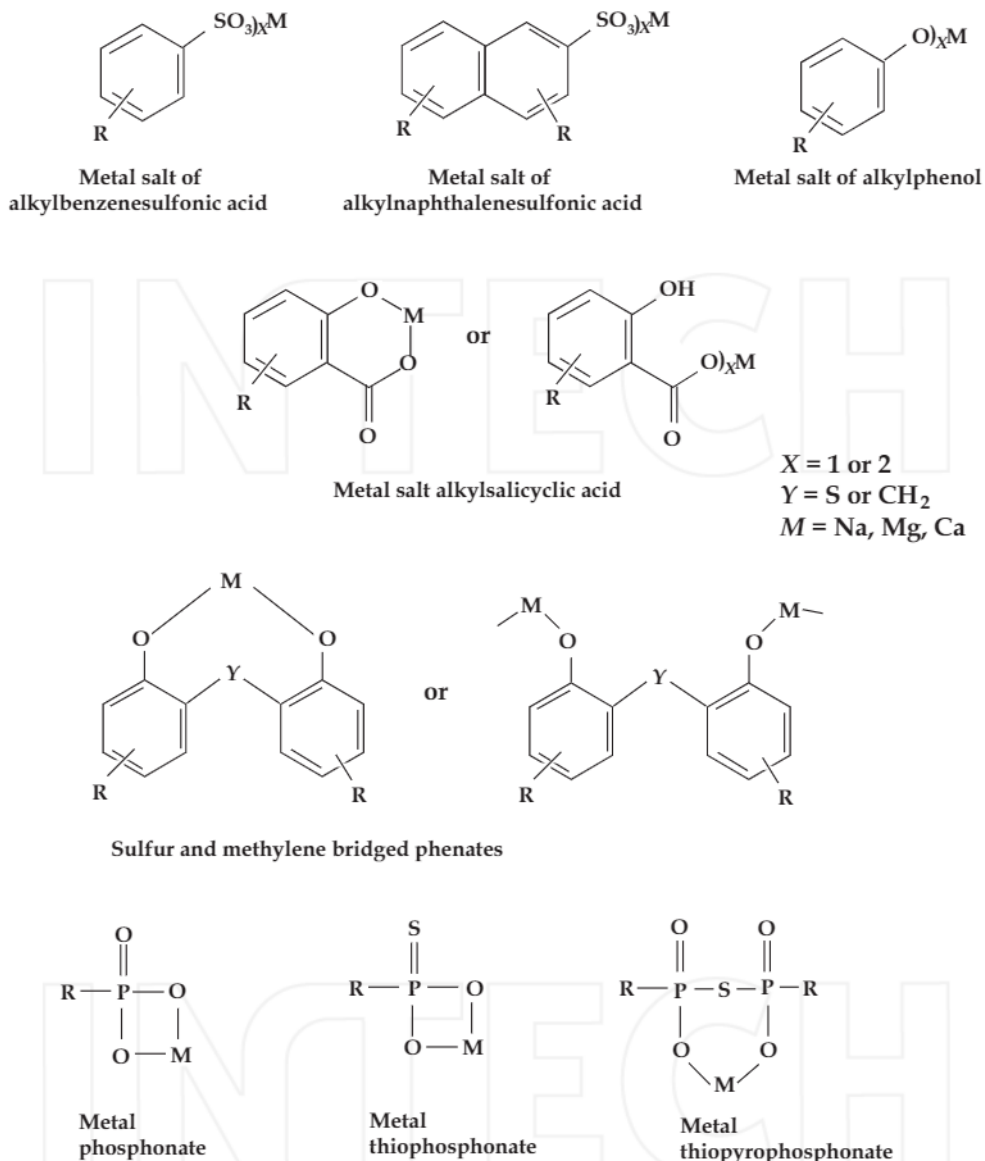


Fig. 1.6 Idealized structures of neutral salts (soaps)

As mentioned, common metals that can be used to make neutral or basic detergents include sodium, potassium, magnesium, calcium, and barium. Calcium and magnesium find most extensive use as lubricant additives, with a preference for calcium due to its lower cost. The use of barium-derived detergents is being curbed due to concerns for barium's toxicity. Technically, one can use metal oxides, hydroxides, and carbonates to manufacture neutral (non-overbased) detergents; for non-overbased detergents, oxides and hydroxides are the

