SECTION - C

MDU (ROHTAK)

B.TECH 1ST YEAR

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(I)CORROSION AND ITS PREVENTION

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(II) LUBRICATION   AND LUBRICANTS

SECTION :- C,

CORROSION AND ITS PREVENTATION

Corrosion is the gradual destruction of material, usually metals, by chemical reaction with its environment. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Rusting, the formation of ironoxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term degradation is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases.

Many structural alloys corrode merely from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

RUSTING OF IRON

Rust is a general term for iron oxides formed by the reaction of iron with oxygen. Several forms of rust are distinguishable visually and by spectroscopy, and form under different circumstances. The chemical composition of rust is typically hydrated iron(III) oxide (Fe2O3.nH2O), and under wet conditions may include iron(III) oxide-hydroxide (FeO(OH)). Rusting is the common term for corrosion of iron and its alloys, such as steel. Although oxidation of other metals is equivalent, these oxides are not commonly called rust.

As rust has higher volume than the originating mass of iron, its buildup may force apart adjacent parts - a phenomenon known as rust smacking.

The rusting of iron is one of the more widely used examples of corrosion. This electrochemical process requires the presence of water, oxygen and an electrolyte and leads to the formation of hydrated iron oxides.

Chemical reactions

Oxidation of iron metal

When impure (cast) iron is in contact with water, oxygen, or other strong oxidants, or acids, it rusts. If salt is present, for example in seawater or salt spray, the iron tends to rust more quickly, as a result of electrochemical reactions. Iron metal is relatively unaffected by pure water or by dry oxygen. As with other metals, like aluminium, a tightly adhering oxide coating, a passivation layer, protects the bulk iron from further oxidation. The conversion of the passivating iron oxide layer to rust results from the combined action of two agents, usually oxygen and water.

Other degrading solutions are sulfur dioxide in water and carbon dioxide in water. Under these corrosive conditions, iron hydroxide species are formed. Unlike iron oxides, the hydroxides do not adhere to the bulk metal. As they form and flake off from the surface, fresh iron is exposed, and the corrosion process continues until either all of the iron is consumed or all of the oxygen, water, carbon dioxide, or sulfur dioxide in the system are removed or consumed.

The rusting of iron is an electrochemical process that begins with the transfer of electrons from iron to oxygen.[3] The rate of corrosion is affected by water and accelerated by electrolytes, as illustrated by the effects of road salt on the corrosion of automobiles. The key reaction is the reduction of oxygen:
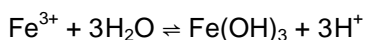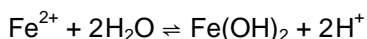
$$O_2 + 4e^- + 2H_2O \quad 4OH^-$$
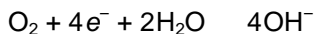
Because it forms <u>hydroxide ions</u>, this process is strongly affected by the presence of acid. Indeed, the corrosion of most metals by oxygen is accelerated at low <u>pH</u>. Providing the electrons for the above reaction is the oxidation of iron that may be described as follows:
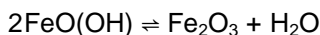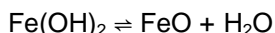
$$Fe \quad Fe^{2+} + 2e^-$$
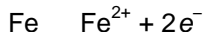
The following <u>redox reaction</u> also occurs in the presence of water and is crucial to the formation of rust:

$$4Fe^{2+} + O_2 \quad 4Fe^{3+} + 2O^{2-}$$

In addition, the following multistep <u>acid-base reactions</u> affect the course of rust formation:

$$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$$

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

as do the following <u>dehydration equilibria</u>:

$$Fe(OH)_2 \rightleftharpoons FeO + H_2O$$

$$Fe(OH)_3 \rightleftharpoons FeO(OH) + H_2O$$

$$2FeO(OH) \rightleftharpoons Fe_2O_3 + H_2O$$

From the above equations, it is also seen that the corrosion products are dictated by the availability of water and oxygen. With limited dissolved oxygen, iron(II)-containing materials are favoured, including <u>FeO</u> and black <u>lodestone</u> (Fe_3O_4). High oxygen concentrations favour <u>ferric</u> materials with the nominal formulae $Fe(OH)_{3-x}O_{x/2}$. The nature of rust changes with time, reflecting the slow rates of the reactions of solids.

Furthermore, these complex processes are affected by the presence of other ions, such as $\underline{Ca^{2+}}$, both of which serve as an electrolyte, and thus accelerate rust formation, or combine with the <u>hydroxides</u> and <u>oxides</u> of iron to precipitate a variety of Ca-Fe-O-OH species.

A chemical rust indicator can be used for testing the presence of Fe^{2+}. Fe^{2+} turns the rust indicator from yellow to blue.

Prevention

Because of the widespread use and importance of iron and steel products, the prevention or slowing of rust is the basis of major economic activities in a number of specialized technologies. A brief overview of methods is presented here; for detailed coverage, see the cross-referenced articles.

Rust is permeable to air and water, therefore the interior metallic iron beneath a rust layer continues to corrode. Rust prevention thus requires coatings that preclude rust formation.

Rust-resistant alloys

Stainless steel forms a <u>passivation</u> layer of <u>chromium(III) oxide</u>. Similar passivation behavior occurs with <u>magnesium</u>, <u>titanium</u>, <u>zinc</u>, <u>zinc oxides</u>,<u>aluminium</u>, <u>polyaniline</u>, and other electroactive conductive polymers.

Special "weathering steel" alloys such as Cor-Ten rust at a much slower rate than normal, because the rust adheres to the surface of the metal in a protective layer. Designs using this material must include measures that avoid worst-case exposures, since the material still continues to rust slowly even under near-ideal conditions.

Galvanization

Galvanization consists of an application on the object to be protected of a layer of metallic zinc by either hot-dip galvanizing or electroplating. Zinc is traditionally used because it is cheap, adheres well to steel, and provides cathodic protection to the steel surface in case of damage of the zinc layer. In more corrosive environments (such as salt water), cadmium plating is preferred. Galvanization often fails at seams, holes, and joints where there are gaps in the coating. In these cases, the coating still provides some partial cathodic protection to iron, by acting as a galvanic anode and corroding itself instead of the underlying protected metal. The protective zinc layer is consumed by this action, and thus galvanization provides protection only for a limited period of time.

More modern coatings add aluminium to the coating as **zinc-alume**; aluminium will migrate to cover scratches and thus provide protection for a longer period. These approaches rely on the aluminium and zinc oxides re-protecting a once-scratched surface, rather than oxidizing as a sacrificial anode as in traditional galvanized coatings. In some cases, such as very aggressive environments or long design life, both zinc and a coating are applied to provide enhanced corrosion protection.

Elecrtoplating

Rusting can completely degrade iron. Note the remaining dull silver-colored galvanization on the unrusted portions.

Zinc plating :(galvanized iron/steel): iron or steel coated with zinc metal layer. Hot-dipped method or zinc-blasting method may be used.

Tin plating: mild steel sheet coated with a tin layer.

:**Chrome plating:** a thin layer of chromium is electrolytically applied to the steel, providing both rust protection and a highly polished, bright appearance. Often used on the bright silver-colored components of bicycles, motorbikes, and automobiles.

Cathodic protection

Cathodic protection is a technique used to inhibit corrosion on buried or immersed structures by supplying an electrical charge that suppresses the electro-chemical reaction. If correctly applied, corrosion can be

stopped completely. In its simplest form, it is achieved by attaching a sacrificial anode, thereby making the iron or steel the cathode in the cell formed. The sacrificial anode must be made from something with a more negative electrode potential than the iron or steel, commonly zinc, aluminium, or magnesium. The sacrificial anode will eventually corrode away, ceasing its protective action unless it is replaced in a timely manner.

Cathodic protection can also be provided by using a special-purpose electrical device to appropriately induce an electric charge on the metal to be protected.

Coatings and painting

Rust formation can be controlled with coatings, such as paint, lacquer, or varnish that isolate the iron from the environment. Large structures with enclosed box sections, such as ships and modern automobiles, often have a wax-based product (technically a "slushing oil") injected into these sections. Such treatments usually also contain rust inhibitors. Covering steel with concrete can provide some protection to steel because of the alkaline pH environment at the steel-concrete interface. However rusting of steel in concrete can still be a problem, since expanding rust can fracture or slowly "explode" concrete from within.As a closely related example, iron bars were used to reinforce stonework of the Parthenon in Athens, Greece, but caused extensive damage by rusting, swelling, and shattering the marble components of the building.

When only temporary protection is needed for storage or transport, a thin layer of oil, grease, or a special mixture such as Cosmoline can be applied to an iron surface. Such treatments are extensively used when "mothballing" a steel ship, automobile, or other equipment for long-term storage.

Special anti-seize lubricant mixtures are available, and are applied to metallic threads and other precision machined surfaces to protect them from rust. These compounds usually contain grease mixed with copper, zinc, or aluminum powder, and other proprietary ingredients.[

Inhibitors

Corrosion inhibitors, like gas-phase or volatile inhibitors, can be used to prevent corrosion inside sealed systems. They are not effective when air circulation disperses them, and brings in fresh oxygen and moisture

Corrosion removal

Often it is possible to chemically remove the products of corrosion. For example phosphoric acid in the form of naval jelly is often applied to ferrous tools or surfaces to remove rust. Corrosion removal should not be confused with electropolishing, which removes some layers of the underlying metal to make a smooth surface. For example, phosphoric acid may also be used to electropolish copper but it does this by removing copper, not the products of copper corrosion.

Resistance to corrosion

Some metals are more intrinsically resistant to corrosion than others (for some examples, see galvanic series). There are various ways of protecting metals from corrosion including painting, hot dip galvanizing, and combinations of these.

Intrinsic chemistry
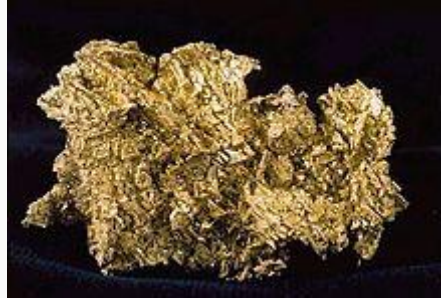
Gold nuggets do not naturally corrode, even on a geological time scale.

The materials most resistant to corrosion are those for which corrosion is thermodynamically unfavorable. Any corrosion products of gold or platinum tend to decompose spontaneously into pure metal, which is why these elements can be found in metallic form on Earth and have long been valued. More common "base" metals can only be protected by more temporary means.

Some metals have naturally slow reaction kinetics, even though their corrosion is thermodynamically favorable. These include such metals as zinc, magnesium, and cadmium. While corrosion of these metals is continuous and ongoing, it happens at an acceptably slow rate. An extreme example is graphite, which releases large amounts of energy upon oxidation, but has such slow kinetics that it is effectively immune to electrochemical corrosion under normal conditions.

Passivation

Passivation refers to the spontaneous formation of an ultrathin film of corrosion products known as passive film, on the metal's surface that act as a barrier to further oxidation. The chemical composition and microstructure of a passive film are different from the underlying metal. Typical passive film thickness on aluminium, stainless steels and alloys is within 10 nanometers. The passive film is different from oxide layers that are formed upon heating and are in the micrometer thickness range – the passive film recovers if removed or damaged whereas the oxide layer does not. Passivation in natural environments such as air, water and soil at moderate pH is seen in such materials as aluminium, stainless steel, titanium, andsilicon.

Passivation is primarily determined by metallurgical and environmental factors. The effect of pH is summarized using Pourbaix diagrams, but many other factors are influential. Some conditions that inhibit passivation include high pH for aluminium and zinc, low pH or the presence of chloride ions for stainless steel, high temperature for titanium (in which case the oxide dissolves into the metal, rather than the electrolyte) and fluoride ions for silicon. On the other hand, unusual conditions may result in passivation of materials that are normally unprotected, as the alkaline environment of concrete does for steel rebar. Exposure to a liquid metal such as mercury or hot solder can often circumvent passivation mechanisms.

Corrosion in passivated materials

Passivation is extremely useful in mitigating corrosion damage, however even a high-quality alloy will corrode if its ability to form a passivating film is hindered. Proper selection of the right grade of material for the specific environment is important for the long-lasting performance of this group of materials. If

breakdown occurs in the passive film due to chemical or mechanical factors, the resulting major modes of corrosion may include pitting corrosion, crevice corrosion and stress corrosion cracking.

Pitting corrosion

The scheme of pitting corrosion

Certain conditions, such as low concentrations of oxygen or high concentrations of species such as chloride which complete as anions, can interfere with a given alloy's ability to re-form a passivating film. In the worst case, almost all of the surface will remain protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause *corrosion pits* of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases due to an autocatalytic process. In extreme cases, the sharp tips of extremely long and narrow corrosion pits can cause stress concentration to the point that otherwise tough alloys can shatter; a thin film pierced by an invisibly small hole can hide a thumb sized pit from view. These problems are especially dangerous because they are difficult to detect before a part or structure fails. Pitting remains among the most common and damaging forms of corrosion in passivated alloys, but it can be prevented by control of the alloy's environment.

Crevice corrosion

Corrosion in the crevice between the tube and tube sheet (both made of type-316 stainless steel) of a heat exchanger in a seawater desalination plant

Crevice corrosion is a localized form of corrosion occurring in confined spaces (crevices), to which the access of the working fluid from the environment is limited. Formation of a differential aeration cell leads

to corrosion inside the crevices. Examples of crevices are gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, spaces filled with deposits and under sludge piles.

Crevice corrosion is influenced by the crevice type (metal-metal, metal-nonmetal), crevice geometry (size, surface finish), and metallurgical and environmental factors. The susceptibility to crevice corrosion can be evaluated with ASTM standard procedures. A critical crevice corrosion temperature is commonly used to rank a material's resistance to crevice corrosion.

Microbial corrosion

Microbial corrosion, or commonly known as microbiologically influenced corrosion (MIC), is a corrosion caused or promoted by microorganisms, usuallychemoautotrophs. It can apply to both metallic and non-metallic materials, in the presence or absence of oxygen. Sulfate-reducing bacteria are active in the absence of oxygen (anaerobic); they produce hydrogen sulfide, causing sulfide stress cracking. In the presence of oxygen (aerobic), some bacteria may directly oxidize iron to iron oxides and hydroxides, other bacteria oxidize sulfur and produce sulfuric acid causing biogenic sulfide corrosion.Concentration cells can form in the deposits of corrosion products, leading to localized corrosion.

Accelerated low-water corrosion (ALWC) is a particularly aggressive form of MIC that affects steel piles in seawater near the low water tide mark. It is characterized by an orange sludge, which smells of hydrogen sulfide when treated with acid. Corrosion rates can be very high and design corrosion allowances can soon be exceeded leading to premature failure of the steel pile.[5] Piles that have been coating and have cathodic protection installed at the time of construction are not susceptible to ALWC. For unprotected piles, sacrificial anodes can be installed local to the affected areas to inhibit the corrosion or a complete retrofitted sacrificial anode system can be installed. Affected areas can also be treated electrochemically by using an electrode to first produce chlorine to kill the bacteria, and then to produced a calcareous deposit, which will help shield the metal from further attack.

High-temperature corrosion

High-temperature corrosion is chemical deterioration of a material (typically a metal) as a result of heating. This non-galvanic form of corrosion can occur when a metal is subjected to a hot atmosphere containing oxygen, sulfur, or other compounds capable of oxidizing (or assisting the oxidation of) the material concerned. For example, materials used in aerospace, power generation and even in car engines have to resist sustained periods at high temperature in which they may be exposed to an atmosphere containing potentially highly corrosive products of combustion.

The products of high-temperature corrosion can potentially be turned to the advantage of the engineer. The formation of oxides on stainless steels, for example, can provide a protective layer preventing further atmospheric attack, allowing for a material to be used for sustained periods at both room and high temperatures in hostile conditions. Such high-temperature corrosion products, in the form of compacted oxide layer glazes, prevent or reduce wear during high-temperature sliding contact of metallic (or metallic and ceramic) surfaces.

Protection from corrosion

Surface treatments

Applied coatings

Galvanized surface

Plating, painting, and the application of enamel are the most common anti-corrosion treatments. They work by providing a barrier of corrosion-resistant material between the damaging environment and the structural material. Aside from cosmetic and manufacturing issues, there are tradeoffs in mechanical flexibility versus resistance to abrasion and high temperature. Platings usually fail only in small sections, and if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an unplated surface would. For this reason, it is often wise to plate with active metal such as zinc or cadmium. Painting either by roller or brush is more desirable for tight spaces; spray would be better for larger coating areas such as steel decks and waterfront applications. Flexible polyurethane coatings, like Durabak-M26 for example, can provide an anti-corrosive seal with a highly durable slip resistant membrane. Painted coatings are relatively easy to apply and have fast drying times although temperature and humidity may cause dry times to vary.

Reactive coatings

If the environment is controlled (especially in recirculating systems), corrosion inhibitors can often be added to it. These form an electrically insulating or chemically impermeable coating on exposed metal surfaces, to suppress electrochemical reactions. Such methods obviously make the system less sensitive to scratches or defects in the coating, since extra inhibitors can be made available wherever metal becomes exposed. Chemicals that inhibit corrosion include some of the salts in hard water (Roman water systems are famous for their mineral deposits), chromates, phosphates, polyaniline, other conducting polymers and a wide range of specially-designed chemicals that resemble surfactants (i.e. long-chain organic molecules with ionic end groups).

Anodization

Aluminium alloys often undergo a surface treatment. Electrochemical conditions in the bath are carefully adjusted so that uniform pores several nanometers wide appear in the metal's oxide film. These pores allow the oxide to grow much thicker than passivating conditions would allow. At the end of the treatment, the pores are allowed to seal, forming a harder-than-usual surface layer. If this coating is scratched, normal passivation processes take over to protect the damaged area.

Anodizing is very resilient to weathering and corrosion, so it is commonly used for building facades and other areas that the surface will come into regular contact with the elements. Whilst being resilient, it must be cleaned frequently. If left without cleaning, panel edge staining will naturally occur.

Biofilm coatings

A new form of protection has been developed by applying certain species of bacterial films to the surface of metals in highly corrosive environments. This process increases the corrosion resistance substantially. Alternatively, antimicrobial-producing biofilms can be used to inhibit mild steel corrosion from sulfate-reducing bacteria.

Cathodic protection

Cathodic protection (CP) is a technique to control the corrosion of a metal surface by making that surface the cathode of an electrochemical cell. Cathodic protection systems are most commonly used to protect steel, water, and fuel pipelines and tanks; steel pier piles, ships, and offshore oil platforms.

Sacrificial anode protection

Sacrificial anode in the hull of a ship.

For effective CP, the potential of the steel surface is polarized (pushed) more negative until the metal surface has a uniform potential. With a uniform potential, the driving force for the corrosion reaction is halted. For galvanic CP systems, the anode material corrodes under the influence of the steel, and eventually it must be replaced. The polarization is caused by the current flow from the anode to the cathode, driven by the difference in electrochemical potential between the anode and the cathode.

Impressed current cathodic protection

For larger structures, galvanic anodes cannot economically deliver enough current to provide complete protection. Impressed current cathodic protection(ICCP) systems use anodes connected to a DC power

source (such as a <u>cathodic protection rectifier</u>). Anodes for ICCP systems are tubular and solid rod shapes of various specialized materials. These include high silicon <u>cast iron</u>, graphite, mixed metal oxide or platinum coated titanium or niobium coated rod and wires.

Anodic protection

Anodic protection impresses anodic current on the structure to be protected (opposite to the cathodic protection). It is appropriate for metals that exhibit passivity (e.g., stainless steel) and suitably small passive current over a wide range of potentials. It is used in aggressive environments, e.g., solutions of sulfuric acid.

Rate of corrosion

A simple test for measuring corrosion is the weight loss method.[The method involves exposing a clean weighed piece of the metal or alloy to the corrosive environment for a specified time followed by cleaning to remove corrosion products and weighing the piece to determine the loss of weight. The rate of corrosion (R) is calculated as

$$R = KW/(At)$$

where *k* is a constant, *W* is the weight loss of the metal in time *t*, *A* is the surface area of the metal exposed, and   is the density of the metal (in g/cm³).

SOIL CORROSION

Soil contains water and dissolved minerals responsible for damaging an underground tank. All soil contains water. Even desert sand contains underground moisture.

Let's assume that you are responsible for deciding whether or not corrosion will affect a new tank to be installed at a new home in the desert. First, let's begin with the questions:

Will it ever rain or snow there? Will the new owner ever plant grass, flowers, shrubs or trees over or near the tank? Will ground moisture condense on the outside surface of the tank? Will water condense out of thin air on the surface of a cold container? Will the grass, flowers or shrubs over the tank be fertilized? Will the tank ever be near a sidewalk or down gradient from a driveway? Will the owner ever throw salt or calcium chloride on the pavement to melt snow and ice? Will magnesium chloride ever be used to control road dust nearby? Will the tank ever be located near or downhill from livestock where salt and urea from animal waste will leach into the earth? Does the irrigation water contain salt or alkali salts? If a tank is set in a hole blasted from solid rock, does the rock contain pyrites, graphite or acidic rocks that will be fractured and exposed to the oxidizing effect of air and water?
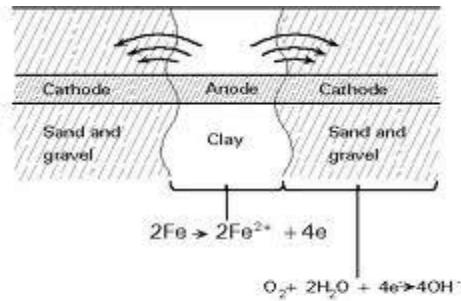
Figure 1 Differential aeration corrosion resulting
from variations in soil conditions

Lubrication and lubricants

A **lubricant** is a substance introduced to reduce friction between moving surfaces. It may also have the function of transporting foreign particles. The property of reducing friction is known as lubricity.

A good lubricant possesses the following characteristics:

- High boiling point.
- Low freezing point.
- High viscosity index.
- Thermal stability.
- Corrosion prevention.
- High resistance to oxidation.

One of the single largest applications for lubricants, in the form of motor oil, is protecting the internal combustion engines in motor vehicles and powered equipment.

Typically lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Vegetable oils or synthetic liquids such as hydrogenated polyolefins,esters, silicones, fluorocarbons and many others are sometimes used as base oils. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance tocorrosion and oxidation, aging or contamination, etc.

Lubricants such as 2-cycle oil are added to fuels like gasoline which has low lubricity. Sulfur impurities in fuels also provide some lubrication properties, which has to be taken in account when switching to a low-sulfur diesel; biodiesel is a popular diesel fuel additive providing additional lubricity.

Non-liquid lubricants include grease, powders (dry graphite, PTFE, Molybdenum disulfide, tungsten disulfide, etc.), PTFE tape used in plumbing, air cushion and others. Dry lubricants such as graphite, molybdenum disulfide and tungsten disulfide also offer lubrication at temperatures (up to 350 °C) higher than liquid and oil-based lubricants are able to operate. Limited interest has been shown in low friction properties of compacted oxide glaze layers formed at several hundred degrees Celsius in metallic sliding systems, however, practical use is still many years away due to their physically unstable nature.

Another approach to reducing friction and wear is to use bearings such as ball bearings, roller bearings or air bearings, which in turn require internal lubrication themselves, or to use sound, in the case of acoustic lubrication.

In addition to industrial applications, lubricants are used for many other purposes. Other uses include cooking (oils and fats in use in frying pans, in baking to prevent food sticking), bio-medicalapplicationson humans (e.g.lubricants for artificial joints, ultrasound examination, internal examinations for males and females, and the use of personal lubricant for sexual purposes.

Purpose

Lubricants perform the following key functions.

- Keep moving parts apart
- Reduce friction
- Transfer heat
- Carry away contaminants & debris
- Transmit power
- Protect against wear
- Prevent corrosion
- Seal for gases
- Stop the risk of smoke and fire of objects

Types of lubricants

In 1999, an estimated 37,300,000 tons of lubricants were consumed worldwide.[1] Automotive applications dominate, but other industrial, marine, and metal working applications are also big consumers of lubricants. Although air and other gas-based lubricants are known, e.g., in fluid bearings), liquid and solid lubricants dominate the market, especially the former.

Lubricants are generally composed of a majority of base oil plus a variety of additives to impart desirable characteristics. Although generally lubricants are based on one type of base oil, mixtures of the base oils also are used to meet performance requirements.

Base oil groups

Mineral oil term is used to encompass lubricating base oil derived from crude oil. The American Petroleum Institute (API) designates several types of lubricant base oil:[2]

- Group I – Saturates <90% and/or sulfur >0.03%, and Society of Automotive

  Engineers (SAE) viscosity index (VI) of 80 to 120

  Manufactured by solvent extraction, solvent or catalytic dewaxing, and hydro-finishing processes. Common Group I base oil are 150SN (solvent neutral), 500SN, and 150BS (brightstock)

  - Group II – Saturates over 90% and sulfur under 0.03%, and SAE viscosity index of 80 to 120 Manufactured by hydrocracking and solvent or catalytic dewaxing processes. Group II base oil has superior anti-oxidation properties since virtually all hydrocarbon molecules are saturated. It has water-white color.

    - Group III – Saturates > 90%, sulfur <0.03%, and SAE viscosity index over 120 Manufactured by special processes such as isohydromerization.Can be manufactured from base oil or slax wax from dewaxing process.

      - Group IV – Polyalphaolefins (PAO)
      - Group V – All others not included above such as naphthenics, PAG, esters.

    In North America, Groups III, IV and V are now described as synthetic lubricants, with group III frequently described as synthesised hydrocarbons, or SHCs. In Europe, only Groups IV and V may be classed as synthetics.

      The lubricant industry commonly extends this group terminology to include:

      - Group I+ with a Viscosity Index of 103–108

- Group II+ with a Viscosity Index of 113–119
- Group III+ with a Viscosity Index of at least 140

Can also be classified into three categories depending on the prevailing compositions:

- Paraffinic
- Naphthenic
- Aromatic

Lubricants for internal combustion engines contain additives to reduce oxidation and improve lubrication. The main constituent of such lubricant product is called the base oil, base stock. While it is advantageous to have a high-grade base oil in a lubricant, proper selection of the lubricant additives is equally as important. Thus some poorly selected formulation of PAO lubricant may not last as long as more expensive formulation of Group III+ lubricant.

Biolubricants made from vegetable oils and other renewable sources

These are primarily triglyceride esters derived from plants and animals. For lubricant base oil use the vegetable derived materials are preferred. Common ones include high oleic canola oil, castor oil, palm oil, sunflower seed oil and rapeseed oil from vegetable, and Tall oil from tree sources. Many vegetable oils are often hydrolyzed to yield the acids which are subsequently combined selectively to form specialist synthetic esters. Other naturally derived lubricants include lanolin (wool grease, a natural water repellent).

Whale oil was a historically important lubricant, with some uses up to the latter part of the 20th century as a friction modifier additive for automatic transmission fluid.[3]

In 2008, the biolubricant market was around 1% of UK lubricant sales in a total lubricant market of 840,000 tonnes/year.[4]

Lanolin is a natural water repellent, derived from sheep wool grease, and is an alternative to the more common petro-chemical based lubricants. This lubricant is also a corrosion inhibitor, protecting against rust, salts, and acids.

Water can also be used on its own, or as a major component in combination with one of the other base oils. Commonly used in engineering processes, such as milling and lathe turning.

Synthetic oils

- Polyalpha-olefin (PAO)
- Synthetic esters

- Polyalkylene glycols (PAG)
- Phosphate esters
- Alkylated naphthalenes (AN)
- Silicate esters
- Ionic fluids

Solid lubricants

PTFE: polytetrafluoroethylene (PTFE) is typically used as a coating layer on, for example, cooking utensils to provide a non-stick surface. Its usable temperature range up to 350 °C and chemical inertness make it a useful additive in special greases. Under extreme pressures, PTFE powder or solids is of little value as it is soft and flows away from the area of contact. Ceramic or metal or alloy lubricants must be used then. "Teflon®" is a brand of PTFE owned by DuPont Co.

Inorganic solids: Graphite, hexagonal boron nitride, molybdenum disulfide and tungsten disulfide are examples of materials that can be used as solid lubricants, often to very high temperature. The use of some such materials is sometimes restricted by their poor resistance to oxidation (e.g., molybdenum disulfide can only be used up to 350°C in air, but 1100°C in reducing environments).

Metal/alloy: Metal alloys, composites and pure metals can be used as grease additives or the sole constituents of sliding surfaces and bearings. Cadmium and Gold are used for plating surfaces which gives them good corrosion resistance and sliding properties, Lead, Tin, Zinc alloys and various Bronze alloys are used as sliding bearings, or their powder can be used to lubricate sliding surfaces alone, or as additives to greases.

Flash point and Fire point

Flash point

It is lowest temperature at which the oil gives off enough vapour that ignite for a moment, when a small flame is brought near it.

Fire point

It is the lowest temperature at which the vapour of the oil burns continuously for at least 5 seconds, when a small flame is brought near it. Generally the fire point is 5-40°C higher than flash point.

Significance

A knowledge of flash and fire point is useful in providing protection against fire hazard during transport

and storage. Lubricating oils of paraffinic base possess higher flash points than those of naphthenic base. Hence the determination of flash and fire points is helpful in identifying the type of lubricating oil. A good lubricating oil should have flash and fire points higher than the operating temperature of the machine.

Determination
Flash and fire points can be determined using the same apparatus. An oil is heated at a prescribed rate in an open cup (Cleve Land's) apparatus or closed cup (pensky Martin's) apparatus of standard dimensions. A small test flame is periodically applied over the surface of the oil. The temperature at which a distinct flash is seen is the flash point. The heating and periodical application of test flame is continued. The temperature at which the oil vapour catches fire and burns continuously for 5 seconds is noted as the fire point

Cloud and pour point

Cloud point
When an oil is cooled slowly the temperature at which the oil becomes cloudy in temperature is called its cloud point.

Pour point
The temperature at which the oil ceases to flow or pour is called its pour point.

Significance
Most of the petroleum based lubricating oils contain dissolved paraffin wax and asphaltic impurities. When the oil is cooled these impurities undergoes solidification which cause jamming of the machine. So the cloud and pour points indicate the suitability of the lubricants in cold condition.
A good lubricant must have cloud point and pour point.

Determination
An oil is taken ina flat bottomed tube enclosed in an air jacket and it is cooled in a freezing mixture (ice + CaCl2). Thermometers are introduced into the oil and freezing mixture. As the cooling takes place via the air jacket temperature of the oil falls. The temperature at which the cloudiness appears is noted as the Cloud Point. The cooling is furthered continued. The temperature at which the oil does not flow in the test tube for 5 seconds on tilting it to the horizontal position is noted as the pour point.

How to improve cloud and pour point
Pour point of lubricating oil can be lowered by
(i) Dewaxing
(ii) Adding a pour point depressant.
Example
Poly alkyl benzene called "para flow' is a commonly used pour point depressant.

Oiliness

Oiliness is the capacity of a lubricating oil to stick on to the surface of the machine parts under heavy load or pressure.

Significance
Lubricating which have oiliness stay in between the lubricated surfaces, when they are subjected to high load and pressure. But lubricants with poor oiliness will be squeezed out of the machine parts under this condition. A good lubricant should have good oiliness.

How to improve oiliness
Mineral oils have poor oiliness where as vegetable and animal oils have high oiliness. Hence oiliness of mineral oil is improved

Viscosity

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. In everyday terms (and for fluids only), viscosity is "thickness" or "internal friction". Thus, water is "thin", having a lower viscosity, while honey is "thick", having a higher viscosity. Put simply, the less viscous the fluid is, the greater its ease of movement (fluidity).[1]

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. For example, high-viscosity felsic magma will create a tall, steep stratovolcano, because it cannot flow far before it cools, while low-viscosity mafic lava will create a wide, shallow-sloped shield volcano.

With the exception of superfluids, all real fluids have some resistance to stress and therefore are **viscous**. A fluid which has no resistance to shear stress is known as an **ideal fluid** or **inviscid fluid**. In common usage, a liquid with the viscosity less than water is known as a **mobile**liquid, while a substance with a viscosity substantially greater than water is simply called a **viscous** liquid.

The study of flowing matter is known as rheology, which includes viscosity and related concepts.

Viscosity index

Viscosity index (VI) is an arbitrary measure for the change of viscosity with temperature. It is used to characterize lubricating oil in the automotive industry.

The viscosity of liquids decreases as temperature increases. The viscosity of a lubricant is closely related to its ability to reduce friction. Generally, the least viscous lubricant which still forces the two moving surfaces apart is desired. If the lubricant is too viscous, it will require a large amount of energy to move (as in honey); if it is too thin, the surfaces will rub and friction will increase.

As stated above, the Viscosity Index highlights how a lubricant's viscosity changes with variations in temperature. Many lubricant applications require the lubricant to perform across a wide range of conditions: for example, in an engine. Automotive lubricants must reduce friction between engine components when it is started from cold (relative to engine operating temperatures) as well as when it is running (up to 200 °C/392 °F). The best oils (with the highest VI) will not vary much in viscosity over such a temperature range and therefore will perform well throughout.

The VI scale was set up by the Society of Automotive Engineers (SAE). The temperatures chosen arbitrarily for reference are 100 and 210 °F (37.8 and 98.9 °C). The original scale only stretched between VI=0 (worst oil, naphthalene) and VI=100 (best oil, paraffin) but since the conception of the scale better oils have also been produced, leading to VIs greater than 100 (see below).

VI improving additives and higher quality base oils are widely used nowadays which increase the VIs attainable beyond the value of 100. The Viscosity Index of synthetic oils ranges from 80 to over 400.

The viscosity index can be calculated using the following formula:

$$V = 100\frac{(L-U)}{(L-H)}$$

where V indicates the viscosity index, U the kinematic viscosity at 40°C, and L & H are various values based on the kinematic viscosity at 100°C available in ASTM D2270.

Saponification value

Saponification value (or "saponification number"/"Koettstorfer number", also referred to as "sap" in short) represents the number of milligrams of potassium hydroxide required to saponify 1g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most of the mass of a fat/triester is in the 3 fatty acids, it allows for comparison of the average fatty acid chain length. The long chain fatty acids found in fats have a low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat as compared to short chain fatty acids. If more moles of base are required to saponify N grams of fat then there are more moles of the fat the chain lengths are relatively small, given the following relation:
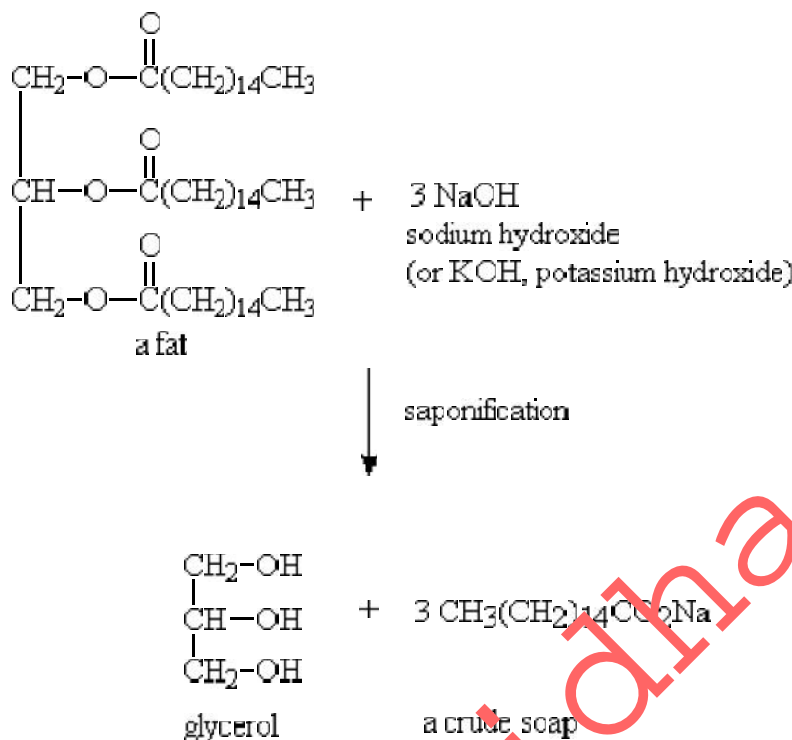
Number of moles = mass of oil/relative atomic mass

The calculated molar mass is not applicable to fats and oils containing high amounts of unsaponifiable material, free fatty acids (>0.1%), or mono- and diacylglycerols (>0.1%).

Handmade soap makers who aim for bar soap use NaOH (sodium hydroxide). Because saponification values are listed in KOH (potassium hydroxide) the value must be converted from potassium to sodium to make bar soap; potassium soaps make a paste, gel or liquid soap. To convert KOH values to NaOH values, divide the KOH values by the ratio of the molecular weights of KOH and NaOH (1.403).

Biodegradable Lubricants

The use of vegetable oils and animal fats for lubrication purposes has been practiced for many years. With the discovery of petroleum and the availability of inexpensive oils, alternatives became unattractive and were left by the wayside. Attention was refocused on vegetable oils during wartime and oil shortage situations. For example, during World War I and World War II, the use of vegetable oils for fuel, lubricants, greases and energy transfer increased rapidly. Also, the oil embargo of 1973 brought needed attention to alternatives for petroleum oils.

Over the past two decades, a renewed interest in vegetable oil-based lubricants has occurred as environmental interest has increased. In Europe during the 1980s, various mandates and regulations were

placed on petroleum products necessitating the use of biodegradable lubricants. During the 1990s, many American companies began developing biodegradable products. A prime example is when the Mobil corporation introduced its Environmental Awareness Lubricants (EAL) line of hydraulic fluids. The Lubrizol Corporation also developed considerable quantities of additives and sunflower oil-based lubricants. However, the lack of regulatory mandates in the United States, as well as the availability of post-Desert Storm low-cost oil, made biodegradable oils too expensive to compete.

The next decade will recognize more advances in the use of biodegradable lubes and greases than in any other time in history. There are at least three major reasons for this upbeat prediction:

1. Patterning after European farmers, U.S. growers' associations have begun spending considerable sums of money on research in nonfood "new uses" areas to reduce crop surpluses.

2. The federal government has introduced initiatives to promote the use of environmentally friendly products within federal agencies.

3. There have been advancements in biodegradable lubricants technology and genetic enhancement to **seed oils.**

Vegetable Oils
Vegetable oils can and have been used as lubricants in their natural forms. They have several advantages and disadvantages when considered for industrial and machinery lubrication. On the positive side, vegetable oils can have excellent lubricity, far superior than that of mineral oil. Lubricity is so potent that in some applications, such as tractor transmissions, friction materials need to be added to reduce clutch slippage. Some crude vegetable oils tested at UNI-ABIL have passed hydraulic pump/wear tests, such as ASTM D2882 and ASTM D2271, in their natural form.

Vegetable oils also have a very high Viscosity index (VI); for example, 223 for soybean oil vs. 90 to 100 for most petroleum oils. Restated, the viscosity of a high VI oil changes less than that of a low VI oil for a given temperature change. The oil's viscosity does not reduce as much when exposed to high temperatures, and does not increase as much as petroleum oils when exposed to cool temperatures.

Another important property of vegetable oils is their high flash/fire points; 610°F (326°C) is the flash point of soybean oil compared to a flash point of approximately 392°F (200°C) for mineral oils.

Most importantly, vegetable oils are biodegradable, in general are less toxic, are renewable and reduce dependency on imported petroleum oils. Additionally, using lubricants and greases made of soybean oil helps reduce soybean surpluses and helps stabilize soy prices for American farmers. For most industrial machinery users these products offer considerable public relations benefits and goodwill within the agricultural community.

On the negative side, vegetable oils in their natural form lack sufficient oxidative stability for lubricant use. Low oxidative stability means, if untreated, the oil will oxidize rather quickly during use, becoming thick and polymerizing to a plastic-like consistency. Chemical modification of vegetable oils and/or the use of antioxidants can address this problem, but increase the cost. Chemical modification could involve partial

hydrogenation of the vegetable oil and a shifting of its fatty acids. The challenge with hydrogenation is to determine at what point the process is to cease. Full hydrogenation of oil can lead to solid products like margarine. Depending on the needed liquidity and pour point of the oil, optimum hydrogenation is determined. Recent advances in biotechnology have led to the development of genetically enhanced oilseeds that are naturally stable and do not require chemical modification and/or use of antioxidants. A soybean seed developed through DuPont technology, for example, presents more than 83 percent oleic acid as compared to only 20 percent oleic acid content in conventional soybean oil. Originally developed for frying applications, this oil has shown about 30 times more oxidative stability and viscosity stability in hydraulic pump tests conducted at the UNI-ABIL Research Program. High oleic varieties of canola oil, rapeseed, sunflower and soybean are now becoming standard base oils for biodegradable lubricants and greases. The primary advantage of soybean is that it is U.S.-grown and has a well-established infrastructure to deliver the quality, quantity and economy for these alternative products.