FRICTION, WEAR AND LUBRICATION

MEMM 1343

Greases

Greases are not simply very viscous lubricating oils.

They are in fact mixtures of lubricating oils and thickeners.

The thickeners are dispersed in lubricating oils in order to produce a stable colloidal structure or gel. Thus, a grease consists of oil constrained by minute thickener fibres. Since the oil is constrained and unable to flow it provides semi-permanent lubrication.

For this reason, greases are widely used, despite certain limitations in performance. The most widespread application of greases is as low-maintenance, semipermanent lubricants in rolling contact bearings and some gears.

The grease may be packed into a bearing or gear set and left for a period of several months or longer before being replaced. Inaccessible wearing contacts, such as are found on caterpillar track assemblies or in agricultural machinery, are conveniently lubricated by this means.

Low maintenance items are also suitable candidates for grease lubrication. The lubricating performance of greases is inferior to mineral oils except at low sliding speeds where some greases may be superior.

Greases have to meet the same requirements as lubricating oils but with one extra condition, the grease must remain as a semi-solid mass despite high service temperatures.

If the grease liquefies and flows away from the contact then the likelihood of lubrication failure rapidly increases.

Furthermore, grease is unable to remove heat by convection as oil does, so unlike oil, it is not effective as a cooling agent.

It also cannot be used at speeds as high as oil because frictional drag would cause overheating.

The lifetime of a grease in service is often determined by the eventual loss of the semi-solid consistency to become either a liquid or a hard deposit.

Manufacturing of greases

Greases are manufactured by adding alkali and fatty acid to a quantity of oil. The mixture is then heated and soap is formed from the alkali and fatty acid.

After the reaction, the water necessary for soap formation is removed and the soap crystallizes.

The final stages of manufacture involve mechanical working of the grease to homogenize the composition and allow blending in of additives and the remaining oil.

Careful control of process variables is necessary to produce a grease of the correct consistency.

Several cycles of mixing and “maturing” are often needed to obtain the required grease properties.

Most greases are made by a batch process in large pots or reactors, but continuous production is gaining acceptance.

Composition

Greases always contain three basic active ingredients:

A base mineral or synthetic oil
Additives and
Thickener.

For thickeners, metal soaps and clays are used. In most cases the mineral oil plays the most important role in determining the grease performance, but in some instances the additives and the thickener can be critical.

The type and amount of thickener (typically 5% - 20%) have a critical effect on grease properties.

Very often additives which are similar to those in lubricating oils are used.

Sometimes fillers, such as metal oxides, carbon black, molybdenum disulphide, polytetrafluoroethylene, etc., are also added.

Base oils

Mineral oils are most often used as the base stock in grease formulation. About 99% of greases are made with mineral oils. Naphthenic oils are the most popular despite their low viscosity index. They maintain the liquid phase at low temperatures and easily combine with soaps.

Paraffinic oils are poorer solvents for many of the additives used in greases, and with some soaps they may generate a weaker gel structure.

On the other hand, they are more stable than naphthenic oils, hence are less likely to react chemically during grease formulation.

Synthetic oils are used for greases which are expected to operate in extreme conditions. The most commonly used are synthetic esters, phosphate esters, silicones and fluorocarbons. Synthetic base greases are designed to be fire resistant and to operate in extremes of temperature, low and high. Their most common applications are in high performance aircraft, missiles and in space. They are quite expensive.

Vegetable oils are also used in greases intended for the food and pharmaceutical industries, but even in this application their use is quite limited.

The viscosity of the base oil used in making a grease is important since it has some influence on the consistency, but the grease consistency is more dependent on the amount and type of thickener used.

Thickener

The characteristics of a grease depend on the type of thickener used.

For example, if the thickener can withstand heat, the grease will also be suitable for high temperature applications.

If the thickener is water resistant the grease will also be water resistant, etc.

Hence the grease type is usually classified by the type of thickener used in its manufacture. As there are two fundamental types of thickener that can be used in greases, the commercial greases are divided into two primary classes: soap and non-soap based.

Soap-type greases are the most commonly produced.

According to the principles of chemistry, in order to obtain soap it is necessary to heat some fats or oils in the presence of an alkali, e.g., caustic soda ($NaOH$).

Apart from sodium hydroxide ($NaOH$), other alkali can be used in the reaction, as for example, lithium, calcium, aluminium, barium, etc. Fats and oils can be animal or vegetable and are produced from cattle, fish, castor bean, coconut, cottonseed, etc.

The reaction products are soap, glycerol and water. Soaps are very important in the production of greases. The most commonly used soap-type greases are calcium, lithium, aluminium, sodium and others (mainly barium).

In non-soap type greases, inorganic, organic and synthetic materials are used as thickeners.

Inorganic thickeners are in the form of very fine powders which have enough porosity and surface area to absorb oil. The most commonly used are the silica and bentonite clays. The powders must be evenly dispersed in the grease so either high-shear mechanical mixing or some special dispersing additives are required during grease formulation. Because of their structure these types of greases have no melting point, so their maximum operating temperature depends on the oxidation stability of the base oil and its inhibitor treatment. When properly formulated these greases can successfully be applied in high temperature applications. They are usually considered as multipurpose greases and are widely applied in rolling contact bearings and in the automotive industry.

Synthetic and organic thickeners such as amides, anilides, arylureas and dies are stable over a wide temperature range and they give superior performance to soap-based grease at high temperatures. They are used for special applications, such as military and aerospace use.

The thickeners form a soft, fibrous matrix of interlocking particles. The interlocking structure forms tiny pockets of about 10^{-6} (m) in which the oil is trapped. A diagram of the fibrous structure of a soap based grease is shown in Figure 1.

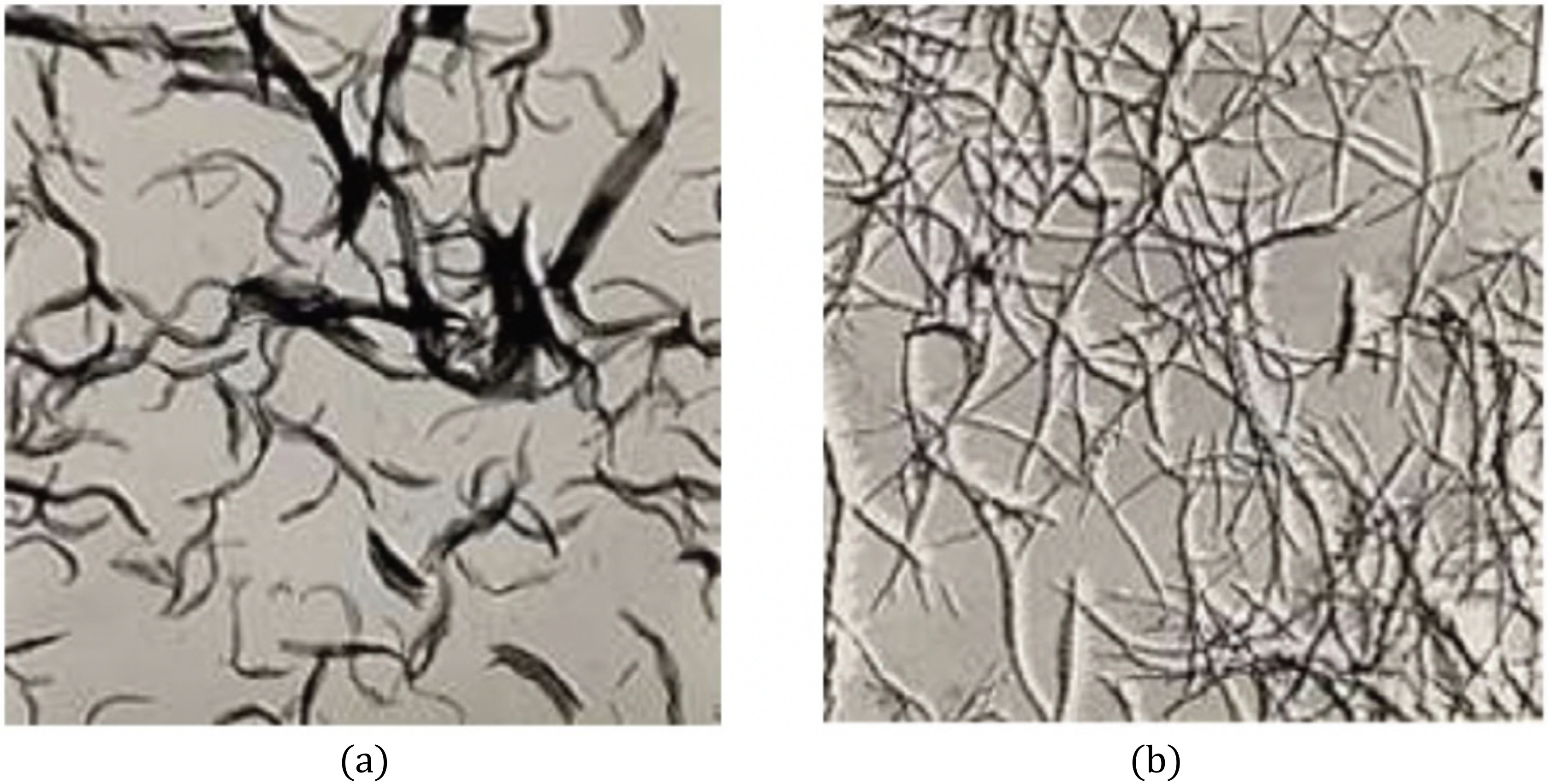

Figure 1: Thickener fiber/micelle structure of two grease compounds (a) Lithium Stearate (b) Lithium 12-hydroxystearate.

Additives

The additives used in grease formulations are similar to those used in lubricating oils. Some of them modify the soap, others improve the oil characteristics.

The most common additives include:
anti-oxidants
rust and corrosion inhibitors
tackiness
antiwear and
extreme pressure (EP) additives.

Anti-oxidants must be selected to match the individual grease. Their primary function is to protect the grease during storage and extend the service life, especially in high temperature applications.

Rust and corrosion inhibitors are added to make the grease non-corrosive to bearings operating in machinery. The function of corrosion inhibitors is to protect the non-ferrous metals against corrosion whereas the function of rust inhibitors is to protect ferrous metals. Under wet or corrosive conditions the performance of most greases can be improved by a rust inhibitor. Most of the multipurpose greases contain these inhibitors.

Tackiness additives are sometimes added to impart a stringy texture and to increase the cohesion and adhesion of the grease to the surface. They are used, for example, in open gear lubricants.

Antiwear and extreme-pressure (EP) additives improve, in general, the load-carrying ability in most rolling contact bearings and gears.

Extreme-pressure additives react with the surface to form protective films which prevent metal to metal contact and the consequent scoring or welding of the surfaces. Although the EP additives are intended to improve the performance of a grease, in some cases the operating temperature is far too low for these additives to be useful.

It has also been found that some thickening agents used in grease formulations inhibit the action of EP additives.

The additives most commonly used as anti-seize and anti-scuffing compounds are graphite and molybdenum disulphide.

Fillers

Fillers are sometimes used as fine solids in grease formulations to improve grease performance.

Typical fillers are graphite, molybdenum disulphide, metal oxides and flakes, carbon black, talc and others.

Graphite, for example, can minimize wear in sliding bearing surfaces, while molybdenum disulphide minimizes wear in gears.

Zinc and magnesium oxide are used in the food processing industry since they neutralize acid.

Metal flakes and powdered metals such as lead, zinc, tin and aluminium are used as anti-seize compounds in lubricants for pipe threads.

Talc is used in die and drawing lubricants.

Lubrication mechanism of greases

Despite the practical importance of greases, there has been surprisingly little research into their lubrication mechanism.

The question is, how do greases lubricate and what is the mechanism involved?

The mechanism of oil lubrication might be hydrodynamic, elastohydrodynamic or boundary, depending on the operating conditions.

The lubrication mechanism of greases, however, will be different since they have a different structure from oil. The structure of grease is gel-like or semi-solid.

It is often assumed that grease acts as some sort of spongy reservoir for oil. It was thought for some time that oil trapped between the soap fibres was slowly released into the interacting surfaces.

The question of whether the grease bleeds oil in order to lubricate, or lubricates as one entity, is of critical importance to the understanding of the lubrication mechanism involved. Studies conducted disprove the oil bleeding model. Experiments were performed where different fluorescent colours were added to the soap thickener and to the oil of a grease. Mixing of the dyes was prevented by selecting a water-soluble dye for the thickener and an oil-soluble dye for the oil. Dispersal of the colours, red and blue, enabled observation of grease disintegration.

Separation of the grease was not observed when it was used to lubricate a rolling bearing. After a few hours of operation, an equal amount of oil and thickener was found on the interacting surfaces.

It was therefore concluded that the bleeding of oil from the grease was not the principal mechanism of lubrication. It appears that the thickener, as well as the oil, takes part in the lubrication process and that grease as a whole is an effective lubricant.

In practice, a large quantity of grease is applied to a system, despite the fact that only a very small amount of grease is needed for lubrication.

The surplus of grease acts as a seal which prevents the lubricant from evaporating and from contamination, while also preventing the lubricant from migrating from the bearing. The surplus of lubricant also plays an important role as a reservoir from which grease feeds to the operating surfaces when needed.

It is thought that the following mechanism is acting: as the thickness of the lubricating film decreases there is an accompanying slight increase in generated frictional heat. As the temperature of grease in the vicinity of the contact increases, the grease expands and softens and more grease smears onto the interacting surfaces.

This has been confirmed in an experiment where the oil and grease film thickness between gears has been measured. Contact voltage drop has been used in experiments to assess the operating film thickness.

It was found that when an oil was used as the lubricant, the contact resistance was relatively steady in comparison to the case when grease was used as the lubricant. This is shown in Figure 2, where the voltage drop for oil and grease is shown for two operating gears under load.

It is evident from Figure 2 that when grease is used as the lubricant, intermittent contact between gears occurs.

The initial failure of the grease film causes the overall temperature to rise, eventually leading to softening and melting of the grease, resulting in the restoration of the lubricating film.

Furthermore, when grease is used, the gear temperatures are usually higher despite lower loading. Average contact load limit for oil is 2,020 (kN/m) and for grease 1,344 (kN/m).

It was also found that the instability of a grease film increases the likelihood of gear failure by scuffing, and gear loading must be reduced by a factor of 0.7 compared to the equivalent load for a gear lubricated by a mineral oil.

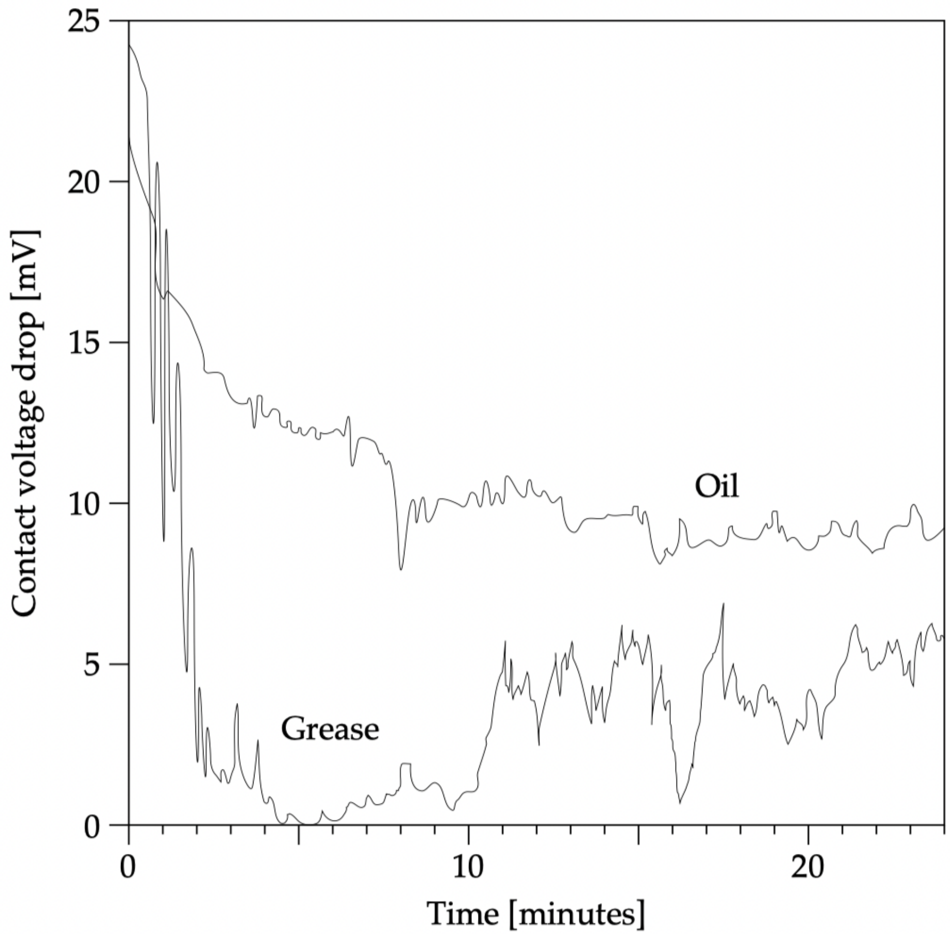

Figure 2: Fluctuations of oil film thickness between two gears, one lubricated by oil and the other by grease.

Greases are commonly used in machinery operating under the elastohydrodynamic lubrication (EHL) regime, i.e., in rolling contact bearings and some gears.

The question is, how does the grease behave in the EHL regime? Experiments revealed that the measured film thickness of grease under EHL conditions is greater initially than if the base oil contained in the grease were acting alone.

With continued running, however, the film thickness of the grease declines to about 0.6 of that of the base oil. The initial thick grease layer is rapidly removed by the rolling or sliding element and the lubrication is controlled by a thin viscous layer which is a mixture of oil and degraded thickener.

The decline in film thickness can only be explained in general terms of scarcity of grease in the contact. Grease is a semi-solid so that once expelled from the contact it probably returns only with difficulty.

It has also been suggested that conveyance of oil by capillary action from the bulk grease to the wearing contact is possible. However, there has been no detailed work conducted as yet to test this hypothesis.

Grease characteristics

There are several performance characteristics of greases which are determined by well established procedures.

The most commonly used in the characterization of greases are:

Consistency
drop point
evaporation loss
oxidation stability
apparent viscosity
stability in storage and
use, colour and odour.

Consistency of greases

Consistency or solidity is a measure of the hardness or shear strength of the grease.

It is defined in terms of grease penetration depth by a standard cone under prescribed conditions of time and temperature (ASTM D217, ASTM D1403).

A schematic diagram of a typical grease penetration apparatus is shown in Figure 3.

The grease is placed in the cup and the surface is smoothed out to make it uniform and is maintained at a temperature of 25°C during the test. The cone tip is adjusted so it just touches the grease surface. The cone release mechanism is then activated and the cone is allowed to sink into the grease for 5 seconds.

The indicator dial shows the penetration depth which is the measure of the consistency of the grease. The test is usually repeated at various temperatures and is used in conjunction with a standard grease-worker described in the next section. The consistency forms the basis for grease classification and its range is between 475 for a very soft grease and 85 for a very hard grease.

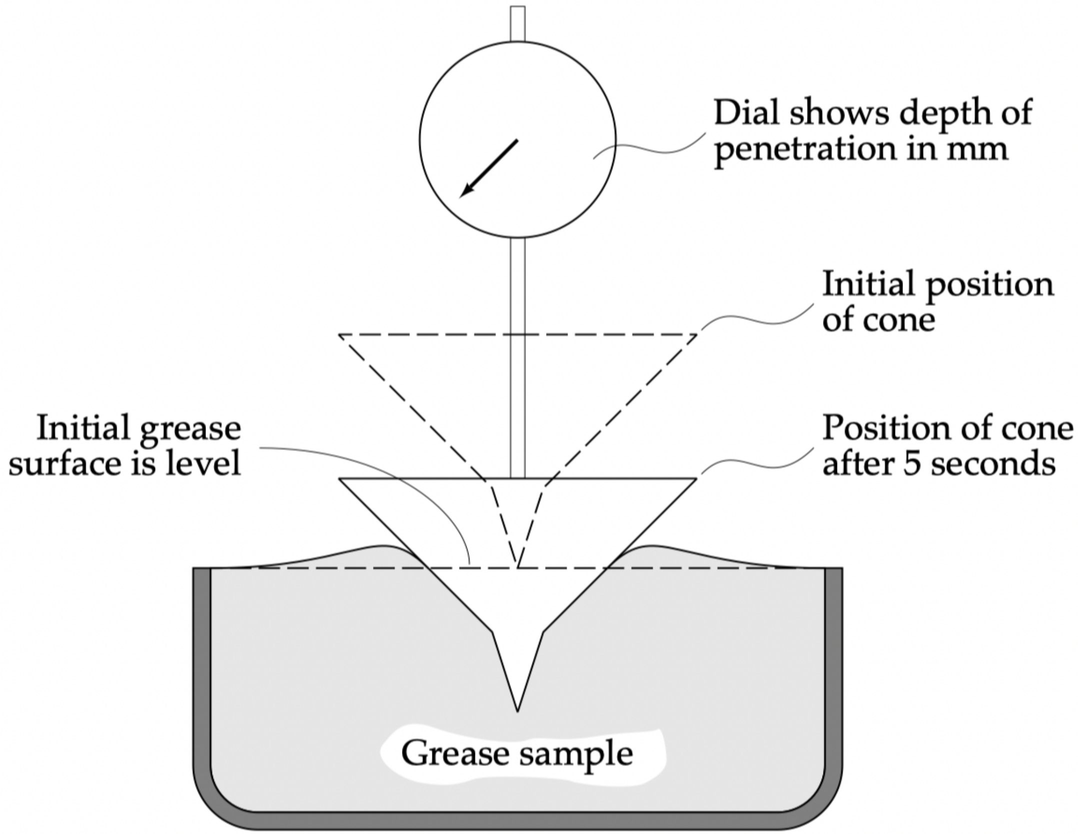

Figure 3: Schematic diagram of a typical penetration grease apparatus.

Although consistency is rather poorly defined, it is a very important grease characteristic.

The hardness of the grease must be sufficient so that it will remain as a solid lump adjacent to the sliding or rolling contact. This lump may be subjected to loads from centrifugal accelerations in rolling bearings and may also be subjected to frictional heat.

However, if the grease is too hard “channelling” may occur where the rolling or sliding element cuts a path through the grease and causes lubricant starvation. Excessively hard greases are also very difficult to pump and may cause blockage of the supply ducts to the bearings.

Consistency of a grease also refers to the degree of aggregation of soap fibres. If the soap fibres are present as a tangled mass then the grease is said to be “rough” and when the grease fibres have joined together to form larger fibres, the grease is said to be “smooth”.

Roughness or smoothness has a strong influence on the stable operation of rolling bearings. If the grease is too smooth, then stable lumps of grease will never form in a rolling bearing during its operation. The grease will continue to slump and circulate in the bearing, and high operating temperatures and short grease life will result.

The trade term for this problem is that the grease has failed to “clear”.

For some unknown reason, a very rough grease will be expelled from the bearing and the bearing will rapidly wear out.

A grease that is neither too rough nor too smooth usually gives the lowest operating temperatures and least wear.

Mechanical stability

The consistency of a grease can change due to mechanical shearing. Even if at the beginning of the service grease possesses the optimum consistency for a particular application, mechanical working will damage the soap fibres and degrade the grease.

Greases differ significantly in the level of damage they will incur due to mechanical working.

For example, greases working in gear boxes and bearings or being pumped through pipes are subjected to shear. The changes in grease consistency depends on the stability of the grease structure.

In some cases greases may become very soft, or even flow, but in most cases there is only slight softening or hardening of the grease. Consistency of the grease is often specified for worked and pre-worked conditions. The grease is worked in the test apparatus which consists of a container fitted with a perforated metal plate plunger which is actuated by a motor driven linkage. The schematic diagram of this apparatus is shown in Figure 4.

There is a large clearance between the piston and the cylinder and the piston is perforated by a series of small holes. The piston is moved up and down and the grease is extruded through the holes and hence is subjected to shearing action. Usually the grease is worked through 60 double strokes of the piston and then the consistency is determined.

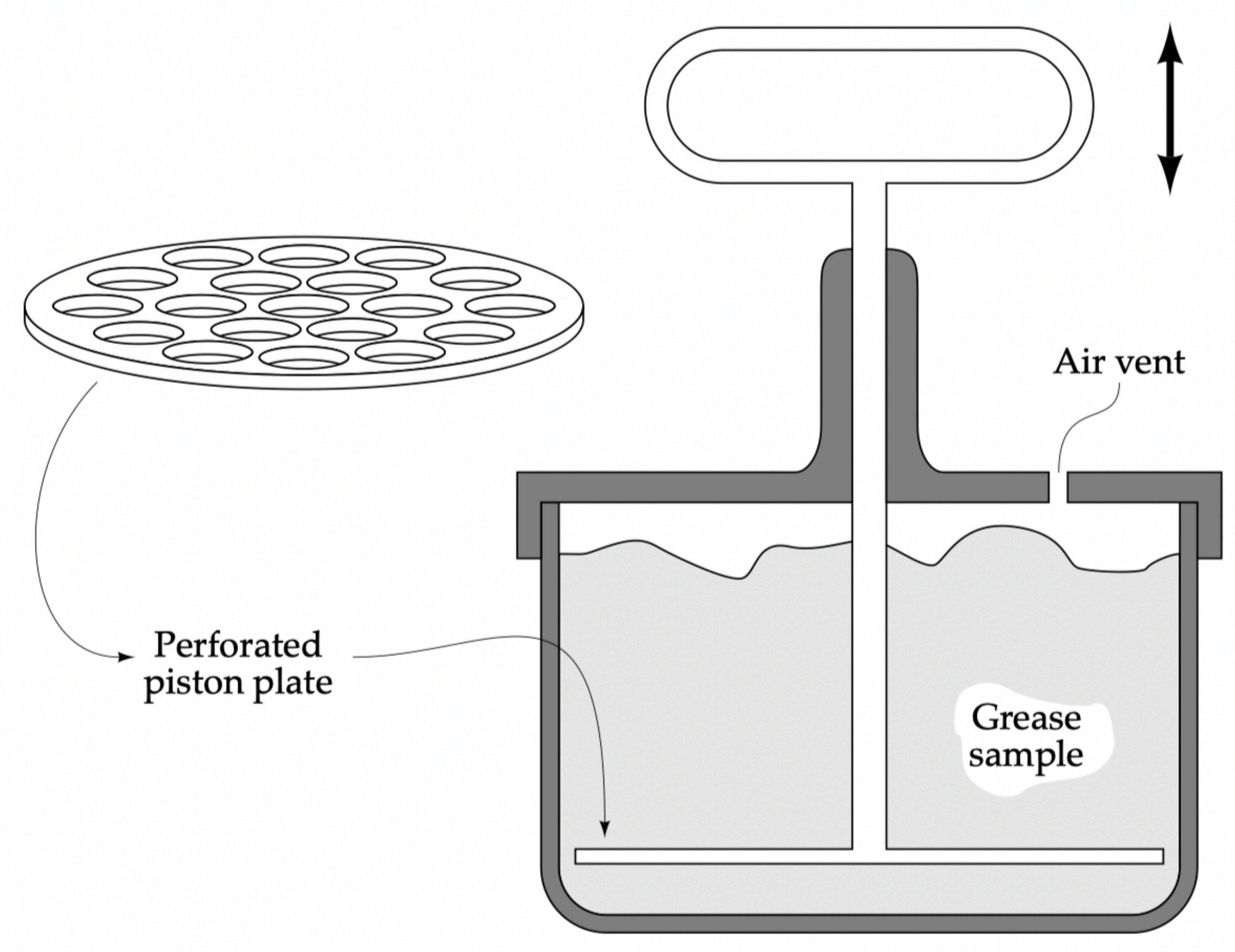

Figure 4: Schematic diagram of a grease-worker.

The consistency of greases made from several thickening agents has been measured after varying periods of mechanical working. It was found that all greases were softened by mechanical working to some extent, but when calcium tallow soap was the thickening agent, little damage resulted.

Lithium hydroxystearate and sodium tallow stearate suffered significant damage initially, but thereafter their consistency reached a stable value. Lithium stearate and aluminium stearate, however, showed a continuous progression in damage.

It was also found that if the grease in a rolling bearing fails to clear then the continued mechanical working of the grease makes the situation even worse.

The high operating speeds of rolling bearings accelerate the mechanical degradation of grease and it is advisable to operate the bearing at slightly less than the maximum rated speed.

A design level of 75% of maximum rated speed has been suggested.

Drop point

The drop point is the temperature at which a grease shows a change from a semi-solid to a liquid state under the prescribed conditions.

The drop point is the maximum useful operating temperature of the grease. It can be determined in an apparatus in which the sample of grease is heated until a drop of liquid is formed and detaches from the grease (ASTM D566, ASTM D2265). The schematic diagram of a drop point test apparatus is shown in Figure 5.

Although frequently quoted, drop point has only limited significance as a grease performance characteristic. Many other factors such as speed, load, evaporation losses, etc. determine the useful operating temperature range of the grease.

Drop point is commonly used as a quality control parameter in grease manufacturing.

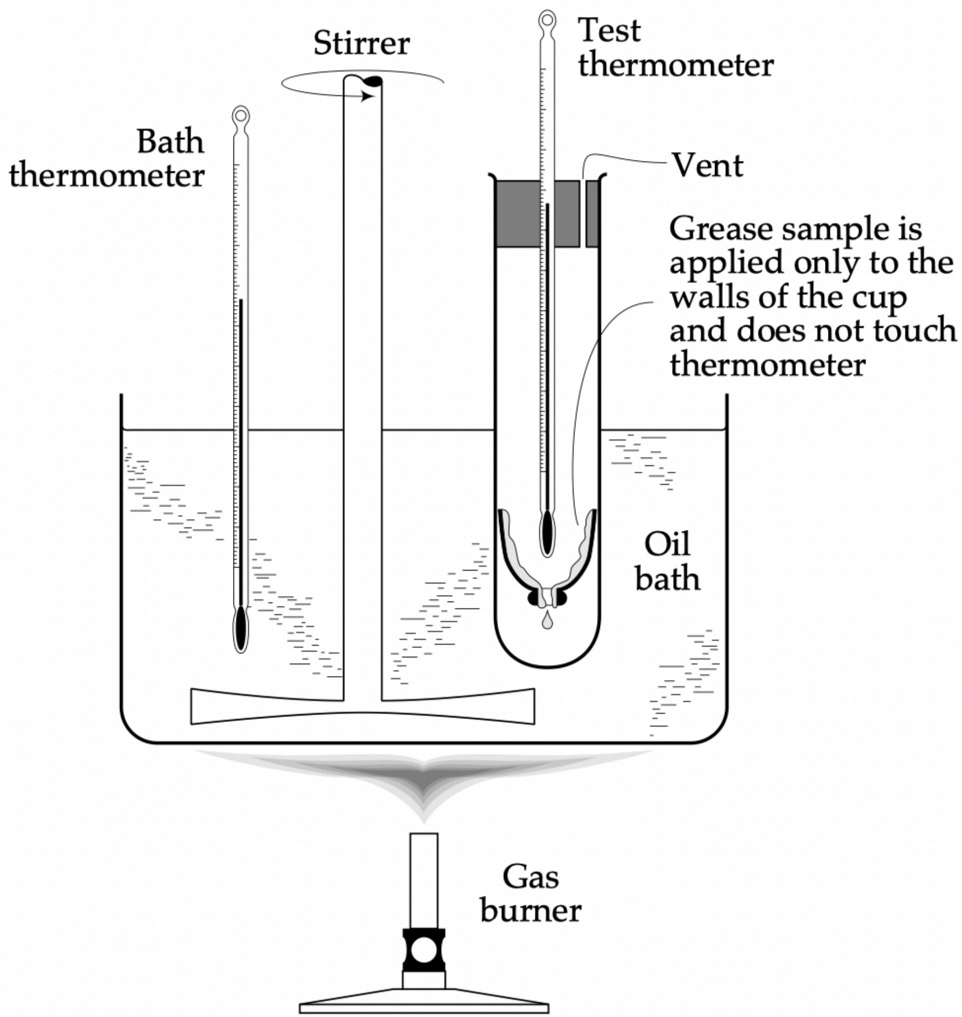

Figure 5: Schematic diagram of a drop point test apparatus.

Oxidation stability

The oxidation stability of a grease (ASTM D942) is the ability of the lubricant to resist oxidation. It is also used to evaluate grease stability during its storage. The base oil in grease will oxidize in the same way as a lubricating oil of a similar type. The thickener will also oxidize but is usually less prone to oxidation than the base oil.

Oxidation stability of greases is measured in a test apparatus in which five grease dishes (four grams each) are placed in an atmosphere of oxygen at a pressure of 758 (kPa).

The test is conducted at a temperature of 99°C and the pressure drop is monitored.

The pressure drop indicates how much oxygen is being used to oxidize the grease. The schematic diagram of the grease oxidation stability apparatus is shown in Figure 6.

Oxidized grease usually darkens and acidic products accumulate in the same manner as in a lubricating oil.

Acidic compounds can cause softening of the grease, oil bleeding, and leakage resulting in secondary effects such as carbonization and hardening. In general the effects of oxidation in greases are more harmful than in oils.

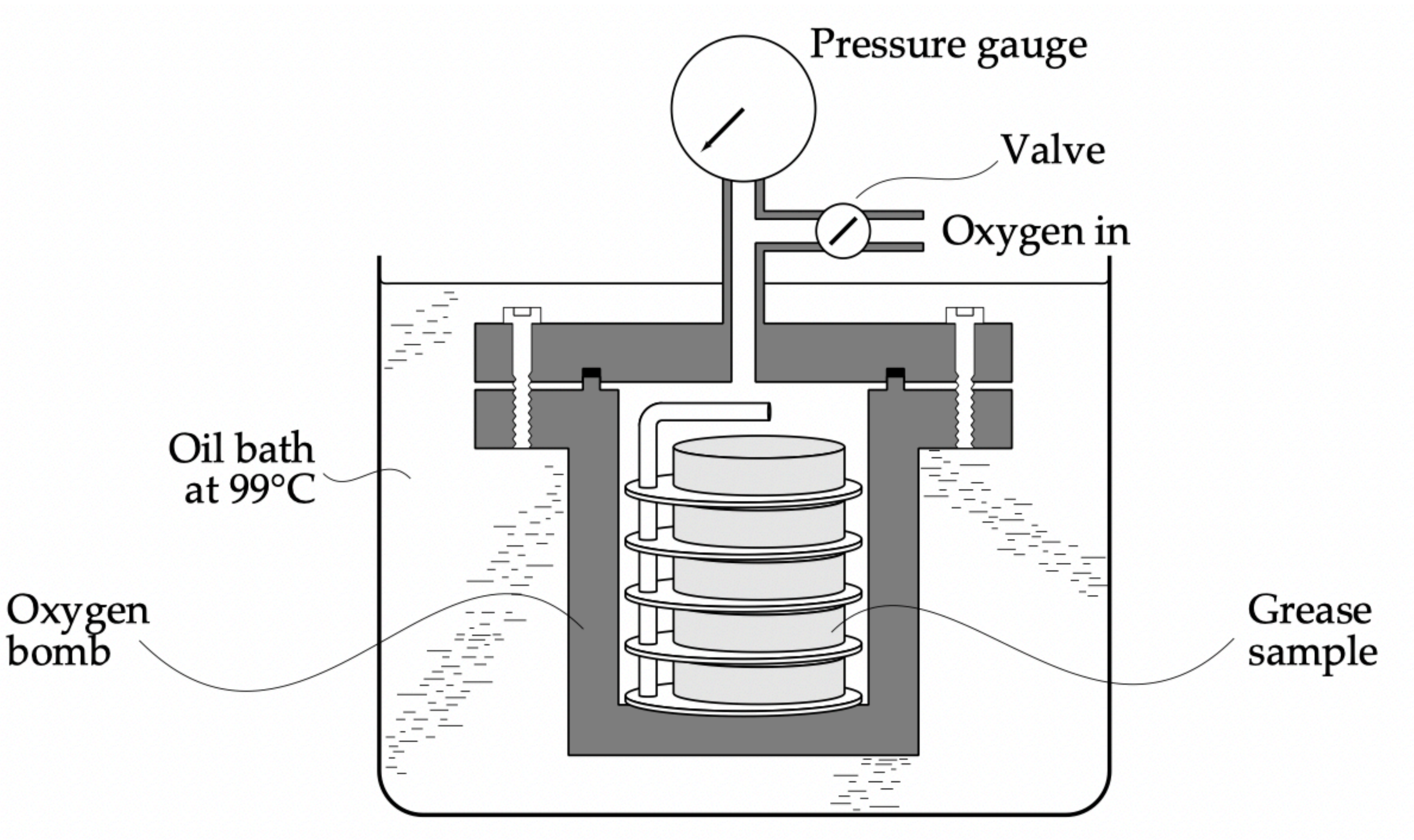

Figure 6: Schematic diagram of the grease oxidation stability apparatus.

Thermal stability

Greases cannot be heated above a certain temperature without starting to decompose.

The temperature limits for greases are determined by a number of grease characteristics such as oxidation stability, drop point and stiffening at low temperature.

Evaporation loss

As in oils, weight losses in greases due to evaporation can be quite significant.

Volatile compounds and products of thermal degradation contribute to the losses, resulting in thickening of the lubricant, higher shear resistance and higher temperatures.

The testing method involves placing the test sample in a heating bath and passing evaporating air over the sample's surface for 22 hours at temperatures ranging between 99°C and 150°C (ASTM D972, ASTM D2595).

The percentage weight loss is then determined.

Grease viscosity characteristics

Greases exhibit a number of similar characteristics to lubricating oils, e.g., they shear thin with increased shear rates, the apparent viscosity of a grease changes with the duration of shearing and grease consistency changes with temperature.

Apparent viscosity of a grease is the dynamic viscosity measured at the desired temperature and shear rate (ASTM D1092, ASTM D3232). Measurements are usually made in the temperature range between -53°C and 150°C in specially designed pressure viscometers.

Apparent viscosity, defined as the ratio of shear stress to shear rate, is useful in predicting the grease performance at a specific temperature. It helps to predict the leakage, flow rate, and pressure drop in the system, the performance at low temperature and the pumpability.

The apparent viscosity depends on the type of oil and the amount of thickener used in the grease formulation.

Classification of greases

The most widely known classification of greases is related to their consistency and was established by the National Lubricating Grease Institute (NLGI).

It classifies the greases into nine (9) grades, according to their penetration depth, from the softest to the hardest, as shown in Table 1.

Table 1: NLGI grease classification.

NLGI grade	Worked (60 strokes) penetration range [$\times 10^{-1}$ mm] at 25°C
000	445 - 475
00	400 - 430
0	355 - 385
1	310 - 340
2	265 - 295
3	220 - 250
4	175 - 205
5	130 - 160
6	85 - 115

Depending on the application a specific grease grade is selected.

For example, soft greases, No. 000, 00, 0 and 1, are used in applications where low viscous friction is required, e.g., enclosed gears which are slow, small and have a tendency to leak oil. In open gears grease must effectively be retained on the gear surface and tacky or adhesive additives such as bitumen are used in its formulation to improve adhesion.

Greases No. 0, 1 or 2 are used depending on the operating conditions such as speed, load and size of the gear.

In rolling contact bearings greases No. 1, 2, 3 and 4 are usually used.

The most commonly applied is No. 2.

Harder greases are used in large bearings and in applications where there are problems associated with sealing and vibrations. They are also used for higher speed applications. In plain, slowly moving bearings (1 - 2 (m/s)) greases No. 1 and 2 are used.

In general practice the most commonly used grease is Multipurpose Grease which is a grease No. 2 according to the NLGI classification, with aluminium or lithium soap thickeners.

The selection of a grease for a specific application mainly depends on the temperature at which the grease is expected to operate.

For low temperature applications, the important factor is the low-temperature limit of a specific grease, which is determined by the viscosity or pour point of the base oil.

Examples of low temperature limits for selected greases are shown in Table 2.

Table 2: Low temperature limits for selected greases.

Base oil	Thickener	Minimum temperature [°C]
Mineral oil	Calcium soap	-20
Mineral oil	Sodium soap	0
Mineral oil	Lithium soap	-40
Mineral oil	Bentonite clay	-30
Diester	Lithium soap	-75
Diester	Bentonite clay	-55
Silicone	Lithium soap	-55
Silicone	Dye	-75
Silicone	Silica	-50

The maximum operating temperature for a grease is limited by the drop point and the oxidation and thermal stability of the base oil and the other grease components.

It is interesting to note that at temperatures above the drop point, a grease may still provide effective lubrication but it will no longer be a grease since it will have changed its phase and become a liquid.

Environmental factors must also be considered in grease selection. Industries such as mining, pharmaceuticals, food processing, textiles, aero-space and others operate in specific environments where different types of greases are required.

In some applications, due to their semi-solid nature, greases are essential. For example, in dirty environments such as mining, greases are ideal since they reduce the risk of fire and have good sealing properties.

In the pharmaceutical and food industry they are widely applied because they seal against dirt and prevent leakages which might otherwise contaminate the product. The type of thickener and base oil that can be used in grease formulation is restricted and controlled in these industries, so that, any accidental contamination of the product will not pose a health risk.

In aerospace applications, greases are expected to operate in extreme conditions.

For example, aviation greases are expected to operate at the temperatures encountered by some of the high altitude military aircraft which range from -75°C to 200°C.

Synthetic lubricants are used in these applications.

In space, greases must have exceptionally low volatility to withstand high vacuum. Evaporation losses in space are controlled by specially designed seal systems.

Grease compatibility

Two lubricating oils, provided that they are of the same type (i.e., mineral, silicone, silane, diester, etc.), should not present any problems with compatibility when mixed.

The general rule, however, is that, two greases should not be mixed, even if they are formulated from the same base oil and thickener, as this may lead to complete failure of the system.

The particular risk is that an oil added may dissolve or soften the thickener.

Degradation of greases

Even though grease is prone to a greater number of degradation modes than oil, it is required to spend a greater period of time as a functioning lubricant. Grease remains packed within the rolling bearing, gear, etc., whereas oil is circulated from a sump.

Grease failure often does not occur immediately but small changes in operating conditions, particularly temperature, may cause problems associated with grease degradation.

The modes of grease degradation are base oil oxidation, separation of oil from the thickening agent and breakdown of the thickening agent.

Base oil oxidation proceeds in a similar manner to that already discussed for plain mineral oils.

Separation of the oil and thickening agent, or “bleeding”, and breakdown of the thickening agent are peculiar to grease.

Even in storage, where oil can be stored in a sealed container almost indefinitely, greases may separate, soften or harden or even become rancid as in the case of some soap thickened greases.

The composition and physical form of the soap control the likelihood of “bleeding” or “loss of consistency”.

Loss of consistency means either that the grease has become too soft or too hard for the intended application or that the rheological and tribological characteristics have deteriorated.

The soap may be present in the oil as a tangled mass of fibres or as discrete crystals. It is only these fibres or crystals that prevent either the oil separating from the grease or the grease degenerating to a simple liquid.

If a grease liquefies, this is called “slumping” and is a major cause of grease failure.

As mentioned earlier, the soap fibres are vulnerable to temperature and excessive mechanical working. Elevated temperature attacks the grease in two ways:

1) The base oil loses viscosity and therefore separates from the grease more readily, and
2) The soap fibres melt, in some cases even at quite low temperatures.

If the soap fibres melt (or soften when there is no clear melting point), the grease disintegrates. Rolling bearings and gears can reach temperatures well in excess of 100°C during operation and special soaps, as opposed to the traditional calcium stearate, have been developed to meet these demands.

An example is lithium hydroxy-stearate which does not soften up to 190°C, and other greases capable of withstanding even higher temperatures are also manufactured.

The lifetime of any grease declines with temperature. For example, at 40°C the lifetime of a lithium hydroxy-stearate grease is approximately 20,000 hours, whereas at 140°C its lifetime is only 500 hours.

Grease failure in these circumstances is caused by hardening of the grease and formation of deposits on bearing surfaces.

Most greases are reasonably resistant to damage by water despite their soap content.

Whilst lithium and aluminium based greases are scarcely affected by water, sodium based greases are quite vulnerable to it.

Calcium based greases, on the other hand, exhibit intermediate levels of water resistance.

Solid lubrication

A solid lubricant is often defined as any solid material which reduces friction and/or wear of contacting surfaces in relative motion.

A vast range of materials and coatings could be judged to behave as solid lubricants on the basis of this definition. Whilst various systems have been used to classify the different types of solid lubricants, an arbitrary–but useful–approach is to classify them as structural lubricants, mechanical lubricants, soaps, and chemically active lubricants (including chemically active additives).

The main purpose of all these substances is to build up a continuous adherent hard or soft film on the rubbing surfaces.

Such films can be applied by a variety of mechanical, chemical, electrochemical or physical processes that include dipping, lapping, painting, immersion, electrolysis, electrophoresis, spraying, plating, welding, baking, cupping, sintering, or ionic plating in vacuum.

Structural lubricants

Currently, the most widely used solid lubricants are graphite and molybdenum disulfide, the highly satisfactory lubricating properties of which are assumed to result from their layered lattice structures.

In addition to these two substances can be included other solids such as metal halides and sulfides that have, in the main, inherent lubricant properties, a lamellar hexagonal crystal structure, and which are usually anisotropic.

Structural lubricants other than graphite and molybdenum disulfide which are not yet used extensively in industry, include:
graphite fluoride
molybdenum diselenide
tungsten disulfide
tungsten
diselenide
niobium disulfide
tantalum disulfide
titan disulfide
barium hydroxide
cobalt chloride
boron nitride and
borax.

Mechanical lubricants

There are different types of substances within this class, the lubricating effect of which is based on different physical and mechanical properties or special conditions.

A common classification divides these lubricants into self-lubricating substances, substances that require a supporting medium to create lubricating properties, and those with indirect lubricating properties based on their hardness.

Self-lubricating substances

These can be classified as organic compounds, metal films, chemical surface layers, and glasses.

Organic compounds can be linear polymers (thermoplastic types such as polytetrafluoroethylene (PTFE), fluoroethylenepropylene (FEP), perfluoroalkoxy (PFA), polyethylene (PE), polypropylene (PP), polyurethane (PU,) polyamide, polyacetals, polyterephthalate, polysiloxanes, Nylon), or crosslinked polymers (thermosetting types such as phenol–formaldehyde, epoxy resin, unsaturated polyester resin, and polyimides.

The sliding characteristics of polymers depend on their chemical nature and the mating partner.

The permissible load is a function of the heat dissipation.

Whilst temperature changes have very little influence on the friction characteristics of polymers, the addition of MoS_2 , graphite, and metal powder improves the frictional characteristics of the polymers and increases their hardness.

Graphite also increases the elasticity module of PTFE.
Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer of tetrafluoroethylene and is a PFAS that has numerous applications. The commonly known brand name of PTFE-based composition is Teflon by Chemours, a spin-off from DuPont, which originally discovered the compound in 1938.

Self-lubricating metal films:

Friction can be reduced by coating the body material surfaces with a thin film of a soft metal, because the friction depends on the shear strength of the soft metal film.

The durability depends on the film hardness, homogeneity, and adhesion.

The lubricating effect of soft metal layers is limited by their melting point (e.g., lead, tin, copper or copper alloys).

Chemical surface layers (conversion films):

In addition to the naturally occurring oxide films present on the surface of most base materials exposed to air, other solid lubricant films can be formed by chemical or electrochemical action on the metal surface.

Chemical surface coatings such as zinc, iron, or manganese phosphates behave similarly to soft metal coatings, but consist not of a metal but rather of metal salts.

Bonderization (phosphate treatment) creates a thin, microcrystalline, strongly adhering phosphate layer on the metal surface; this reduces the coefficient of friction and the danger of seizure during the running-in period.

The lubricating efficiency of the layer, which is normally 2–5 mm thick, is based on its lower shear strength in comparison with the metal.

Glasses:

The structure of glasses consists of random three-dimensional (3-D) networks in which the formation of chains or sheets is possible. The constituents of glass are divided into network formers (SiO_2 , B_2O_3 , Al_2O_3 , Na_2O, etc.) and network modifiers (K_2O, MgO, CaO, PbO, etc.).

The strongest bonds in these glasses are the Si–O bonds, with an average bond distance of 1.62 A.

There is no absolute Si–O bond distance in a glass because of the absence of symmetry, which means that glass softens and has no fixed melting point. The lubrication properties of glass depend on the composition.

The coefficient of friction at a given temperature is a function of the viscosity, the thermal conductivity, the rate of shear, the area of shear, the capacity to dissolve different amounts of oxide from the surface of the material to be lubricated, and the contact angle between the glass and the material, because this determines the capacity of the glass to wet the material. The importance of glasses used as lubricants is specially to be seen in metal-forming operations with operating temperatures up to approximately 1500°C.

Substances that need a supporting medium

These can be classified as inorganic compounds and metal powders.

Inorganic compounds are metal fluorides, metal phosphates, metal hydroxides $Ca(OH)_2$, $Mg(OH)_2$, $Zn(OH)_2$, metal oxides PbO, ZnO, FeO, and Fe_2O_3.

Natural oxide films on metals, which are usually approximately 100 Å thick, have been investigated by Whitehead with regards to their influence on the coefficient of friction.

Their action was found to depend primarily on the relative mechanical properties of metal and oxide. It is generally accepted that the oxide film reduces surface damage, makes sliding smooth, and often reduces friction.

Sulfides, fluorides, phosphates, and hydroxides are each claimed to act as a supporting agent or a catalyst by producing friction- and wear-reducing layers.

Calcium hydroxide, for example, supports the production of a layer of Fe_3O_4 on the rubbing surface of steel. This oxide has better tribological properties than the more common alpha-Fe_2O_3, possibly because of its more favorable close-packed cubic lattice structure compared to the corundum-like lattice structure of Fe_3O_4. The process of formation of these layers depends on the chemical composition of steel and, in particular, on its surface chemistry.

Phosphate layers can also be applied by galvanic techniques. Such procedures are mainly used to create phosphate layers as precoatings for dry-film application, and as lubricant carriers in cold metal forming processes.

In addition to acting as a lubricant carrier, the phosphate coating can be plastically deformed with the steel slug and, therefore, in conjunction with the lubricant, prevents metal-to-metal contact so as to reduce surface friction and wear.

The three main types of phosphating solutions contain zinc, iron, and manganese phosphates, of which zinc phosphate is probably the most widely used.

In contrast to structural lubricants and self-lubricating mechanical lubricants, the lubricating properties of the other mechanical lubricants are mainly based on the supporting effect of a carrier substance or a binder.

The main purpose of these substances, which include Pb, Sn, Zn, Cu, Ag, and In, is to improve the adhesion and cohesion properties of the non-self-lubricating mechanical lubricants.

Soaps:

Soaps are the metal salts of the higher saturated and unsaturated fatty acids and of resin acids, and they are sometimes understood to include salts of naphthenic acids and synthetic fatty acids.

The most effective of these are polar compounds with active groups in a long-chain molecule, presumably because the reactive group attaches itself to the surface being lubricated and resists removal.

They often give the lowest coefficients of friction obtainable with solid lubricants, but in general cannot be used above their melting points, or at high loads. The main function of soaps in lubrication technology is in the preparation of greases.

The main use of soaps as lubricants in their own right depends on their formation in situ on a metal surface, by the chemical attack of a fatty acid on the metal.

Products containing solid lubricants

Powders

In order to ensure that solid lubricants in the form of powder provide sufficient coverage in a tribological system, these lubricants must have the appropriate properties to enable them to create a film (cohesive properties) and also to adhere (adhesive properties). Three requirements result from this:

1) The level of adhesion between the lubricant film and the surface of the material must be great enough to ensure that this lubricant film adheres to this surface when it is subjected to friction.
2) The internal cohesion of the film must be sufficiently large that the film does not split when subjected to friction.
3) The adhesion between the particles and layers in the shearing direction should be as small as possible to keep the resistance to friction low.

These main requirements can be met only by self-lubricating dry lubricants. MoS_2, because of its crystalline structure (layer grid) and bonding type (covalent bonding of a metal (Mo) and strong polarizing effect of a non-metal (S) with a high degree of polarization), meets these requirements as well as can be achieved; it is, as a result, the most commonly used.

Other solid lubricants which are applied in powder form are organic compounds such as PTFE and graphite, although these fulfill the requirements listed above to a limited extent only.

Before the solid lubricant powder can be applied, the surface of the material must be thoroughly cleaned.

Roughing the surface mechanically or with phosphates improves adhesion, and therefore also the lifetime.

The lubricant can be effectively applied by simple rubbing with cloths, sponges, brushes, or polishing pads or polishing buffs, by applying it using suitable carriers, and coating by cathode evaporation in an ultra-high vacuum.

Solid lubricants in carrying media

As mentioned above, very few solid lubricants have the appropriate adhesive and cohesive properties which enable them to create an effective lubricating layer with low friction coefficients while providing a sufficient lifetime.

Most substances used as solid lubricants require a carrying medium, a bonding agent, and/or pre-treatment of the material surface, to help create or improve their adhesive and film-creating properties.

The substances commonly used as bonding agents include: organic binding agents, such as resins; inorganic binding agents, such as silicates; and oils, greases, and water.

It is also advantageous to pre-treat the surfaces by degreasing, sandblasting, corroding, etching, phosphating, anodizing, and also by activation, for example with a low-pressure plasma.

Dispersions and suspensions

Dispersions and suspensions in carrying liquids with low volatility are mainly used in areas where, for tribological reasons, a dry lubricating film should be created, but where the effective application of a powder is not possible for technical reasons. The same types of solid lubricant are used here in the same way as for powders.

Dispersions and suspensions of solid lubricants in water are usually used to coat mass elements for cold and hot forming.

The most commonly used substances here are salts, special white solid lubricants, and graphite.

Dispersions and suspensions in oils also act as aids in forming techniques, and they are also used as additions in gear- and oil-lubricating systems.

The solid lubricants used here in forming techniques are the same types as those used as dispersions and suspensions in water.

MoS_2 plays a dominant role as an additive to lubricating gears and for general use in oil lubricating systems.