Lubrication Beyond Oil and Grease

*How Anti-Seize Pastes and Anti-Friction Coatings Reduce Wear, Optimize Friction and Perform Under Extreme Environmental Conditions*

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Molykote® brand Lubricants from Dow Corning Corporation
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Introduction

Tribology – the science and engineering of interacting surfaces in relative motion – is used to study effects of different lubricants on friction and wear. Starting with a discussion of basic tribosystems and types of lubrication regimes, this paper describes different forms of lubrication, including solid lubricants and how they function. Evidence is provided that anti-seize pastes and anti-friction coatings, fortified with different types and levels of solid lubricants, can provide effective lubrication beyond oils and greases in certain applications and support oils and greases in other applications. Available as Molykote® brand Smart Lubrication™ solutions from Dow Corning, these anti-seize pastes and anti-friction coatings (AFCs) can reduce wear, optimize friction and perform under extreme environmental conditions.

Tribosystems and Lubrication Regimes

Basic Tribosystem: A tribosystem, as shown in Figure 1, consists not simply of lubricants employed to manage friction and wear, but also includes opposing parts and their material and surface properties, the loads and relative motions presented by the application under investigation, and the environment under which this entire system is expected to perform. The properties and characteristics of a typical tribosystem work synergistically to mitigate friction and wear in an effort to improve performance and prolong usefulness of the asset or component within the operating context of the application.

Lubrication Regimes: Tribological films are formed in different ways. In general, film formations are described as being hydrodynamic regimes ... elastohydrodynamic regimes ... or boundary regimes. The mixed regime combines elements of boundary and hydrodynamic regimes. Lubrication or friction regimes are formed as a function of many different properties and characteristics of the tribosystem. Most important are the speeds, loads, component geometries, substrate material properties and lubricant material properties involved in the application.

In hydrodynamic regimes, fluid lubricants are forced between opposing surfaces as a result of relative motion (speed), and they respond to forces (loads) applied on the opposing component surfaces. The fluid response is to separate one opposing surface from the other with dynamic pressure.

In elastohydrodynamic, or EHD, regimes, as loads and speeds increase dynamic pressure, the fluid is compressed to a point at which it begins behaving like a solid. This leads to elastic deformation of the component surfaces, and a transition is made into the EHD regime.

Boundary regimes are not created by fluid under pressure, but rather by surface-active materials that form boundary films on and between the substrate surfaces. Surface-active substances like anti-wear and extreme-pressure additives and solid lubricants can adhere to component surfaces as well as cohere to themselves to provide boundary layers. These can protect the substrate from wear by reducing friction. Adhesion and

Figure 1. Components of a typical tribosystem include the parts in relative motion, the tribological film (lubricant), loads and operating environment.
cohesion of surface-active materials are keys to the effectiveness of boundary films.

**Mixed regimes** occur when both hydrodynamic and boundary regimes may be present. Under most application conditions, the tribological films will experience each type of lubrication regime at one point or another. For example, during start-up and shutdown periods or in transient events that involve shock loads, conditions can occur in which the relative motion and/or the distance between surfaces converge toward zero. At these points, both partial hydrodynamic films and boundary films are in play.

**Concept Example:** A water skier can demonstrate the concepts of these different lubrication regimes. Referring to Figure 2, imagine the ski as surface 1 and the lake bed as surface 2. The skier represents the load, while the water represents the lubricant. Graphically, the film thickness and frictional coefficient can be plotted relative to speed (velocity) of the skier. On the left, the example begins with the load (the skier) on surface 1 (the ski), while surface 1 (the ski) is resting on surface 2 (the lake bed). This marks the **boundary regime**, or solids contact. As the skier’s velocity increases, water is forced between the ski and the lake bed. This marks the **mixed regime** – the boundary regime moving toward the hydrodynamic regime. Dynamic fluid pressure begins to “lift” the ski from the lake bed, increasing film thickness between the ski and the lake bed. As the film thickness increases, the coefficient of friction decreases.

The point at which the ski no longer touches the lake bed marks the end of boundary lubrication. At this time, the thin film of water between the ski and lake bed is under enough pressure to deform the surface of the ski and/or lake bed (imagine rocks shifting as the skier passes by), and the frictional coefficient is the lowest. This marks the **elastohydrodynamic (EHD) regime**. As velocity continues to increase, the fluid film becomes thicker. As a result, the internal fluid friction of water and the friction between the ski and the water begins raising the frictional coefficient. This marks the full-film **hydrodynamic regime**.

**Surface-Active Materials:** Think back to the beginning, when the skier’s velocity was low or if the load was extremely high. Imagine coating the ski with wax and/or the lake bottom with small pebbles. The wax and pebbles can be thought of as surface-active materials to reduce the coefficient of friction when the hydrodynamic film cannot be formed.

This is the basic principle behind using solid lubricants to improve lubrication effectiveness and prolong usefulness of assets or components in a given operating application.

**From Concept to Machine**

In industrial applications, a machine or component requiring lubrication will have a primary lubrication regime based on its steady-state operation. Remember that the lubrication regime is a function of speed, load, material properties and more. As such, different lubricant forms may be required to provide proper lubrication for the primary regime. In typical applications, fluids (generally oils and greases) are used to meet requirements of hydrodynamic and elastohydrodynamic regimes. Solid lubricants and long polymer-chain additives are used to meet the requirements of boundary regimes. A combination of fluids, additives and solids can be used in the mixed regime.

Subsequently, finished lubricant formulations come in a myriad of forms to meet different application requirements. For example, a bearing requiring hydrodynamic lubrication will require a lubricant fluid to form the hydrodynamic film. In contrast, a low-speed, highly loaded gear set will require a solid lubricant to form adhesive and cohesive boundary layers to protect gear teeth from wear. A component subject to start-stop conditions and shock loads may need a combination of lubricant forms.

As shown in Figure 3, the boundary regime normally requires solid lubricants, pastes and anti-friction coatings. The mixed regime is best handled with greases and dispersions containing solid lubricants. And the requirements of the hydrodynamic regime can typically be met with oils and greases.
Constituents in Lubricant Forms

- Oils
- Greases
- Anti-Seize Pastes
- Anti-Friction Coatings (AFCs)

Base Oil: ~90%
Additives, including solid lubricants: up to 10%

Base Oil: ~65 to 95%
Thickener: ~5 to 35%
Additives, including solid lubricants: ~0 to 10%

Base Oil: ~40 to 60%
Solid lubricants: ~40 to 60%
Solvents: ~55%
Resins: ~12%
Additives: ~3%

In general, the listed lubricant forms perform best in the specific lubrication (or friction) regimes, yet some overlap occurs. This is especially true for instances of the mixed regime in which both the boundary regime and the hydrodynamic regime are present. An examination of the typical formulation constituent components in different lubricants will help explain how and why different forms work better in different regimes.

Different Lubricant Constituents

In Figure 4, the typical constituents of four common types of lubricant forms are listed. These include oils, greases, pastes and anti-friction coatings. As shown, a base oil (fluid basestock) is the predominant constituent component in oils and greases. This is the primary reason that oils and greases are best for providing hydrodynamic films; lubrication is primarily provided by fluid.

In similar fashion, solid lubricants are the predominant component in anti-seize pastes and anti-friction coatings (AFCs). This explains why pastes and AFCs are best for providing boundary lubrication films; lubrication is primarily provided by surface-active materials. Note that oils and greases may contain low levels of solid lubricants for supplemental surface-wear protection.

AFC Solvent: Some may question the use of solvents in the anti-friction coating formulations. Similar to paints that use water or solvents to facilitate spreading color pigments, AFCs use solvents to aid in dispensing and dispersing the solid lubricant and resin components onto the application surface. These solvents evaporate upon application and provide little or nothing to the tribological film formation.

Oils and Greases: As previously stated, oils and greases rely on fluid to provide the hydrodynamic lubricating films. For these hydrodynamic films to form, relative motion between the opposing surfaces must be present. Some other significant or considerable factors are rooted in the relationship between viscosity, temperature, pressure and film formation. This will not be explored in this discussion. A key point, however, is that fluid viscosity changes with temperature and pressure, and film thickness changes with viscosity. As a result, in a hydrodynamic regime, the lubricant film thickness will change with temperature and pressure.

In addition, fluids are volatile and subject to issues relating to oxidation, evaporation and the effects of gravity. These inhibit the ability of the fluid to stay where it is needed – between the component surfaces.

As a general statement, based on this and other discussion points, lubricant fluids may be unable to form effective tribological films under static loads and high loads, as well as at low speeds (slow relative motion).

Solid Lubricants: Unlike the fluids in oils and greases, the solid lubricants that make up a dominant portion of the film-forming functional constituents of anti-seize pastes and anti-friction coatings are relatively

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Figure 3. Different lubricants are used to meet the requirements of the boundary, mixed and hydrodynamic regimes.

Suitable Lubricant Forms for Different Frictional States

<table>
<thead>
<tr>
<th>Boundary Friction</th>
<th>Mixed Friction</th>
<th>Hydrodynamic Friction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid lubricants</td>
<td>Greases with solid lubricants</td>
<td>Greases</td>
</tr>
<tr>
<td>Pastes</td>
<td>Dispersions</td>
<td>Oils</td>
</tr>
</tbody>
</table>

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Figure 4. Different lubricant forms contain different constituent components to meet regime requirements.

<table>
<thead>
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<th>Constituents in Lubricant Forms</th>
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<tbody>
<tr>
<td>Oils</td>
</tr>
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<td>Base oil: ~90%</td>
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</tr>
<tr>
<td>Anti-Seize Pastes</td>
</tr>
<tr>
<td>Base oil: ~40 to 60%</td>
</tr>
<tr>
<td>Solid lubricants: ~40 to 60%</td>
</tr>
<tr>
<td>Anti-Friction Coatings (AFCs)</td>
</tr>
<tr>
<td>Solvents: ~55%</td>
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<tr>
<td>Solid lubricants: ~30%</td>
</tr>
<tr>
<td>Resins: ~12%</td>
</tr>
<tr>
<td>Additives: ~3%</td>
</tr>
</tbody>
</table>
unaffected by temperature and pressure. As temperatures and pressures increase or decrease, boundary films formed by solid lubricants can maintain steady thickness without changing as fluids do.

Additionally, because these lubricant materials are in a solid state, they are not subject to evaporation. Oxidation temperatures exceed 399°C (752°F) or higher for solid lubricants. Particle size and adhesive and cohesive properties enable solid lubricants to stay in place, even under gravitational influence.

Perhaps the most important difference between solid lubricants in pastes and AFCs, compared to the fluid lubricants in oils and greases, is that solid lubricants do not rely on relative surface speeds to form tribological films. This can be advantageous under static and high load conditions as well as at slow speeds.

In particular, solid lubricants can provide benefits when used in support of fluid lubricants to help protect surfaces during transient events.

These can include start-up and shutdown events when surface motion is transitioning from low speed to high speed or from high speed to low speed. The same applies to events with shock loads brought on by system upsets like pump cavitation or dead-heading, compressors being flooded with liquids, bearings under abnormally high vibration, and other such conditions.

**How Solid Lubricants Work**

This discussion has covered principles of how fluids form tribological layers in hydrodynamic regimes. It also noted that solid lubricants can provide advantages in boundary regimes. Understanding how solid lubricants work is important for selecting the most effective lubricant for certain applications. Some of the basic principles of solid lubricants are shown in Figure 5.

Solid lubricants are produced as fine-particle powders. These particles are able to fill in, smooth and cover surface asperity peaks and valleys found on component surfaces. As relative motion and loads are applied to the interacting surfaces, the solid particles adhere to the substrate material. The result is the formation of protective layers to control friction and reduce surface wear.

In addition, because of the particle and surface intermolecular charges, solid lubricants adhere strongly to the surface material and also cohere to each other to form lubricating layers.

However, solids in powder form are relatively difficult to apply to a surface with much consistency, and keeping them on the surface can be difficult, despite the intermolecular attraction. So, solid lubricants in high quantities normally are applied as a constituent of anti-seize pastes and anti-friction coatings.

**Anti-Seize Pastes**

A paste is a convenient form for easy application of solid lubricants. Typically, such pastes can be used to aid assembly and disassembly of...
components by providing a consistently lower coefficient of friction than component surfaces alone, even at extreme temperatures.

Paste Constituents: The two primary constituent components in anti-seize pastes are solid lubricants and base oils. Paste formulations typically contain 40 to 60 percent solid lubricants. Various choices for solid lubricants include molybdenum disulfide (MoS₂); graphite; calcium hydroxide; metal phosphates; inorganic oxides; and various metals, like copper, tin, lead, zinc, aluminum and nickel.

The second primary component in pastes is a base oil, which functions to carry the solid lubricants to the point where lubrication is required. The oil volume will vary between 60 and 40 percent, depending on the level of solid lubricants. These carrier oils can be mineral-oil-based or synthetic in nature. Synthetic carriers include poly-alpha olefins (PAO), polyalkylene glycols (PAG), diesters (DE), polyol esters (POE), silicones and perfluoropolyethers (PFPE).

Paste Types: Paste types are often characterized by color, as this suggests the types of solid lubricants employed in a particular formulation. The different types are summarized in Figure 6, along with their typical solid-lubricant content and common applications.

<table>
<thead>
<tr>
<th>Paste Type</th>
<th>% Solid Lubricants</th>
<th>Typical Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black pastes</td>
<td>60% MoS₂, graphite and other solid lubricants</td>
<td>Assembly, thin-film</td>
</tr>
<tr>
<td>White pastes</td>
<td>60% white solid lubricants</td>
<td>Assembly, thin-film</td>
</tr>
<tr>
<td>Metal pastes</td>
<td>60% metal powders and other solid lubricants</td>
<td>Threaded connections</td>
</tr>
<tr>
<td>Grease pastes</td>
<td>25% solid lubricants</td>
<td>Thick-film, lifetime lubrication</td>
</tr>
<tr>
<td>Oil pastes</td>
<td>10 to 20% solid lubricants</td>
<td>Lifetime lubrication, corrosion protection</td>
</tr>
<tr>
<td>Metal-free pastes</td>
<td>60% black and white solid lubricants</td>
<td>Assembly, threaded connections</td>
</tr>
</tbody>
</table>

Some paste formulations may contain small amounts of thickeners, similar to those used in greases, to give some additional consistency and provide “lifetime” lubrication. These are commonly referred to as grease pastes, and they typically have about 25 percent solid lubricants. Oil pastes have a reduced amount of solid lubricants – 10 to 20 percent, for example – with the balance predominantly oil. These oil pastes are often good for lifetime lubrication and can provide additional corrosion protection and adhesion.

Metal-free pastes are becoming more popular as users seek to become more eco-friendly. These pastes typically use forms of inorganic oxides like zirconium as the solid lubricants. Metal-free pastes are often applied as other pastes are used, but most commonly when high temperatures exist and where solder embrittlement and stress-corrosion cracking can be factors.

Anti-Friction Coatings

The second form in which solid lubricants can be applied to surfaces is as an anti-friction coating. AFCs are paint-like products in which solid lubricants in a solvent carrier are bound to a surface by a resin material. Like paint, the AFC dries or “cures” to form a thin, dry layer of solid lubricants as the solvent evaporates. The solids provide lubrication for boundary regimes, while the resins as well as the solid-film layers provide some degree of corrosion protection.

AFC Constituents: Typical AFC formulations will contain solid lubricants, resins, additives and solvents. Respectively, solids, resins and additives constitute about 30 percent, 12 percent and 3 percent of the formulation and make up the functional “coating” or film. Solvents make up the balance – about 55 percent – of the formulation and serve as agents to aid dispensing and dispersing the solids.

Like pastes, the functional lubricants in an AFC are solids. These solids can include many of the same materials used in pastes, such as molybdenum disulfide (MoS₂), graphite and polytetrafluoroethylene (PTFE). Solid-lubricant materials, like graphite and
MoS₂, typically provide higher load-carrying capacity (up to 1,000 N/mm²), while PTFE and other resin waxes provide lower load-carrying capacity (up to 250 N/mm²) but are typically good at providing a low coefficient of friction in sliding conditions.

The resin or binder system in an AFC provides adhesion of the solid lubricants to the substrate. Resins often have chemical and corrosion-resistance properties that complement the surface protection that the solid-lubricant layers provide. In general, the higher the concentration of resin is in the formulation, the better the corrosion protection. Resins can be epoxy, polyamide, phenolic, acrylic or titanate in nature, each offering different cure conditions as well as different adhesion and robustness properties. Organic resins are best for lower application temperatures of 250°C (482°F) and below, while inorganic resins are needed for higher application temperatures up to 600°C (1,112°F).

Solvents help maintain the AFC in a fluid form to aid application and proper substrate coverage. Solvent concentration helps regulate the viscosity during the application process, much like paint thinners can be used to thin paint and promote smooth, even coverage. These solvents may be organic or water-based.

Additives play a role in anti-friction coatings, similar to their functional role in oils, greases and pastes. Selected additives can be used to impart additional, desirable properties to the AFC and/or the substrate.

**Coating Application:** An AFC is typically applied to the surface as a wet film about 30 microns thick. As the solvents evaporate, the resin matrix cures to bind the solid lubricants to the substrate surface in a dry film approximately 15 microns thick. Curing (drying) conditions vary from one AFC formulation to another. This is predominantly controlled by the different resins or binder systems used in the various coating formulations. Cure temperatures can vary from ambient to as high as 250°C (482°F). Cure times also can vary from as short as five minutes to as long as 120 minutes.

AFCs can be applied effectively in a few ways similar to how paints are applied, such as by spraying, brushing or dipping. Additional methods – like dip-spinning (in which a centrifuge is employed to spin off excess material) or screen printing – can help promote even film thickness and uniform appearance.

The application process impacts the total cost of using anti-friction coatings. For example, a dip-spinning process will make up approximately 70 percent of the total cost of applying an AFC due to additional equipment and process time. The material cost will be only about 30 percent. Total cost-in-use, however, may be far less than an alternative lubrication method if the need for relubrication is reduced or eliminated.

Just as in painting, AFC effectiveness and service life depend on pretreatment processes. Paint will not adhere to an improperly prepared surface, and neither will an anti-friction coating. Pretreatments, such as degreasing, sandblasting and even acid washing, may be required to remove surface contaminants and allow the resin binder in the AFC to adhere the solid lubricants properly to the substrate.

Additional surface treatments, such as anodizing, phosphating or galvanizing, may be considered to help ensure corrosion resistance or provide other desirable properties. AFC resins will still adhere to such pretreated substrates and deliver an extra measure of corrosion protection.

**AFC Advantages:** Anti-friction coatings offer many advantages for controlling friction and wear on a surface. Cured AFCs are dry, will not attract dust and dirt, and will work effectively in the presence of dust and dirt. The solid lubricants and resins in AFCs are not susceptible to aging and evaporation like conventional oil and grease lubricants. AFCs can often be used in place of surface treatments like galvanizing to provide both lubrication and corrosion protection. In the event a machine component must sit idle in a prolonged shutdown, AFCs will remain fully effective, unlike oils and greases that may degrade and evaporate. Because solids are used as the primary lubricants, AFCs protect and lubricate across a very wide service temperature range. And AFCs also can be more aesthetically pleasing; when applied correctly, they have a smooth and even surface appearance.

**AFC Limitations:** Typically, anti-friction coatings are not used as primary lubricants in relatively high-speed, rolling applications. Higher speeds typically require lubricating films for hydrodynamic regimes, and rolling applications typically require lubrication for elastohydrodynamic regimes. These regimes are best served by fluid-containing lubricants like oils and...
greases. Yet, AFCs may be used as secondary, emergency or transient-event lubricants to support a primary oil or grease lubricant. An example would be using an AFC to protect a pump shaft at start-up or shutdown, when shaft speeds are such that sleeve bearings are not operating at speeds where hydrodynamic films can be formed.

Another downside to AFCs is that the application process can be somewhat costly. Special equipment, extra handling and trained coating shops may be needed. Also, required cure times may not always fit into existing manufacturing processes; components may require coating by other resources. As noted, however, such added costs can be overcome by reducing or eliminating relubrication requirements.

**AFC Applications:** There are countless applications for AFCs. Generally, these include low-speed and high-load applications that require boundary-regime lubrication. AFCs also are good for dusty or dirty environments in which oil and grease lubricants can attract contaminants that may lead to accelerated abrasive wear. Applications where oscillatory motion and vibration can cause fretting corrosion also are good candidates for an anti-friction coating. In addition, AFCs can help reduce premature machine wear from initial start-up and run-in operations. They also can provide good corrosion protection, replacing heavy metal coatings to prolong asset life and enhance environmental friendliness. Applications with sliding friction and wear mechanisms – such as cams, slides, ways and springs – also are ideal for AFCs.

**Conclusion**

In summary, tribosystems are made up of surfaces, lubricants, loads and relative motion within a known environment. From resisting the effects of dust and dirt to withstanding temperature extremes, effective lubrication must provide hydrodynamic and boundary lubrication to reduce wear and friction on surfaces of machinery components. Different lubricant forms are needed for different lubrication or friction regimes. Oils and greases can be effective in hydrodynamic regimes but cannot provide proper film formation in boundary regimes. Solid lubricants can be applied as a component of anti-seize pastes and anti-friction coatings to offer protection under boundary conditions. These same solid lubricants can support lubrication solutions for the mixed regime.

Effective lubrication for boundary regimes is needed in applications with static or heavy loads, components operating at low speeds, or with shock loads or transient conditions that might cause component failures. Anti-seize pastes and anti-friction coatings, fortified with high levels of lubricant solids, can go beyond traditional oils and greases to reduce wear; optimize friction; and provide long-lasting, effective lubrication in extreme environmental conditions.
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