WHITE PAPER

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Lubrisense™

DESIRABLE PARTICLES

”Utilisation of particles in lubricating greases from toxic metallic powders to renewable materials”

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Greases containing solid particles

AXEL CHRISTIERNSSON

UTILISATION OF PARTICLES IN LUBRICATING GR
FROM TOXIC METALLIC POWDERS TO RENEWAB


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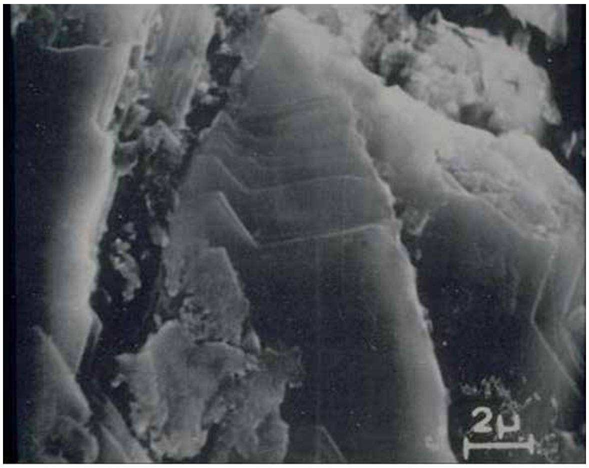
Obviously, the primary function of a lubricating grease is to lubricate i.e. to perform as a surface separator and a friction modifier, but even other advantages such as sealing ability, corrosion protection and providing a matrix to carry solid particles into the contact zones can be achieved. By definition, lubricating grease is a multiphase system consisting of a fluid lubricant and a thickener (gelling agent). This thickening agent gives lubricating grease the rheological properties of a solid at rest whereas, at a given level of shear stress, the grease will begin to flow like a liquid and perform as a lubricant in a dynamic situation.

For many years now, the authors have noted many grease manufacturers' ignorance about and lack of attention to particle technology and its potential for their business. A tremendous amount of resources has been spent on studying and developing oils, thickener systems and additives but with the clear exception of solid particles. This statement can easily be verified by studying patents and articles published over the last 50 years. There are, however, some companies who have discovered and utilised the advantage of introducing "suitable" and "desirable" particles in lubricating grease in order to upgrade a so-called multipurpose grease into a problem solver.

It is well known that by adding solid particles to a lubricating grease, certain properties can be enhanced. These include surface separation (especially at high loads, slow speeds and high temperatures), increased load carrying capacity, reduction of wear and friction and the facilitation of performance under oscillatory conditions. The effect of these particles is most useful in the boundary and mixed-lubrication regimes where they can protect the metal surfaces, build lubricating films and prevent metal to metal contact.

EASE ...

LE MATERIALS

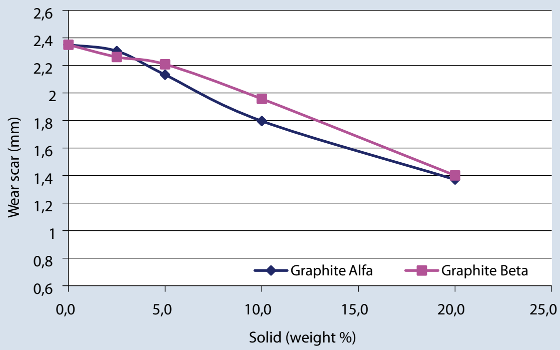


THE LAYERED STRUCTURE OF MOS_2
PHOTO COURTESY CLIMAX MOLYBDENUM

Perhaps the most important particle for lubricating grease is *molybdenum disulphide*, MoS_2. Lubricating grade MoS_2 is a highly refined form of the mineral molybdenite. Typically, for lubrication purposes, >98% purity grades are used. MoS_2 has excellent adhesion and successfully burnishes onto the metal surfaces. It is most effective at temperatures up to 350°C and for high load applications. In fact, its effectiveness in reducing friction increases with the contact force. MoS_2 has a layered hexagonal crystal lattice structure which allows for low friction when the lamellas slide across each other and allows it to form a transfer film on the metal surfaces. The lowest friction is observed in the absence of moisture due to the chemical reactivity of the crystalline edges. Tungsten disulphide, WS_2, which offers a wider working temperature than MoS_2, and bismuth sulphide Bi_2S_3, which has improved EP characteristics in lithium grease due to the facilitated formation of intermetallic compounds of bismuth-iron, are becoming interesting alternatives. This is especially true when the price of MoS_2 is high and the price difference decreases or is even in favour of the alternatives. Emerging technologies using inorganic fullerenes like IF-MoS_2 have reduced reactivity due to the absence of edges which reduces the friction. This opens up new possibilities to achieve excellent lubrication and protection of surfaces. However, none of the nano-MoS_2 particles (or any other particles for that matter) should be used as a straight replacement for 2H-MoS_2 in greases. For example, the use of dispersion aids as well as the nano-size of the particles can lower the affinity to metal surfaces and alter the lubrication mechanism. Needless to say, as with all particle introduction, this requires the optimisation of their useful range in terms of concentration, temperature, contact pressure, sliding velocity, surface type and topography as well as interactions with other components in the grease etc.

Beside MoS_2, *graphite* is the other most frequently utilised particle in lubricating greases. It has low friction, low chemical reactivity, and low abrasive-

THE LAMELLAR STRUCTURE OF GRAPHITE
PHOTO COURTESY TIMCAL FRANCE



COMPARISON OF DIFFERENT TYPES OF GRAPHITE IN THE SAME GREASE (GRAPHITE A IS FOUR TIMES MORE EXPENSIVE THAN GRAPHITE B)*

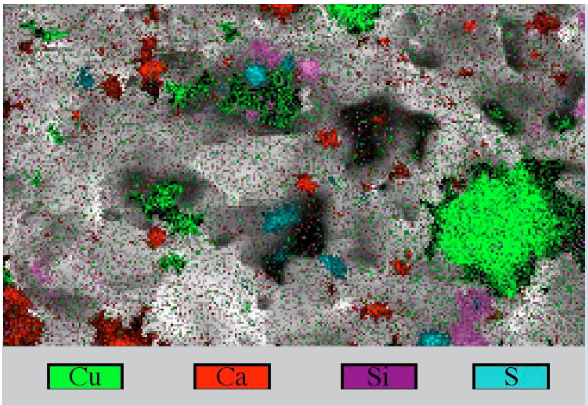
ness, high thermal and electrical conductivity and high thermal stability. Just like MoS_2, it has a lamellar structure with strong covalent bonds within each layer and weaker *van der Waal* bonds between the layers. The incorporation of graphite, as well as other particles, is less problematic in greases compared to other lubricants since the inherent high viscosity prevents particle settling. Since graphite requires adsorbed vapours for its lubricity, it works better in regular atmospheric conditions rather than in vacuum. Its synergistic effect with MoS_2 is well documented for normal conditions. Under humid conditions, however, where MoS_2 is susceptible to cause corrosion, or at high temperatures, graphite is more effective on its own. The useful temperature range for graphite is up to 450°C in an oxidising atmosphere compared to 350°C for MoS_2. The level of oxidation stability depends quite simply on the quality of the graphite. It is therefore of the utmost importance to understand (know-why) under which conditions the more high purity and thus more expensive graphite will be needed, i.e. will the grease be exposed to prolonged periods of high temperatures where the oxidation stability of the particle is an issue? Note however that a more expensive solid does not provide improved properties to the grease under all conditions. One type of graphite can cost four times more than another type but, in terms of performance in the 4 ball wear test, there is virtually no difference.

Metallic powders are also used in some types of lubricants, in particular thread compounds and

GREASES CONTAINING SOLID PARTICLES

There are many lubricating greases available on the market today containing solid particles of different sorts, shapes and sizes. Whether or not these particles are actually necessary for the intended applications is a completely different story. However, when particles actually can make a significant contribution to enhancing performance, a lubricating grease is, for obvious reasons, a much better "carrier" of these than a fluid oil. For applications where it is impossible or difficult to maintain a continuous hydrodynamic film, one way of keeping the surfaces apart and reducing friction is to create a "third body" by transporting suitable types of solid materials into the contact zone.

Typical examples of such applications are where there are exceptionally low speeds or where there is oscillating motion. Large construction vehicles are enormous pieces of equipment, often heavily loaded, and do not travel at particularly high speeds. In the mining industry, huge vehicles are used to transfer materials from their point of origin to other locations on site for further treatment. The wheels on these "monsters" can be up to several meters anti-seize compounds. These compounds are generally similar to lubricating greases in their composition but contain much higher amounts of the solid materials in question. In such compounds, surface separation properties are of the highest importance allowing adjacent bodies (pipes, drills, screws, bolts etc.) to be separated again after having been pressed together under considerable force. Other properties such as sealing ability, friction coefficients, and corrosion inhibition are also vital to a properly functioning compound. In addition to the traditional particles used in lubricating greases, thread and anti-seize compounds commonly contain substantial quantities of soft metals such as lead, copper and zinc. A typical thread compound can, as defined for instance in API 5 A2, contain up to 60% metallic powder. The lubricating properties of soft metals such as gold, silver, copper, zinc, lead, bismuth, antimony and indium arise from their face-centred structure which has considerably more slip planes than hard metals or metal alloys such as steel. They can form self-repairing lubricating films at slow speeds. Also nano-particles of soft metals can deposit on the friction surface and compensate for the loss of mass, giving rise to the so-called "mending effect". It should however also be mentioned that these types of soft metals are toxic and have an especially high detrimental impact on the marine environment. Furthermore, greases containing copper are analogous to products with traditional fillers in terms of corrosivity. Copper and copper oxide are also strong promoters of oxidation.



MICROGRAPH OF DIFFERENT PARTICLES IN A COMMERCIAL THREAD COMPOUND USING ENVIRONMENTAL (LOW VACUUM) SEM COUPLED WITH EDS

PTFE (poly-tetra-fluoro-ethylene) is a particle which can be used for its ability to lubricate even once frictional heat increases in the contact, due to its high softening point. It has one of the lowest static and dynamic friction coefficients of solid lubricants and is also chemically inert. Since particles can build networks within a grease, they also serve as thickening agents. *Clays and fumed silicas* are particles that have been extensively used as thickeners in greases, in particular for greases intended for high temperature applications. In a grease thickened with bentonite clay, for instance, other filler particles may act as a "reinforcement" creating a stronger network and providing a higher shear strength. For soap thickened greases, the interaction between the particles and the soap molecules is even more complex and the order of adding the components during production can influence the rheological characteristics of the grease.

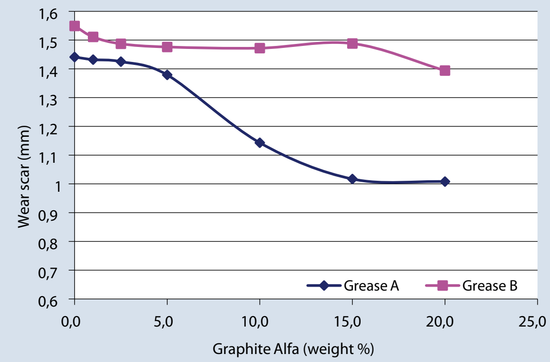
The use of overbased detergent systems can generate particles in-situ in a grease. The most common material of this type in lubricating greases is calcium carbonate $CaCO_3$. For enhanced lubricating properties, it is imperative that the right crystal form is produced i.e. metastable polymorph vaterite, originally produced from the amorphous form of $CaCO_3$, must be transformed into the softer calcite form for improved EP properties. These particles are dispersed with oil soluble surfactants, generally aromatic in nature such as alkyl benzene sulphonate, providing a suspension of well dispersed nano-particles in the finished lubricant. Note that the term micelle is quite often erroneously used in this context. However, a *micelle* is, in fact, an aggregate of surfactant molecules dispersed in a liquid phase whereas particles dispersed in a liquid medium form a *suspension*.

The tribological action of particles can be seen as threefold, to separate surfaces, to fill in voids on the contacting surfaces in order to increase the real contact area and to form EP films. It is therefore natural to consider the *size* of the particles in relation to the roughness of the lubricates surfaces. To act as a surface separator, the particle needs to be large in relation to the roughness whereas even nano-particles can cluster together and fill the valleys. For particles imparting EP properties, there may be an issue about competition for the surface with other EP additives.

in diameter and it is therefore difficult to maintain a proper lubricant film due to the slow rotational speed of the bearings. In many cases, the base grease for such applications is therefore relatively soft and reinforced with MoS_2 to ensure performance. In addition, on excavators, front loaders, draglines and similar pieces of equipment, plain bearings and bushings are commonly used and these do not rotate. Instead, they oscillate slowly backwards and forwards, often under heavy shock loading (a digger hitting a large hidden rock, for instance). Grease for such applications are almost always "black moly" products i.e. they contain varying amounts of MoS_2 or other "equivalent" black particles. There is a lot of discussion on the optimal types and amounts of particles here but most such products contain somewhere between 1% and 3% of MoS_2. To reduce the cost of the lubricant, the MoS_2 is sometimes replaced partly or completely by equivalent amounts of graphite. On the other hand, one important OEM specification advocates the use of 5% MoS_2 and this makes such "approved" products very expensive indeed. AXEL has published a short "flyer" entitled "Black is Black" comparing MoS_2 and graphite and this is available to interested parties. Applications where similar types of conditions prevail can be found in other areas, both automotive and industrial. In some types of constant velocity joints(CVJ), because of the intricate geometries involved in their design, there is considerable oscillating

For grease formulators, the *cost* of the particle needs to be balanced against the required performance of the finished product. Mixtures of particles are commonly used for this very reason. Graphite is therefore often used in combination with MoS_2 at ratios of approximately 3:1. Another reason to mix graphite and MoS_2 may be the fluctuating availability of MoS_2.

Particles can also behave very differently depending on the chemistry and consistency of the continuous phase (different lubricating greases in this particular case) and this adds considerable complexity to the situation. Individual test results should therefore never be extrapolated from one grease to another nor should the effect of a given particle concentration be extrapolated into a range wider than actually investigated. When formulating a lubricating grease or thread compound, it is necessary to recognise that the effect of adding a specific particle is not determined solely by the particle properties in isolation but also by the grease matrix including the other particles present in the grease. The particle *concentration* is, of course, very important but the effect on the load carrying properties of a given particle will eventually level



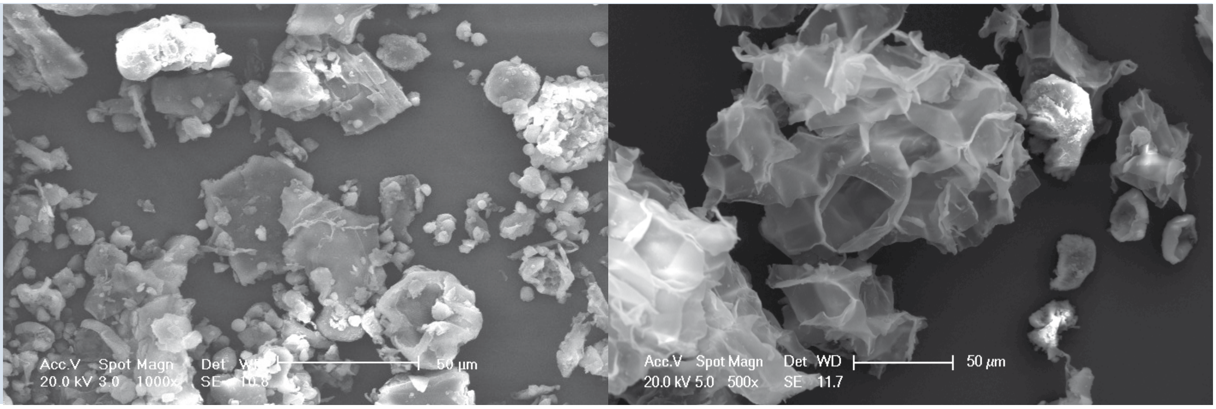
COMPARISON OF THE SAME GRAPHITE IN DIFFERENT TYPES OF GREASE*

out at higher concentrations. The addition of particles may also affect the rheological characteristics of the grease. When adding particles the rheology will change depending on the type and amount of particles as well as their interaction with other grease components. As a rule of thumb, viscosity tends to increase with higher particle concentration, reduced particle size, improved particle distribution, a narrower particle size

motion and greases for these units often contain MoS_2. In steelworks and paper mills, there are many types of equipment and machines which are either extremely heavily loaded or run in different directions (reciprocal motion) and this requires extremely shear stable greases containing MoS_2 or graphite. Couplings are another example of such an application. Greases containing ultra-small nano-particles of both MoS_2 and WS_2 (tungsten disulphide) can nowadays be found for very special applications.

Graphite is preferred where there is an excess of water/humidity or when the temperatures are excessively high. It is, for instance, the most widely used solid component in open gear greases and many OEM specifications stipulate a minimum of 10% graphite. The great majority of rail phlange greases also contain graphite and the trend here is to use a biodegradable base grease as the carrier. In a steel mill, material is transported in and out of ovens in special wagons. These are often lubricated with a graphite grease. The carrier in this case is, however, a polyglycol which evaporates completely in the high temperature conditions inside the oven, leaving the graphite to do the job.

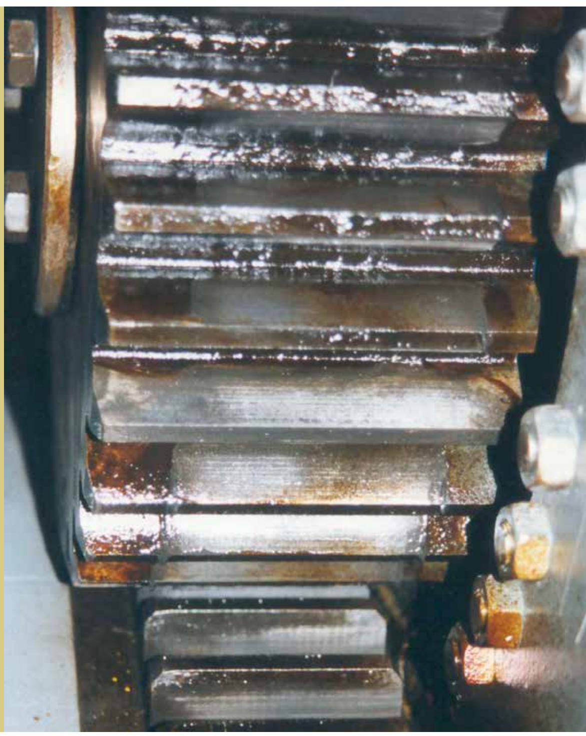
One cosmetic disadvantage of both MoS_2 and graphite is that greases containing these particles become pitch black in colour and this can be perceived as dirty,



SEM ILLUSTRATIONS OF TWO DIFFERENT TYPES OF RENEWABLE PARTICLES (a & b)

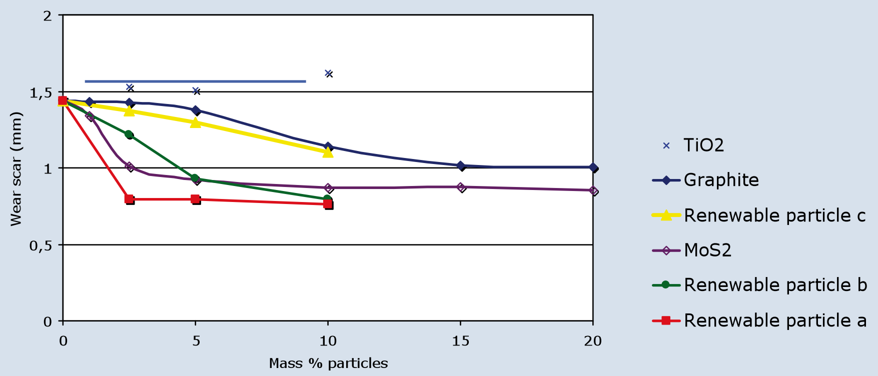
distribution and attraction forces between different particles.

Yet another emerging technology is the use of *renewable particles*. These exist in natural abundance and are derived from different types of renewable (organic) materials. Some of them can even be produced from waste products which will contribute to a lesser environmental impact through new-life reuse. A number of these materials have shown great promise and some even outperform conventional particles such as MoS_2. As an additional advantage, the renewable particles are not only completely biodegradable and non toxic but also often the cheapest materials which can be used in both greases and thread compounds. In a joint project between YKI and AXEL, several of these renewable particles were studied in the



unhealthy and perhaps even old fashioned. In response to this, greases containing white particles have been developed and these are now readily available. Examples of such materials include PTFE, calcium carbonate, the oxides and phosphates of both zinc and calcium, titanium dioxide, talc, polymers, waxes and many others. One particular area where this is extremely important is in lubricants for the foodstuffs industries where the white colour is seen as clean and healthy.

As has been indicated above, in the white section, nano-particles of $CaCO_3$ can be formed in-situ in greases and these can be found in calcium sulphonate complex products which are excellent for heavy industrial and

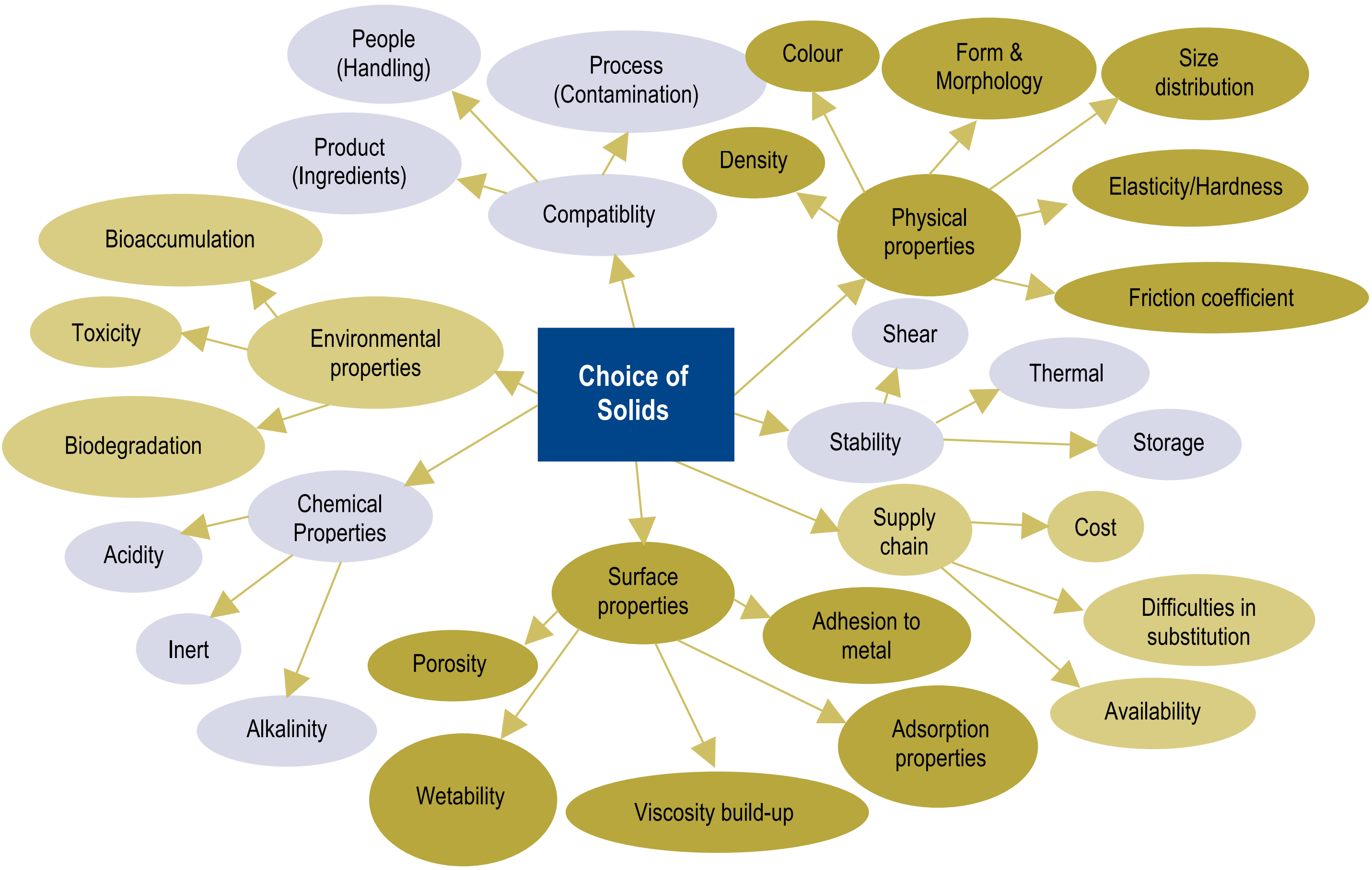


COMPARISON OF DIFFERENT TYPES OF RENEWABLE PARTICLES WITH MORE CONVENTIONAL PARTICLES*

context of more environmentally acceptable thread compounds. As an illustrative experiment, three different renewable particles were compared to more traditional particles such as MoS_2, graphite and TiO_2 (titanium dioxide) in the 4 ball wear test. A limiting wear scar level was obtained at higher concentrations for all particles. MoS_2, as expected under these particular test conditions, provided improved wear protection compared to graphite at equivalent concentrations. TiO_2 contributed to an increasing of the wear scar, even higher than the base grease itself. All three renewable materials contributed to a significant reduction of the wear scar, all better than graphite. One particular renewable material showed the best performance of all, even better than MoS_2. Results from this project have contributed to the development of new prototype thread compounds for sensitive marine

marine applications. Suspensions of such particles are also to be found in multi-metal complex greases which can perform successfully in these environments and which are especially advantageous in large open gears , for instance on rotating kilns used in heavy industries like cement manufacturing. Such particles contribute to the thickener system of the grease as well as to water stability and load carrying capacity. Other particles used to thicken greases include bentonite clays, fumed silica, PTFE, graphite etc and these types of greases are mostly used for special purposes. Bentone and silica-gel thickened greases are used for general high temperature applications due to the absence of a dropping point, for low temperature applications such as aviation due to low elasticity, for food-grade applications, and where the use of a soap thickened product is simply not suitable for some reason or another. PTFE can be used together with a fluorinated base fluid for extreme applications such as radiation, contact with highly reactive fluids and gases (oxygen), and in vacuum environments (outer space).

Thread compounds, anti-seize compounds and rock drill greases contain much higher quantities of solid particles compared to conventional lubricating greases. As well as most of the particles previously mentioned, other types of materials can come into consideration here and factors such as size, shape and packing geometries become vital. Even minerals such as mica and other "flakes" can



be incorporated into the formulation of such "dopes" as well as many different soft metal powders. Environmental demands in sensitive marine environments such as the North Sea have triggered the development of more suitable compounds for offshore applications and this has resulted in some innovative products. These contain particles emanating from the ocean itself and their impact on the environment is obviously much less than when using toxic metals. No matter what we do however, these types of minerals are not biologically degradable and, to meet the full requirements of the national and international authorities, all lubricants used offshore, including both the base grease itself and the particles involved should preferably be completely biodegradable. In the white section, our guest authors have described a development project on the possible use of organic particles and these have proven to be as good as, and in some cases better than, the conventional particles. This fits in well with the demands in the USA to maximise the use of what is termed "bio-mass". So particle technology in greases of the future will involve the use of naturally occurring organic waste products and this will hopefully limit any significant threat to Mother Nature.

environments incorporating such renewable particles into biodegradable base products.

It is clear that particle technology is an area which is important for the formulation of both lubricating greases and thread & anti-seize compounds and that there is an abundance of potential particles that still remains unexplored. The authors' strong recommendation to grease formulators is therefore to explore and utilise the full potential of particle technology. This includes both conventional and unconventional materials and also the emerging particles stemming from the area of nanotechnology. Some of the issues that need to be considered when choosing particles are shown in the diagram opposite. In conclusion, we wish you a fruitful exploration of the possibilities particles can bring to your lubricating needs.

*Wear scar results shown in the three graphs are according to DIN 51350:5, load 1400N, time 60s

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NEXT ISSUE

The next issue of the Lubrisense™ White Papers will be Part 2 of our focus on particles. Whereas this issue deals with desirable particles in lubricating greases, the next issue will highlight the problems that can occur when a lubricating grease is contaminated with deleterious particles. These particles can emanate from the raw materials, from the production process or from the surrounding environment in which the grease is expected to perform. Such contaminants can drastically reduce the service life of greases and bearings. Cleanliness has therefore become a new quality assurance parameter in many OEM grease specifications in line with equivalent demands for hydraulic fluids and other types of lubricants.

As usual, we encourage reader contribution, feedback and proposals for future editions of the White Paper series.

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