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Monitoring programs and biocide use for maximizing lubricant system performance are suggested based on an explanation of the contribution of microbes to lubricant degradation.

Biocides for lubricant rancidity and biofouling prevention

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INDUSTRIAL lubricants are increasingly providing a rich environment for microbial growth and proliferation. Most of the knowledge of lubricant biodeterioration has been extrapolated from field and laboratory experience with metalworking fluids. Compositionally more complex than most lubricants, metalworking fluids are either solutions or emulsions of 5 to 10% coolant concentrate in water. The fatty acids, sulfurized oils, glycols and other organic components of metalworking fluids and other lubricants provide a rich food source for microbes. Coolant recirculation provides aeration to support aerobic microbial activity. Most lubrication systems do not share this characteristic with metalworking fluid systems. Lubricant flow tends to be slower and absorbs less entrained air. Recirculating systems provide an ideal environment for biofilms to grow. Large systems may have several square miles of surface area for oxygen to be exposed to lubricant. Except for fire retardant hydraulic fluids, with their high water content, moisture enters the system through condensation.

Microbes are most prevalent on system surfaces where condensation co-mingles with lubricant to support development. The microbes inhabiting the biofilms that form on these surfaces act like fixed-film biological reactors; drawing nutrients from the coolant and excreting waste products back into the stream. The net effect is lubricant biodeterioration.

The objective of contamination control is primarily to prevent biodeterioration. A secondary, but often consequential objective is to minimize biomass accumulation. Properly used as part of an overall lubricant management strategy, biocides play a major role in inhibiting both biodeterioration and biomass accumulation.

Biocides

Biocides may be used as preservatives or disinfectants. When used as preservatives, biocides are added to uncontaminated fluids to prevent microbes from proliferating.

Lubricants are typically formulated water-free (except for high water-content specialty lubricants). However, the term water-free is relative. A lubricant containing 0.2% water has 2 gal of water for every 1000 gal of product. This may appear insignificant, but relatively simple calculations reveal a different perspective. A moderate microbial load in lubricant-associated water is 10,000 bacteria/millilitre. One gallon contains 3.78×10^3 millilitres. Thus, 2 gal of water in a 1000-gal system contains approximately 1×10^7 bacteria.

Any contamination introduced during blending or drumming can proliferate in-drum during storage. Although coolant concentrates rarely turn rancid in-drum, unpreserved concentrate can be a significant contamination vector for metalworking fluid systems. Used as in-drum preservatives, biocides prevent coolant concentrates from contributing to microbial loads in metalworking systems.

At the customer's site, biocides are used to maintain a check on spoilage microbes. In this situation, the biocide's role is not to achieve sterility. The objective is to control biodeterioration. Alternative strategies for achieving contamination control will be discussed subsequently.

Lubricant biodeterioration

The objective of this article is, primarily, biocides, not microbial activity in lubricants. However, an understanding of microbes forms a basis for making informed decisions regarding biocide selection or use strategies.

Lubricant rancidity is relatively rare compared with metalworking fluid rancidity. However, as refinery operations have evolved to meet increasingly stringent clean air act regulations, the chemistry of lubricant base-stocks has shifted toward lower aromatic and higher paraffinic organic compound contents. Consequently, it is more biodegradable (not necessarily a disadvantage if the concern is waste treatment).

In lubricant systems, microbes exist in a relatively steady state, operating as consortia, unless disturbed. In a consortium, the overall effect of the microbial community is greater than the sum of the activities of its individual members. Some species secrete biosurfactants that trap hydrocarbons into small micelles, or invert emulsion oil in water droplets. Species that can attack base-stock or other lubricant components secrete metabolic wastes that other microbes can use as food. This microbial food chain has the net effect of accelerating biodeterioration. Microbial activity is a continuous process. Microbes excrete low molecular weight (C1 to C4) fatty acids, mercaptols, skatols and other volatile, organoleptic molecules (Fig. 1). Microbes are continuously active, even if there is only an occassional awareness of their symptoms.

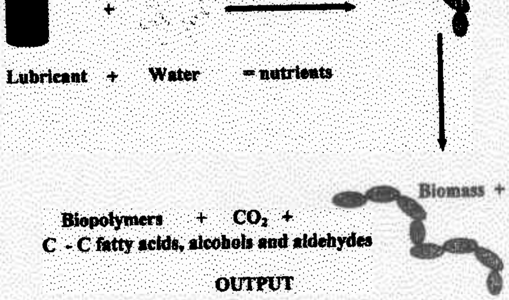

Fig. 1 — Bioconversion of lubrication constituents into new biomass: carbon dioxide; low molecular weight organic molecules (odorous); and biopolymers (biofilm/slime).

A second conventional wisdom holds that microbes are not a problem until there is a visible slime formation. It requires approximately a billion individual bacteria to form a 1/8-in. dia colony. By the time equipment is covered with a microbial mat, it is too late to consider either preventive measures, or control though biocide use alone.

Microbes attack lubricants and lubrication systems both directly and indirectly. The principal form of direct attack is to use lubricant components as food. Bacteria and fungi can use many lubricant additive and base-stock chemistries as primary food sources. Smaller molecules and paraffins tend to be attacked before more complex molecules. Consequently, lubricant components will be depleted selectively. This upsets the balance among formulation components and leads to performance failure.

As discussed previously, microbes produce substantial volumes of low molecular weight organic acids, as waste by-products, or metabolites. These acidic metabolites react with and neutralize coolant formulation amines. When they accumulate locally, as in biofilms, they can etch metal surfaces, inducing or accelerating corrosion. The organic acids may also destabilize emulsions, inducing oil to split from the water-phase (for example, in high water-based hydraulic fluids). Depending on the prevailing conditions, microbes can emulsify or demulsify lubricants.

Monitoring for microbial contamination

There are four general types of observations that systems operators can make in recognizing microbial contamination:

- Gross.
- Physical.
- Chemical.
- Microbiological.

Any monitoring or contamination control program must be designed with clear objectives. It is possible to monitor too frequently and to use biocides aggressively. Not all observations need to be made with the same frequency. A short list of flag parameters should be identified. These are easily made observations that indicate that a potential problem exists and that additional testing may be needed to determine the basic cause of the problem. For each parameter, define control criteria. Also, define specific actions to be taken if measurements fall outside the control limits: change is being measured. Conditions in a freshly charged system serve as the benchmark. Statistical process charts indicate whether a system is in control or not. Any method that is adopted must be applied consistently, otherwise, the changes observed may be due to procedural variations rather than system changes.

Most gross observations can be made during a visit to the shop floor. Unusual odors, slime on or around system components or corrosion on surfaces, uncontrolled microbial contamination could be the cause.

Physical observations may require instrumentation. Haze and visible, nonmetallic particulates are the first sign of significant microbial contamination.

Simple chemical tests for water-phase samples include pH, alkalinity and corrosivity. Most lubricants are built with excess base. The total base number (TBN) is a measure of a lubricant's basicity. If a used lubricant's TBN is <75% of a fresh product's TBN, microbial contamination is a likely cause. More sophisticated test procedures can be used to track concentrations of specific lubricant components or microbial metabolites.

Microbiological tests can be categorized as direct observation, viable cell enumeration or chemical assay. Viewing samples under a microscope is direct observation. This approach is rarely practical at industrial or power generation sites. Variations on the viable cell enumeration method are the most common means of monitoring microbial loads. Many plants use dip-slides coated with microbial growth media to estimate the number of living bacteria or fungi in coolants. Viable cell enumeration results tend to underestimate population densities. Moreover, viability results are not necessarily correlated with biodeterioration. Microbes that are active in the lubrication system but do not form colonies go undetected. Other microbes that might be dormant in the lubricant may grow luxuriantly on microbiological growth media. Possibly, the major limitation to viable cell enumeration values is the incubation period. By the time the data are reported (24 to 72 hr), lubricant system conditions may have already deteriorated to the point where refined tests are superfluous. There are several commercial chemical assays that can be used to detect microbes. These provide speed and simplicity, enabling operators to take timely corrective action when necessary. The catalase test[1] is a commonly used rapid assay. A new lipopolysaccahride assay[2] has recently been introduced into the metalworking industry. The potential of this method as a lubricant screening tool has yet to be determined.

In summary, there are a variety of methods for determining whether systems have uncontrolled microbial contamination that is adversely affecting operations.

Strategies

Biocide use can be divided into two categories:

- In-drum.
- In-application.

Each of the two categories can be further divided in sub-categories. In-drum biocide use can be intended for either lubricant concentrate preservation (discussed previously) or product enhancement. When formulators expect biocides that have been built into lubricant formulations to inhibit microbial contamination in lubricant systems, they are using the biocides as performance additives. By law, any product that makes anti-microbial claims must be registered under the regulations of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). (FIFRA regulations are found in 40 CFR 152 to 186.) Few lubricant compounders use sufficient biocide concentrations, in formulations, to provide in-use biocide performance. However, since specific anti-microbial claims are not made, either in the product literature or on drum labels, they do not register their coolant formulations.

Biocides may be used in-application to either prevent uncontrolled microbial contamination problems or correct them once they have occurred. Preventive treatment strategies fall into two categories; periodic and proportional. In periodic treatment programs, biocide is added either in accordance with a pre-determined schedule or based on monitoring data. Scheduled additions are convenient in that they become part of the plant routine. However, they do not take system variability into account. For example, variations in water to coolant make-up rates have a significant impact on biocide demand. Biocides are consumed as they kill microbes. Moreover, they may react with dissolved metal ions and other coolant systems chemicals, or become irreversibly bound to particles and other surfaces. The net rate at which biologically active biocide disappears from the systems is called the biocide demand. Failure to compensate for this variation can translate into either under-dosing or over-dosing with biocide. Similar problems can occur if the assumptions on which the scheduled addition program was designed are not valid (turnover rates, biocide demand, microbial contamination rates, etc).

Data-driven periodic biocide addition is generally more cost effective and safer than a scheduled addition. One or more of the parameters discussed previously are used to determine when biocide is needed (for example TBN and catalase activity). Generally, microbial growth increases when biocide concentrations fall below effective levels (Fig. 2). Consequently, data-driven treatment prevents over-dosing the system. It is important to monitor systems both before and after treatment. Occasionally, populations that are resistant to a particular biocide gain predominance as biocide sensitive microbes are suppressed. This phenomenon has sometimes been confused with biocide resistance mutations that make the initially sensitive species less susceptible to disinfection (Fig. 3a). Population mutation shifts are more likely to occur in systems routinely treated with sub-lethal biocide doses (Fig. 3b). The effects of alternative treatment strategies on bioburden are illustrated in Fig. 4.

Sub-lethal treatment is most likely to occur in systems treated proportionately with biocide. Some end-users consider this approach as a means of insuring that their systems are receiving continuous treatment. However, the arguments against scheduled, periodic treatment apply in this case as well. It is rarely advisable to add biocide (or any other additive) without a data-supported basis for the addition. Moreover, given the relatively large volume of biocide consumed through proportional treatment, plant operators may choose to use lower than recommended doses. Chronic sub-lethal treatment is the best stimulant for mutant population selection (Fig. 3a). In addition, virtually all toxic substances exhibit an oligodyanamic effect.

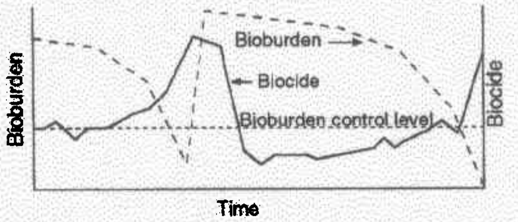

Fig. 2 — Effect of biocide concentration on bioburden.

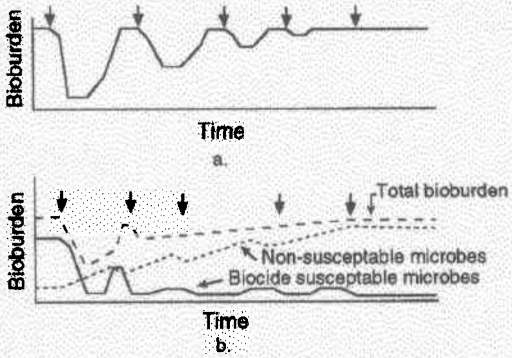

Fig. 3 — Effect of biocide treatment: a. Mutation following biocide treatment; and b. Population succession following biocide treatment. (Arrows indicate biocide treatments.)

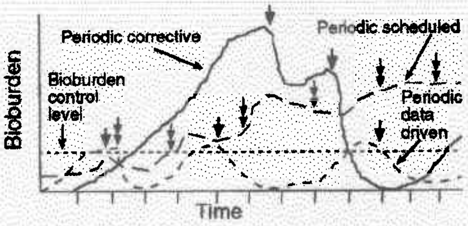

Fig. 4 — Effect of alternative biocide treatment on bioburden: periodic corrective dosing; periodic, scheduled preventive dosing; and periodic, data-driven preventive. (Arrows indicate biocide treatment: single arrow, periodic corrective; and double arrow, periodic scheduled.)

The oligodynamic effect, illustrated in Fig. 5, occurs when a chemical is toxic at concentrations above a certain threshold level. At the threshold, it has no effect, but at lower doses it is a stimulant. At 125 ppm or higher concentrations, the biocide illustrated in Fig. 4 effectively kills microbes. At 75 ppm it has no effect. The microbial level in fluid treated with 25 ppm biocide is 2000 times higher than that in the untreated control. Under-treatment can create worse problems than no treatment at all.

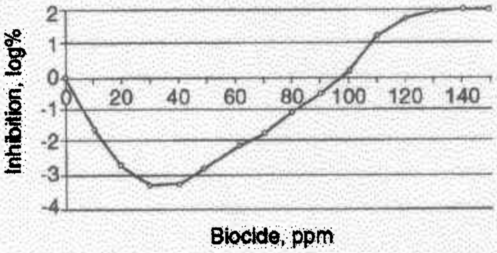

Fig. 5 — Olygodynamic effect. (Inhibition, log % = log CFU = log $CFU_{treated\ population}$/m litre + log $CFU_{control\ (untreated)\ population}$/m litre.)

The least desirable biocide application strategy is corrective treatment. Although it is actually a variation on data-driven periodic preventive treatment, corrective dosing provides too little, too late. Biocide demand, as discussed previously, is a critical but generally an unrecognized factor in overall biocide performance. Once a system has gross evidence of serious microbial contamination, the coolant has already been damaged beyond recovery. Thick biofilms can protect embedded microbes from biocide molecules. The heavy over-dosing needed to bring such systems under control may cause respiratory irritation or dermatitis. Moreover, as biofilm embedded microbes are killed, large flocs of biological debris come free from system surfaces. These flocs can plug filters or spray nozzle heads. They can also be deposited on work-piece surfaces, adversely affecting finishes.

In summary, under most conditions, in-drum preservation coupled with data-driven, periodic, preventive tank-side biocide addition is the most cost effective strategy for coolant microbiological contamination control.

Biocide selection

At present, there are over thirty USEPA registered active ingredients for lubricant biocides. (Each registered biocide contains one or more biologically active chemicals, known as active ingredients. Most biocides also contain biologically inert chemicals as solvents, dispersants or stabilizers. One active ingredient may appear in many biocide formulations.) There are two general approaches to biocide classification:

- Target microorganism(s).
- Active ingredient chemistry(ies).

When classified by target microorganism, products are designated as:

- Bactericides — target bacteria, generally ineffective against fungi.
- Fungicides — target fungi (yeasts and molds), not particularly effective against bacteria.
- Microbicides — broad spectrum, kill both bacteria and fungi.

The boundaries among these groups are not necessarily clean. At high concentrations (2 to 3 times the dose used to control bacteria), many bactericides will also kill fungi. Fungicides will also kill bacteria at high dose levels. However, cost-effective performance is most readily achieved when products from the appropriate group are selected.

Chemical classification is more complicated. Alternative classification schemes are based on overall molecular structure (alkanes, heterocyclics, phenolics, etc), elemental composition (nitrogen compounds, organo-sulfur compounds, organo-metallic compounds, etc) or synthetic intermediates (formaldehyde condensate, etc). Each approach provides useful information to some community. However, classification schemes may also be confusing. Active ingredients with similar molecular structures might be expected to react similarly. For example, aldehyde biocides (formaldehyde, glutaraldehyde; 2-hydroxy-2-nitro-1,3-propanediol) all denature endotoxins associated with gram negative bacteria cell walls.[3] Information on chemical classification or inorganic ions in biocide molecules also enable coolant formulators to predict potential chemical synergies or incompatibilities between biocides and other formulation components. Classification by reactive intermediate is the approach most likely to cause confusion. Uninformed potential users make biocide choices (more often negative choices in the form of product brands) based on their understanding of the toxicity of one or more of a biocide's reactive intermediates. The recent controversy over formaldehyde condensate biocides is an example. Although formaldehyde is a suspect carcinogen, formaldehyde condensate biocides are not.[4]

The first step in biocide selection is defining the application strategy. Products with relatively short half-lives or with chemical incompatibilies are generally inappropriate candidates for in-drum preservation. However, they may be excellent biocides for tank-side use to treat systems with 7 to 10% daily turnover rates. If fungal contamination is the principal problem, then fungicidal products need to be evaluated. Biocide performance is lubricant specific and often system specific. This reflects the variability of conditions between recirculating systems, even when superficially they appear to be identical. Inadequate treatment spectra are often confused with mutant selection.

The growth pattern typically seen when bioresistant mutants of a particular species succeeds their biocide labile parents is illustrated in Fig. 3a. More often, members of the microbial community that go undetected because other (biocide susceptible) microbes are faster growing, or compete more successfully for available nutrients, flourish, once their competitors have been inhibited (Fig. 3b). Total plate count data may yield similar results (the population no longer responds to biocide treatment). Proper dosage prevents mutant survival. Broad spectrum treatment guards against selection for different microbial species. Once the use strategy and target microbes are defined, one or more candidate products can be selected for laboratory screening. Commonly run bench tests are ASTM D3946,[5] E-686[6] and E-979.[7] The biocide or biocide combination that gives the most cost effective control in bench tests should then be subjected to field trials. Continuing treatment should be data driven; no two systems are identical in their treatment requirements.

Biocides and bioresistant molecules

Recently, a number of companies have introduced bioresistant lubricant additives into their product lines. In some cases, these are bona fide neutralizing amines, anti-corrosion products or other functional molecules. However, there are also companies marketing chemicals that provide no other benefit than reducing a lubricant's tendency to go rancid. These products may be simply un-registered biocides. A bioresistant additive has no U.S. EPA registration. This means that there are few or no toxicity data available and the product container will have a short label. This is legal if the additive meets the following two criteria:

- Does not kill microbes.
- Does provide non-biological performance properties to the formulation.

The difference between a biocidal and bioresistant additive is illustrated in Fig. 6. When a challenge inoculum is added to a preserved lubricant, the microbial population is killed off quickly (curve a). However, in a bioresistant lubricant the population slowly declines as it essentially starves (curve b). If a putatively bioresistant additive performs like a biocide, then it probably is. However, biocidal chemicals are routinely used that are *not* registered pesticides. Muriatic acid, pickling solutions, caustic, etc, have clearly defined performance properties other than disinfection. However, in concentrated form, they are all toxic. Since they are not used as biocides, they do not have to be registered as pesticides. Before adopting an additive recommended as being bioresistant, verification should be made that it is not an illegal, unregistered pesticide.

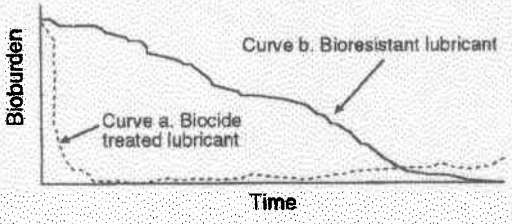

Fig. 6 — Dynamics of population die-off in biocide-treated and bioresistant lubricant formulations.

Regarding biocides, there is a misconception that more information means more toxicity. Unlike many other equally toxic substances used in metalworking plants, biocides are strictly regulated. They receive registration only after lenghty toxicity testing and USEPA data review. Label information on registered pesticides is defined by law. Each product label is individually approved by the USEPA. Consequently, pesticide labels contain considerable product information. Besides listing all active ingredients, the label provides handling and spill clean-up instructions, guidance for container disposal and recommended use levels. In contrast, most hazardous chemicals have a greatly reduced amount of information. Even with current hazardous material communication regulations, non-pesticide labels provide substantially less product information than will be found on a biocide label. A longer label (more information) is not equivalent to greater risk. Used in accordance with their label instructions, metalworking fluid biocides pose no unusual risk to plant operators.

Summary and conclusions

Lubricant systems provide a good environment for microbial communities. Growing most abundantly on surfaces, microbes can change lubricant performance properties by selectively depleting functional additives. Moreover, microbial metabolites can stimulate corrosion and induce invert emulsion formation.

The keys to microbial contamination control are good industrial hygiene, monitoring and timely treatment. There are more than 30 USEPA registered metalworking fluid biocides. Each has an application where it provides cost-effective protection. Biocides should be selected based on performance in a particular coolant and system. Most often, biocides with limited solubility in non-polar solvents work better in lubricants. Bench tests provide a relatively inexpensive method for evaluating alternative treatments. Bench test data need to be confirmed through field evaluations. Bioresistant additives that have no obvious functionality other than replacing registered biocides should be considered with care.

Properly used as one component of a complete lubricant system management program, data-driven biocide use can extend lubricant life dramatically, reduce downtime and create a healthier work environment.

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World Crude Steel Production Reaches 384.5 Million Tonnes at Mid-Year

Total June crude steel production reported by 66 steel producing nations to the International Iron and Steel Institute (IISI) was 65.1 million tonnes, 6.6% more than production in the same month last year. World total production for the first half of this year reached 384.5 million tonnes, topping last year's production of 364.5 million tonnes for that same period by 5.4%. Excepting the former U.S.S.R., Africa and Oceania, all regions reported increasing production growth.

June 1997 production of 15.0 million tons in Western Europe was 10.8% higher than in June 1996. In the European Union, overall production at 13.7 million tonnes was more than 11.0% higher compared to results in the same month last year. In all major steel producing countries in the EU region, production continued to rise considerably, ranging from a 3.0% increase in the U.K. to a 34.8% increase in Finland.

In Eastern Europe, total June 1997 production was estimated at 2.8 million tonnes, 6.5% above output in the same month last year. Total output in the former U.S.S.R. rose slightly, by 0.4%, with production of a estimated 2.2 million tonnes in the Ukraine up 12.8% from the June 1996 level, but down 7.4% in Russia, to an estimated 3.9 million tonnes.

North American production in June rose by 4.3%, to 10.7 million tonnes. Production in NAFTA countries U.S. (8.1 million tonnes), Canada (1.3 million tonnes) and Mexico (estimated at 1.2 million tonnes) rose above the June 1996 level by 3.5%, 3.6% and 10.5%, respectively.

South America's major producer, Brazil, reported June 1997 production of crude steel at 2.3 million tonnes, 9.7% more than in the same month last year. Total production in the region in June 1997 was 3.1 million tonnes, a rise of 7.3% over the year-earlier figure.

In Africa, June crude steel production fell by 3.9%, to 1.0 million tonnes, with production in South Africa down by 3.2 %, to 678,000 tonnes. June 1997 output in the Middle East reached 810,000 tonnes, 11.8% above last year's sixth-month result, despite a 2.2% production fall in Saudi Arabia, to 218,000 tonnes. However, in Iran output rose by more than 20.0%, to 540,000 tonnes.

In Asia also, June 1997 results were an improvement on year-earlier figures in all major steel-producing countries. In P.R. China output was estimated to have reached 8.9 million tonnes, 6.4% more than in June last year. In Japan, production rose by 5.6%, to 8.7 million tonnes. In the Republic of Korea, production was up by 7.6%, to 3.5 million tonnes. In India, June 1997 output reached 1.8 million tonnes, up 1.6% from year-earlier results, and production in Taiwan was estimated at 1.4 million tonnes, 50.5% more than in the same month last year. Total regional output in June 1997 reached 24.3 million tonnes, a 7.7% increase over year-earlier results.

June 1997 production in Oceania (Australia and New Zealand) was 720,000 tonnes, 4.8% less than in the same month last year. ▲