

Synthetic submarine hydraulic oil

A newly developed PAO-based fluid handles stressful operating conditions better than a mineral oil-based lubricant.

KEY CONCEPTS:

- **The current submarine lubricating oil is a mineral oil-based fluid that has not adequately handled stressful operating conditions and has failed too quickly, leading to a potentially hazardous environment and higher disposal costs.**
- **A newly developed PAO-based synthetic fluid exhibits a superior oxidation induction time, lower wear scars in four-ball testing and a much higher viscosity index.**
- **The PAO-based fluid is undergoing additional testing and a submarine trial is anticipated in the near future.**

Lubricant fluids used in submarine propulsion systems must meet very challenging operating conditions. Submarines function very independently, which means their operating systems need to perform reliably over long time periods. If a problem occurs with a submarine at sea, the chances for outside assistance are remote.

A lubricating fluid in a submarine must therefore be very reliable. STLE members Dr. Richard Sapienza, CEO of METSS Corp., Westerville, Ohio, and William Ricks, senior research scientist for METSS Corp., say, "Space constraints in a submarine mean that it cannot carry too many materials. Lubricants must not only be reliable but also multifunctional."

The current lubricating oil used in submarines (known as 2190-TEP) is a mineral oil-based fluid that meets the military specification MIL-PRF-17331. Sapienza says, "This oil has been used in submarines for the past 40 years without any difficulties. It is prepared from well-refined petroleum basestocks (Group I or II) and contains a mild extreme pressure additive package."

But the U.S. Navy has increased the severity of the operating conditions in its fleet. Sapienza comments, "The U.S. Navy has the goal of faster, hotter and longer with respect to its submarines. Faster refers to the new drive systems that have much higher gear-to-fluid volume interactions. Hotter corresponds to the higher operating temperatures which lead to more thermal efficiency." In addition to submarines, newer surface ships with controllable pitch-propeller systems have placed additional demands on the 2190-TEP lubricant.

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Another significant application for the lubricating oil is in air compressors. Sapienza says, "The submarine compressor oil is the most severe application for the mineral base hydraulic oil. The oil is stressed by temperatures as high as 200 C and pressures as high as 4,500 psi."

The net result of these more stressful operating conditions is that the existing mineral oil-based hydraulic fluid is failing more quickly, leading to high oil replacement and disposal costs. Three of the problems seen are (1.) high depletion of antioxidants in the mineral oil-based fluid, (2.) sharp increases in total acid number and (3.) severe off-gassing events. Degradation is leading to the formation of components such as formaldehyde and carbon monoxide that can be particularly hazardous in the close operating conditions of the submarine. Estimated disposal costs of \$28/gallon have also been incurred, according to Sapienza.

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The more rigorous performance conditions that cannot be handled by a mineral oil-based lubricant necessitate the switch to a synthetic basestock. Such a product has been developed and is in the process of being evaluated.

PAO-BASED FLUID

METSS has developed a synthetic-based fluid that exhibits superior performance as compared to the existing mineral oil-based oil. The new fluid, designated Nye 2190-S, is now available commercially through specialty lubricant manufacturer Nye Lubricants, Inc., of Fairhaven, Mass. Sapienza says, “We have been able to develop a synthetic fluid that displays improved thermal stability and oxidation resistance, better lubricity and an improved viscosity index.” The synthetic fluid is formulated with a PAO basestock and a complementary additive package. This fluid is compatible with the existing mineral oil, which minimizes any difficulty during changeover.

Oxidation testing using the Rotating Pressure Vessel Oxidation Test (RPVOT – ASTM D2272) shows a substantial improvement with the synthetic fluid. Ricks says, “The oxidation induction time (OIT) for our PAO fluid is over 2,500 minutes, which is far better than the 330 minutes value obtained from the mineral oil product. We also found that addition of the synthetic fluid to the mineral oil-based product also improves performance. In a 50:50 blend of the two fluids, the properties of the PAO fluid dominate and OIT values in excess of 1,000 minutes are observed.”

Lubricity testing was conducted using the four-ball wear test (ASTM D4172). Testing using both 52100 steel under a 40 kg load and 440 C steel under a 20 kg steel load leads to lower wear scars for the PAO-based synthetic fluid.

The viscosity index for the PAO fluid is 138, which is much higher than the value of 94 for the mineral oil-based product. Ricks adds, “This result is very significant because it means that the synthetic fluid can better tolerate the higher operating temperatures now seen in submarine propulsion systems.” This is particularly important to ensure ease of valve operations.

A series of additional performance tests was conducted by a major supplier of hydraulic components to the U.S. Navy. Samples of the mineral oil- and PAO-based fluids were taken

before and after this testing and are shown in Figure 1. The former fluid has significantly darkened after testing while the PAO fluid remained unchanged.

Sapienza says, “We did additional testing on these samples and found that the RPVOT results for the mineral oil-based fluid had dropped from 330 to 65. In contrast, the synthetic fluid had not seen any reduction in performance.” The concentration of antioxidants in the mineral oil-based fluid had also declined while no

change was observed with the synthetic.

Two other important characteristics are degassing and microbial contamination. Degassing is a test that assesses the volatile degradation products that can be formed after the fluid is heated for a specific period of time. Sapienza says, “Typically, a fluid is heated at 85 C for 24 hours and then the head space is analyzed for degradation components. This test is particularly important for any fluid that is being used in the closed environment of a submarine. The PAO fluid passed the test.”

Algae and bacteria are two microbes that have been found in the hydraulic fluid systems of submarines using the mineral oil-based fluid. Sapienza says, “These microbes can attack and degrade the fluid. Testing of the PAO fluid has shown that it is so pure that no microbes grow in it and, as a result, we do not need to include any biocides in the formulation.”

Further testing of the PAO-based fluid is ongoing. Sapienza hopes that the U.S. Navy will set up a trial in a submarine in the near future. He adds, “We are also looking to evaluate the PAO fluid in the wind turbine industry. Many of the issues faced in submarines are also seen in wind turbines, which need to operate over long operating time intervals in remote locations.”

Additional information can be obtained at the METSS Corp. Web site: www.metss.com or by contacting Sapienza at rsapienza@metss.com.

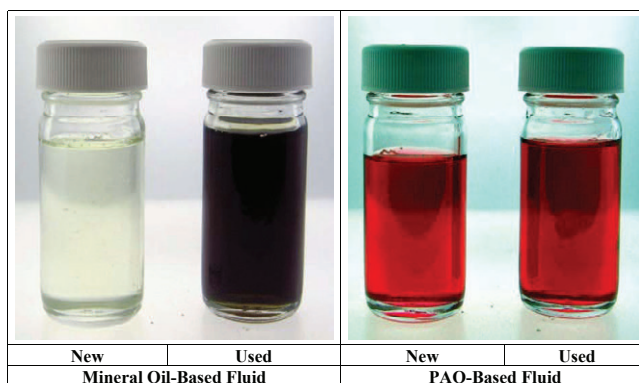


Figure 1 | Performance testing conducted on the current mineral oil-based submarine fluid and a potential replacement based on PAO shows that the former fluid on the left significantly darkens while the latter fluid on the right remains unchanged. (Courtesy of METSS Corp.)

A new alternative to hexavalent chromium conversion coatings

Researchers discover an environmentally friendly alloy with lower wear and superior corrosion protection.

KEY CONCEPTS:

- Hexavalent chromium has been very effective as a coating to protect metal alloys for over 60 years, but health and safety concerns have led the metal-finishing industry to look for an alternative.
- A nickel-tungsten alloy has been developed that exhibits lower wear and superior corrosion protection. This alloy is also environmentally friendly.
- The properties of the nickel-tungsten alloy can be tailored for specific applications.

Hexavalent chromium has been a mainstay in protecting metal alloys for more than 60 years. But the metal-finishing industry is looking for alternatives because of health and safety concerns with hexavalent chromium that has been found to be a carcinogen.

The European Union RoHS (Restriction of Hazardous Substances) directive allows for a maximum concentration of hexavalent chromium of 0.1% in conversion coatings. Development of alternatives has been difficult because hexavalent chromium displays a combination of unique characteristics. Christopher Schuh, associate professor of materials science and engineering at MIT, says, “Hexavalent chromium exhibits a unique slate of properties that include a high degree of hardness, excellent corrosion and wear resistance and a shiny visual appearance.”

The most difficult property to match is hardness, according to Schuh. He adds, “Hardness is a show stopper for most alternatives, though it is not as important a property as wear resistance.”

Schuh indicates that chromium displays excellent hardness because this metal inherently develops a nanoscale structure when it forms a coating. He adds, “Very few other metals form such a structure naturally during deposition, though nanocrystalline forms of other metals can be prepared, which leads to a boost in hardness.”

Besides a nanoscale structure, Schuh believes two other steps are required to prepare an alternative with comparable properties to hexavalent chromium. The second step is to make and keep the nano-grain size small. Finally, a process needs to be developed to control the size of the nanocrystals used in preparing the coating.

A suitable alternative that can match the properties of hexavalent chromium without the health and safety problems has not been developed until now.

NICKEL-TUNGSTEN ALLOY

When processed into nanocrystalline forms, nickel coatings display comparable hardness to hexavalent chromium in the short term. But the nickel crystals gradually lose their high hardness characteristics because they expand in size to become microscale grains.

The researchers found that combining nickel with tungsten produces a coating that displays comparable and in some cases superior performance to hexavalent chromium. The coating fulfills the three steps that Schuh indicates are necessary. He says, “Tungsten is mainly used for thermodynamic reasons to enhance processing and to assist with stability of the nanostructure.”

The reason that a superior performing coating can be developed is due to a unique manufacturing procedure. In a conventional electroplating process used to prepare conventional hexavalent chromium, DC current flows from the anode to the cathode. Metallic ions in the solution are attracted to and plate out on the mate-

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Preparation of the nickel-tungsten alloy coating is conducted by a pulse-reverse waveform technique. Schuh explains, "We flip the direction of the current which enables us to put down metal and then strip some of the metal off during the plating process. This enables us to precisely manipulate the structure of the nanocrystalline coating."

Evaluation of the nickel-tungsten alloy was conducted vs. a hexavalent chromium coating and an electroless nickel coating. A ball-on-disk/pin-on-disk tribometer was used to evaluate the sliding wear resistance of the coatings. The counterbody involved in the testing was a six-millimeter tungsten carbide sphere.

A wear load of three newtons was employed for the nickel-tungsten alloy and the hexavalent chromium while the electroless nickel could only handle a one-newton load. The latter did not have the characteristics to tolerate the higher load. Schuh says, "Profilometer evaluation of the wear tracks for each coating showed that the nickel-tungsten alloy exhibits a lower wear rate than hexavalent chromium by an order of magnitude and a greater-than-two orders of magnitude lower wear rate as compared to electroless nickel run at the lower load."

Corrosion inhibition was assessed through the use of the salt spray test conducted by the ASTM B117 method. As shown in Figure 2, a 12-micron coating of the nickel-tungsten alloy on steel displayed no rust after 1,100 hours of salt spraying. In contrast, the same thickness of hexavalent chromium coating on the same substrate rusted after only 48 hours.

Schuh pointed out that performance tradeoffs are seen with coatings such as electroless nickel and hexavalent chromium. He says, "Electroless nickel is typically baked to improve its hardness. But this process causes this coating to crack, which leads to a sacrifice in corrosion protection. Hexavalent chromium loses hardness when heated at elevated temperature. In contrast, the nickel-tungsten alloy

hardens substantially after baking without sacrificing other performance characteristics."

In fact, Schuh indicates that the properties of the nickel-tungsten alloy can be tailored during processing to optimize specific properties. He says, "We have figured out a way to control the structure of the nickel-tungsten alloy coating. This allows us to tailor the properties of the coating to meet

specific hardness, wear resistance and corrosion protection requirements for a particular application."

Properties are optimized by mixing and matching the size of nanocrystals. Grain sizes between 2 and 200

nanometers can be prepared, according to Schuh.

The performance of the nickel-tungsten alloy coating was evaluated in an ink transfer application. A rotating gravure ink wheel transfers ink to a wire. Mechanical contact wear is generated as embossed letters on the wheel are exposed to an ink and pressed against a substrate. A 12-micron coating of the nickel-tungsten alloy on a wheel facilitated the printing of 135 kilometers of printed wire, prior to the process leading to unacceptable printed letter quality. A hexavalent chromium coating was only able to satisfactorily print 13.5 kilometers of wire.

The nickel-tungsten alloy technology has been licensed to Xtalic Corp., Marlborough, Mass., which is commercializing the plating process. Further information can be obtained by contacting John Kinne at jkinne@xtalic.com.

Schuh is working with other metals in an effort to develop high-strength coatings for lightweight nonferrous alloys. Further information on the nickel-tungsten alloy can be found in a recent presentation made at the 2009 Sur/Fin Conference.¹

REFERENCE

1. Jones, A., Hamann, J., Lund, A. and Schuh, C. (2009), "Nanocrystalline Ni-W Alloy Coating for Engineering Applications," *Proceedings of the 2009 SUR/FIN Conference, Louisville, Ky.*



Figure 2 | After 1,100 hours of salt spray testing, a steel specimen coated with the nickel-tungsten alloy displays no rust in the top figure. In contrast, the same steel specimen coated with hexavalent chromium shows extensive rust in the bottom figure after only 48 hours. (Courtesy of the Massachusetts Institute of Technology)

Bridging the waste-treatment gap

A polymeric material is available that removes oil and hydrocarbon droplets between 0.1 and 15 microns.

KEY CONCEPTS:

- No techniques have been available to remove oil and hydrocarbon droplets with sizes ranging between 0.1 micron and 15 microns.
- A new polymeric technology known as a Hydrocarbon Removal Matrix incorporates oil droplets in the 0.1 micron to 15 microns range into a polymeric material. The effectiveness rate for this technology is over 99-plus% after one pass.
- The Hydrocarbon Removal Matrix also removes oil and oil-soluble components from most aqueous fluids including emulsions.

Process wastewater generated by manufacturing facilities needs to be treated prior to discharge in order to meet local, state and federal requirements. If the waste is discharged through a sewer system, then one of the main challenges is ensuring that the wastewater does not interfere with the operation of the municipality's Publicly Operated Treatment Works (POTW). A secondary challenge is to process wastewater treatment on-site or recycle the water where it is either less available or very costly to obtain.

Key pollutants that can cause difficulties in treatment of effluent are mineral oil, fatty oils and other oil-soluble organic compounds. These compounds are collectively designated as fats, oils and greases (FOG) and are known to cause difficulties in plugging up sewer pipes and in the operation of POTWs. These same substances will damage membrane treatment systems if these are contemplated for on-site treatment or water recycle.

There are a number of techniques available to remove mineral oil and oil-soluble organic compounds from effluent streams. High concentrations of oils can be removed through conventional techniques such as centrifuges, coalescers and skimmers. This accounts for oils with droplet sizes above 15 microns.

In most process waste-treatment systems, high concentrations of particulates and oils are removed in this fashion, however, sufficient oil and hydrocarbon organic compounds remain at levels causing either POTW permit violations or plugging and high-pressure buildup across the membrane process equipment.

Paul Greco, senior vice president of business development for MyCelx® Technologies Corp., Gainesville, Ga., says, "A gap is present between those techniques that remove large concentrations of oil in the effluent (as large droplets) and those that remove very small droplets. This gap covers oil particles with sizes between 0.1 micron and 15 microns."

A technique that can bridge this gap by removing oil and hydrocarbon organic compounds from process wastewater effluent would be welcomed to ensure that effluent meets POTW guidelines or that effluent will not damage membrane processes in-use or contemplated for recycle.

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A major benefit of the Hydrocarbon Removal Matrix is its ability to extract oil and oil-soluble components from most aqueous fluids.

HYDROCARBON REMOVAL MATRIX

The challenge of process wastewater treatment within this treatment gap is breaking the oil-surfactant-water bonds that exit. Greco says, "We have developed a polymeric material that can change the properties of hydrocarbons upon contact. Oil is literally incorporated into this polymeric material, which we have designated as a Hydrocarbon Removal Matrix."

The polymeric material is designed to extract oil droplets in the 0.1 to 15 micron range that could not be removed by any other techniques. In addition, the Hydrocarbon Removal Matrix is used in some cases to economically remove oil with a droplet size above 15 microns.

The polymeric material reacts with oil and oily hydrocarbons in less than one second. This high reaction time does not differentiate droplet size but permits capture in a very small treatment footprint. Greco adds, "The Hydrocarbon Removal Matrix traps oils predominantly, but it also can remove hydrocarbons that are soluble in oil or slightly soluble in water. Compounds such as polychlorinated biphenyls, trichloroethylene and methyl tert-butyl ether (MTBE) are representative of these."

The Hydrocarbon Removal Matrix has an effectiveness of more than 99-plus% in extracting insoluble oils from an effluent stream after one pass, according to Greco. Compounds with higher water solubility may require two passes.

A major benefit of the Hydrocarbon Removal Matrix is its ability to extract oil and oil-soluble components from most aqueous fluids. It provides a robust, efficient, cost-effective and operationally simple method of removal that can reduce the cost of an overall treatment process.

Highly stable emulsions cannot be treated as readily if they have low oil droplet sizes. Greco says, "Oil in emulsions with droplet sizes below 0.1 micron cannot be removed." This represents emulsions with very fine droplet sizes that are even smaller than most microemulsions.

Greco says, "Our technology has been used successfully to remove oil from the waste stream of many industrial plants. A recent example involves a glass plant that has a wastewater stream containing a percussion air-tool oil, a polyalphaolefin (PAO)-based gear oil and a vegetable oil. The effluent contains a high concentration of dirt particles and free and emulsified oils. Less than 1 ppm of oil remains in the effluent after a five-stage process is used to remove dirt particles and the oils."

Once the effluent stream passes through the polymeric material, it can be directly discharged. Figure 3 shows an image of the effluent prior to treatment in the beaker on the left. After one pass through, the clearer effluent is seen in the jar on the right. Greco indicates that ultimately the glass plant would like to recycle the used water.

The Hydrocarbon Removal Matrix is provided in cartridges that can be easily replaced. Saturation of the polymeric material is detected when oil is seen in the effluent via oil content monitors or moves through the process cartridges to a visual indicator cartridge. Greco says, "Saturation of the Hydrocarbon Removal Matrix is a function of the viscosity of the oil. As the viscosity drops, the saturation point also declines."

In general, this means that a decrease in viscosity can reduce the amount of oil removed by a 10-inch segment of the polymeric material from 300 to 400 grams down to 100-200 grams. The spent polymeric material can be disposed of in a similar fashion as mineral oil-based hydraulic fluid.

Further information on the Hydrocarbon Removal Matrix can be found at www.mycelx.com or by contacting Greco at greco@mycelx.com.



Neil Canter heads his own consulting company, Chemical Solutions, in Willow Grove, Pa. Ideas for Tech Beat items can be sent to him at neilcanter@comcast.net.



Figure 3 | The polymeric material known as the Hydrocarbon Removal Matrix can efficiently remove oil from wastewater effluent streams with droplet sizes between 0.1 micron and 15 microns. The beaker on the left shows the effluent from a glass plant prior to treatment. The clearer effluent after one pass through is seen in the jar on the right. (Courtesy of MyCelx® Technologies Corp.)