



THE STUDY OF UNIQUE ADDITIVE CHEMISTRY IN ENVIRONMENTALLY ACCEPTABLE LUBRICANTS

In all mechanical operations, lubrication is necessary to reduce the friction and wear from the long-term use of machinery. If left unlubricated, the metal-on-metal grinding will create heat due to friction, causing parts of the machinery to weld together and tear apart, leading to the overall damage of the machine. For this reason, it is vital to find or create a lubricant that perfectly aligns with the specificities of your machine. The most commonly used lubricants are lubricating oils, in which friction modifiers play a crucial role in reducing the coefficient of friction between the two surfaces of the machine that come in contact with each other. However, the application of the lubricant heavily determines what materials can be used in lubrication. For example, lubrication must be zinc-free if its intended use is on machinery composed of silver alloy. Furthermore, benefits such as being able to extend the life of catalytic converters and prevent the blockage of the diesel particulate filter (DPF), phosphorus-free additives are used. With the lubricant market's focus being shifted heavily towards environmental sustainability, it has made finding appropriate friction modifiers, such as zinc dialkyl dithiophosphate (ZDDP), more challenging as they are limited in dosage due to environmental regulations. The use of specific materials in the development of high-performance friction modifiers that are environmentally friendly has become the primary focus of research for the lubricant industry.

For a lubricant and its additives to display high performance, certain qualities are sought after. Firstly, the lubricant's viscosity is vitally important to its functionality, more specifically finding the ideal balance in the viscosity. When a lubricant is too viscous (like honey), the lubrication requires too much energy to flow through the system creating blockages. If a lubricant is not viscous enough, the lubricant proves to be ineffective as the two surfaces still come in contact with each other. Generally, it is ideal for the lubrication to be the least viscous possible while still achieving fluid-bearing conditions. Secondly, the lubricant as a whole must display excellent temperature resistance. Temperature stability is crucial when considering the application of a lubricant as the internal temperature of heavy industrial machinery can reach extreme temperatures while in operation. If the lubrication can not withstand these conditions, it will surely lose its chemical structure (and therefore losing its usefulness as a lubricant) or worse, combust and causing expensive damage to the machinery and the facility. The lower extreme of temperature is also crucial to consider as if the lubricant cools too much and congeals to a near solid state it will prevent flowing, leaving portions of the machine unlubricated, resulting in the death of the machine as previously described. This also ties back into viscosity with a metric known as viscosity index (VI) which is a unitless measurement describing the stability of the lubricant's viscosity over temperature fluctuations in which a high VI means greater stability. Finally, the corrosiveness of the lubricant's molecular compound should be limited. This would entail limiting the presence of halogens and phosphorus as these

elements can produce unnecessary wear on the machine surfaces through corrosion over time which shortens the machine's life.

For this reason, organic molybdenum friction modifiers such as Molyvan 855 (a sulfur and phosphorus-free lubricant additive) have seen an increase in popularity in the automotive industry, heavy industry machinery, and aerospace field due to its anti-wear, anti-friction, temperature resistance, enhancement of engine efficiency, and biodegradability. As friction modifiers containing sulfur and phosphorus rapidly get phased out due to the restrictions posed by environmental regulations, organic molybdenum will likely take its place. Furthermore, nitrogen-containing heterocyclic compounds such as thiadiazole are also vital in the future of enhancing the performance of environmentally friendly lubricants. This is because thiadiazole intrinsically possesses an excellent load-bearing capacity as well as anti-oxidation and anti-corrosion properties meaning the thiadiazole will decompose during friction to create a protective film on the surface of the machinery. Being that both additives are environmentally friendly, it is inevitable that we will see an increase in products containing these additives due to their ability to not only comply with the strict environmental regulations but also their ability to possess high performance with a wide range of applications. There have already been many attempts, many of which successful, to combine molybdenum and thiadiazole compounds with environmentally acceptable base oils derived from vegetable oils to create an environmentally acceptable lubricant with outstanding performance and range of application.

One of these tests ran on these novel lubricant additives had them be added to trimethylolpropane trioleate (TMPT, an oil derived from the esterification of oleic acid found in sunflower seeds) base oil. The resulting oil displayed a reduced friction coefficient and an enhancement of the anti-wear properties and the pressure resistance of the base oil. Lastly, the decay of the thiadiazole due to friction works well when combined with molybdenum compounds as the sulfur and molybdenum would theoretically react in the heat caused by friction to reform itself, being uniquely self-sustaining.

The self-sustaining ability of the mixture is perhaps the most interesting and potentially valuable aspect of these additives. These additives would never be able to be self-sustaining forever as that would break the laws of conservation, so the lubrication would need to be replaced eventually as it wears out. But as far as research is concerned there are very few lubricant additives, especially additives that are environmentally acceptable, that have this property. Lubricants that contain these molybdenum and thiadiazole compounds as additives were proven to reduce the coefficient of friction and load by nearly 40% over extended periods without being replaced. This is important as this product develops further as industries such as the automotive industry, heavy industry machinery, and aerospace field all rely heavily upon lubricants. These industries can look to this product as a means of passively saving income by requiring less overall lubrication as it performs for longer.

This self-sustaining property of the lubrication additives is not just purely theoretical conjecture that does not occur in practice. In the aforementioned experiment where the molybdenum and thiadiazole additives were added to TMPT, EDX spectroscopy was utilized to analyze the distribution of elements on the worn surfaces of the machine after the lubrication with organic molybdenum and thiadiazole compounds had been used. It was found that the surface contained S and Mo elements that could participate in a tribochemical reaction with each other under high enough temperatures and pressures which could be provided by normal operating conditions of the machine. They then ran the machine again for a longer period, reanalyzed the surface using EDX and SEM analysis, and found that their theory proved correct and MoS₂, an excellent solid lubricant due to its layered structure, formed on the surface. This when further applied to the surfaces of the machine generates a tribofilm exhibiting excellent antiwear properties which extend the lifetime of the machinery.

Of course, all of the previous benefits of organic molybdenum and thiadiazole compounds as lubricant additives would not amount to anything if they did not function well when added to environmentally acceptable lubricants (EALs). As the lubricant market shifts to being dominated by EALs, poor compatibility with biodegradable base oils (such as those derived from vegetable oils) would be a major blow to the future implications and applications of these additives. Luckily, organic molybdenum and thiadiazole compounds perform amazingly as additives in EALs. Not only were the excellent friction reduction and load-bearing properties observed when applied to TMPT, but it was also observed that it increased the lubrication's resistance to extreme pressure and temperature. Furthermore, the biodegradable properties were not only still observed but were enhanced. The finished product with the organic molybdenum and thiadiazole additives decomposes at a faster rate than without additives and since the thiadiazole contains nitrogen, it would also theoretically provide nutrients for aquatic microorganisms making it environmentally beneficial.

In conclusion, organic molybdenum and thiadiazole additives have proved to be effective and environmentally beneficial. Organic molybdenum lubricant additives have been proven to exhibit outstanding anti-friction, anti-wear, wide temperature accessibility, and anti-oxidation characters. All of which contribute to the overall greater mechanical efficiency of the engine and fuel economy. In addition, nitrogen-containing heterocyclic compounds such as thiadiazole also exhibit excellent tribological properties individually. Thiadiazole will decompose during friction and undergo chemical reactions on the metal surface to generate a protective film rich in carbon and sulfur which makes

it intrinsically possess excellent load-bearing capacity, lubricating properties, thermal stability, anti-oxidation, and corrosion resistance, which can satisfy the special requirements of the mechanical equipment and the environment while also enhancing a lubricants environmentally friendly nature by providing nitrogen for microorganisms to feed off of. These properties make the additives useful individually as EAL additives; however, the unique self-sustaining properties that occur as Mo and S formed by the decomposition of the lubricant undergo tribological reaction under the heat and pressure generated by the machine reforming MoS₂. This regeneration is a rare characteristic that is seldom displayed elsewhere with lubricant additives that have proven to be beneficial at providing a sustained anti-wear film to the surfaces and extending how long the lubricant can last in the machine. All of these properties are made all the more valuable since the additives apply to lubricants such as TMPT and other vegetable oil-derived lubricants. This makes the combination of the two additives very valuable and powerful, warranting further research and experimentation into broadening the applications of the product.

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