

Using conventional molybdenum and boron lubricant additives in electric vehicles

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Introduction

Organomolybdenum friction modifiers reduce friction and enhance wear protection in lubricant formulations through the in-situ formation of lubricious molybdenum disulfide tribofilms (MoS_2) [1]. Boron based antiwear / extreme pressure additives work by reacting with iron oxide surfaces forming a hard borate-iron glassy network [2]. Therefore, lubricant additives based on molybdenum and boron have been used extensively in traditional drivetrains. The unique benefits and challenges of these additives may present significant opportunities within the electric vehicle (EV) market. Additionally, because of the relative newness of the field, preconceived notions of traditional additive incompatibility with EV requirements may unduly relegate some time-honoured lubricant additives as unusable in EV fluids. This work investigates additive combinations of three traditional organometallic friction and wear modifiers in EV-focused low viscosity fluids. Concerns regarding corrosion, friction, wear, and electrical conductivity are addressed.

Development of new fluids for electric vehicles includes some of the same challenges as with fluids designed for internal combustion engines (ICE), but there are significant differences. First, the average overall operating temperature of a lubricant in a plug-in hybrid engine is lower than that of an ICE, by as much as 25% [3]. In the context of traditional

molybdenum and boron additives, which often require a high activation temperature to be functional, lower operating temperatures may pose a significant barrier to the effectiveness of these additives. An additional concern is yellow metal corrosion. In the context of EV, there is a significant increase in the possibility of the lubricating fluid contacting copper components and electronics. As such, the issue of fluid conductivity comes into play in EV-based systems. A high conductivity fluid can promote short circuiting and current leaks. A low conductivity fluid in turn acts as an insulator and/or capacitor. This can result in the build-up of a large charge gradient, which will eventually equilibrate through electrical discharge [4].

For electrical properties, the use of organo-metallic ligand chemistry is in its relative infancy. One element of interest is boron. Boron is a metalloid element possessing both ionic and covalent bonding characters due to the availability of its three electrons in its outer shell. Its presence at interfaces contributes significantly to effective lubrication through two primary mechanisms. The first is through the interaction with oxygen and nitrogen, leading to the formation of lubricating compounds like B_2O_3 and BN, which exhibit low friction properties due to their lamellar structure. The second is through the interaction with metals, in particular iron. This results in the creation of a tribofilm consisting of a very hard iron-borate glass network, which serves to reduce wear [2]. As

such, boron, most commonly in the form of boric acid, has been used as a lubricant modifier as early as the 1880's [5]. There was a particular increase in the use of borates beginning in the 1940's with the increased use of ester chemistry and polyol chemistry in lubricants [6].

During this time, the solubility of the boric acid in lubricating compositions was increased via chemical modification through dehydration coupling reactions to esters, polyols and long chain alcohols [7]. While a beneficial step in the use of boron as an additive in mineral based lubricants, these simple borate esters are known to suffer from hydration in the presence of moisture, and often revert to boric acid, which can result in both fallout and increased acidity in lubricants. To combat this hydrolytic stability issue, amide stabilised borate esters were introduced [8]. It has been demonstrated that borates of this structure have a significantly increased hydrolytic stability relative to other borates [9].

In the current ICE lubricant market, borates have found a home as anti-wear agents, extreme pressure modifiers, and anti-corrosion agents. All of these properties are of key interest to EV applications, but the use of borated additives in EV based lubricants has been mixed due to potential concerns of a significant increase in electrical conductivity in the lubricant. Some studies indicate that organoborates may possess very high conductivity [10]. Polyamine based dispersants, and particularly borated polyamine based dispersants are understood to be significant conductivity promoters and have been employed in such manner [11]. In contrast, other work has shown that borates may possibly be employed to reduce conductive deposits in lubricating compositions [12]. The discrepancy in behaviour is most likely due to the ligand composition rather than the presence of boron itself within the lubricant, and may falsely lead to the exclusion of boron based additives from future EV formulations.

A second additive class of some concern are molybdenum based organometallics. Molybdenum additives, particularly in the form of molybdenum dithiocarbamates (Mo-DTCs) have been used as excellent friction modifiers in lubricating formulations going back to the 1960's [13]. Non-sulphur containing oil-soluble molybdate were also entering the lubricant landscape as both molybdate salts of organic acids [14], and as esters of long chain alcohols [15]. As with the borate chemistry, hydrolytic stability of many of these early molybdate ester additives was an issue. Using a similar approach to the stabilised borate chemistry, the incorporation of electron donating nitrogen can increase the hydrolytic stability of the organomolybdate [16]. By introducing the nitrogen in the form of an amide, resistance to hydration is further increased [17].

Both molybdates and borates used in hydrocarbon lubricants have a high degree of polarisability [18]. There is a common understanding that polarisability and conductivity are related and that an increase in polarisability corresponds in an increase in conductivity [19]. This understanding extends to lubricant formulations, where increased concentrations of highly polarisable additives will significantly increase the conductivity of a lubricant [20]. Yet evidence exists showing that contribution of additives such as molybdenum dithiocarbamates (Mo-DTCs) to the overall electrical conductivity of an EV fluid may be low, and in some instance these additives may act to lower the overall electrical conductivity of the system [21].

In this experiment combinations of three friction modifiers, based on molybdenum and boron, are explored to assess their effects on low friction onset, wear, corrosion, and conductivity in an EV style formulation. The borate compound in this study is a hydrolytically stable ester amide based on a naturally sourced C₁₂ ester (B-AMIDE). The two molybdate additives represent two separate molecular architectures. One molybdate friction modifier

(Mo-AMIDE) is sulphur free, and is based on the same naturally sourced C_{12} ligand chemistry as the B-AMIDE [22]. The second molybdate friction modifier contains sulphur and is a molybdenum dithiocarbamate (Mo-DTC) similar to that described in EU Patent 2697342 [23].

Experimental

A base electric vehicle style formulation was prepared using a low viscosity Group IV PAO 4cSt base stock. The formulation contained a partial package of additives typically found in an EV or automatic transmission fluid. This formulation was topped with combinations of the three friction and wear modifiers as described in TABLE 1. Each additive is charged within a typical concentration range used in ICE formulations.

Additive ID	Description	Concentration Range (ppm metal)
Mo-DTC	Molybdenum dithiocarbamate	0 – 0.3%wt (0-300 ppm Mo)
Mo-AMIDE	Molybdate Ester/Amide	0 – 0.3%wt (0-300 ppm Mo)
B-AMIDE	Borate Ester/Amide	0 – 1%wt (0-100 ppm B)

Table 1: Friction modifiers and concentrations.

The additive combinations used in this study are shown in [Figure 1], with minimum and maximum values of each additive representing the range of 0% to 100% charge. Formulations A through C represent singular component top-treats. Formulations D through F represent binary component top-treats, and formulations G through I represent ternary component top-treats to the base formulation and package.

In addition to testing freshly prepared samples, lubricant samples were also aged by a bulk oxidation method of 48 hours at 160 °C under an oxygen bubble. This was done to simulate oil after an extended in-use period.

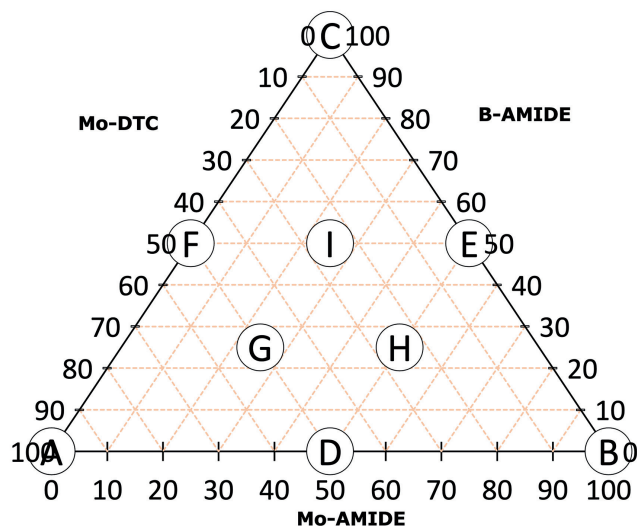


Figure 1: Composition of ternary mixtures.

Extended Copper Strip Corrosion (CSC) testing was performed on fresh oils in a modified ASTM D130 test, with separate tests running at 24, 168, and 336 hours at 160 °C, and including ICP analysis of solvated copper from each run. Bulk electrical conductivity was measured using an Epsilon+ dielectric meter in a temperature range of 40 -160 °C. Mini-Traction Machine (MTM) Stribeck curves were obtained using a 35 N load, 100% SRR, and 3-3000 mm/s rolling speed, and in temperature steps from 40 -140 °C, in 20 °C increments, with reporting of the average of triplicate measurements at each temperature.

SRV was run using a custom profile of 4N, 1mm stroke, ball on disc, reciprocating at 50Hz. A temperature ramp was imposed from 40°C to 140°C with 10 minutes rubbing at each temperature followed by a 5 minute temperature ramp. Rubbing time was extended to 15 minutes at the final 140°C. Wear scars on the test pieces were then measured using an optical profilometer.

Results and Discussion

Extended Cu Corrosion (Modified ASTM D130)

The ICP results of the extended copper corrosion [Figure 2] show the increasing solubilised Cu with increasing time. Copper leaching is relatively low (max

136 ppm Cu, average 85 ppm Cu at 336 hours across all formulations). The increase in dissolved copper over time follows a modified Arrhenius behaviour. Copper strip ratings at 336 hours range from 1a to 3a. The lowest corrosion being Formula D, containing only Mo-AMIDE.

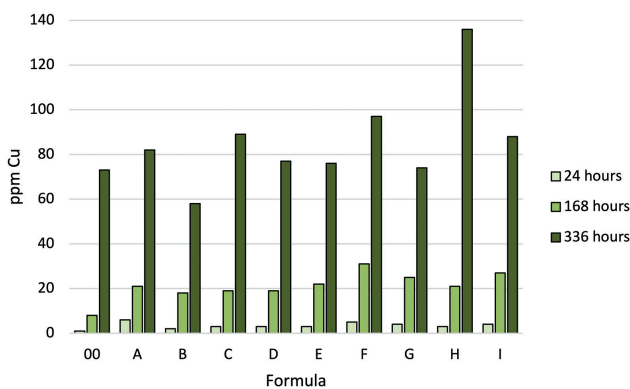


Figure 2: Dissolved copper by ICP (Extended D130 @ 160°C).

A visual comparison of the copper strips over the course of two weeks [Figure 3] demonstrates a minimal amount of corrosion on the bare copper. There is an inherent amount of baseline corrosion due to other componentry, as noted in the appearance of Formula 00. The singular addition of Mo-DTC (A) and Mo-AMIDE (B) contributes little beyond that.

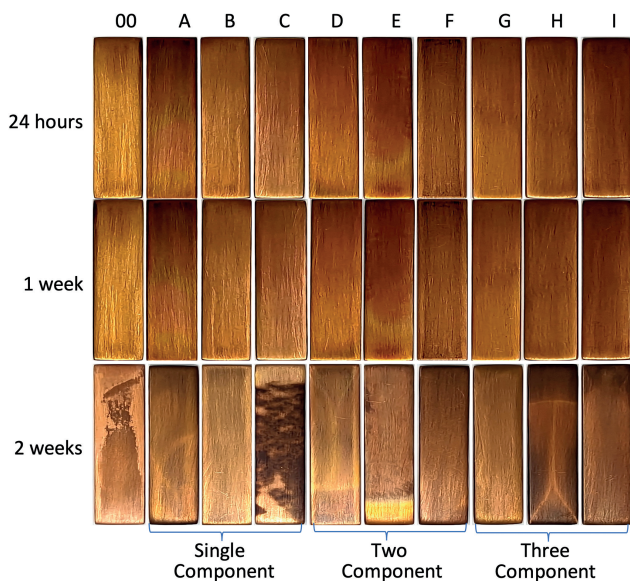


Figure 3: Visual appearance of Cu Strips (Extended D130 @ 160°C).

It was somewhat unexpected that the singular top-treat of B-AMIDE (C) increased corrosion, since many borates are actually employed for their anti-corrosion properties. This detriment is easily mitigated, through binary and ternary combinations of the borate with the two molybdate additives.

Electrical conductivity

All formulations, fresh and aged, yield electrical conductivities in a range similar to current EV specific fluid technology [Figure 4]. The conductivities with respect to temperature follow no specific trend when measured in fresh oil, other than the expected result that conductivity increases with temperature. This increase is a known property with most fluids and is most likely a direct result of reduced viscosity with the higher temperatures. A lower viscosity allows for easier flow of material and correspondingly, an easier flow of electrons.

The electrical conductivity of the fluids after oxidative ageing presents a less random behaviour than fresh oil. In general, the conductivities are higher than the respective fresh oil measurements. The viscosity changes in these oils are extremely minimal relative to the fresh oil, therefore, the observed conductivity changes are most likely the results of oxidative changes in the oils, with the increased polarity of the oxidative products driving the increase in conductivity.

From the aged oil data, none of the molybdenum or boron based additives are working as antioxidants, as all show an increase in conductivity above baseline oil 0. That being said, most combinations of the additives do show a greater resistance to oxidation than formulas using only the individual additives. Of particular note are Formula F, which is comprised of B-AMIDE and Mo-DTC, and Formula I, which is comprised of B-AMIDE, Mo-DTC, and Mo-AMIDE. In terms of conductivity, these two formulas demonstrated the least amount of oxidative degradation relative to baseline.

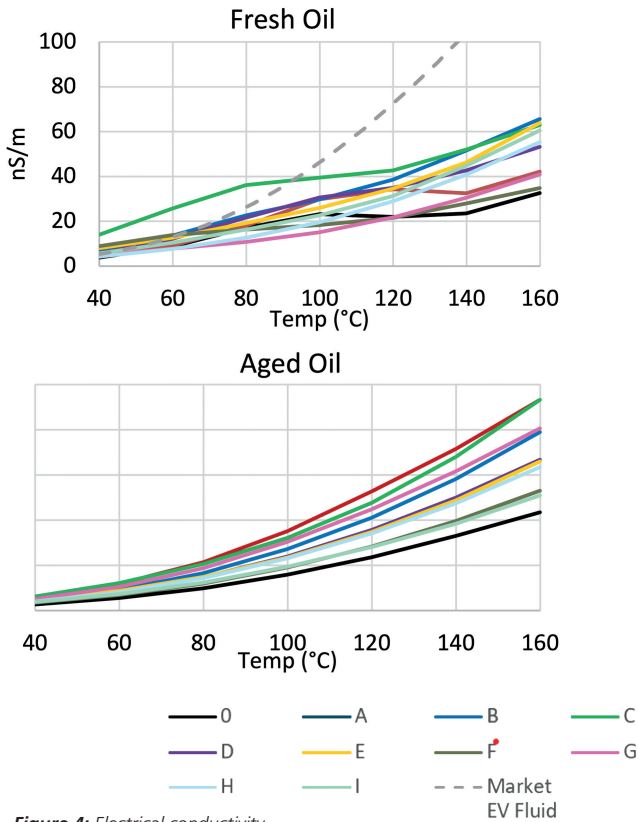


Figure 4: Electrical conductivity.

Friction coefficient (via MTM)

Stribeck curves were taken on both fresh and aged oils at temperatures from 40 °C to 140 °C. Of greatest interest are the results shown below in Figure 5. A common issue with Mo-DTCs is that they tend to show excellent anti-friction behaviour when tested in fresh oils, but lose that benefit with ageing. This is shown in Figure 5, with higher friction values observed for the aged Mo-DTC, relative to the fresh oils. The B-AMIDE similarly demonstrates relatively high friction in aged oils, but since its primary use is as an anti-wear additive, the higher friction value is not unexpected. The interesting benefit is seen when these two additives are combined, as with Formula F. With the combination, a synergistic friction benefit is observed between the two additives. The benefit is minimal at higher temperatures, but more pronounced at 40 °C. This may be significant in the context of EV formulations, where operating temperatures are much lower than in conventional ICE engines.

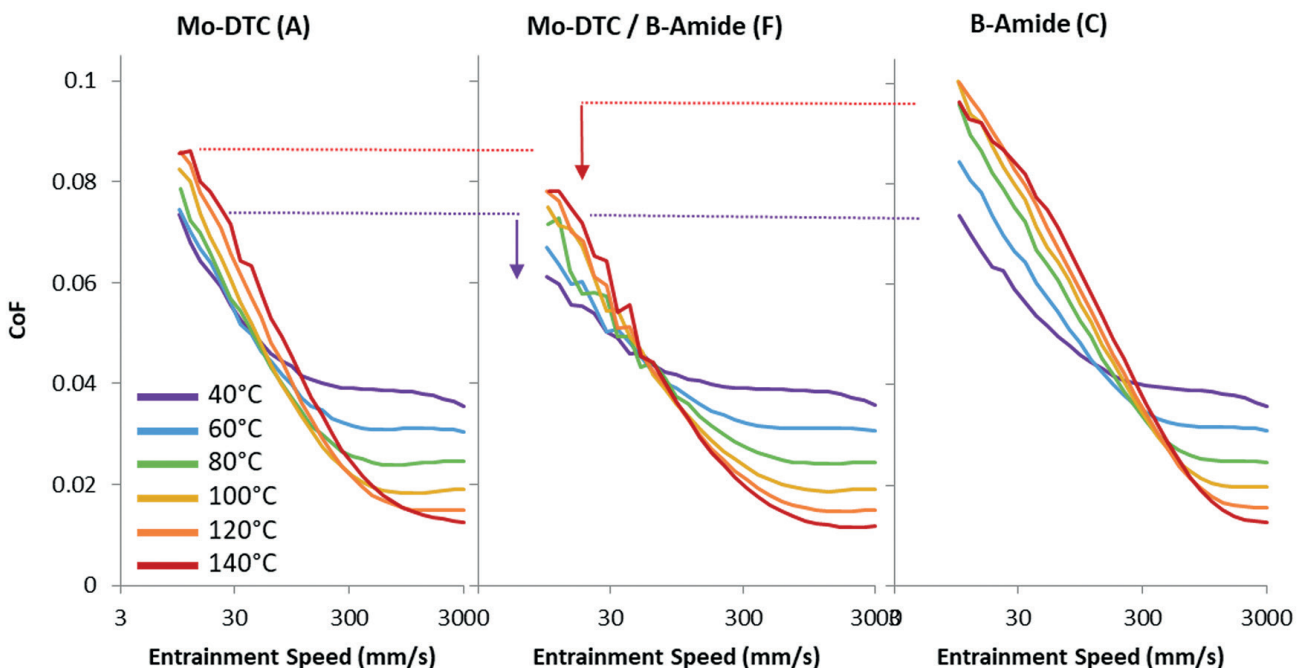


Figure 5: MTM Stribeck friction curves of Aged Oils.

SRV friction and wear

SRV was used to further explore the temperature component in tribofilm formation. Figure 6 shows the results for the custom temperature ramp friction profile for both fresh and aged oils. The benefit of Mo-DTC in fresh oil (Formula A) is well demonstrated in this test. Beginning at 80 °C, there is a significant drop in friction when using Mo-DTC in fresh oil. Likewise, the diminished returns of Mo-DTC in aged oil is also seen, such that a 100 °C activation temperature is needed in aged oil. Above this temperature, lower friction is achieved, but it never achieves the same low value as seen in fresh oil. This loss in aged-friction can be mitigated somewhat through a combination of Mo-DTC and Mo-AMIDE (Formula D). With this combination, a consistent friction performance can be achieved across both fresh and aged oils.

The SRV data also demonstrates that aged oil performance can be significantly different than that of fresh oil, independent of formulation. As a single component B-AMIDE (Formula C) becomes a friction modifier in this EV formulation, with activation around 80 °C. It outperforms the traditional Mo-DTC friction modifier (Formula A) until 120 °C, and then matches performance from thereon. Likewise binary additive combinations of B-AMIDE with either of the molybdenum friction modifiers gives a similar performance (Formulas E and F).

Two of the three ternary additive combinations outperform all other additive combinations in the aged oil. Both Formulas G and H contain a minor fraction of B-AMIDE. The major fraction is split 2:1 between the two molybdenum friction modifiers, with Mo-DTC being the majority in FORMULA G, and Mo-AMIDE being the majority in Formula H. Both formulas G and H consistently give lower friction across the entire temperature range, and the lowest activation temperature of all formulations, at approximately 60 °C.

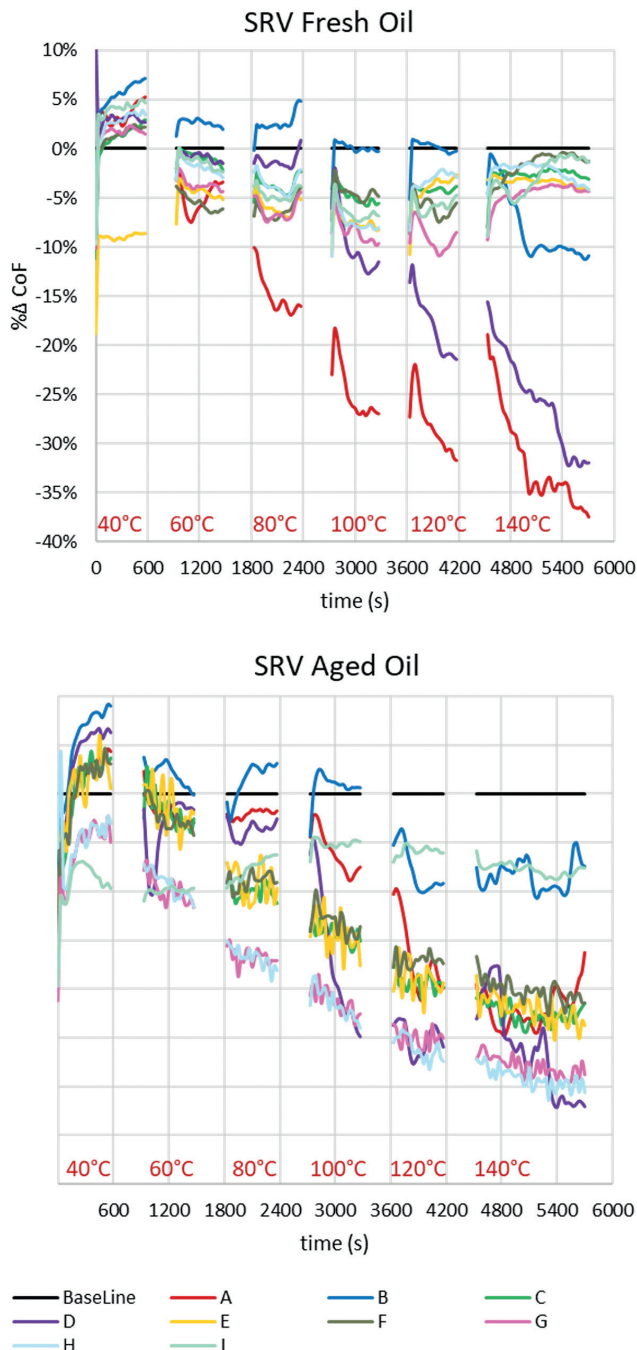


Figure 6: SRV friction profile relative to baseline formula 00.

Wear volume results for each of the formulations run in the SRV are shown in Figure 7. For the fresh oil, all formulations are statistically similar to the baseline, indicating no additional wear benefit in this

test. The exceptions are Formulas A and C, which are the singular top-treats of Mo-DTC and B-AMIDE, respectfully. Aged data is similar for singular top treats, but as with the friction benefit, multiple additive combinations yield a statistical improvement in wear.

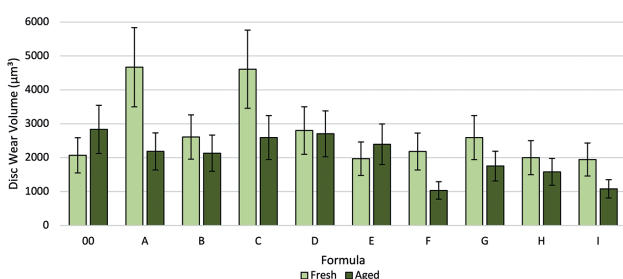


Figure 7: Disc wear volumes from SRV experiment.

Conclusion

In this experiment, traditional lubricant additives based on boron and molybdenum are incorporated in a low viscosity lubricant for use in applications where copper corrosion and electrical conductivity may be of concern. Results indicate that combinations of B-AMIDE, Mo-AMIDE and Mo-DTC can be effectively used in an EV based fluid without detriment to electrical conductivity or corrosion. Of particular merit is a combination of molybdenum dithiocarbamate and borate ester which provides both a very low impact on electrical conductivity, and a synergistic response to friction in aged oils. In terms of extended oil life, conductivity and friction remained low with this combination.

While formulation differences will always affect performance of any individual additive, it is important not to preemptively rule out traditional additive technology. Older technology may not only work in newer EV formulations without detriment, but may also bring unexpected benefit.

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