Influence of polymeric friction modifiers in the lubrication of DLC contacts when used alone or in the presence of MoDTC

Croda's polymeric friction modifiers (PFM) Perfad™ 3000, Perfad 3006 and Perfad 3050 demonstrate unique frictional characteristics on steel-steel contacts and they also exhibit unique performance in DLC - steel contacts, helping to reduce friction and minimise wear.

It is very important to consider both friction and wear when conducting experiments, as low friction does not necessarily equate to low wear. Sometimes it can be observed that low friction is actually the direct result of high wear (as can be observed when using MoDTC), so additives which have the ability to reduce both friction and wear are highly desirable. Two pieces of work have been conducted to investigate the influence of friction modifiers on DLC lubricated surfaces, using a commercial moly-free 5W30 European Oil (ACEA C3) as a reference fluid: (1) Reciprocating sliding test – University of Leeds (2) Uni-directional sliding test – Croda.

Three different types of DLC coating have been investigated. Their approximate structure composition can be visualised in figure 1 and will be described in more detail.

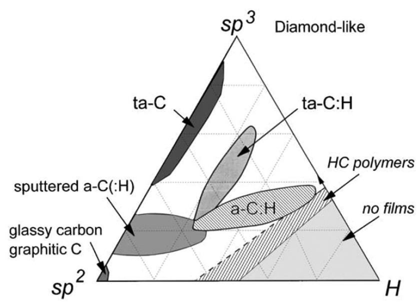

Figure 1. DLC triangle – J.Robertson, Materials Science and Engineering, 2002 (129-281)

1. Reciprocating Sliding Tests

Work commissioned by Croda was undertaken at the University of Leeds, United Kingdom (Dr. Shahriar Kosarieh, Dr. Farnaz Motamen Salehi et al). The test arrangement was a reciprocating cast iron pin on a DLC plate. The coating was prepared by Oerlikon and was nominally a-C:H15 DLC coating applied to a HSS M2 grade steel plate. The pin was 20mm in length, 6 mm in diameter and had a 40mm radius curvature. The test was conducted at an oil temperature of 100°C, reciprocating speed of 20mm/s and a frequency of 1 Hertz for 20 hours. A load of 390N was applied, giving an initial Hertzian pressure of 0.7GPa.

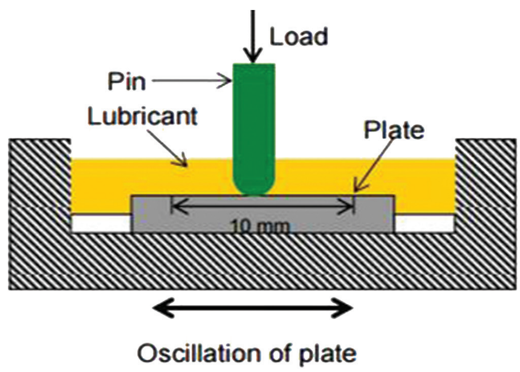

Figure 2. Test arrangement for cast iron – a-C:H15 DLC plate flooded with lubricant

1.1 Friction as a Function of Time (5W30 ACEA C3 Oil)

Polymeric friction modifiers have a positive influence in reducing friction in a sliding contact configuration of cast iron – aC:H15 DLC, when top-treated into the 5W30 ACEA C3 engine oil (figure 3). PFMs at a teat-rate of 0.5% resulted in a 5% reduction in friction, with 1% PFM contributing 20% reduction in friction.

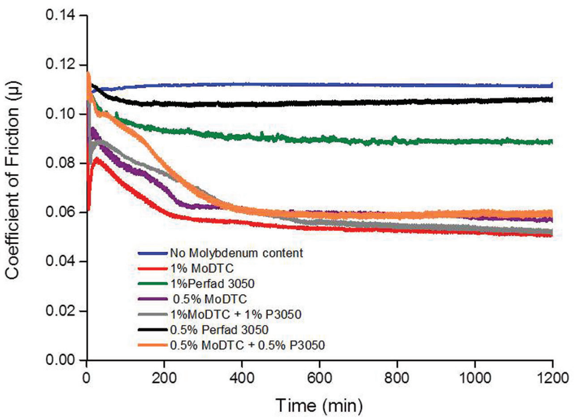

Figure 3. *Friction data for 5W30 ACEA C3 reference oil and top-treated reference oil*

MoDTC at a treat-rate of 1% resulted in >50% reduction in friction but this was accompanied by a very significant increase in wear and transfer of the a-C:H15 DLC coating from the plate to the pin (figure 4).

Figure 4. *Transfer of a-C:H15 DLC coating from plate to pin for MoDTC containing oils*

Combinations of PFM with MoDTC resulted in the same final friction coefficient but the PFM interfered with the friction in the early stages of the test. Whilst the overall friction profile was not as good as MoDTC alone, including PFM in the formulation significantly reduced wear and eliminated the transfer of a-C:H15 DLC from the plate to the pin (figure 5).

Figure 5. *No transfer of coating from a-C:H15 plate to pin for PFM containing oils*

1.2 Influence of MoDTC and PFMs on Wear Profile

The 5W30 reference oil, without any top-treatment of friction modifiers showed wear on the cast iron pin (22 x $10m^{-18}m^3/NM$) but no observable wear on the a-C:H15 DLC plate (figure 6).

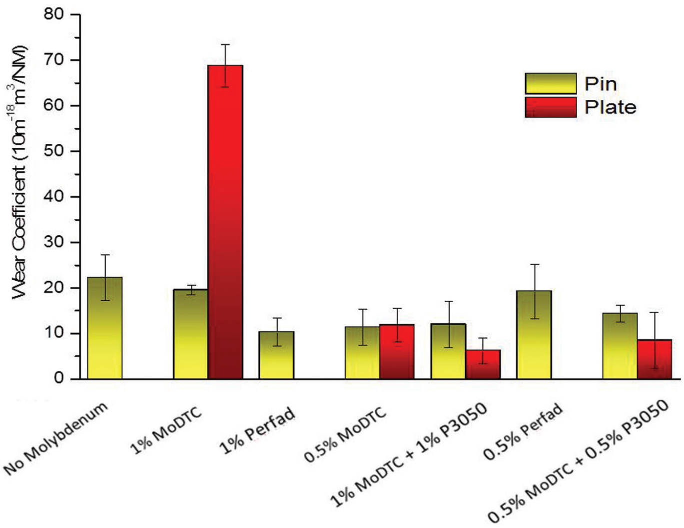

Figure 6. *Pin and plate wear for cast iron - aC:H15 DLC plate reciprocating – sliding contact*

PFMs when top-treated into the 5W30 ACEA C3 engine oil provided wear protection to the cast iron pin. At 1% treat-rate the wear on the cast iron pin was reduced by approximately 50% (11 x $10m^{-18}m^3/NM$). The a-C:H15 DLC plate remained wear free as far as was observable under these test conditions.

Including MoDTC as a friction modifier in the 5W30 ACEA C3 engine oil resulted in wear taking place on the a-C:H15 DLC disc. The wear rate is a function of MoDTC concentration, with 1% producing very high levels of wear (68 x $10m^{-18}m^3/NM$) on the a-C:H15 DLC plate and similar wear rates on the cast iron pin (20 x $10m^{-18}m^3/NM$), when compared to the 5W30 reference fluid.

The inclusion of 1% PFM into the reference oil also containing 1% MoDTC prevented the transfer of a-C:H15 DLC coating from the plate to the cast iron pin. This combination also resulted in a very significant reduction in wear on both the pin (12 x $10m^{-18}m^3/NM$) and the a-C:H15 DLC plate (7 x $10m^{-18}m^3/NM$) when compared to the 5W30 oil containing MoDTC. It must be noted that even with the inclusion of PFM it was not possible under these conditions to completely eliminate the wear on the a-C:H15 DLC plate due to the presence of MoDTC.

2. Croda In-House MTM Testing (Steel disc – DLC ball)

In a parallel project, the effectiveness of PFMs on two other types of DLC was investigated. The structure and composition of the two types of DLC used are summarised in table 1.

Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.110 page 3

One DLC is described as 50%sp^3; 40% hydrogen content; the second DLC is described as sp^2;Cr doped; 0% hydrogen. Both types of DLC ball were provided by PCS Instruments.

Parameters	Uncoated steel ball	50% sp^3; 40% hydrogen ball	sp^2;Cr doped; 0% hydrogen ball
Elements	-	C, H	C, Cr
Structure	-	50% sp3	sp2
Disc Hardness (HV)	720-780	1600	1500
Disc Roughness (µmRa)	< 0.01	< 0.04	< 0.04
Ball Hardness (HV)	800-920	1600	1500
Ball Roughness (µm Ra)	< 0.02	< 0.05	< 0.05

Table 1. *Steel ball and DLC ball profiles used in MTM sliding contact*

The effect of friction modifiers in a steel ball – steel disc contact was also investigated and compared to DLC ball – steel disc arrangement.

Friction and Wear tests were conducted using a PCS Instruments Mini Traction Machine, using the following test profile:

- Determination of an initial Stribeck curve:
    - Ball on disc: Pure Sliding
    - Virgin surfaces
    - Load 36N (1.01 GPa Hertzian Pressure)
    - Lubricant temperature 80ºC
    - Entrainment speeds between 0.05 m/s and 3.0 m/s
    - No running-in profile, friction measured from high speed to low speed
- Run a rubbing test profile; pure sliding, 0.05 m/s at 30 N and 80ºC for 120 mins
- Determination of a Second Stribeck curve using the same conditions described above for the initial Stribeck curve. Friction and wear performance was determined after the second Stribeck curve was generated.

Following completion of the second Stribeck curve, wear profiles for both balls and discs were studied using 3D imaging (Bruker 3D Optical Profilometer Contour GT).

Figure 7 shows examples of both grey scale images and computer enhanced images of the wear scar observed on the ball. Using these images the volume of the wear scar can be estimated.

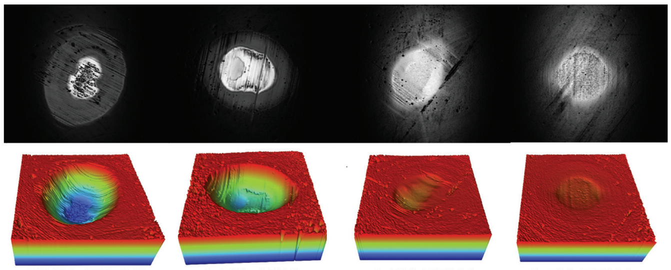

Figure 7. *Grey-scale and computer enhanced wear images*

Figure 8 shows an example of how the wear scar of the disc is estimated. Unlike the ball, it is not possible to measure the wear across the whole circumference of the disc therefore only a small cross-section of the disc is examined. This type of measurement was taken at 8 different points around the wear track and an average value calculated. Whilst we do not measure the whole wear track, the measurement allows quantitative comparisons between oils to be measured.

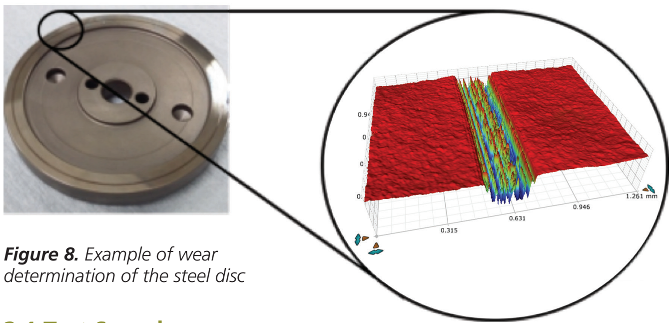

Figure 8. *Example of wear determination of the steel disc*

2.1 Test Samples

The 5W30 European ACEA C3 oil was once again used as the base line reference fluid. Friction modifiers were added to this reference oil in order to determine the influence of MoDTC, polymeric friction modifiers and a conventional organic friction modifier, namely glycerol mono-oleate (GMO).

The test samples and tests conducted are shown in Table 2.

Sample	Mo content / ppm	50% sp^3; 40% hydrogen ball – steel disc	sp^2;Cr doped; 0% hydrogen ball - steel disc	Steel ball – steel disc
5W30	0	Y	Y	Y
5W30 + 0.5% MoDTC	400	Y	Y	Y
5W30 + 0.5% PFM 1	0	Y	Y	Y
5W30 + 0.5% MoDTC + 0.5% PFM 1	400	Y	Y	Y
5W30 + 0.5% GMO	0	Y	Y	Y
5W30 + 0.5% MoDTC + 0.5% GMO	400	Y	Y	Y

Table 2. *Samples and tests conducted using MTM sliding conditions*

2.2 DLC 50% sp³; 40% hydrogen Ball – Steel Disc

The 5W30 ACEA C3 reference oil is a high friction oil (coefficient of friction 0.11 in the boundary regime - figure 9) but resulted in only a small amount of wear (figure 10) on both the 50% sp³; 40% hydrogen DLC ball (4000 μm³) and steel disc (12,600 μm³).

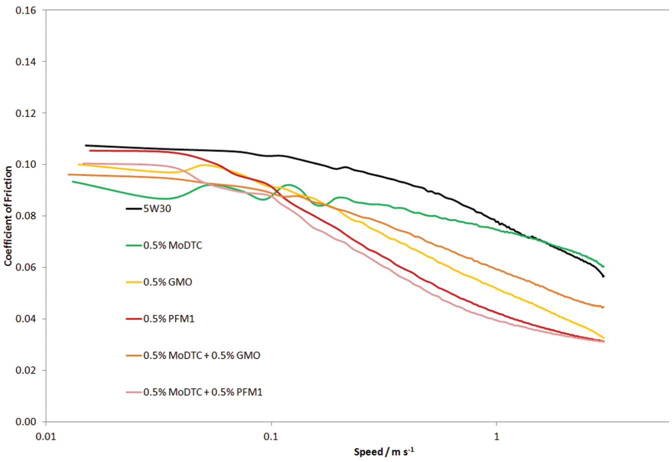

Figure 9. *Stribeck Curves for 50% sp³; 40% hydrogen DLC Ball – Steel Disc*

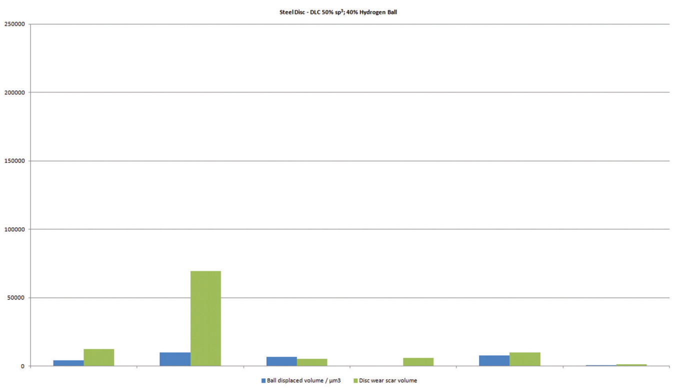

Figure 10. *Stribeck Curves for 50% sp³; 40% hydrogen DLC Ball – Steel Disc*

Introducing 0.5% MoDTC into the formulation resulted in a decrease in friction (0.09) in the speed range of 0.1m/s – 0.03 m/s. However, wear on the 50% sp³; 40% hydrogen DLC ball (10,000 μm³) increased by 150% and by 450% on the steel disc (70,000 μm³) due to the presence of MoDTC.

Glycerol mono-oleate at a treat-rate of 0.5% also provided a reduction in friction (0.10) compared to the 5W30 reference oil. It also proved to be lower in friction than the MoDTC containing oil at higher entrainment speeds (>0.1m/s). Whilst the wear volume of the steel disc (5300 μm³) was decreased by >50%, the wear on the 50% sp³; 40% hydrogen DLC ball (6700 μm³) increased by almost 70% relative to the reference oil but was much lower than the oil containing MoDTC (70,000 μm³).

Addition of GMO to the oil containing MoDTC resulted in a blend with a similar friction profile to the reference oil + 0.5% GMO, that is, slightly higher in the boundary regime but lower than MoDTC in the mixed lubrication regime.

The combination of GMO and MoDTC resulted in a moderate decrease in wear on the 50% sp³; 40%-H DLC ball and a significant decrease in wear on the steel disc compared to that observed for the oil containing only MoDTC (figure 11). MoDTC drastically increased disc wear compared to the 5W30 reference oil alone which was 12,600 μm³.

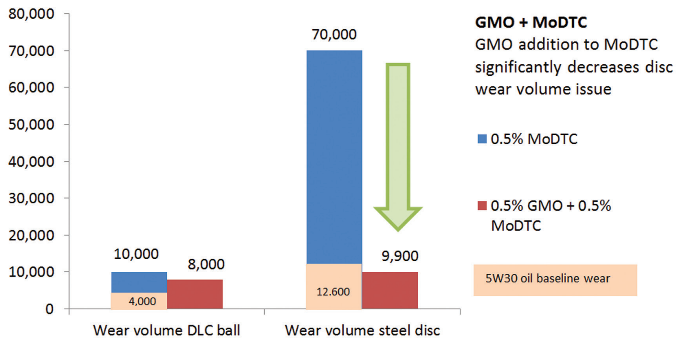

Figure 11. *Addition of GMO to MoDTC, effect on wear volume*

The most effective friction modifiers for this particular DLC – steel arrangement were the polymeric friction modifiers. Whilst PFMs did not demonstrate any significant friction reducing properties at very low speed, they did provide the lowest friction in the mixed lubrication regime.

Used alone, PFMs reduced the wear on the 50% sp³; 40%-H DLC ball by 90% and by >50% on the steel disc (figure 12).

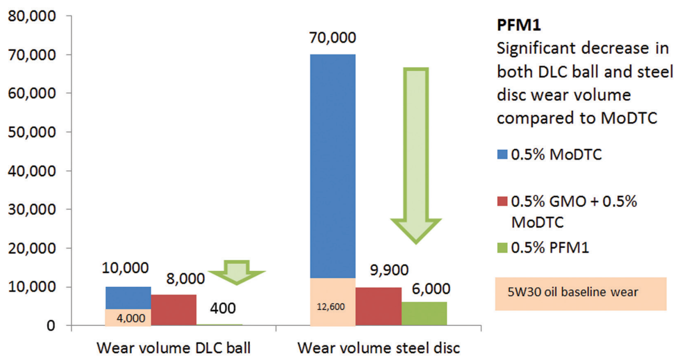

Figure 12. *PFM1, reduction of wear volume*

Figure 13 shows that a combination of MoDTC and PFMs, together acted to reduce the wear on both the DLC ball and the steel disc by more than 80%, a considerable achievement given that MoDTC alone actually caused wear to increase on both the 50% sp³; 40% hydrogen DLC ball and steel disc.

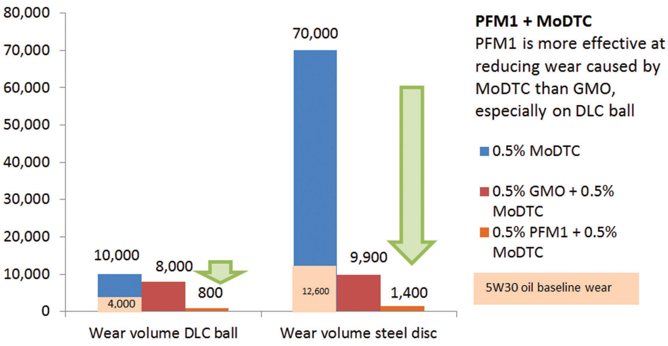

Figure 13. Addition of PFM1 to MoDTC, even further reduction of wear volume

2.3 DLC sp^2;Cr doped; 0% hydrogen Ball - Steel Disc

The sp^2;Cr doped; 0% hydrogen DLC ball is a higher friction surface than the 50% sp^3; 40% hydrogen DLC ball. Using the same 5W30 ACEA C3 oil, the sp^2;Cr doped; 0% hydrogen DLC ball – steel disc arrangement had a coefficient of friction ≥0.12 at slow speeds (figure 14), compared to 0.11 for the 50% sp^3; 40% hydrogen ball – steel disc arrangement.

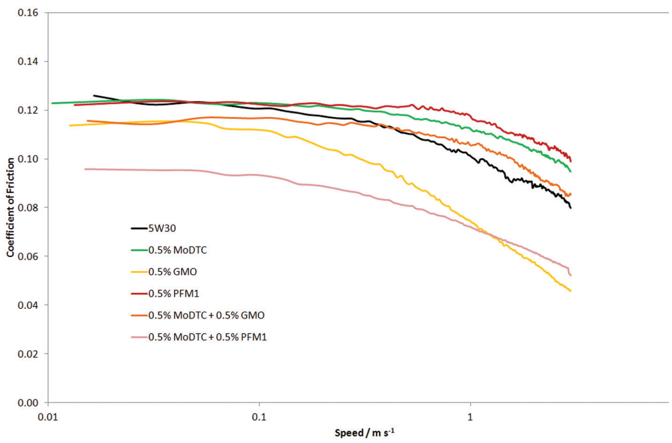

Figure 14. Stribeck Curves for sp2;Cr doped; 0% hydrogen DLC ball – steel disc

The sp^2;Cr doped; 0% hydrogen DLC ball was also shown to be much less durable than the 50% sp^3; 40% hydrogen ball, as can be seen in figure 15.

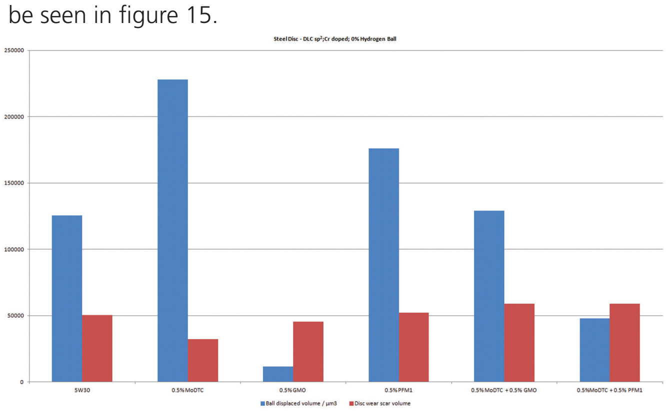

Figure 15. Wear profiles for sp^2;Cr doped; 0% hydrogen DLC ball – steel disc

At the end of test, the measured wear volume on the sp^2;Cr doped; 0% hydrogen DLC ball was 125,000 μm^3, compared to <5000 μm^3 for the 50% sp^3; 40% hydrogen DLC ball. The steel disc in contact with the sp^2;Cr doped; 0% hydrogen DLC ball also experienced higher wear (50,000 μm^3) compared to the steel disc in contact with the 50% sp^3; 40% hydrogen ball (120,000 μm^3).

MoDTC did not lead to any reduction in friction with the sp^2;Cr doped; 0% hydrogen DLC ball but still resulted in 65% increase in wear (230,000 μm^3) on the DLC ball. There was a 36% reduction in wear (32,000 μm^3) observed on the steel disc counter-surface compared to the reference oil alone.

Glycerol mono-oleate, when used as the only friction modifier top-treated into the 5W30 ACEA C3 oil, gave the best performance in reducing both friction (0.115) and wear with the sp^2;Cr doped; 0% hydrogen DLC ball. Compared to the reference oil, the oil containing GMO gave a 10% reduction in boundary friction and >10% in the mixed lubrication regime. GMO reduced the wear (11500μm3) on the sp^2;Cr doped; 0% hydrogen DLC ball by 90% and by 10% on the steel disc counter-face (45500 μm^3).

Including MoDTC in the GMO containing formulation resulted in a product which had friction and wear properties similar to the ACEA C3 reference oil, suggesting that MoDTC and GMO were counteracting each other (figure 16).

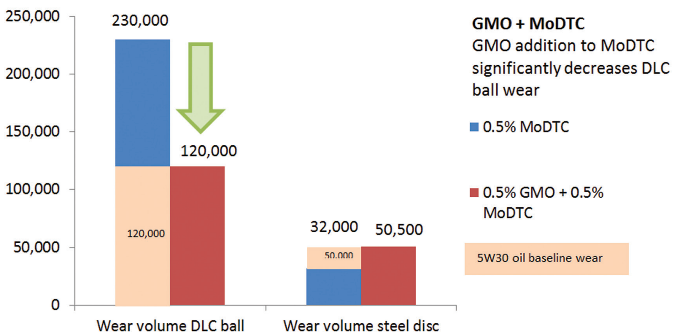

Figure 16. Addition of GMO to MoDTC, effect on wear volume sp2 DLC

Including PFM alone in the ACEA C3 engine oil resulted in higher friction than the reference oil and also higher wear on the sp^2;Cr doped; 0% hydrogen DLC ball, an increase of 40%. The wear on the steel disc counter-face was very similar to the reference oil without any additional FM added (figure 17).

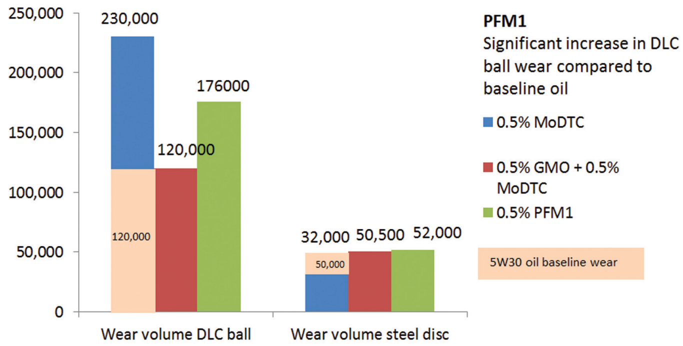

Figure 17. *PFM1, increase of wear volume on sp² DLC ball*

The combination of MoDTC and PFM gave a surprisingly good performance compared to either additive used alone. Whilst not achieving the level of wear protection provided by GMO only, this combination resulted in the lowest friction profile (<0.10; >20% reduction compared to the ACEA C3 reference oil). With respect to wear, the combination of PFM and MoDTC provided a 40% reduction in wear on the sp²;Cr doped; 0% hydrogen DLC ball (48,000 µm3) but a 20% increase in wear on the steel disc counter-face (59,000 µm³).

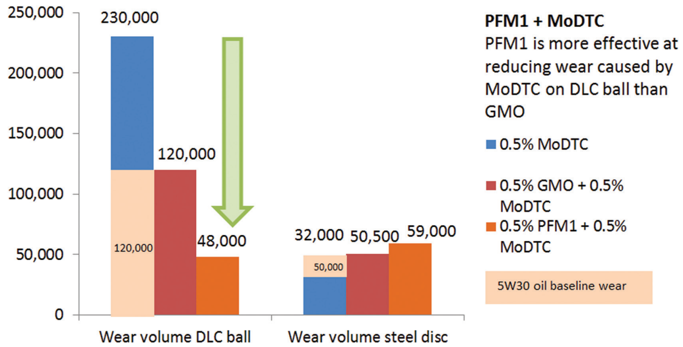

Figure 18. *Addition of PFM1 to MoDTC, surprising reduction in sp² DLC ball wear*

2.4 Steel Disc – Steel Ball

To complete the study, the results for steel-steel friction and wear were repeated for all the FM and FM combinations.

In comparison to the two DLCs investigated as part of the Croda in-house work, steel ball – steel disc contact is the highest friction contact, with the 5W30 ACEA C3 reference oil having a coefficient of friction of 0.14 in the boundary regime (figure 19).

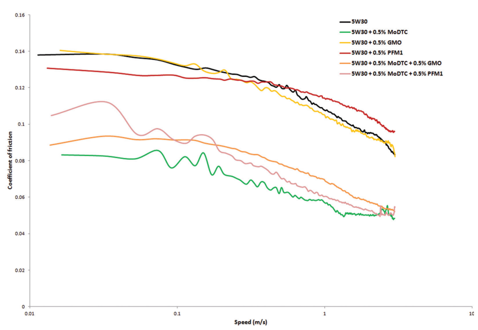

Figure 19. *Stribeck Curves for Steel Ball – Steel Disc*

When comparing the wear performance of the 5W30 baseline oil, the steel – steel contact demonstrated ball wear of a similar magnitude to the sp²;Cr doped; 0% hydrogen DLC ball, which was 30 times greater than the ball wear observed with the 50% sp³; 40% hydrogen ball (figure 20). The disc wear was lower than was observed in the sp²;Cr doped; 0% hydrogen DLC ball – steel disc configuration but 2.5 times greater than the level of the steel disc wear observed with the 50% sp³; 40% hydrogen DLC ball – steel disc contact.

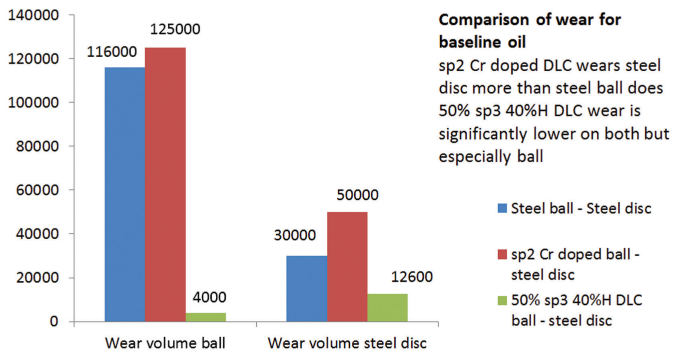

Figure 20. *Comparison of wear for 5W30 baseline oil in different configurations*

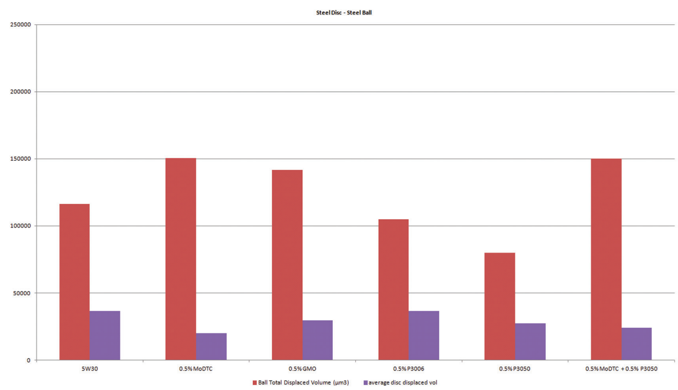

Figure 21. *Wear profiles for steel ball – steel disc*

The reference oil top-treated with GMO showed no reduction in friction and GMO may be responsible for an increase in wear (140,000 µm³) compared to the 5W30 reference fluid under these test conditions (116,000 µm³).

MoDTC provides a substantial reduction in friction (0.08; 40% decrease), compared to the reference oil. However, a 30% increase in ball wear (150,000 µm³) was observed. Disc wear was lower (20,000 µm³) than the 5W30 ACEA C3 reference fluid (36,000 µm³).

GMO + MoDTC when used in combination also provided a very strong reduction in friction (0.09; 35% decrease) compared to the reference oil but not as low as MoDTC by itself. This combination of inorganic and organic friction modifier resulted in the lowest wear measured on both steel ball and steel disc.

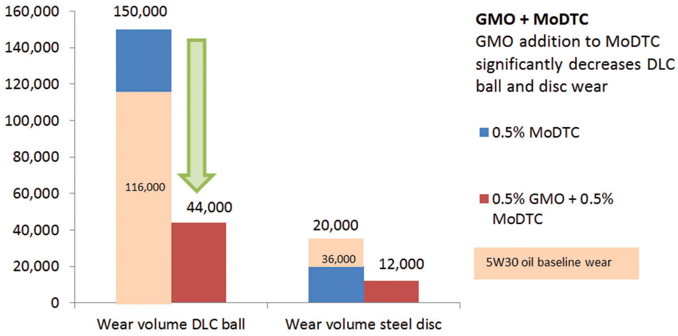

Figure 22. *GMO addition reduces wear caused by MoDTC on both ball and disc*

In comparing PFM with GMO and MoDTC only containing formulations, it was observed that the PFM provided the highest level of wear protection for both the ball and the disc (figure 23). The PFM gave a modest reduction in friction (0.13; 5% reduction) compared to reference oil when used at 0.5% treat-rate.

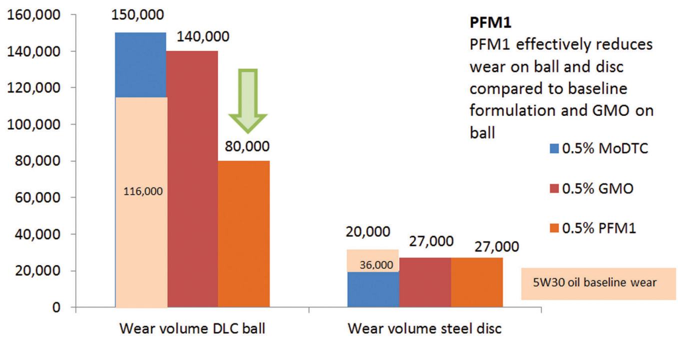

Figure 23. *PFM1 reduces wear on ball and disc compared to baseline formulation*

Like the GMO + MoDTC combination, the combination of PFM and MoDTC resulted in lower friction (0.11) but not as low as for MoDTC alone (0.08). PFM and MoDTC combined were observed to result in wear on both the steel ball and on the steel disc comparable to those observed for MoDTC alone and GMO + MoDTC formulations. Under these test conditions it appears that wear results directly from the presence of MoDTC.

3. Comparison of FMs by Contact Type

Table 3 summarises the effectiveness of the different FMs and combination of FMs for all three types of DLC in contact with either the cast iron pin or steel counter-face, and a steel – steel contact. Green boxes indicate a strong positive effect in reducing friction or wear, yellow indicates some positive effect in reducing friction or wear and red indicates no evidence of a positive effect on friction and wear, and indeed may result in higher friction and wear.

	sp^2;Cr doped; 0% hydrogen ball - Steel Disc		sp^2/sp^3; 15% hydrogen plate – cast iron pin		50% sp^3; 40% hydrogen ball – steel disc		Steel Ball – Steel Disc	
	friction	wear	friction	wear	friction	wear	friction	wear
5W30								
5W30 + 0.5% MoDTC								
5W30 + 0.5% GMO								
5W30 + 0.5% PFM								
5W30 + 0.5% MoDTC + 0.5% GMO								
5W30 + 0.5% MoDTC + 0.5% PFM								

Table 3. *Traffic light table indicating relative performance of FMs and combinations of FMs*

The following observations are based on the effect of friction modifiers when top-treated into a 5W30 ACEA C3 engine oil:

3.1. MoDTC

a. MoDTC had a strong positive effect in reducing friction in a steel – steel contact (the lowest friction of any additive or combination of additives) but it came at the expense of increased wear.

b. MoDTC did not reduce friction in a sp^2;Cr doped; 0% hydrogen DLC ball – steel disc contact and resulted in very high wear of the DLC coating.

c. MoDTC did reduce friction in a sp^2; 15% hydrogen DLC plate – cast iron contact but resulted in very high wear of the DLC coating and a transfer of the coating from disc to cast iron pin.

d. MoDTC did reduce friction in a 50% sp^3; 40% hydrogen DLC ball – steel disc contact but resulted in very high wear of the DLC coating.

3.2. Glycerol Mono-Oleate

a. GMO has a negative effect on friction and wear in a steel – steel contact.

b. GMO did reduce friction in a sp^2;Cr doped; 0% hydrogen DLC ball – steel disc contact and resulted in lower wear of the DLC coating. Of all the FMs and combinations of FMs, GMO was the most effective friction modifier on sp^2;Cr doped; 0% hydrogen DLC in minimising DLC wear.

c. GMO did reduce friction in a 50% sp^3; 40% hydrogen DLC ball – steel disc contact and provided some reduction in wear of the DLC coating.

3.3. Polymeric Friction Modifier

a. PFMs have a positive effect in reducing friction in a steel – steel contact and they provided the highest wear protection of any single FM or combination of friction modifiers.

b. PFMs did not reduce friction in a sp^2;Cr doped; 0% hydrogen DLC ball – steel disc contact and resulted in high wear of the DLC coating.

c. PFMs did reduce friction in a sp^2; 15% hydrogen DLC ball – cast iron pin contact and provided the highest wear protection of all friction modifiers or combinations of friction modifiers.

d. PFMs did reduce friction in a 50% sp^3; 40% hydrogen DLC ball – steel disc contact and provided the highest wear protection of all friction modifiers or combinations of friction modifiers.

3.4. MoDTC / GMO Combined

a. MoDTC / GMO combination had a strong positive effect on friction and wear in a steel – steel contact. Of all the additives and combinations tested, this combination gave the lowest wear in the steel – steel contact.

b. MoDTC / GMO combination did not reduce friction in a sp^2;Cr doped; 0% hydrogen DLC ball – cast iron pin contact but did result in lower wear of the DLC coating. The combination of MoDTC and GMO gave inferior performance compared to GMO alone in a sp^2;Cr doped; 0% hydrogen DLC ball – steel disc configuration.

c. MoDTC / GMO did reduce friction in a 50% sp^3; 40% hydrogen DLC ball – steel disc contact but did not provide any significant additional wear protection compared to the reference oil or to GMO alone.

3.5. MoDTC / PFM Combination

a. MoDTC / PFM combination had a positive effect in reducing friction in a steel – steel contact but the level of wear protection was not improved relative to the reference oil. Both the friction and wear performance were dominated by MoDTC.

b. MoDTC / PFM combination gave the lowest friction in a sp^2;Cr doped; 0% hydrogen DLC ball – steel disc contact and resulted in significantly lower wear of the DLC coating. With sp^2;Cr doped; 0% hydrogen DLC there appears to be a synergistic effect between the inorganic FM and the polymeric FM, as the friction and wear results were significantly improved compared to either of the two individual friction modifiers.

c. MoDTC + PFM combination did reduce friction in a sp^2; 15% hydrogen DLC ball – steel disc contact to a level similar to that of MoDTC by itself but the time to reach the minimum was longer due to the presence of the PFM. Whilst having a negative influence on the initial friction reduction, the PFM did provide an increase in wear protection of the DLC surface from MoDTC erosion but it did not reach the level of protection provided by the PFM alone.

d. MoDTC / PFMs did provide a reduction in friction in a 50% sp^3; 40% hydrogen DLC ball – steel disc contact and provided a high level of wear protection, similar to that provided by PFM alone.

4. Conclusions

1. DLC type has a very important role to play in influencing friction and wear and friction modifier selection:

- H-free sp^2 type responds very well to GMO but not in the presence of MoDTC
- sp^2/sp^3 H-containing DLCs respond positively to polymeric type FMs, even in the presence of MoDTC
- No single FM is optimal for all DLC – Fe and all Fe – Fe contacts, compromises may be required
- PFMs alone can provide excellent friction and wear performance on DLC surfaces

2. PFMs and MoDTC can act synergistically

3. Low friction can be associated with high wear, especially with MoDTC

4. Optimisation of MoDTC / PFMs / Add Packs could yield greater improvements in DLC contacts (friction and wear)

John Eastwood
Head of Global Business Development

©Croda Europe Ltd 2017. All rights reserved.

LINK
www.crodalubricants.com