

1 Interactions between Organic Friction 2 Modifier Additives[†]

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1 Abstract

2 The interactions of different additives in engine oils can create synergistic or antagonistic effects. This
3 paper studies how mixing different organic friction modifier additives affects friction reducing
4 properties of lubricants in the boundary lubrication regime. Amines of different degree of saturation
5 were mixed with either glycerol monooleate (GMO) or oleic acid in hexadecane. The model lubricants
6 thus formed were characterised with Fourier-transform infrared spectroscopy. Friction tests in
7 reciprocating motion using ball-on-disc steel-steel contacts were conducted to examine the
8 tribological performance of these lubricants. Worn surfaces were examined using X-ray photoelectron
9 spectroscopy. Oleic acid and oleylamine, a primary amine. Were found to form a partial ionic liquid,
10 providing synergistic friction reduction. This positive interaction reduces with increasing degree of
11 saturation of the amine. No synergistic effect was observed between GMO and oleylamine, suggesting
12 that GMO does not hydrolyse into a carboxylic acid within a rubbing contact in the presence of amine.

13 Keywords: Boundary Lubrication, Additives, Friction

14 Abbreviations: organic friction modifier (OFM); glycerol monooleate (GMO); ionic liquid (IL);
15 oleylamine (OA); diocylamine (DA); trihexylamine (TA); dimethylhexadecylamine (DM16); high
16 frequency reciprocating rig (HFRR); X-ray photoelectron spectroscopy (XPS).

17 1 Introduction

18 Lubricants are commonly used to reduce friction and wear of rubbing surfaces. They are most effective
19 when a sufficient amount of lubricant exists between the two surfaces, i.e. in full film lubrication
20 regime. When there is insufficient lubricant in the contact, as in the case of the mixed and boundary
21 lubrication regimes, surface contact occurs. Under mixed and boundary lubrication conditions, friction
22 modifiers are frequently added into the lubricant for friction reduction.

23 Organic Friction Modifiers (OFMs) are friction modifiers which contain only carbon, nitrogen, oxygen
24 and hydrogen atoms. OFMs are typically amphiphilic surfactant molecules with a polar head group
25 and a hydrocarbon tail group. These additives have been used since the early 1920's. Oleic acid was
26 the first "oiliness additive". Due to its corrosive nature, it is not commonly used and glycerol
27 monooleate (GMO) and other surfactant molecules are used instead [1]. OFMs reduce friction by
28 adsorbing to metal surfaces [2–4]. The adsorbed layer has friction reducing properties but its
29 properties may change during rubbing [5,6]. Rubbing may encourage multilayer formation [7], or
30 tribochemical reaction. For example, GMO is thought to hydrolyse to a carboxylic acid molecule within
31 rubbing contacts [8].

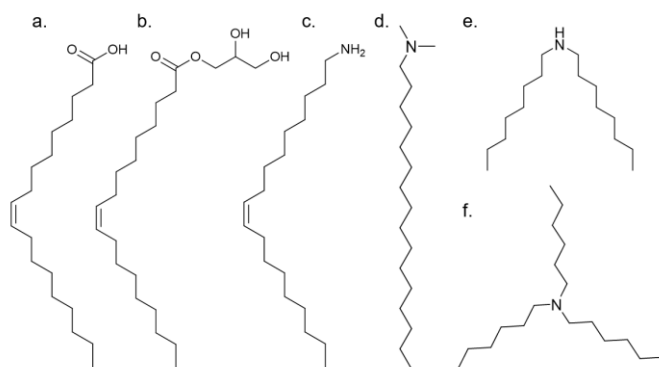
1 Fully formulated lubricants contain multiple additives, some of which may interact with OFMs. The
2 interactions between OFMs and zinc dialkyldithiophosphates, an extreme pressure (EP) additive, have
3 been shown to be synergistic [9,10] or antagonistic [11] depending on the chemistry and
4 concentration of the OFM additives. Antagonistic effect has been observed between a sulphur based
5 EP additives and OFMs due to competitive surface adsorption [12]. Mixing GMO with an overbased
6 calcium sulphonate detergent also produced antagonistic effects when measuring the lifetime for
7 parts in the hydroforming process [13]. Various OFM additives were added to a continuously variable
8 transmission (CVT) lubricant: oleic acid provided no improvement in friction reduction and removed
9 the detergent from the surface, while GMO improved friction reduction but reduced wear protection
10 when added into the CVT oil [14]. In cases where multiple friction modifiers were used, no synergistic
11 effect was observed between GMO and oleylamide, but synergistic interactions were observed when
12 GMO is mixed with a polymeric friction modifier [15].

13 Ionic liquids (ILs) are molten salts which are liquids below 100 °C. ILs have been shown to have
14 promising tribological properties [16]. They can also be used as additives [17]. Much of the literature
15 on oil soluble ILs studies phosphorous ILs, which are effective antiwear and friction modifier additives
16 [18–23]. Protic ionic liquids (PILs) are ionic liquids which form through a simple Brønsted acid-base
17 reaction, with the most heavily researched PILs being amine based [24]. Even in pure form, PILs are
18 not fully ionic, with the level of proton transfer from the acid to the base depends on the structure of
19 the reacting species. One study showed that the proton transfer is more complete with primary
20 amines compared to tertiary amines [25]. This is caused by the level of hydrogen bonding that can
21 occur within an ionic liquid, which then impacts on the physicochemical properties of the IL [26].
22 Mixing OFMs and PILs has been shown to improve the tribological properties of the lubricant. It is
23 thought that the IL may enhance the hydrogen bonding within the OFM adsorbed layer, giving rise to
24 lower friction [27].

25 A PIL formed by mixing oleylamine and oleic acid has been shown to be non-corrosive and provide
26 good friction and wear reducing properties as a pure ionic liquid [28]. Note that both oleylamine and
27 oleic acid are used individually as OFM additives [1]. Thus it is hypothesized that a synergistic effect
28 exists when they are used together as lubricant additives. This study tests this hypothesis. Since it has
29 been suggested that GMO breaks down to oleic acid during rubbing [8], the effect of mixing oleylamine
30 and GMO in a lubricant is also investigated. The performance of oleylamine, a primary amine, will be
31 compared to that of a secondary and a tertiary amine to shed light on the interactions between amine,
32 oleic acid and GMO and their effects on friction.

2 Materials

All chemicals were $\geq 99\%$ purity and were purchased from Sigma Aldrich. Hexadecane was cleaned through a filter of activated alumina, molecular sieves and silica gel before use. All other chemicals were used as received. All tests were conducted with 1 mM OFM solutions in hexadecane. The OFM additives tested, as shown in Figure 1, were oleic acid, glycerol monooleate (GMO), oleylamine (OA), dioctylamine (DA), trihexylamine (TA) and dimethylhexadecylamine (DM16) and their concentrations are 368 ppm, 461 ppm, 346 ppm, 312 ppm, 348 ppm and 348 ppm respectively if only one OFM is used in the solution. Two types of OFM solutions were prepared: a single-component system, consisting of only one type of OFM in hexadecane; and a two-component system, consisting of two types of OFMs in hexadecane.



11

12 *Figure 1. Structures of the OFM additives tested, (a) oleic acid, (b) glycerol monooleate (GMO), (c) oleylamine (OA), (d)*
13 *dimethylhexadecylamine (DM16), (e) dioctylamine (DA), (f) trihexylamine (TA).*

14 A 1 mM single-component solutions was prepared by adding the additive to hexadecane, which
15 underwent magnetic stirring for 3 hours at 60 °C. A two-component solution was prepared by mixing
16 equal volumes of two 1 mM single-component solutions at 60 °C for 1 hour. Hence the concentration
17 of individual components in a two-component solution was 0.5 mM. The test solution have similar
18 viscosities to that of hexadecane (1.72 mPa·s at 50 °C).

19 Oleic acid and GMO are both commonly tested OFM additives. A primary (oleylamine, OA), a
20 secondary (dioctylamine, DA) and two tertiary (trihexylamine, TA and dimthethylhexadecylamine,
21 DM16) amines were tested to examine how the structure of the amine affects its effectiveness in
22 friction reduction. All chosen amines have similar molecular weights. OA has previously been
23 suggested to form an ionic liquid with oleic acid [28].

1 3 Methods

2 A ball-on-disc geometry, consisted of a stationary steel disc and a steel ball undergoing linear
3 reciprocating motion, was adopted for friction tests. Both the balls (diameter = 6 mm) and the disks
4 (diameter = 8 mm) were made of AISI52100 steel, with the latter hardened to 800 Hv. Their surface
5 roughness (R_a) are < 50 nm and < 10 nm respectively. Prior to test, they were immersed in toluene and
6 placed in an ultrasonic bath for 30 minutes. They were then rinsed with toluene, followed by cleaning
7 with oxygen plasma for 1 minute to remove any surface residue.[29]

8 Friction tests were carried out on a high frequency reciprocating rig (HFRR) from PCS instruments. The
9 contact was fully flooded with 2 ml of lubricant used within the holder. The tests were run with a
10 stroke distance of 1 mm, frequency of 50 Hz, at a temperature of 50 °C. An applied load of 500 g was
11 used. This gave a maximum Hertzian pressure of 1.16 GPa and a Hertzian contact diameter of 90 μm .
12 The maximum speed at mid-stroke was 0.157 m/s. The calculated minimum film thickness from the
13 Hamrock-Dowson formula [30] was about 1.7 nm, which was much smaller than the roughness of
14 rubbing surfaces. So tests were conducted in the boundary lubrication regime. Each test was run for
15 3 hours. The friction coefficients and electrical contact resistance (ECR) experienced by the contact
16 were recorded throughout the test. Note that ECR measures the electrical resistance between the ball
17 and disk, with increased contact between them resulting in a lower electrical resistance. Three tests
18 were conducted for each condition and the results were highly reproducible (see S11).

19 After each test, the ball and the disk were rinsed with hexane before the wear scars were examined
20 with a light microscope. Roughly circular wear scars were observed on the steel balls (see S1-3 for
21 images) and their diameters were obtained as the average of the width along the two axes parallel
22 and orthogonal to the rubbing direction. Ex-situ chemical analysis was performed on the wear scars
23 of the steel disks (see S4-6) using X-ray photoelectron spectroscopy (XPS). XPS is a surface sensitive
24 technique which bombards the surface with X-rays, causing core shell electrons to be removed from
25 the molecular orbitals of an atom. The energy of the released electrons from atoms on the top 5 nm
26 of the surface can be measured. This energy is related to the environment of the atom the electron
27 originated and is compared to known binding energies to identify what chemical species are on the
28 surface. A Thermo Fisher K-Alpha system with an X-ray beam energy of 1486 eV was used. The spot
29 size of the X-ray beam was 400 μm . An average over 20 scans and 40 scans were applied to the C_{1s}
30 spectra and the lower intensity N_{1s} spectra respectively.

31 Chemical analysis of the OFM solutions was carried out with transmission infrared spectroscopy using
32 a Perkin Elmer Frontier FTIR system. A liquid cell with KBr plates and a 1 mm PTFE spacer were used.
33 A spectrum of pure hexadecane was removed from spectra of OFM solutions to show the impact of

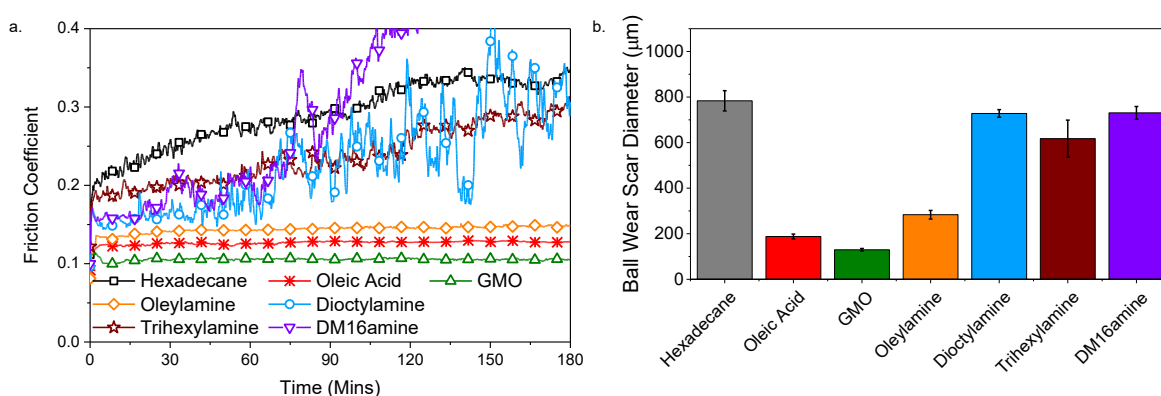
1 the OFM on the carboxyl peaks (1766 and 1713 cm^{-1}) and the primary amine peak (1620 cm^{-1}). Other
2 potentially relevant peaks were not measured due to the noise caused by the absorption of the
3 solvent.

4 4 Results

5 4.1 Tribological performance of OFMs

6 4.1.1 Single-component systems

7 The friction coefficients from single-component OFM solutions and the diameters of the resulting
8 wear scars are compared to those from pure hexadecane, as shown in Figure 2a and Figure 2b
9 respectively. For pure hexadecane (black squares), the friction coefficient increases slowly from ~ 0.2
10 to ~ 0.33 . The behaviour of the OFM solutions can be divided into two groups. 1 mM GMO (green
11 triangles), oleic acid (red asterisks) and OA (orange diamonds) have stable low friction coefficients.
12 Among the three, GMO has the lowest friction coefficient of 0.11. This is followed by oleic acid and
13 OA, which both have an oleyl tail group. The second group consists of secondary and tertiary amine,
14 whose friction coefficients are initially stable, then increase gradually. DA (blue circles), a secondary
15 amine, shows relatively low initial friction (~ 0.15) for the first 30 mins of the test. Its friction
16 coefficient then fluctuates substantially and its average increases with time. TA (brown stars), a
17 tertiary amine, shows an initially stable friction coefficient of about 0.19 for 40 mins before rising to
18 ~ 0.3 . Interestingly, while the coefficient of friction (~ 0.15) of the less sterically hindered tertiary
19 amine, DM16 (purple inverted triangles), is lower than TA initially, it increases rapidly after $t = 60$ mins
20 and has the highest friction of all single-component OFM solutions after 90 mins of rubbing.



21
22 *Figure 2. For single-component OFM solutions: (a) the averaged friction traces; and (b) the diameter of the wear scar on the*
23 *ball after friction tests.*

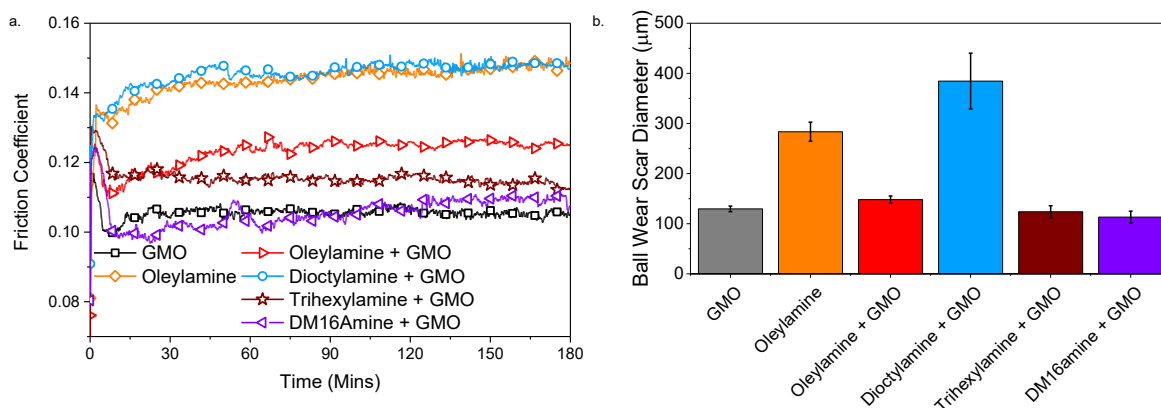
24 Single-component OFM solutions that give low stable friction also have smaller wear scars on steel
25 balls (Figure 2b). GMO gives the smallest wear scar, followed by those from oleic acid and OA. DA and

1 DM16 produce larger wear scars than TA. This is also reflected by the friction test results, with DA
2 having large friction fluctuations while DM16 sees its friction increases rapidly.

3 4.1.2 Two-component systems: effect of mixing two OFMs

4 The effect of mixing GMO with amines on friction is shown in Figure 3. Results from 1 mM single-
5 component solutions of GMO (black squares, ~ 0.105) and OA (orange diamonds, ~ 0.145) are also
6 included for comparison. Note 0.5 mM and 1 mM GMO solutions have similar friction coefficients (see
7 S7). None of the 4 amines tested enhance the friction reduction performance of GMO. Mixing GMO
8 with a primary amine (GMO-OA, red inverted triangles) gives a friction coefficient in between those
9 of single-component GMO and OA solutions. This suggests that both additives contribute to friction
10 reduction and they do not interact. A similar effect is seen when GMO is mixed with DA (GMO-DA,
11 blue circles), with the friction coefficient being between those of the two individual additives, See S8.
12 The GMO-TA solution (brown stars) shows a slightly higher friction coefficient than that of the GMO
13 solution, while the GMO-DM16 solution follows a similar friction trace to that of the GMO solution.
14 These results suggest that the addition of tertiary amines have little effect, i.e. GMO dominates the
15 performance of these two-component solutions.

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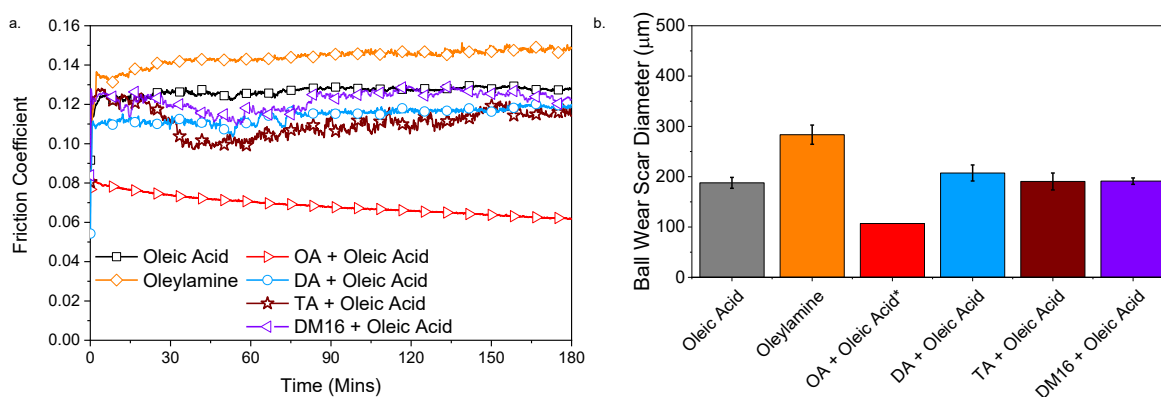
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18 *Figure 3. The effect of mixing GMO with amines: (a) the averaged friction traces; and (b) the diameter of the wear scar on*
19 *the ball after friction tests.*

20 When two-component GMO-amine solutions were used, GMO controls the size of the wear scar in
21 most cases (Figure 3b). The GMO-DA solution is the exception. The diameter of its wear scar is in
22 between those of single component GMO and DA solutions and is roughly half of that from the DA
23 solution.

24 The effect on mixing oleic acid with amines on friction is shown in Figure 4a. Results from 1 mM single
25 component solutions of oleic acid (black squares ~ 0.12) and OA (orange diamonds, ~ 0.145) are also
26 included for comparison. All oleic acid-amine solutions show similar (as in the case of oleic acid-DM16

1 solution, purple triangles) or improved performance in friction and wear reducing capabilities
 2 compared to 1 mM oleic acid solution. Oleic acid-DA (blue circles) and oleic acid-TA (brown stars)
 3 solutions show a $\sim 10\%$ drop in friction coefficients compared to 1 mM oleic acid solution. Note that
 4 oleic acid-OA solution (red inverted triangles) gives the greatest reduction in friction coefficient, from
 5 0.12 to 0.07. The low initial friction observed with the oleic acid-OA solution may suggest that this
 6 mixture has stronger surface adsorption than other mixtures used in this study at 50 °C [6].



7
 8 *Figure 4. The effect of mixing oleic acid with amines: (a) the averaged friction traces; and (b) the diameter of the wear scar*
 9 *on the ball after friction tests.*

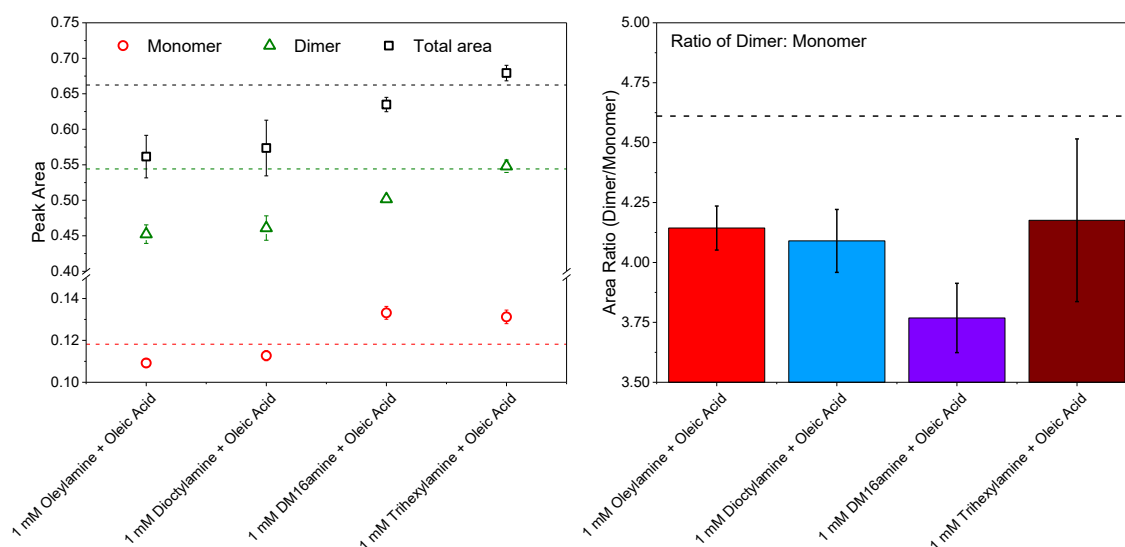
10 Since the friction coefficients of most of the oleic acid-amine solutions are similar or only slightly lower
 11 than to that of oleic acid solution, it is not surprising that they produce wear scars of similar size. The
 12 exception is oleic acid-OA solution which gives the lowest friction. It gives no visible wear scar on the
 13 disks and only small wear scars are seen on some of the balls.

14 4.2 Interactions between oleic acid and amines in hexadecane

15 The origin of the synergy between oleic acid and amines requires further exploration. FTIR spectra of
 16 0.5 mM oleic acid solution and 1 mM oleic acid-amine solutions were obtained (see S9). Note that all
 17 2-component solutions contain 0.5 mM oleic acid. Carboxylic acids are known to form dimers through
 18 hydrogen bonding in solution [7]. The “free” carboxylic acid molecule (monomer) has a C=O stretch at
 19 1766 cm^{-1} and the dimer has a C=O stretch of 1713 cm^{-1} . The change in intensity of these peaks with
 20 concentration is non-linear and is determined by the equilibrium constant of the carboxylic acid [31].

21 The concentrations of oleic acid monomers and dimers in the solution are correlated to their peak
 22 intensities, which can be quantified by estimating the area of each peak. The results are shown in
 23 Figure 5a. The intensity of the dimer peak is clearly affected by the type of amine used in the oleic
 24 acid-amine solutions (triangles) which in an ascending order: oleic acid-OA < oleic acid-DA < oleic acid-
 25 DM16 < oleic acid-TA \approx oleic acid. For the intensity of the monomer peak (circles, Figure 5a), primary

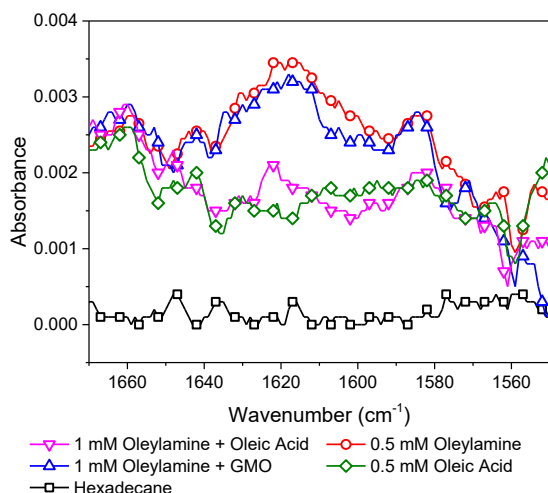
1 and secondary amine mixtures have lower, while tertiary amine mixtures having greater peak intensity
2 than that of 0.5 mM oleic acid solutions.



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4 *Figure 5. The average values measured by FTIR of a) dimer peak intensity, monomer peak intensity, combined monomer and*
5 *dimer peak intensity; and b) ratio of dimer: monomer peak areas. The dash lines are values for 0.5 mM oleic acid solution.*

6 The combined area of the monomer and dimer peaks of the FTIR spectra (squares, Figure 5a) follows
7 a similar trend to that of the dimer peak. This suggests that there is less unreacted acid when oleic
8 acid is mixed with OA, DA and DM16, than oleic acid-TA and single-component oleic acid solutions.

9 The ratio of the area of the dimer to monomer peaks for oleic acid-amine solutions are shown in Figure
10 5b. The addition of amine reduces the ratio compared to that of 0.5 mM oleic acid (dashed line). For
11 oleic acid-OA and oleic acid-DA solutions, this may be partly due to a reduction in carboxylic acid (see
12 squares, Figure 5a) which shifts the equilibrium in favour to the formation of monomers in solution
13 (see S10d). For the oleic acid-tertiary amine solutions, the tertiary amine may promote the formation
14 of monomer in solution (see also circles in Figure 5a). This is in agreement with previous work which
15 showed that a tertiary amine would destabilise a carboxylic acid dimer through the interaction with
16 the lone pair [32]. Hence oleic acid-DM16 solution has the lowest ratio because of its reduced
17 concentration of unreacted oleic acid and the promotion of monomer formation by DM16.



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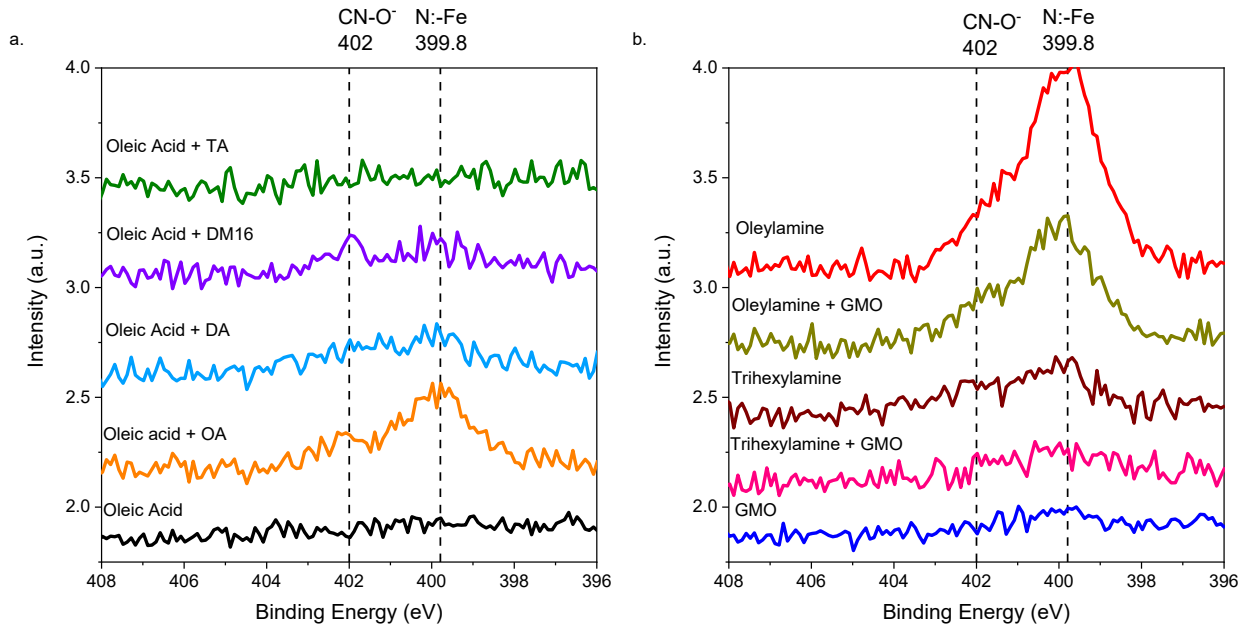
2 *Figure 6 IR absorbance of the primary amine peak of 0.5 mM oleic acid, 0.5 mM oleylamine, 1 mM GMO-oleylamine and 1*
 3 *mM oleic acid-oleylamine solutions.*

4 The primary amine peak (1620 cm^{-1}) was compared among different oleylamine solutions, Figure 6.
 5 Compared to 0.5 mM oleylamine (red circles), there is a suppression of this peak when oleylamine is
 6 mixed with oleic acid (pink inverted triangles), whereas it is unchanged when mixed with GMO (blue
 7 triangles). This suggests that in oleic acid-oleylamine solution, the amine molecule is no longer a
 8 primary amine but potentially an ammonium salt. No change in the chemical structure of amine
 9 molecule is suggested in GMO-oleylamine solution.

10 4.3 Boundary films formed in oleic acid-amine solutions

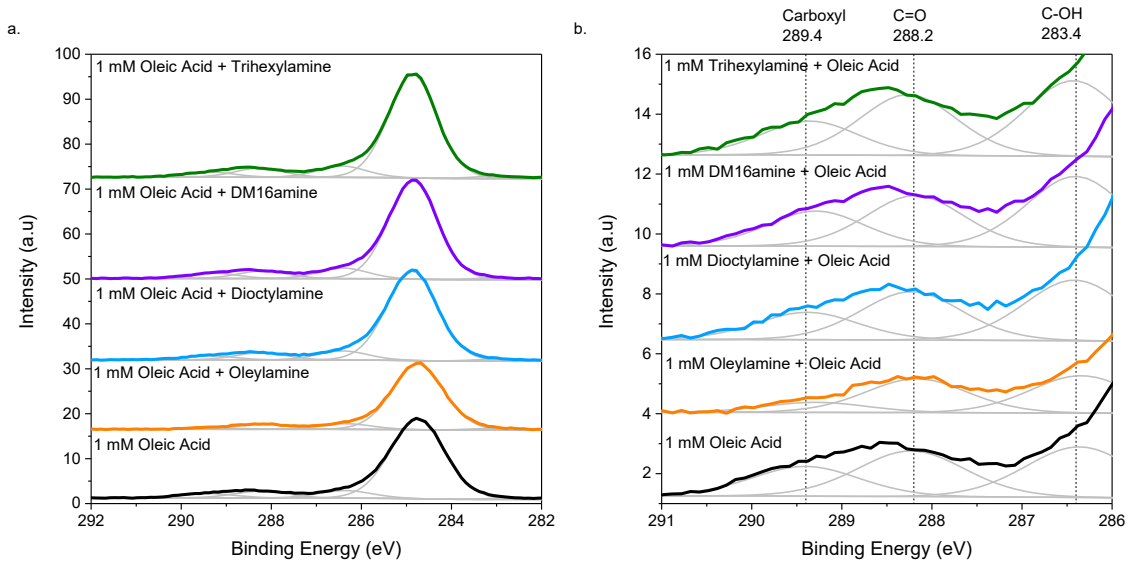
11 Wear tracks on steel disks were analysed using XPS, as shown in Figure 7 and Figure 8. The wear tracks
 12 formed in all oleic acid-amine solutions have lower nitrogen peak signals than those from their
 13 respective single-component amine solutions. This is partly due to the lower concentration of amine
 14 in the mixtures. The nitrogen peaks, as shown in Figure 7a, show that there is a higher nitrogen
 15 concentration within the wear scar formed in oleic acid-OA solution (orange) than those in other oleic
 16 acid-amine solutions. Some signals from nitrogen peaks can also be observed with oleic acid-DA
 17 solution (cyan). Very low signals are measured on wear tracks formed in the two oleic acid-tertiary
 18 amine solutions, suggesting these tracks have very small amount of, if any, amine.

19 Note that the amount of nitrogen in the wear track formed in oleic acid-OA (orange, Figure 7a) is less
 20 than that formed in GMO-OA (dark yellow, Figure 7b). This is also the case with the TA mixtures but
 21 the peaks are much smaller. The strong interaction between oleic acid and oleylamine in hexadecane
 22 is reflected in the nature of the boundary film formed by oleic acid-OA solution.



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Figure 7. The N1s XPS spectra from within wear tracks on steel discs after HFRR tests in (a) oleic acid-amine solutions, and (b) GMO-amine solutions. Curves are offset for clarity.



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Figure 8. The C1s XPS spectra from within wear tracks on steel discs after HFRR tests for oleic acid and oleic acid-amine solutions: (a) spectra for Binding energy 292 -282 eV; (b) an expansion of (a) focusing on binding energy from 291 to 286 eV. Curves are offset for clarity.

9 Figure 8 shows the C1s spectra of wear tracks of oleic acid-amine mixtures. The carboxyl peak (at 289.4
10 eV) on the wear tracks formed in oleic acid solution (black) and oleic acid-tertiary amine solution
11 (purple and green) have similar intensity, indicating they have similar surface carboxyl concentration

1 despite that only 0.5 mM acid is in oleic acid-amine solutions. The oleic acid-DA mixture (cyan) has a
2 smaller carboxyl peak, and the oleic acid-OA mixture (orange) having the smallest peak.

3 5 Discussion

4 5.1 Oleic Acid mixtures with Amines

5 In hexadecane, oleic acid interacts with amine, as shown by FTIR analysis in Figure 5. The addition of
6 amine reduces the intensities of the carboxyl peaks within the solution. This effect is especially visible
7 with oleylamine, a primary amine. The effect is less significant with dioctylamine, a secondary amine
8 and diminishes further with tertiary amines.

9 The reduction of the carboxyl peaks shows a reduction in the amount of free acid in the solution which
10 can be attributed to the formation of a protic ionic liquid, as suggested in [28]. The carboxyl group
11 reacts to form a carboxylate should show a FTIR peak shift from 1766 cm^{-1} to 1550 cm^{-1} for the
12 asymmetric COO^- stretch [33], although this peak is not visible due to the hexadecane peaks. Note
13 that results in Figure 6 indicate that there is a depletion of the primary N-H stretch in the oleylamine-
14 oleic acid solution. Taken together, our results support that oleylamine and oleic acid react to form a
15 partial ionic liquid additive in hexadecane, which lessens with the saturation of the amine. This agrees
16 with previous work which shows that primary amines form a higher degree of proton transfer than
17 tertiary amines [25].

18 The nature of the surface layers formed by oleic acid-amine solutions impact the friction and wear
19 results. For oleic acid-amine solutions that contain secondary or tertiary amines which only interact
20 weakly with oleic acid, oleic acid preferentially adsorbs. This is supported by the XPS spectra taken in
21 wear tracks formed in these solutions having similar peak intensity from the carboxyl groups (Figure
22 8) to that formed in 1 mM oleic acid solution. This explains why these solutions give rise to comparable
23 friction and wear to that of 1 mM oleic acid solution. Note that friction coefficient fluctuates more
24 with 0.5 mM oleic acid solution than with 1mM oleic acid solution and oleic acid-tertiary amine
25 solutions. Since our results suggest minimal amine on the rubbed surface (see Figure 7), the beneficial
26 effect of the addition of tertiary amine in this case may be caused by the tertiary amines destabilising
27 the oleic acid dimer, as shown in Figure 5. This could have an impact on the adsorption of the acid to
28 the surface, with the heat of adsorption being greater for the un-hydrogen bonded monomer than
29 the dimer [34]. This could then have an impact on the friction coefficient as the kinetics of surface
30 adsorption has been linked to the friction reduction for OFM solutions [35]. This effect could help in
31 the stabilisation of the friction coefficient.

1 For oleic acid-OA solutions, whose components form an ionic liquid additive, both components of the
2 additive are evident on the wear track. They form a boundary layer which has the lowest friction and
3 minimal wear compared to one component 1 mM oleic acid and 1 mM oleylamine solution. This is
4 followed by oleic acid-dioctylamine solution, whose friction coefficient is consistently lower than that
5 of oleic acid by 0.01. Note that XPS results of the wear track formed in oleic acid-DA solution also
6 shows evidence of the existence of amine. This suggest that the more ionic bonded oleic acid-amine
7 solution provides the lowest friction and minimal wear.

8 Overall, the addition of amines to an oleic acid solution shows benefits to the friction and wear
9 reducing properties with a primary amine showing the greatest benefit. Note that the synergetic effect
10 is unlikely to be achieved if oleic acid and oleylamine barely co-adsorbed on the surface. Hence our
11 result offer strong supports that strong specific interaction occurs between oleic acid and oleylamine,
12 as in this case by the formation of an ionic liquid additive.

13 5.2 GMO mixtures with Amines

14 When GMO is mixed with a primary or a secondary amine, friction coefficients of these mixtures are
15 between those of the two individual solutions, implying that the amine and GMO are both on the
16 surface. For GMO-tertiary amine mixtures however, their friction and wear performance was similar
17 to those of GMO solution, suggesting that in this case, the surfaces are mainly occupied by GMO. This
18 is supported by XPS results (Figure 8b) which show that there is much less amine within the wear track
19 formed in GMO-trihexylamine solution than in GMO-oleylamine solution.

20 It is likely that the amine additives and GMO are all acting independently. Compositions of surface
21 layers are thus a mere result of competitive surface adsorption, with the propensity to adsorb on steel
22 surfaces decreases with the degree of saturation of amine. Note that hydrogen bonding may occur
23 between GMO and amines in the hexadecane solution. The presence of an N-H in primary and
24 secondary amines, which can be a hydrogen bond donor, is not available to a tertiary amine. Possible
25 strong hydrogen bonding between GMO and primary and secondary amine, may promote co-
26 adsorption of GMO and these two amine additives. The weak interaction between tertiary amine and
27 GMO allows the more polar GMO molecule to preferentially adsorb on surfaces, dominating the
28 friction reduction.

29 It has long been hypothesized that GMO goes through hydrolysis and forms a carboxylic acid and
30 glycerol in the contact [8]. The results that GMO and amine do not show that same synergy observed
31 between oleic acid and amine in terms of friction reduction is thus perhaps surprising. This may
32 suggest that the hydrolysis process of GMO, if exists, may be altered by the addition of amine, or that
33 GMO does not form a carboxylic acid molecule at all.

1 6 Conclusion

2 This research shows how interactions among OFM additives can be explored to achieve improved
3 friction and wear properties. Mixing oleic acid and oleylamine in hexadecane has a synergistic effect
4 resulting in a large reduction in friction and wear. This is because the two additives form a partial ionic
5 liquid in the solution. As the saturation of the amine increases, this effect decreases, with tertiary
6 amines having minimal interactions with the oleic acid in hexadecane and as a result no improved
7 friction reduction. For the primary amine, both the acid and amine were observed in the wear track
8 whereas for the tertiary amine, no amine was observed as oleic acid was preferentially adsorbed.

9 Since it is suggested that GMO may hydrolyse to form oleic acid, the effect of mixing GMO and amine
10 was also investigated. Unlike what is observed with oleic acid-amine mixtures, no synergetic effect in
11 friction is observed when mixing amines with GMO in hexadecane. This means that it is unlikely that
12 GMO has hydrolysed to a carboxylic acid when mixed with amine in hexadecane. The composition of
13 the boundary layer in a GMO-amine mixture is likely governed by competitive adsorption between
14 additives. When mixing GMO with primary or secondary amines, both GMO and amine molecules are
15 evident on the wear track, leading to a friction coefficient between that of the individual additives.
16 GMO-tertiary amine mixtures provide friction reduction equivalent to an individual GMO solution,
17 with minimal nitrogen observed in wear track, hence GMO preferentially adsorbs in these mixtures.

18 The existence of N-H bonds is the likely cause of the interaction between amines and other OFM
19 additives in hexadecane. In this particular study, we show that the greater the amount of hydrogen
20 bond donors on the amine, the greater the interaction with oleic acid. Such interaction between amine
21 and oleic acid gives rise to a synergetic effect potentially through the formation of an ionic liquid
22 additive in hexadecane.

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