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**Article:**

Onumata, Y, Zhao, H, Wang, C et al. (2 more authors) (2018) Interactive Effect between Organic Friction Modifiers and Additives on Friction at Metal Pushing V-Belt CVT Components. *Tribology Transactions*, 61 (3). pp. 474-481. ISSN 1040-2004

<https://doi.org/10.1080/10402004.2017.1355502>

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## **TITLE**

Interactive Effect between Organic Friction Modifiers and Additives on Friction at Metal Pushing V-belt CVT Components

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## **ABSTRACT**

The interactions between organic Friction Modifiers (FMs) and other additives in a CVT fluid (CVTF) are investigated aimed at optimizing friction management of metal pushing V-belt CVTs. Three types of FMs (oleic acid, oleyl alcohol and glycerol mono-oleate (GMO)) were formulated in Poly- $\alpha$ -olefin (PAO) and a fully-formulated CVTF, and the friction performance was evaluated in a reciprocating test apparatus (TE77). For estimating their effect at the major frictional components in the CVTs, a steel belt-pulley and a torque converter clutch, the tribotests were carried out with both steel/steel and paper/steel sliding configurations. Then, the post-test materials were assessed by surface analysis techniques to observe the chemical nature of any reacted layers at the surface.

The results indicate that the friction on the steel surface was significantly influenced by a combination of the FMs and the CVTF additives as well as the functional group of the FMs. Although oleic acid and GMO typically present more friction reduction than oleyl alcohol in most of the conditions, oleic acid did not decrease friction at the steel/steel contact with the presence of the other additives in the CVTF formulation; the friction reduction effect was poisoned by the presence of other additives. Surface analysis of the post-test specimens implied that it was interactions with the calcium detergent that inactivated the FM effect of oleic acid.

## **KEY WORDS**

Friction Modifiers, Continuously Variable Transmissions (CVT), Automatic Transmission Fluids

## **INTRODUCTION**

The emission of CO<sub>2</sub> from automobiles is a global concern; the legislative pressures and environmental demands are annually being increased. In order to comply with the legislation, car manufacturers put their priority on improving fuel-efficiency, and some advanced transmission systems, such as metal pushing V-belt continuously variable transmission (CVT) or dual clutch transmission (DCT) have been developed to increase their market share (1-3). The CVT is capable of improving the fuel efficiency by continuously changing the gear ratio, which makes it possible to operate the engine under more efficient conditions. This continuous gear shift is achieved by a steel belt-pulley mechanism (4), where a torque input from the engine is transferred through steel/steel contact between the belt and the pulley as shown in Fig. 1. Minor slip generally occurs at the belt-pulley contact as a result of the

mechanical configuration (5, 6), therefore, the steel/steel contact friction at low sliding speeds should be kept at a sufficient level to reduce the risk of macroscopic slip, leading to damage in the transmission. On the other hand, a paper clutch system is also installed at a torque converter of the CVT. It consists of a paper clutch plate and a counter steel plate, and the clutch engagement should be controlled appropriately to prevent vibration, often referred to as shudder (7). It is generally considered that a relationship between the friction coefficient ( $\mu$ ) and the sliding speed ( $V$ ) of the clutch paper material ( $\mu$ - $V$  characteristics) is an essential factor as the theoretical analysis reported by Kugimiya (8) indicated that a positive  $\mu$ - $V$  slope is capable of preventing a self-induced vibration. Therefore, it is preferable to manage the friction lower at a low sliding speed region (9).

In summary, the tribological demands for the CVT system are complex; the friction at low speed should be modified to be higher at the steel belt pulley, while lower at the paper clutch. An issue is that both of these requirements need to be satisfied with the use of one lubricant. In terms of the friction control at transmission components, organic Friction Modifiers (FMs) are key additives. They generally consist of a polar group and a hydrocarbon chain, and the polar group is capable of adsorbing onto a substrate surface forming an adsorption film, which tends to reduce friction at low sliding speed (10-12). For application to CVTFs, the effect of the FMs needs to be controlled appropriately to satisfy the frictional requirements (13).

The working mechanism of the FMs has been of interest to researchers and discussed in a large number of papers. Ratoi (14) investigated adsorption of carboxylic acids onto metal substrates by measuring the oil film thickness utilizing ultrathin film interferometry, concluding that the adsorption was influenced by moisture in the test environment as well as the substrate material and the chemical structure of the acids. The adsorption mechanism of carboxylic acids was also reported by Li (15). Behavior of acetic acid adsorbed on Au/Pd

alloy surfaces was assessed using RAIRS (reflection-adsorption infrared spectroscopy) under elevated temperature conditions, and the molecule desorption as a function of the temperature was discussed. Furthermore, in-situ AFM measurement was carried out by Kalin (16) in order to observe the adsorption film on steel and DLC surfaces. The island structures formed by chemical adsorption of alcohol FMs were detected on the substrates after tribotest.

In addition, interactions between FMs and other additives in automotive lubricants has been recognized to be an important factor for friction modification. Miklozic (17) investigated the influence of ZDDP tribofilm on the friction reduction performance of FMs. Interestingly, some FMs (amine or amide) showed a synergetic effect with the ZDDP film, while other FMs (poly-condensed fatty acid/ester) were affected in an antagonistic manner. A similar relationship was also reported by Ratoi (18); their paper assessed an interaction between FMs and ZDDP in a fully-formulated engine oil. It revealed that the FMs inhibited the formation of ZDDP tribofilm, and the friction reduction of the FMs was dependent on the chemical structure.

The behavior of the FMs on paper clutch material has also been studied extensively. However, the number of the reports is less than for steel. Derevjanik (19) focused on an interaction between FMs and calcium detergents on metal and paper clutch materials, and concluded that some combinations of the additives presented a synergetic effect on friction modification on metal and paper clutch substrates. A series of research papers by Zhao (20, 21) investigated behavior of amine FMs on paper clutch material by surface analysis of the post-test specimens to support the observations of friction tests. They indicated that ZDDP and calcium detergent showed a negative influence on the friction modification by the FMs.

Looking at previous research, it seems that interactions between the FMs and the other additives will be a key factor to satisfy the competing frictional requirements for the CVTFs.

An ideal scenario would be that the effect of the FMs could be inhibited by the other additives on the steel surface, while they could keep working on the paper clutch material.

This study aims to elucidate an effective chemical structure of the FMs appropriate for the CVTFs and reveal the working mechanism. The friction coefficient was measured using a reciprocating tribometer (TE77), then the chemical nature on the post-test substrate was analyzed using XPS, SEM/EDX and ATR-FTIR. For the purpose of investigating the interactive effect with the CVTF additives, the FMs were assessed in both synthetic base oil and a fully-formulated CVTF.

## **EXPERIMENTAL METHODS**

### **Test Oil Formulations**

Three organic friction modifiers were investigated for this study; oleic acid, oleyl alcohol and glycerol mono-oleate (GMO). The chemical structures are shown in Fig. 2. Each of the FMs has an oleic hydrocarbon chain in common, while the polar group was different; a carboxylic acid in oleyl acid, a hydroxyl group in oleyl alcohol and an ester and two hydroxyl groups in GMO. Technical grade reagents were used as the FMs in this study. Although they have minor amount of hydrocarbon structures different from oleic group as impurity, the composition was similar among the three FMs. It is therefore considered that the primary factor which controlled the effect of the FMs was their polar group structures.

The FMs used in this study are widely applied to commercial transmission fluids, and there have been a large number of reports regarding their effect on steel and paper clutch surfaces (22-24). However, the working mechanism in CVTFs has not been discussed in detail based on the analytical observations from the surface chemistry. In addition, the effect of the FMs should be evaluated on both steel and paper surfaces using the same oils in order to realize

the specific effect depending on the substrates. The knowledge gained from this analysis will be useful for designing CVTFs.

The FMs were formulated in two base fluids, poly- $\alpha$ -olefin (PAO) and a fully-formulated CVTF, respectively. PAO is a standard synthetic base fluid, which was chosen for the purpose of investigating the pure effect of the FMs without influence from the other additives. On the other hand, the CVTF base fluid consisted of PAO as base oil and following typical CVTF additives (25) except for the FMs; a phosphorous anti-wear agent (P; 300 ppm), an overbased calcium sulfonate detergent (Ca; 300 ppm), a poly-isobutenyl succinic imide dispersant (3 wt%), a poly-methacrylate viscosity modifier (8.5 wt%) and anti-oxidants (alkyl diphenylamine and hindered phenol types; 1.0 wt% in total). The combination effect of the FMs and the additives on the frictional properties was investigated with the use of the CVTF base fluid. The detailed test oil formulations are shown in Table 1. The concentration of the FMs was determined at 0.03 mol/kg considering the practical dosage in commercial fluids and the solubility.

### **Friction Test**

The friction coefficient was measured by TE77 pin-on-plate reciprocating tester (Cameron-Plint) using both steel/steel and paper/steel contacts as shown in Fig. 3. The reciprocating sliding configuration was adopted by Narita (26) for simulating the actual belt-pulley contact at the CVT showing a good agreement with an actual torque capacity. Although less reports have been published regarding the reciprocating tests with the paper clutch (27), it is possible to evaluate friction reduction effect of the FMs on the paper at low speed conditions, which is required for the smooth clutch control without vibration.

The detailed tribotest conditions are summarized in Table 2. A combination of a steel pin (AISI 52100) and a steel plate (AISI 4140, 42CrMo4) was used for simulating the steel belt-pulley, while a steel pin (AISI 52100) and a steel plate coated with JASO M 349 paper clutch material (28) was used for assessing the effect of the FMs on the paper clutch system. The contact pressure was controlled at 1.0 GPa for steel/steel contact and at 6.0 MPa for paper/steel contact, respectively. The test temperature was 100°C, and the sliding speed was 0.20 m/s (frequency; 20 Hz, sliding width; 5.0 mm) for both conditions. The sliding speed at 0.20 m/s is considered to be appropriate to simulate the friction at the belt-pulley system (26) as well as to estimate the  $\mu$ -V characteristics at the torque converter clutch (11). Each of the friction tests was performed for 60 minutes, and the friction coefficient at the end of the test was reported in the results.

### **Surface Analysis Techniques**

The post-test specimens after the TE77 sliding test under the steel/steel contact were assessed in order to analyze chemical nature as well as the wear on the steel surface.

The wear scar on the post-test steel pins was measured by a non-contact optical interferometer, NPFLEX (Bruker Corporation), and the wear depth was compared. X-ray Photoelectron Spectroscopy (XPS) analysis was performed with Thermo Scientific Theta Probe (Thermo Fisher Scientific, Inc.) to estimate the chemical nature of the FMs on the steel plate. A sampling depth of the XPS is generally a few nm (29), therefore, the results reflect information on the uppermost steel surface, which should include the adsorption film formed by the FMs. The XPS spectra were acquired using a monochromatic Al K $\alpha$  source with a spot size of 150  $\mu$ m. Both the survey and the C 1s spectra were collected, and the acquired data were analyzed by using CasaXPS software. The charge was corrected by fitting a C 1s peak

of saturated hydrocarbon at 285.0 eV (30). Energy Dispersive X-ray spectroscopy (EDX) analysis was applied using Carl Zeiss EVO MA 15 (Carl Zeiss AG). The measurement depth of the EDX on metal is around 1  $\mu\text{m}$ , so that the EDX results should present chemical compositions formed by the CVTF additives on the steel surface. Additionally, Attenuated Total Reflectance-Fourier Transformed InfraRed spectroscopy (ATR-FTIR) was also utilized with Perkin-Elmer Spectrum 100 FT-IR Spectrometer with a UATR accessory (Perkin-Elmer, Inc.). The ATR crystal material was germanium with a 100  $\mu\text{m}$  diameter contact area and one-time reflection in the optical pass. Because of the passing depth of the IR beam into the steel at around 1  $\mu\text{m}$ , it is considered that the obtained spectra mainly reflect the chemical structure of the reaction film. The penetration depth of the apparatuses are summarized in Fig. 4.

## **RESULTS AND DISCUSSION**

### **TE77 Friction Measurement**

The friction coefficient measured by TE77 is shown in Fig. 5. The values shown in the graph are the friction at the end of the 60 minutes of the sliding test when they reached steady state. In the steel/steel contact, oleic acid and GMO presented a FM effect in PAO, reducing friction coefficient at approximately 0.025, while no reduction was observed with oleyl alcohol. When formulated with the CVTF additives, the friction reduction effects by oleic acid and GMO were obviously decreased, particularly oleic acid did not present any effect on the friction coefficient. In the paper/steel contact, each of the FM was able to reduce friction according to the following order; oleyl alcohol < GMO  $\leq$  oleic acid. Oleyl alcohol showed a slight friction decrease in the paper system. In addition, on the contrary to the steel/steel contact, the effect of the FMs was not affected by the CVTF additives, showing the consistent

friction reduction either in PAO or the CVTF base fluid. For the purpose of elucidating the reason of the specific trends observed at the steel/steel contact, the post-test steel specimens were assessed.

## **Surface Analysis**

### **NPFLEX Results**

Wear depth on the post-test TE77 steel pins after the steel/steel sliding test was measured by NPFLEX as shown in Fig. 6. The wear volume of the PAO without the FM was significantly larger than the others as expected, then followed by oleyl alcohol and GMO with PAO. The contact pressure at 1.0 GPa was determined to simulate the belt-pulley, and as such it was possibly too severe for the PAO formulations without the other additives. Interestingly, oleic acid presented an excellent anti-wear performance even in PAO showing the wear depth at around 0.25  $\mu\text{m}$  which was the same level as the CVTF formulations. Therefore, it is considered that oleic acid was capable of building a strong film on the steel surface, and some reaction with steel surface probably helped this film formation. All the CVTF formulations had wear depth less than 0.5  $\mu\text{m}$ , which should be due to the reaction film formed by the additives.

### **XPS Results**

The wear track on the TE77 steel plates was analyzed by XPS to characterize the chemical nature of the tribofilm on the outermost surface to approximately 5 nm depth. The C 1s spectra of the PAO and the CVTF formulations are shown in Fig. 7 and Fig. 8, respectively.

In terms of the PAO formulations, the spectra appeared to be similar showing the following peaks; 288.7–289.0 eV attributed to O=C-O and 286.5-286.6 eV to C-O, in addition to a peak

from saturated hydrocarbon (SHC) at 285.0 eV. Those peaks are commonly observed in C 1s spectra due to adventitious carbon contamination, therefore, it should be reasonable to consider that the peaks observed in PAO (Fig. 7(a)) and PAO+alcohol (Fig. 7(c)) were derived from the contamination not from the adsorption film considering their deep wear depth and high friction coefficient. On the other hand, PAO+acid (Fig. 7(b)) and PAO+GMO (Fig. 7(d)), which presented lower friction, had an additional peak at 288.1 eV attributed to O-C-O bond. It could imply a presence of a consistent adsorption film formed by the FMs (21).

The spectra of the CVTF formulations, except for CVTF+GMO, showed a very similar trend with the following three peaks; 288.2-288.4 eV attributed to N-C=O, 286.4-286.7 eV to C-O / C-N and 285.0 eV to SHC. The peaks related to nitrogen bonds were potentially derived from the dispersant or the amine antioxidant. Furthermore, the imide group in the dispersant was detected as the N-C=O peak indicating the dispersant adsorption on the steel surface. CVTF+GMO (Fig. 8(d)) had an additional peak at 289.1 eV suggesting a presence of O=C-O bond estimated to be derived from GMO, while CVTF+acid (Fig. 8(b)) did not show the peaks neither at 288.1 eV from O-C-O nor 289.0 eV from O=C-O, which were detected in the spectrum of PAO+acid. These results show good agreement with the TE77 results; only GMO presented a friction reduction effect in the CVTF formulation.

The element quantification obtained from the XPS survey spectra is summarized in Table 3. The PAO without the FM had a higher concentrations of oxygen and iron than the other PAO formulations with the FM. It suggests generation of iron oxide wear particles due to the severe sliding conditions. Among the CVTF formulations, CVTF+acid spectrum indicated an interesting trend regarding the elements contained in the CVTF additives. The concentration of calcium at 3.0 mass% was significantly lower than the other CVTF formulations, while the phosphorus at 10.8 mass% was obviously higher instead.

In summary, the adsorption of oleic acid on the steel surface was not observed in the presence of the CVTF additives, and the chemical composition of the reaction film showed difference in calcium and phosphorus concentrations. These results imply an interaction of oleic acid with the calcium detergent and the phosphorous anti-wear agent. Oleic acid probably reacted with the calcium on the steel surface, promoting the phosphorus adsorption due to less competition with the FM and the detergent.

### EDX Results

The chemical composition in the wear track of the post-test TE77 steel plates was assessed using EDX. The results are shown in Fig. 9. As an overall trend of the PAO formulations (Fig. 9(a)), the oxygen concentration was significantly higher than the fresh steel plate except for PAO+acid. It was due to iron oxide and oxidative degraded products produced by the severe sliding environment, while PAO+acid appeared to be able to protect the steel surface by film formation as estimated from the NPFLEX and the XPS result. Focusing on the CVTF formulations (Fig. 9(b)), the elements originated from the CVTF additives, phosphorus, sulfur and calcium, were detected on all the steel surface. These elements should be attributed to a reaction film considering the sampling depth of EDX at approximately 1  $\mu\text{m}$ .

Interestingly, the concentrations were different among the test oils. CVTF and CVTF+alcohol showed almost the same result, which implies that oleyl alcohol did not affect the steel surface chemical nature as expected from the TE77 friction result. On the other hand, oleic acid and GMO presented lower phosphorus and calcium concentrations, suggesting the competition between the FMs and the other additives. Furthermore, the calcium concentration of CVTF+acid was much lower than phosphorus, which shows a good correspondence with the XPS survey spectra results. It should be an evidence that oleic acid had a strong

interaction with the calcium detergent on the steel surface because of the highly reactive chemical structure.

#### ATR-FTIR Results

For the further estimation of the chemical structure of the reaction film ( $\sim 1 \mu\text{m}$ ), ATR-FTIR analysis was carried out for the post-test TE77 steel plates of the CVTF formulations. The spectra at the fingerprint region, between  $1,800$  and  $800 \text{ cm}^{-1}$ , are shown in Fig. 10. A peak at around  $1,150 \text{ cm}^{-1}$  was detected among all of the CVTF formulations. Considering the elements detected by EDX, it could be identified as pyrophosphate ( $\text{P}_2\text{O}_5$ ) produced from the phosphorous anti-wear agent (31). It is notable that only the peak of CVTF+acid appeared to be wider and shifted to smaller wavenumber, which might be attributed to phosphate ( $\text{PO}_4$ ). A previous work mentioned that an interaction between a phosphorous anti-wear agent and a calcium detergent lead to a formation of  $\text{P}_2\text{O}_5$  and  $\text{PO}_4$  (26), therefore, it is reasonable to consider that oleic acid changed the quantitative balance between calcium and phosphorus on the steel surface, resulting in a generation of the different phosphorus oxide structure. No peak was detected between  $1,750$ - $1,700 \text{ cm}^{-1}$ , attributed to carboxyl groups, in all the spectra, although CVTF+GMO showed a peak of  $\text{O}=\text{C}-\text{O}$  bond in the XPS C 1s spectrum. It was due to a penetration depth of the IR beam, which reflected much more information of the reaction film.

#### **Mechanistic Behavior of the FMs on the Steel Surface**

The purpose of investigating the FMs in PAO was to assess the pure effect of the FM without the influence from the other additives. The friction coefficient acquired by TE77 shows the significant friction reduction effect of oleic acid and GMO, while oleyl alcohol did not

present any effect. Considering the polar groups contained in the FMs, the carboxylic acid group in oleic acid and the ester group in GMO were capable of reducing the steel friction, however, the hydroxyl group in oleyl alcohol or GMO did not work effectively. The XPS C 1s analysis supports this assumption showing the peak attributed to O-C-O bond only in the spectra of PAO+acid and PAO+GMO.

On the other hand, the interaction between the FMs and the additives had a significant influence on the frictional properties among the CVTF formulations. The first factor should be the competitive adsorption against the other polar additives, such as the phosphorous anti-wear agent or the calcium detergent as detected in the XPS survey spectra. There has been a large number of reports regarding the competitive adsorption between the FMs and the other additives. For example, Murase (22) reported that adsorption of carboxylic acid was strongly inhibited in the presence of phosphite. It should be the reason of the weak friction modification effect of GMO when formulated with the CVTF additives.

However, it is not possible to explain the working mechanism of oleic acid only by the competitive adsorption because CVTF+acid did not show any effect at the steel/steel contact, and the XPS C 1s spectrum did not suggest the presence of oleic acid on the surface. Taking into the account that oleic acid was able to reduce the friction even with the CVTF additives at the paper/steel contact, the oleic acid appears to not be decomposed at the test temperature of 100°C. Therefore, there should be the other interaction with the additives. The XPS survey spectra and EDX results give a good suggestion on the mechanism. The calcium detergent and the phosphorous anti-wear agent generally have a synergetic effect forming a reaction film which consists of  $\text{CaCO}_3$ ,  $\text{CaHPO}_4$ ,  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Fe}_3(\text{PO}_4)_2$  (26). Considering that the XPS survey spectrum of CVTF+acid showed much lower calcium concentration on the uppermost steel surface compared with the other CVTF formulations, oleic acid probably reacted with  $\text{CaCO}_3$  on the steel surface as follows;



Oleic acid and the calcium detergent were consumed by the reaction, resulting in forming the reaction film with less Ca as observed by EDX. The competitive adsorption and the reaction with the other additives diminished the friction reduction effect of oleic acid as shown in Fig. 11.

Based on this study, oleic acid is considered to be appropriate for the CVTFs because it was able to achieve the high friction at the steel belt-pulley as well as the friction modification at the paper clutch system. It should be worth to discuss why oleic acid did not interact with the detergent at the paper/steel contact, resulting in friction reduction. The differences between the steel/steel and the paper/steel contact are the specimen material (steel or paper clutch) and the contact pressure (1.0 GPa or 6.0 MPa), and hence these factors are assumed to affect the behavior of oleic acid. Further study will be carried out to understand the working mechanism of the FMs on the clutch paper surface.

## CONCLUSIONS

The frictional properties of oleic acid, oleyl alcohol and GMO were investigated using TE77 for the purpose of elucidating the working mechanism of the friction modifiers. Oleic acid and GMO generally presented a superior friction reduction effect at both the steel/steel and the paper/steel contact, while oleyl alcohol showed a poor effect. Interestingly, the effect of oleic acid and GMO was reduced in the presence of the CVTF additives only at the steel/steel contact, especially oleic acid lost the effect completely. Because the XPS survey spectra on the post-test steel plates suggest the adsorption of the CVTF additives, such as phosphorous anti-wear agent and the calcium detergent, on the uppermost steel surface, the competitive adsorption between the FMs and the additives is considered to be one of the reason of less

friction reduction effect of CVTF+acid and CVTF+GMO. In addition, the XPS survey spectrum of CVTF+acid shows a lower calcium concentration on the steel surface, and the EDX and the ATR-FTIR result indicate that the reaction film composition was changed in the presence of oleic acid. These result suggests the reaction between oleic acid and the calcium detergent, which should be the other mechanism leading to losing the effect of oleic acid. As a result, oleic acid was not able to adsorb on the steel at all as the XPS C 1s spectrum confirms.

The results suggests that the reaction between the FMs and the other additives as well as the competitive adsorption is a key factor to control the frictional properties on the steel surface. An appropriate combination will be able to satisfy frictional requirements at the belt-pulley and the torque converter clutch simultaneously.

## **ACKNOWLEDGEMENTS**

The authors are grateful to JXTG Nippon Oil & Energy Corporation for financial support for this work. We acknowledge the National EPSRC XPS Users' Service (NEXUS) at Newcastle University for their help in XPS analysis.

## **REFERENCES**

- (1) Murakami, Y. (2005), "Half a century of automatic transmissions for vehicles - The tribology for friction materials and fluids," *Journal of Japanese Society of Tribologists* 50 (9), pp. 665-670.
- (2) Abo, K. and Kobayashi, M. (2000), "Development of a New Metal Belt CVT for High Torque Engines," *SAE Technical Paper Series* (2000-01-0829).
- (3) Matthes, B. (2005), "Dual Clutch Transmissions - Lessons Learned and Future Potential," *SAE Technical Paper Series* (2005-01-1021).
- (4) Okamura, M. (2000), "Trends of metal pushing belt type CVTs," *Journal of Japanese Society of Tribologists* 45 (6), pp. 423-428.

- (5) Oshidari, T. (2001), "Trends of development in CVTs and their tribology," *Journal of Japanese Society of Tribologists* 46 (3), pp. 201-208.
- (6) Ando, T., Yagasaki, T., Ichijo, S., Sakagami, K. and Sumida, S. (2015), "Improvement of Transmission Efficiency in CVT Shifting Mechanism Using Metal Pushing V-Belt," *SAE International Journal of Engines* 8 (3), pp. 1391-1397.
- (7) Yoshimura, N. (1996), "Automatic transmission," *Journal of Japanese Society of Tribologists* 41 (8), pp. 659-662.
- (8) Kugimiya, T., Yoshimura, N. and Mitsui, J. (1998), "Tribology of automatic transmission fluid," *Tribology Letters* 5 (1), pp. 49-56.
- (9) Zhao, H. Y., Morina, A., Neville, A., Durham, J. and Vickerman, R. (2011), "Understanding Friction Behavior in Automatic Transmission Fluid LVFA Test: A New Positive Curve Parameter to Friction Coefficient Ratio Index Evaluation," *Journal of Tribology-Transactions of the Asme* 133 (2), pp. 021802.
- (10) Tang, Z. L. and Li, S. H. (2014), "A review of recent developments of friction modifiers for liquid lubricants (2007-present)," *Current Opinion in Solid State & Materials Science* 18 (3), pp. 119-139.
- (11) Ingram, M., Noles, J., Watts, R., Harris, S. and Spikes, H. A. (2011), "Frictional Properties of Automatic Transmission Fluids: Part I-Measurement of Friction-Sliding Speed Behavior," *Tribology Transactions* 54 (1), pp. 145-153.
- (12) Spikes, H. (2015), "Friction Modifier Additives," *Tribology Letters* 60 (5).
- (13) Mitsui, H. (2000), "Trends and requirements of fluids for metal pushing belt type CVTs," *Journal of Japanese Society of Tribologists* 45 (6), pp. 435-440.
- (14) Ratoi, M., Anghel, V., Bovington, C. and Spikes, H. A. (2000), "Mechanisms of oiliness additives," *Tribology International* 33 (3-4), pp. 241-247.
- (15) Li, Z. J. and Tysoe, W. T. (2012), "The adsorption of acetic acid on clean and oxygen-covered Au/Pd(100) alloy surfaces," *Surface Science* 606 (23-24), pp. 1934-1941.
- (16) Kalin, M. and Simic, R. (2013), "Atomic force microscopy and tribology study of the adsorption of alcohols on diamond-like carbon coatings and steel," *Applied Surface Science* 271, pp. 317-328.
- (17) Miklozic, K. T., Forbus, T. R. and Spikes, H. A. (2007), "Performance of friction modifiers on ZDDP-Generated surfaces," *Tribology Transactions* 50 (3), pp. 328-335.
- (18) Ratoi, M., Niste, V. B., Alghawel, H., Suen, Y. F. and Nelson, K. (2014), "The impact of organic friction modifiers on engine oil tribofilms," *Rsc Advances* 4 (9), pp. 4278-4285.
- (19) Derevjani, T. S. (2001), "Detergent and Friction Modifier Effects on Metal/Metal and Clutch Material/Metal Frictional Performance," *SAE Technical Paper Series* (2001-01-1993).
- (20) Zhao, H. Y., Morina, A., Neville, A. and Vickerman, R. (2013), "Tribochemistry on Clutch Friction Material Lubricated by Automatic Transmission Fluids and the Link to Frictional Performance," *Journal of Tribology-Transactions of the Asme* 135 (4), pp. 041801.
- (21) Zhao, H. Y., Morina, A., Neville, A. and Vickerman, R. (2012), "Anti-Shudder Properties of ATFs-Investigation into Tribofilm Composition on Clutch Friction Material and Steel Surfaces and the Link to Frictional Performance," *Tribology Transactions* 55 (6), pp. 782-797.

- (22) Murase, A. and Ohmori, T. (2003), "TOF-SIMS study on the adsorption behavior of mixtures of a phosphite and a friction modifier onto ferrous material," *Applied Surface Science* 203, pp. 586-589.
- (23) Tasdemir, H. A., Wakayama, M., Tokoroyama, T., Kousaka, H., Umehara, N., Mabuchi, Y. and Higuchi, T. (2013), "Ultra-low friction of tetrahedral amorphous diamond-like carbon (ta-C DLC) under boundary lubrication in poly alpha-olefin (PAO) with additives," *Tribology International* 65, pp. 286-294.
- (24) Kugimiya, T. (2000), "Effects of additives of ATF and components of friction material for AT on mu-nu characteristics," *Journal of Japanese Society of Tribologists* 45 (5), pp. 387-395.
- (25) Sato, T. (2009), "Recent Trend of Metal Pushing Belt Type Continuously Variable Transmission Fluids," *Journal of Japanese Society of Tribologists* 54 (4), pp. 248-253.
- (26) Narita, K. and Priest, M. (2009), "Friction Characteristics and Topography of Tribofilms from Anti-Wear Additives Applied to Metal V-Belt Type CVT Fluids," *Tribology Letters* 35 (1), pp. 45-56.
- (27) Eguchi, M. and Yamamoto, T. (2005), "Shear characteristics of a boundary film for a paper-based wet friction material: friction and real contact area measurement," *Tribology International* 38 (3), pp. 327-335.
- (28) Society of Automotive Engineers of Japan (2012), "JASO Standards: M349-12,"
- (29) Fadley, C. S., Baird, R. J., Siekhaus, W., Novakov, T. and Bergstro.Sa (1974), "SURFACE ANALYSIS AND ANGULAR-DISTRIBUTIONS IN X-RAY PHOTOELECTRON-SPECTROSCOPY," *Journal of Electron Spectroscopy and Related Phenomena* 4 (2), pp. 93-137.
- (30) Beamson, G. and Briggs, D. (1992), "High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database," Wiley, ISBN 9780471935926.
- (31) Socrates, G. (2001), "Infrared and Raman characteristic group frequencies : tables and charts," 3rd Edition, Wiley, Chichester ; New York, ISBN 0471852988.

## FIGURE AND TABLE CAPTIONS

Fig. 1 – Schematic layout of the belt-pulley system in the CVT

Fig. 2 – Chemical structures of oleic acid, oleyl alcohol and glycerol mono-oleate (GMO)

Fig. 3 – Schematic image of the TE77 friction test

Fig. 4 – Schematic image of the penetration depth of XPS, EDX and ATR-FTIR

Fig. 5 – Friction results of the TE77 (a) at the steel/steel contact and (b) at the paper/steel contact

Fig. 6 – NPFLEX wear depth measurement results on the TE77 post-test steel pins

Fig. 7 – XPS C 1s spectra curve-fitting results of the steel plates after the TE77 test using (a) PAO, (b) PAO+acid, (c) PAO+alcohol and (d) PAO+GMO

Fig. 8 – XPS C 1s spectra curve-fitting results of the steel plates after the TE77 test using (a) CVTF, (b) CVTF+acid, (c) CVTF+alcohol and (d) CVTF+GMO

Fig. 9 – EDX results of the TE77 steel plates after testing (a) the PAO formulations and (b) the CVTF formulations

Fig. 10 – ATR-FTIR results of the TE77 steel plate surface after testing the CVTF formulations

Fig. 11 – Schematic images of the behavior of oleic acid on steel (a) in PAO and (b) with the other additives

Table 1 – Test oil formulations in this study (X indicates the presence of PAO or CVTF additives)

Table 2 – Specimens and conditions for TE77 friction test

Table 3 – XPS survey scan results of the post-test TE77 steel plates – Element quantification

## TABLES

Table 1 – Test oil formulations in this study (X indicates the presence of PAO or CVTF additives)

	PAO formulations				CVTF formulations			
	w/o FM	PAO + acid	PAO + alcohol	PAO + GMO	w/o FM	CVTF + acid	CVTF + alcohol	CVTF + GMO
PAO	X	X	X	X	X	X	X	X
CVTF additives					X	X	X	X
Oleic acid      mol/kg		0.03				0.03		
Oleyl alcohol    mol/kg			0.03				0.03	
GMO              mol/kg				0.03				0.03

Table 2 – Specimens and conditions for TE77 friction test

	Steel/steel contact	Paper/steel contact
Test specimens	Steel pin (AISI 52100) Steel plate (AISI 4140)	Steel pin (AISI 52100) Paper plate (JASO)
Pressure (Pmax)	1.0 GPa	6.0 MPa
Temperature	100°C	
Sliding speed	0.20 m/s (Stroke; 5 mm, 20 Hz)	
Test duration	60 minutes	

Table 3 – XPS survey scan results of the post-test TE77 steel plates – Element quantification

mass%	PAO formulations				CVTF formulations			
	w/o FM	PAO + acid	PAO + alcohol	PAO + GMO	w/o FM	CVTF + acid	CVTF + alcohol	CVTF + GMO
C 1s	61.7	69.8	69.5	69.6	59.3	57.5	61.9	56.6
O 1s	33.8	28.1	28.4	29.0	23.4	24.4	21.2	27.7
N 1s	-	-	-	-	3.9	3.7	3.7	2.4
Ca 2p	-	-	-	-	4.6	3.0	5.1	4.8
P 2p	-	-	-	-	8.2	10.8	7.8	7.6
Fe 2p	4.5	2.1	2.1	1.4	0.6	0.6	0.3	0.9