

# Adsorption of ATF additives on wet clutch friction interfaces under water contaminated lubricant conditions

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## Abstract

Stable friction and positive slope of friction-speed is the typical criterion for a good clutch performance. Lubricated friction interfaces used for wet clutches produces different friction behavior depending on the lubricant conditions. Usually the lubricant conditions vary for different automatic transmission fluid (ATF) formulations implying *e.g.* water contamination and these conditions might influence the deterioration of the clutch plates. The aim of this paper is to verify additive adsorption on friction interfaces and ageing of the friction material in wet clutch system for a water contaminated commercial ATF (DEXRON® VI). Standard clutch plates are employed in an automated wet clutch test rig to evaluate the friction characteristics of the tested lubricant. For controlled test conditions (speed, contact pressure, oil temperature) and specific number of test cycles, the mean friction coefficient and the friction vs. speed relations are monitored during sliding test. The resultant tribofilms on the tested friction interface surfaces are characterized by means of Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM- EDS), Attenuated Total Reflectance -Fourier Transform Infrared Spectroscopy (ATR-FTIR) and X-ray Photoelectron Spectroscopy (XPS analysis). The spectroscopic techniques were used to analyse adsorbed additives on friction interfaces and made it possible to correlate measured data to the specific friction behavior obtained after water contamination of the ATF.

**Keywords:** Wet clutch, water contamination, ATF, additive, surface analysis.

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## 1. INTRODUCTION

Automatic transmissions (AT) are now popular choice for today's vehicles for their quick response and convenience. In AT the clutch selects the gear range only, but it is not used when driving. The gear changes automatically. After first introduction by Chrysler in 1941, there have been continuous modifications and improvements to fulfill the automatic gear shifting as well as to facilitate the enhanced performance. In AT oil lubricated wet clutches are mainly used for torque transfer purposes where it is required to handle more heat and energy and to control torque. Lockup clutches in torque converter or shifting device are important applications involving wet clutches in AT [1]. The friction characteristics play an important role to provide

us with the desirable positive friction-speed characteristics [2]. During operation, the wet clutches utilize the sliding friction occurring at the contacting clutch plates to enable the power transfer from the input shaft to the output shaft. One of the contact surfaces is the friction plate and the other is the steel reaction plate. In clutch system these plates are arranged alternately and a typical AT requires a multiple plate clutch system to intensify the torque output with reduced sized plates. The friction material plays an important role as a basic functioning clutch component. Among different friction liner materials the cellulose based materials are now preferred considering the friction-speed characteristics, cost, and environmental aspects. Although there are many different friction materials different friction material

from sintered bronze to recent hybrid materials, medium to high carbon steel (En6 or En42) can be used as counter surface or reaction plate material for all [1, 2]. Commonly, Automatic Transmission Fluid (ATF) is used to lubricate these clutch plates. Need of enhanced performance clutch operation along with the rapid development of AT systems necessitates the development of more effective ATF. ATFs are not only used to remove heat or to clean the sliding clutch surfaces, but also to maintain the friction-speed characteristics to prevent the shudder occurrences. ATFs are generally formulated lubricants with a complex mixture of additives in the base oils [3, 4]. Along with viscosity index improvers, antioxidants and antiwear additives, friction modifiers, metallic detergents, and dispersants are vital ATF additives. Since the dominant lubrication regime during clutch engagement is the boundary lubrication regime, the friction characteristics of the wet clutch depend largely on the interaction among these polar, surface active additives and the friction interfaces [2, 3, 4]. The polar head groups of the amphiphilic surfactants interact with the clutch surface and form monomolecular layers. When the clutch engages the layers of the adsorbed surfactants generally provide the boundary lubrication and reduce sliding friction and wear. Friction modifiers with long hydrocarbon tails solubilized in base oil and the polar head anchored to the friction interfaces or reacting with already adsorbed species may form closely packed arrays of multilayer clusters (as proposed in [5]). Due to Van der Waals forces the molecules in the multilayer clusters tend to align themselves parallel to each other. This layer is hard to compress, but easy to shear thus provide lower friction. FMs (commonly long chain fatty acids, aliphatic ester, long chain amines, amides, phosphonate esters, phosphate esters etc.) are utilized in order to reduce friction in the low speed region. On the other hand, dispersants (succinic imides, succinate esters etc.) and detergents (metallic sulphonates like Ca sulphonates) contribute to increase friction in the high speed region [3, 4]. So the stable and shudder free friction generation actually depends on the tribofilm's nature [2, 5]. The thickness and effectiveness of this friction modifying tribofilm formation is related to a number of factors such as polar groups, chain length, configuration of the molecule, base oil or solvent, concentration, temperature, surface profile, and contaminants [5]. Some previous works [6, 7, 8] evaluates the effect of contaminating water on the wet clutch friction and on the clutch component. It was found that the addition of water in ATF intensified the mean friction coefficient initially, but in the long run the loss of friction was larger with time and that eventually degraded the clutch life faster. It was also reported [7] that the water presence promoted the negative friction-speed slope.

The aim of the present study was to characterize the tribofilm after tested with water contaminated ATF and to investigate the correlations between the tribofilm compositions and the friction characteristics.

## 2. EXPERIMENTAL DETAILS

### 2.1. Test Specimens

The clutch plates used for the tribotest are standard cellulose based friction plate OEM TM# 2420333, supplied by General Motors and slandered steel reaction plate (OEM TM# 8683024, supplied by BorgWarner) used for GM vehicles. A commercially available fully formulated automatic transmission fluid DEXRON® VI introduced for GM Hydra-Matic 6L80 6-speed rear-wheel- drive during 2006 (supplied by Petro Canada Ltd.)

### 2.2. Tribotest Equipment and Test Conditions

A special automated full scale wet clutch test rig was built to study the steady state (constant load 10 kN and constant speed 290 rpm for 5s slip time) friction performance characteristics of wet clutches used for automatic transmission. The test can be divided into three stages i) 500 cycles running in stage (5kN load), ii) 500 cycles reference stage (10 kN load), iii) 1000 cycles regular stage (10 kN load). In between each test cycles the friction interfaces are lubricated with 800 ml ATF flowing at a rate of 1.8 l/min (kept at 90°C). Additionally for the water contaminated test, 20 ml distilled water has been added to oil sump after reference stage and mixed for 15 min. During the test the coefficient of friction (COF) was calculated and monitored. Full details of the test and the test rig can be found in [1, 8].

### 2.3. Posttest Analysis

The terminology used for the post test friction plates are listed below in **Table 1**.

*Table 1: Terminology of the post test samples*

Test Condition	Friction Plate	Reaction Plate
Uncontaminated	FPWOW	RPWOW
Water contaminated	FPWW	RPWW

After the tribotest the posttest friction plates and steel reaction plates were rinsed with n-hexane for few seconds and then dried in vacuum (according to ASTM standard E1829 guide) to prepare them for sensitive surface analysis.

## Scanning Electron Microscopy-Energy Dispersive X-ray spectrometry (SEM-EDS)

A high resolution (ca 0.8 nm) electron microscope (Zeiss Merlin FEG-SEM) admitting energy dispersive X-ray spectrometry (Inca software from Oxford instruments) was used for chemical mapping and.

## Fourier Transform Infrared Spectroscopy (FTIR)

To analyze mainly the functional groups of the organic compounds in the surface film Attenuated Total Reflectance -Fourier Transform Infrared Spectroscopy (ATR-FTIR) was utilized. IR spectra were recorded using a Bruker Vertex 80v FTIR spectrometer equipped with a Diamond Attenuated Total Reflection (ATR) accessory and a DTGS detector. Spectra were recorded under vacuum at room temperature (23°C) and 128 scans were co-added and signal averaged at an optical resolution of 4  $\text{cm}^{-1}$ . Both the friction and the reaction plates were carefully washed with n-hexane to remove base oil before analysis.

## X-ray Photoelectron Spectroscopy (XPS)

XPS analyses were performed using a PHI VersaProbe II Multitechnique XPS microprobe (consist of dual beam 1 eV electron beam and 8 eV Ar beam). The friction plate samples tested with and without water in the ATF (FPWW and FPWOW) were characterized using x-ray beam at 100 W power. The analyzed area was 1400  $\mu\text{m} \times 100 \mu\text{m}$ . Spectra were acquired at a  $10^{-7}$  to  $10^{-8}$  Pa base pressure, using Al  $\text{K}\alpha$  monochromatic source with a spot size of 100  $\mu\text{m}$ . First survey scans was acquired on the samples and for the major detected elements high resolution spectra were recorded. These spectra were used for making chemical state assignments based on reference data for the observed binding energy. By a curve fitting software the data were further analyzed by PHI Multipak curve fitting software.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Tribotest

The mean COF was calculated from friction measurements for each case (tests with or without water contamination in the ATF) during reference and regular stages. Fig.1 illustrates that the mean COF is almost uninterrupted and stable with the number of test cycles for the uncontaminated fluid. Instead the water contaminated fluid shows similar trend of increasing friction after water addition as observed previously [6, 8]. Here the test was continued for 1000 regular test cycles considering the friction behaviour observed in [8] while the coefficient of friction after water addition reached a maximum value and then started to drop. The aim of this tribotest was to analyse the friction change in surface film due to water contamination.

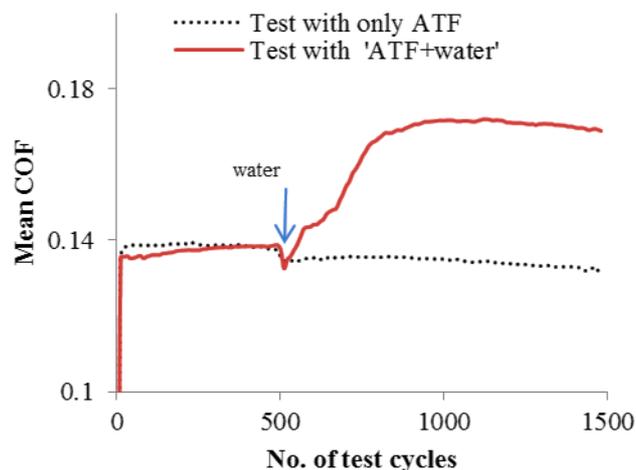


Figure 1: Mean COF vs. number of test cycles

### 3.2. SEM-EDS results

The EDS test results of the post test samples are shown in Table 2. In case of friction plate surfaces, the atomic concentration of O, Si, P, Fe are relatively high in the water contaminated sample. FPWW also shows adsorption of N and Al traces on the surface. Besides, it is interesting that the uncontaminated posttest steel reaction plate RPWOW adsorbed Zn, Ca, S. On the other hand, water contaminated RPWW shows lack of Ca, S, Zn, Si and comparatively higher P content.

Table 2: Atomic concentration comparison of large area EDX analysis for the posttest sample surfaces

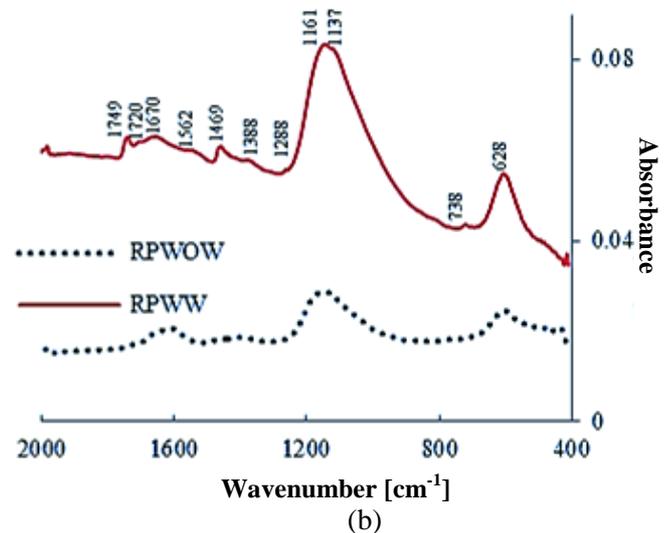
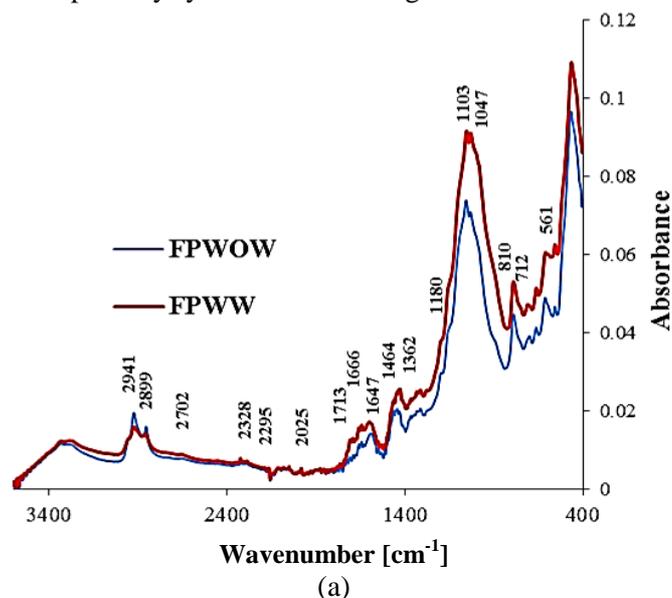
Element	FPWOW	FPWW	RPWOW	RPWW
C K	75.48	44.60	15.97	11.94
N K	-	8.08	-	-
O K	19.05	34.52	6.70	7.81
Al K	-	0.20	-	-
Si K	1.14	2.91	0.34	-
P K	1.60	3.71	0.82	1.15
S K	0.52	0.90	0.38	-
Fe L	1.58	4.25	75.54	79.10
Zn L	0.64	0.83	0.12	-
Ca K	-	-	0.12	-

### 3.3. FTIR results

Fig. 2 demonstrates the FTIR spectra of the post test samples. The FTIR spectra were carefully analysed to identify the functional groups according to their characteristic bands. In the high wavenumber region the two peaks for both samples at 2941  $\text{cm}^{-1}$  and 2899  $\text{cm}^{-1}$  shows stretching mode of  $\text{CH}_2$  and  $\text{CH}_2$  groups. FPWW shows (Fig. 2a) a weak band at 1713  $\text{cm}^{-1}$  that is absent in spectra of FPWOW. This band position usually corresponds to the stretching vibration of  $\text{C}=\text{O}$  in carboxylic acids [9]. The other adjacent bands with peak intensity at 1666 and 1647  $\text{cm}^{-1}$  are showing

absorption due to N-H bending and C=O stretching in primary and secondary amides. The band at  $810\text{ cm}^{-1}$  might be due to infrared absorption from N-H wagging in secondary amines. However, assignments to a specific mode should always be made with caution in the finger print region of infrared spectra because the bands are usually a mixture of vibration modes. Absorption bands in the spectral region between  $1460\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$  are, however, typical for C-H bending vibrations in methylene and methyl groups. Further, the hydrogen bonding region between  $3350$  and  $3200\text{ cm}^{-1}$  (Fig. 2a) shows typical infrared absorption from hydrogen bonded OH and NH functions. The strong and broad band centered at  $1075\text{ cm}^{-1}$  with distinct peaks at  $1103$  and  $1047\text{ cm}^{-1}$  is most probably due to phosphate and C-O vibrations. The band is shifted to lower wavenumber for FPWW compared with the corresponding infrared band observed for the uncontaminated friction plate FPWOW (Fig. 2a) indicating less P=O.

The surface of the water contaminated steel plate (RPWW, Fig. 2b) shows C=O stretching bands at  $1749\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$ . These bands are missing in the spectra of the surface of the friction plates and are typical for ester carbonyls. The two distinct peaks only present in RPWW are at  $1388\text{ cm}^{-1}$ ,  $1288\text{ cm}^{-1}$  and  $738\text{ cm}^{-1}$  possibly for O-C-O stretching in saturated carbon and primary amide N-H bending respectively. The strong and broad band (peaks at  $1161$  and  $1137\text{ cm}^{-1}$ ) centered at  $1150\text{ cm}^{-1}$  for both samples is in the spectral region typical for phosphate vibration. The band is shifted to higher wavenumber compared with the corresponding infrared band observed for the friction plates (Fig. 2a) indicating more of P=O character, although contribution from S=O stretching cannot be excluded. The strong band at might represent the absorption by symmetric stretching of S=O.



**Figure 2:** FTIR measurements for a) post test friction plates (FPWOW, FPWW) and b) posttest steel reaction plates (RPWOW, RPWW)

### 3.4. XPS results

The friction plate surface was further analysed with XPS, since this surface sensitive technique allows determination of the chemical nature of the uppermost (1-2 nm) layer of the tribofilm. The atomic concentration from the survey analysis of the posttest friction plates are shown in Table 3. The comparison between the samples shows that the water contaminated sample FPWW has higher concentration of N, O and P. Moreover, FPWW also confirms the presence of Fe and Si, which are absent in the uncontaminated FPWOW. The possible source of Fe on cellulose surface is the wear product from the steel plate and Si should originate from the cellulose friction liner or from the ATF additives since its concentration in the steel plate is very low (Table 2). A detailed analysis of the high resolution spectra (see Table 4) for chemical species shows that chemical species containing Ca, P, Zn, S and N are similar in both samples. Fe, Ca and Zn are found on the surfaces in oxide forms. N, P and partly S appear to be coupled with the organic matrix (C-N,  $-\text{PO}_4$ ,  $\text{S-CH}_x$ ,  $\text{CH}_x\text{-SO}_2$ ). The presence of C-N,  $\text{CH}_x\text{-SO}_2$  and  $-\text{PO}_4$  indicates interaction involving aramid fiber in friction liner, over-based Ca-sulphonate, and ZDDP/phosphates of FMs respectively. Possible sources of metal sulfides and CaO chemical species in both samples can be the anti-wear additive ZDDP and  $\text{CaCO}_3$  in detergent over-based Ca-sulphonate. The curve fit of the C 1s shows higher amount (17.10%) of C-O/C-N in the uppermost layer of the tribofilm for water contaminated ATF (FPWW) than in the uncontaminated FPWOW system (2.9%). It is also notable that the tribofilm on FPWW shows presence of O-C=O species for C 1s and C-O/SiOC species for O 1s curve fitting. O-C=O suggests the presence of carbonyl groups: ester and/or carboxylic acid groups on

the liner. The possible metal in metal oxides found in both cases for O 1s curve fitting can be Zn or Ca. Possible metal in metal oxides for O 1s curve fitting can be Zn or Ca found in both cases.

**Table 3:** Atomic concentration comparison of XPS analysis of the post test samples FPWOW and FPWW

Element	Atomic Concentration %	
	FPWOW	FPWW
C 1s	87.4	78.8
O 1s	7.2	14.0
N 1s	2.4	3.2
P 2p	1.5	2.0
Ca 2p	0.8	0.3
S 2p	0.4	0.5
Zn 2p3	0.3	0.2
Fe 2p	-	0.5
Si 2p	-	0.5

**Table 4:** XPS curve fitting results of the posttest friction plate surfaces

Atomic Orbital	Chemical State of the Species	Binding Energy, ev (%Area)	
		FPWOW	FPWW
C 1s	C-C	285, 97.10%	285, 80%
	C-O/C-N	287, 2.9%	286, 17%
	O-C=O	-	288, 2%
O 1s	Metal-O/PO <sub>4</sub>	531, 62.57%	531, 38%
	C-O	532, 37.43%	-
	C-O/Si-O	-	532, 62%
N 1s	C-N	400	400
P 2p	-PO <sub>4</sub>	133	133
Si 2p	Si	-	103
S 2p	S-Metal	162, 25.35%	162, 23%
	S-M	163, 42%	163, 9.4%
	S-CH <sub>x</sub>	164, 44%	164, 55%
	CH <sub>x</sub> -SO <sub>2</sub>	168, 13%	168, 20%
Ca 2p	CaO	347	347
Fe 2p	FeO	-	347
	Fe <sub>2</sub> O <sub>3</sub>	-	709

## 4. CONCLUSIONS

In the present paper, different surface analysis techniques were applied to understand the tribofilm formation on posttest clutch plate surfaces in water contaminated ATF lubrication. Moreover, the correlation between tribofilm composition and the characteristic high COF generation [6, 7, 8] was assessed here. The presented results disclose some interesting facts about additive adsorption when water is present in ATF:

- The cellulose surface shows almost similar composition in EDS and FTIR analysis in both water contaminated and uncontaminated situations. However the higher amount of Si, P, Fe and O in the water contaminated sample is analogous to the XPS results. The presence of iron oxides in the tribofilm indicates increased wear of the steel reaction plate.
- Water contaminated reaction plate shows absence of Ca, S, Zn and comparatively higher P content on its surface, which originates mostly from the regular metallic detergents and anti-wear agents used also for stabilizing the friction.
- The FTIR results indicate that all the major functional groups are present in both uncontaminated and contaminated friction interfaces. However, the water contaminated plates show shift in case of C=O stretching and PO<sub>4</sub><sup>-3</sup> absorptions. This indicates hydrogen bonding in presence of water in ATF. Moreover, the water contaminated reaction plate shows the possibility for O-C-O stretching in saturated carbon and primary amide N-H bending.
- The water contaminated friction plate surface showing the presence of O-C=O, C-O/Si-O and higher amount of C-O/C-N groups in the XPS study and O-C-O in the FTIR spectrum suggest water effect on the adsorption of the detergents and friction modifier. The friction modifiers like fatty amide or amine are the usual precursors of the negative charged (due to dipole moment) inorganic C-O/C-N groups.
- Though the presence of Si is noticeable in the water contaminated friction interfaces, the source and effect of Si in this water contaminated tribosystem was not clarified. It can be from the cellulose plate or from additives in the ATF.

From the above results it can be summarized that the presence of formula groups is distinct for the differences in the additives' (specifically friction modifiers, metallic detergents) adsorption in the water contaminated friction interfaces. These differences in the tribofilm composition might be related to the changed polar

additives' action for water presence [8] as well as responsible for the observed high friction for a short period.

## 5. ACKNOWLEDGEMENTS

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