lubricants

Article

Tribological Behaviour of PVD Coatings Lubricated with a FAP⁻ Anion-Based Ionic Liquid Used as an Additive

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Abstract: This paper studies 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate ionic liquid ([BMP][FAP]) as a 1 wt% additive to a polyalphaolefin (PAO 6) in the lubrication of CrN and TiN PVD coatings. Friction and wear behaviour were determined by using a ball-on-plate reciprocating tribometer at two loads (20 and 40 N) and a reciprocating frequency of 10 Hz. The tribological behaviour of this mixture has also been compared to a traditional oil additive, like zinc dialkyldithiophosphate (ZDDP). As an additive, ionic liquid exhibited an important friction and wear reduction compared to the base oil. However, tests conducted with ZDDP show slightly better results. XPS was used to analyse wear surfaces. The interactions of each additive with the surface contributed to improving the tribological behaviour of the lubricants.

Keywords: lubricant additives; PVD coatings; ionic liquids; friction coefficient

1. Introduction

Ionic liquids (ILs) are salts formed by the interaction between a weakly-coordinating inorganic anion and an organic cation. The chemistry and functionality of the salt is usually controlled by the anion, although the cation has a strong impact on the stability. Recently, there has been considerable interest in ILs due to their unique range of properties and particular characteristics, which include negligible vapour pressure, low melting point and flammability, high ionic conductivity and thermo-oxidative stability and controlled miscibility with organic compounds [1–6]. Despite significant cost drawbacks compared to conventional fluids, interest in ILs is driven by the potential versatility of these fluids, particularly for electrochemistry, the development of new materials, extraction technology, organic synthesis, catalysis and tribology [3–6]. Nevertheless, in order to determine the usefulness of the new compound, a much more focused understanding and the associated determination of the physical and chemical properties may be an important goal for the future [2,7]. Despite of the fact that considerable research into ILs as specialty lubricants has been carried out, their tribological properties and mechanism of action remain unclear [1,8].

Ionic liquids have been studied as lubricants of a series of contacts over the last decade, particularly steel–steel [9–15], lightweight materials (aluminium and silicon alloys) [16–20], various engineering surfaces, like nanocrystalline nickel coating [21], phosphor bronze [22], electrodeposited Ni/Si_3N_4 composition coating [23], 1Cr18Ni9Ti stainless steel modified by plasma nitriding [24] and many others [25–27]. Traditionally, a variety of [BF_4] and [PF_6] imidazolium salts (as additives or neat lubricant) that can be obtained at an affordable cost have been used in tribology works, showing good results on both antifriction and anti-wear performance [28,29]. One of the most promising applications of these new lubricants is their use at severe conditions for which conventional lubricants fail [6,12,16,30–32]. Currently, a significant number of research activities is focused on the surface interactions between the material and the ionic liquid, which defines the efficiency of the ionic liquid as a lubricant [5,33]. In conclusion, this kind of lubrication shows improved tribological behaviour compared to synthetic, mineral or engine oils, normally used for different lubricated surfaces [3,4,17,34].

Recently, trifluorotris(pentafluoroethyl) phosphate ([FAP]) has been introduced as a highly hydrophobic anion precursor of ionic liquids. In comparison with the conventional [BF_4] and [PF_6] anions, the excellent hydrolytic stability avoids the corrosion problem, and the flexibility of the cationic moiety in the preparation of ionic liquids provides good lubricant and tribological properties, making this anion highly suitable for use in tribological applications [35]. Most tribological research on ILs has used imidazolium-derived cations [1,11–13,17,18,20,28,29,32,33]. However, Nainaparampil *et al.* [36] used ionic liquids with low volatility and high environmental stability as lubricants, including the one used in this work, for sliding microelectromechanical system (MEMS) devices.

In order to minimize the industrial issues of failures due to wear, an extension of industrial tool life could be achieved by the application of the surface coating technology based on physical vapour deposition (PVD) [37]. The usefulness of these coatings is very different: from decorative through optical and magnetic to medical, being the most common those applications based on the improvement of the tribological properties of machine elements [38]. Chromium nitride (CrN) is a low friction ceramic coating that has been increasingly used not only for its anti-wear properties, but also for its thermal stability, high hardness and anti-corrosive and anti-adhesive properties that produces an excellent protective coating [39,40]. As can be seen in some previous studies, the wear behaviour and corrosion of CrN coating under lubricated conditions were improved in comparison with hard chromium: hence, the former may be considered a potential substitute to replace the latter [41]. Due to the excellent tribological behaviour exhibited by the CrN coating under boundary lubrication conditions, the applications of these coatings in automotive components, especially for shims and piston rings, have increased within the last decade [42]. Additionally, research on the friction, wear characteristics and failure mechanisms of PVD TiN coating have shown that it can improve tribological performance and extend the useful life of components. This coating frequently offers good corrosion protection and surface finish, high wear resistance and a low coefficient of friction [38,43].

It should be noted, however, that few papers have been published on the issue of PVD coatings in lubricated contacts with the presence of ionic liquids. Zeng *et al.* [44] found that amorphous chromium coatings under ionic liquid lubrication exhibit much better corrosion and wear resistance compared to Fe, Cu and nanocrystalline Cr coatings. Chen *et al.* [45] also concluded that imidazolium-based ionic liquid [BMIM][BF_4] lubrication of BCN films improved load carrying capacity, wear resistance, friction and long anti-wear life. Zhengfeng Jia *et al.* [46] showed that synthesized ionic liquid-functionalized borate esters exhibited better friction-reducing and anti-wear properties for a diamond-like carbon (DLC) coating/steel sliding pair than commercial zinc dialkyldithiophosphate (ZDDP) when both were separately added into polyalphaolefin (PAO) as additives. Gonzalez *et al.* [47] studied the ionic liquid used in this work (1-butyl-1-methylpyrrolidinium ([BMP])[FAP]) as neat lubricant and 1 wt% additive to a polyalphaolefin (PAO 6) in the lubrication of TiN, CrN and DLC PVD coatings. The ionic liquid as an oil additive showed a slight friction reduction compared to tests produced with neat PAO 6, but far from the lowest friction coefficient and wear reduction of the pure [BMP][FAP]. Blanco *et al.* [48,49] worked with an ammonium-based ethyl-dimethyl-2-methoxyethylammonium tris(pentafluoroethyl)trifluorophosphate ionic liquid ([(NEMM)MOE][FAP]) as a 1 wt% additive to a polyalphaolefin (PAO 6) in the lubrication of CrN and TiN coatings. This IL provoked, in both cases, a slight friction reduction compared to tests made with neat PAO 6, but far from the lowest friction coefficient and wear reduction of the traditional additive ZDDP in the same weight proportion. Hernández *et al.* [50] analysed the same [(NEMM)MOE][FAP] ionic liquid as a pure lubricant and as an additive (PAO 6 as base oil) within the lubrication of three PVD coatings (TiN, CrN and DLC). The results show an important friction and wear reduction when the IL was used as pure lubricant. Furthermore, a friction reduction was observed when the ionic liquid was used as an additive in comparison with the performance of neat PAO 6.

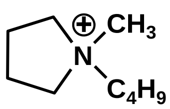
Considering the industrial applications of such coatings in lubricated contacts and the growing research interest of ionic liquids in lubrication, this paper studies the use of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ionic liquid ([BMP][FAP]) as a 1 wt% additive to a polyalphaolefin (PAO 6) in the lubrication of two PVD coatings (CrN and TiN) and includes a comparison with the tribological behaviour of the PAO 6 containing an identical concentration of ZDDP in the lubrication of the above-mentioned PVD coatings.

2. Experimental Section

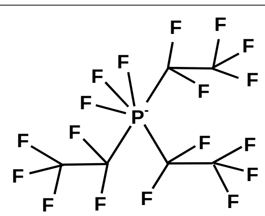
In order to study the effectiveness of the [BMP][FAP] ionic liquid as a lubricant additive, a polyalphaolefin (PAO 6) kindly provided by REPSOL S.A. was used as the base oil. The ionic liquid used in this work was commercially available from Merck KGaA (Darmstadt, Germany). In order to measure the effectiveness of the IL as an additive, a mixture of PAO 6 with a traditional additive, ZDDP, was employed as a reference oil. From the closely-related chemicals constituting the ZDDP chemical category, zinc, bis(2-methylpropoxy)-sulfanylidene-sulfido-λ5-phosphane (CAS No. 68457-79-4) was kindly supplied by REPSOL S.A. and used for this purpose. The characteristics of the materials and specimens used in the experiments are listed in Table 1.

Table 1. Material properties. PAO, polyalphaolefin; ZDDP, zinc dialkyldithiophosphate; [BMP][FAP], 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate ionic liquid.

Materials	**Properties**			
Base Oil/Additive	**Density (g/cm^3) ASTM D 4052 (15 °C)**	**Kinematic Viscosity (mm^2/s) ASTM D 445**		**Viscosity Index ASTM D 2270**
		40 °C	100 °C	
PAO 6	0.826	31.0	5.90	135
ZDDP	2.320	320	14	-
[BMP][FAP]	1.590	58.8	8.6	118
PVD Coatings	**Thickness (µm)**	**Roughness (µm)**	**Hardness (Vickers)**	
TiN	2.9	0.27	1633	
CrN	3	0.26	2137	
Ionic Liquid				
IUPAC name		**Purity (%)**	**Water content (%)**	
1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate		98	<1 (Karl Fisher)	
Cation		**Anion**		
$(C_4H_8)(CH_3)(CH_2CH_2CH_2CH_3)N^+$		$F_3(C_2F_5)_3P^-$		



[BMP]



[FAP]

An ultrasonic probe was utilized for 5 minutes in order to disperse the ionic liquid and ZDDP in the base oil in a concentration of 1 wt%. Unlike ZDDP, which is soluble in the base oil, the stability of the ionic liquid mixture was monitored. A Turbiscan Lab Expert (Formulaction) was employed to analyse the stability of the mixture of base oil and ionic liquid for 72 h. No change in the intensity of backscattered light through a glass vial containing the blend of PAO 6 + 1 wt% [BMP][FAP] as a function of time indicated that the mixture was stable. Although the [BMP][FAP] dispersion in the PAO 6 was guaranteed during the friction and wear tests performed, extensive work on the improvement of ionic liquids' stability in base oils should be done in the future. Phosphorous concentration in the blends was also calculated, indicating a value of 838 ppm for PAO 6 + 1 wt% [BMP][FAP], which is slightly lower than 879 ppm of phosphorous present in the PAO 6 + 1 wt% ZDDP.

In a previous author's work [51], neat PAO 6, PAO 6 + 1 wt% ZDDP and PAO 6 + 1 wt% [BMP][FAP] were examined using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). Due to the low concentration of the additives studied, the resulting spectra of the blends were very similar to the neat PAO 6 result.

For the tribological tests, a CETR-UMT-3 micro-tribometer with a reciprocating ball-on-plate configuration was employed. AISI 52100 chrome steel balls with a 9.5-mm diameter and a hardness of 63 HRC were in sliding contact with ASTM A-569 steel plates ($10 \times 10 \times 3$ mm^3) coated with TiN and CrN, respectively, in the presence of 15 mL of PAO 6 + 1 wt% [BMP][FAP]. In the same conditions, neat PAO 6 and PAO 6 + 1 wt% ZDDP were also tested to compare the results of the mixture containing ionic liquid with the base oil and the mixture with ZDDP.

Friction and wear tests were performed for a period of 30 minutes under normal loads of 20 and 40 N (corresponding to mean contact pressures of 0.9 and 1.14 GPa, respectively), 1 mm of amplitude and a frequency of 10 Hz. Normal load was applied using a closed-loop servomechanism, and normal load and friction force were measured with the strain gages. Three repetitions for each test condition at room temperature were made.

After lubricated tribological tests, the surface topography and wear scar volume of the coated lower plates were studied using a Zygo New View 5000 microscope, which uses white light interferometry to produce images of the surface topography. The chemical composition of the worn surfaces was also determined by X-ray photoelectron spectroscopy (XPS) with a SPECS Phoibos 100 MCD5 system equipped with a hemispherical electron analyser operating in a constant pass energy, using Mg K alfa radiation ($h\nu$ = 1253.6 eV). The background pressure in the analysis chamber was kept below 5×10^{-9} mbar during data acquisition. Individual high-resolution spectra were taken at a pass energy of 30 eV. All spectra were calibrated using C1s peak fixed at 284.6 eV. The binding energies (BE) of N 1s, O 1s, F 1s, Ti 2p and Zn 2p$^{3/2}$ core levels were used to reveal the chemical state of the respective species.

In order to study the possible corrosion damage of the coated surfaces due to their interaction with the ionic liquid, pure [BMP][FAP] was applied on the CrN and TiN surfaces (previously cleaned in an ultrasonic bath with heptane and then air dried), which remained at room temperature for two weeks while the corrosion activity was observed. Additionally, coated surfaces were dipped in to the ionic liquid and maintained at 100 °C for 10 h. After both tests, coated surfaces were analysed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). As a result, no corrosion activity was detected on the surfaces coated with TiN or CrN.

3. Results and Discussion

The friction coefficient was measured during the tests. Average values were obtained from the three replicates performed for each test condition and PVD coating, ensuring that standard deviation values were below 0.009 in every case (Table 2). As is observed, there is a logical increase of the friction coefficient when the applied load rises.

Figure 1 also shows the friction coefficient *versus* time for all tests made with CrN (Figure 2a,b) and TiN (Figure 2c,d) coatings. The first five minutes of the graphs (Figure 2a,c) showed the running-in period. Nearly constant values of the friction coefficient can be observed for all of the lubricants employed when the steady state is reached (Figure 2b,d).

Table 2. Friction results for all tests made. IL, ionic liquid.

Load (N)	Coating	Lubricant	Average	SD	COF Reduction (%)
20	CrN	PAO 6	0.122	0.0061	-
		+1% ZDDP	0.077	0.0033	36.85
		+1% IL	0.099	0.0030	18.38
	TiN	PAO 6	0.132	0.0061	-
		+1% ZDDP	0.072	0.0028	45.42
		+1% IL	0.091	0.0033	36.33
40	CrN	PAO 6	0.130	0.0061	-
		+1% ZDDP	0.098	0.0035	24.14
		+1% IL	0.110	0.0037	15.21
	TiN	PAO 6	0.164	0.0087	-
		+1% ZDDP	0.086	0.0046	47.43
		+1% IL	0.137	0.0043	15.54

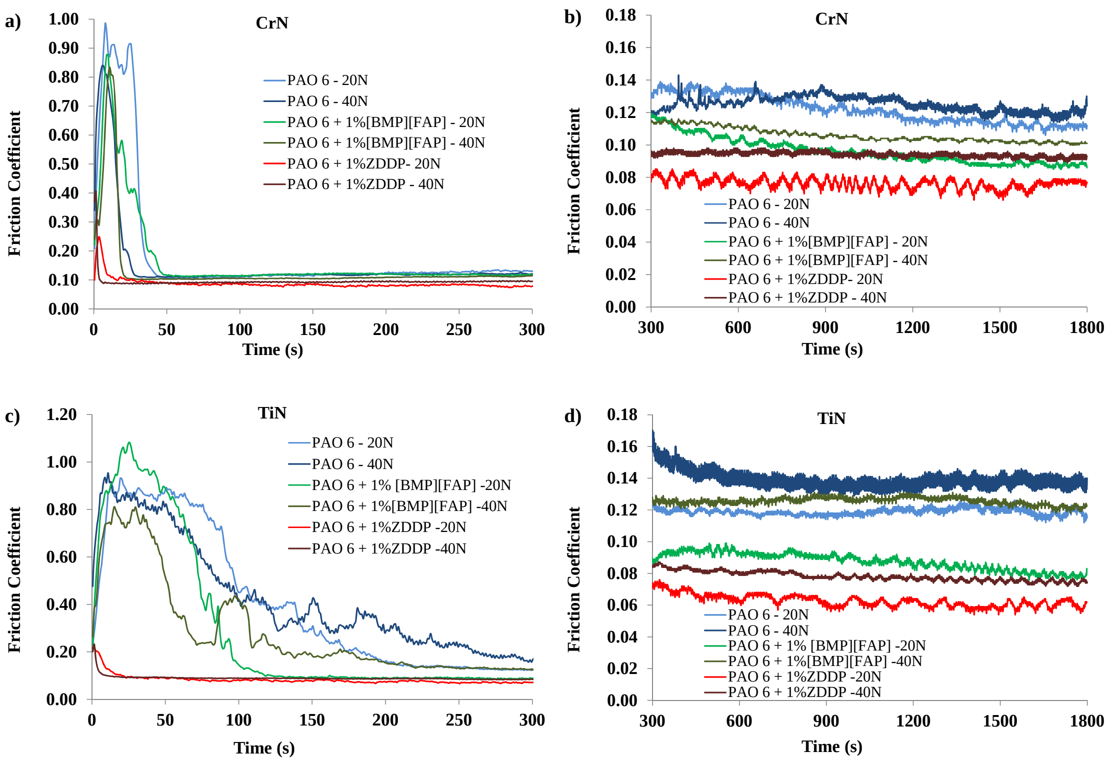


Figure 1. Evolution of the friction coefficient during tribological tests: (**a**) CrN (running-in); (**b**) CrN (steady state); (**c**) TiN (running-in); (**d**) TiN (steady state).

For both PVD coatings (CrN and TiN) under an applied load of 20 N, significant differences between the lubricant samples were detected. The mixture with ZDDP shows the lowest friction coefficient of the three oil samples. The ZDDP mechanism of action can explain this fact because of the additive-metal surface interaction, which avoids welding and reduces friction and wear [52,53]. For tests made with ionic liquid as the additive, a significant friction coefficient reduction compared to neat PAO 6 can also be observed. However, this result was below the performance compared to that obtained when the traditional additive ZDDP was employed.

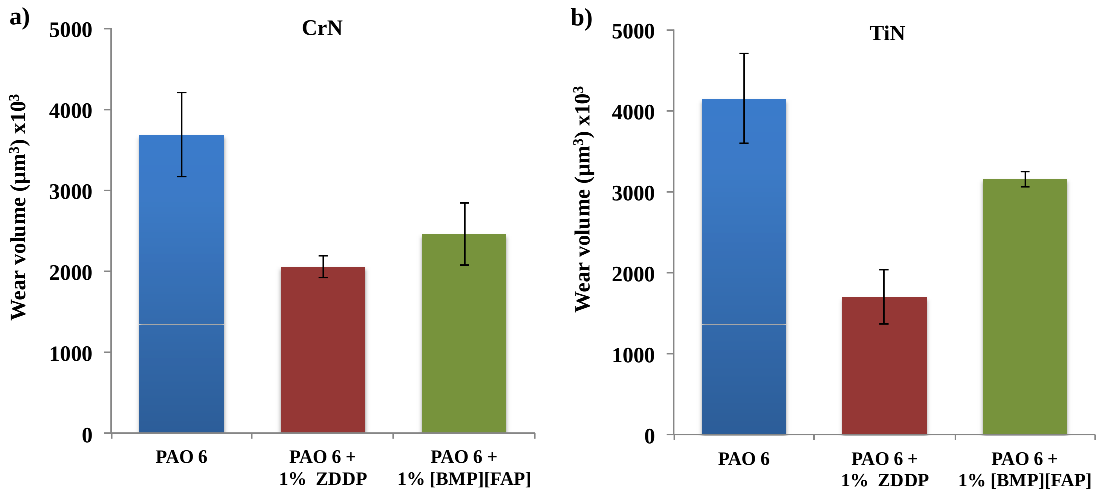


Figure 2. Wear results for tests made at 40 N: (**a**) CrN; (**b**) TiN.

Alternatively, the friction behaviour observed in tests made at 40 N was very similar to that measured at 20 N. The sample containing ZDDP again showed superior antifriction performance, while PAO 6 rendered the worst results. From the point of view of friction reduction, Table 2 also shows that ZDDP is better than ionic liquid for all of the coatings and loads being tested; achieving a greater improvement that reaches 45% in the samples coated with TiN tested at both loads. Moreover, the ionic liquid also improved the performance of PAO 6 under all of the test conditions, showing the best performance at 20 N for both PVD coatings. Alternatively, Figure 2 shows only the wear volume results for the tests made at 40 N, since the wear at 20 N was too low to be measured for both the additives and the coatings. At the lowest applied load, an excellent antiwear performance was observed in the case of ZDDP as the additive, where no significant surface damage was detected (Figure 3).

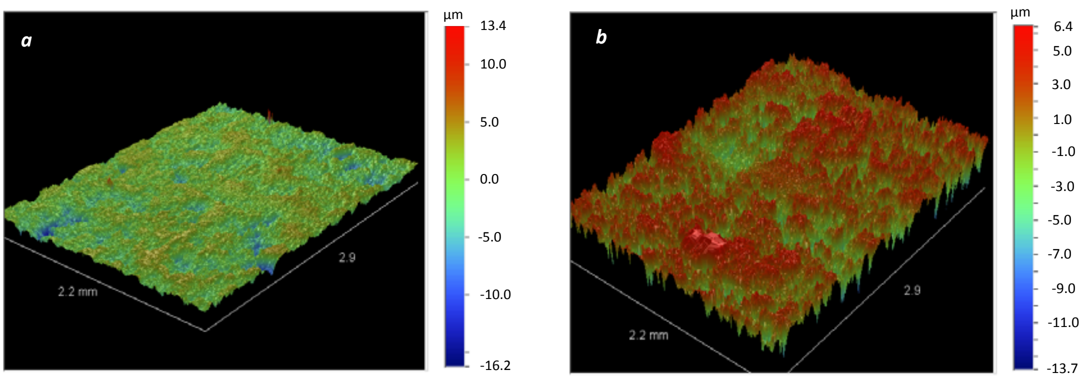


Figure 3. 3D optical wear surfaces of the coatings after reciprocating wear tests at 20 N lubricated with PAO 6 + 1% ZDDP: (**a**) CrN and (**b**) TiN.

These wear results are in agreement with the friction values mentioned earlier in Table 2. Besides, those obtained during the tests performed with neat base oil at 40 N are clearly the maximum measurements. However, a reduction of the damage suffered by the coated surfaces was observed in the test lubricated with PAO 6 + 1 wt% ZDDP and PAO 6 + 1 wt% [BMP][FAP]. The addition of ZDDP additive to the base oil, especially in the lubrication of TiN surfaces, led to a significant wear reduction of nearly 60% compared to neat. However, the results also show a remarkable reduction in wear (over 25%), for both coated surfaces, when the PAO 6 + 1 wt% [BMP][FAP] was used.

Wear surfaces were analysed by XPS to evaluate the chemical mechanisms of the ionic liquid-coating interactions. The XPS experiments were carried out with a magnesium X-ray source (1253.6 eV) with a 1-cm^2 area under ultra-high vacuum conditions. In order to be able to distinguish between the electrons located from the outside of the wear scar and those located from the inside, a 2.5 mm-diameter iris was inserted between the sample and the detector, focusing on the correct area of the sample prior to the scanning procedure. CasaXPS, as well as home-developed software by the authors were used to deconvolute the experimental profiles.

CrN samples loaded at 40 N, with a worse friction coefficient, showed a single F 1s peak at 688.1 eV corresponding to the [FAP] anion [47]. Furthermore, Cr 2p analysis showed two different peaks at 575.7 eV and 574.9 eV assignable to air-exposed CrN and CrN, respectively [52]. According to these results, there seems to be no evidence of interaction between the ionic liquid and the coating at 40 N. However, samples loaded at 20 N showed two F 1s peaks at 687.9 eV and 686.2 eV belonging to [FAP] anion and CrF [48]. The existence of chromium-fluoride compounds was confirmed by analysing the Cr 2p XPS band. In this case, three peaks were obtained at 574.9 eV, 575.7 eV and 579.8 eV, which can be assigned to CrN, air-exposed CrN and CrF, respectively [54,55]. In view of the results, the experiments with the lower load (where better friction coefficients were obtained) showed a F-Cr interaction that could be characterized by XPS. These interactions arise from the tribofilm created over the surface and could be responsible for the reduction in the friction coefficient. Table 3 summarizes these results.

Table 3. Details on the deconvolution of XPS peaks obtained for CrN worn surfaces.

Band	Load (N)	B.E. (eV)	%	Assigned to	Reference
F 1s	20	687.9	88	FAP^-	[47]
		686.2	12	Cr-F	[48]
Cr 2p		574.9	17	CrN	[54]
		575.7	74	Air exposed CrN	[54]
		579.8	9	Cr-F	[55]
N 1s		396.6	61	CrN	[56]
		402.5	39	Cr nitrites/nitrates	[56]
F 1s	40	688.1		FAP^-	[47]
Cr 2p		574.9	14	CrN	[54]
		575.7	86	Air exposed CrN	[54]
N 1s		396.7	57	CrN	[56]
		402.6	43	Cr nitrites/nitrates	[56]

B.E. is binding energy. % refers to the percentage of that assignation for a certain load.

F 1s and Ti 2p$^{3/2}$ photoelectron bands were measured in order to check the modifications of the TiN surface and the possible interaction of fluorine (in the case of ionic liquid) with the coating. For the test made at 20 N, the deconvolution of the Ti 2p photoelectron band suggests that the formation of a tribofilm occurs through reduction of Ti (III) in TiN to Ti°. In fact, Ti° and TiN are the only chemical states for Ti detected in the samples of the best lubricant (PAO 6 + 1% ZDDP). Experiments carried out with PAO 6 + 1% [BMP][FAP] at the same load (20 N) present TiO structures on the surface in addition to those of Ti° and TiN (Table 4). This is probably related to the lower tribological behaviour of this lubricant sample compared to that containing ZDDP. Additionally, titanium fluoride compounds may also be involved in the tribofilm in ionic liquid lubrication. It is important to state that titanium fluoride compounds are expected to appear at high binding energies (458 eV or higher [47,57]). Unfortunately, the Ti 2p$^{1/2}$ band appears at 6 eV above that of the Ti 2p$^{3/2}$ one. Therefore, Ti 2p$^{1/2}$ bands arise from Ti° overlap with Ti 2p$^{3/2}$ from titanium fluoride compounds. As a consequence TiF structures are not easy to detect in Ti°-containing samples. In order to confirm the previous results, the F 1s photoelectron band was also examined (Table 4). F appears as titanium fluorides (TiF, $TiOF_2$) for the test made at 20 N. The situation for samples lubricated with neat PAO 6 is coherent with the presented theory. The analysis for the lowest load does not show Ti°, and therefore, the lubrication performance is worse.

Table 4. Details on the deconvolution of XPS peaks obtained for TiN worn surfaces [57–63].

Band	Load (N)	B.E. (eV)	%	Assigned to	Reference
F 1s	20	685.2	45	$TiOF_2$	[59]
		686.1	55	TiF	[59]
Ti 2p		453.1	54	Ti°	[62]
		455.1	9	TiO	[61]
		455.6	37	TiN	[62]
F 1s	40	686.9	70	Monofluorinated C	[57,58]
		688.0	30	[FAP^-]	[63]
Ti 2p		454.6	58	TiN	[60]
		456.9	42	Ti_2O_3	[61]

B.E. is binding energy. % refers to the percentage of that assignation for a certain load.

According to interferometry data, the TiN coating is almost removed when the highest load (40 N) was used with PAO 6 as the lubricant. This can also be confirmed through XPS experiments, as the coating could not be detected at all in the case of neat base oil; in the case of the other lubricant samples, different titanium oxides were present. These Ti compounds are probably residues of the original TiN coating. At this highest load, fluorine is mainly found as FAP^- or partially-damaged FAP^- (with partially-hydrogenated carbon chains) when [BMP][FAP] was employed as an additive.

4. Conclusions

In this paper, [BMP][FAP] ionic liquid was studied as an additive to PAO 6 in the lubrication of CrN and TiN PVD coatings. In addition, it presents a comparison with the use of ZDDP as additives to PAO 6 in the lubrication of the same coatings. Although the use of the ionic liquid as a 1 wt% additive to PAO 6 resulted in a friction reduction compared to neat PAO 6 for both coatings and applied loads, the lubricant samples containing ZDDP as the additive in PAO 6 always exhibited the lowest friction coefficients. Even though it has been observed that the antifriction and antiwear performance of [BMP][FAP] as a 1 wt% additive is lower than that of ZDDP, the use of this ionic liquid may be interesting as a friction and wear reduction additive in neat PAO 6.

In the case of CrN, the XPS results show that a tribofilm involving the interaction between fluorine and chromium was generated at 20 N of applied load. However, this tribofilm may not be present at 40 N, probably due to the high load that leads to a higher film removal rate than the rate at which film forms at the rubbed surface. The presence (at 20 N) or absence (at 40 N) of this Cr-F interaction was confirmed by analysing the chromium 2p band, showing Cr-F peaks at 20 N, but not at 40 N. These results are also in good agreement with the friction coefficient data.

For the test made at 20 N using [BMP][FAP] or ZDDP as additives in the lubrication of TiN surfaces, friction and wear reduction is associated with the formation of a tribofilm that seems to involve the reduction of the TiN coating to produce a certain amount of Ti°. Depending on the wear conditions, partial reduction of TiN may also occur. From the XPS results, neat PAO 6 is the worst lubricant in the creation of a tribofilm leading to almost complete removal of TiN coating at 40 N.

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