Lubricity Evaluation for Lubricants Used in Refrigeration with HFC-134a

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ABSTRACT

Replacing CFCs by HFCs in refrigeration implies new conditions for compressors and the development of new lubricants. For example, it is common knowledge that the chlorine in CFC is a positive factor in lubrication, particularly in the zones with high contact pressures. As HFCs are chlorine-free, lubricants therefore need to contain specific anti-wear additives.

Experience shows the effective lubrication also depends on compressor design. However, formulators cannot test specific products for every compressor model. For this reason it is essential to develop a wide range of simple friction tests, enabling simulation of a wide variety of operating conditions.

This study presents an interesting example of a lubricity evaluation procedure, and concerns a particularly severe piston-type hermetic compressor operating with 134a refrigerant fluid. The friction tests developed to evaluate lubricants are carried out on FALEX pin and Vee-block, FOUR-BALLS and automated PLINT-CAMERON tribometers.

These tests enable a realistic image to be obtained of the way the system operates on a real mechanical level. A range of grade ISO 22 to ISO 100 lubricants was formulated using this test procedure. In the presence of 134a, these lubricants have better in-service behaviors than those obtained with the couple mineral oil-CFC 12.

INTRODUCTION

As the ozone layer disappears over some regions of the earth's atmosphere, CFC 12 (CF_2Cl_2) refrigerant, currently used in domestic refrigeration and for automobile air conditioning units, is being phased out and replaced by HFC-134a ($CH_2F\ CF_3$). This change implies the formulation of new lubricants as the mineral oils used conventionally with CFC 12 will not combine with HFC-134a. Lubricant manufacturers have started to develop synthetic fluids, and research approachs were based on two main groups : esters and polyalkyleneglycols (PAGs).

During formulation the properties of the mixtures obtained must be verified at every instant. Generally speaking, it is quite easy to evaluate the chemical or physico-chemical behaviour of oils rapidly, using simple tests, including :

- miscibility with HFC-134a
- chemical stability
- aggressivity in terms of metals (Cu, Fe, Al), seals and other polymers
- hygroscopicity (the affinity of a lubricant for the absorption of water)
- ...

On the other hand it is much more difficult and delicate to determine a priori the lubricant effectiveness of an oil on a given piece of equipment, from simple laboratory tests. Lubricants have several basic functions which it is quite difficult to demonstrate on a simple tribometer.

In this article, after having examined the most common mechanical tests and the difficulty of extrapolating results obtained with these tests to true operating conditions, an original and rapid evaluation method developed by the ELF Research Center will be presented and some important results will be listed and discussed.

1 GENERAL REMARKS

1.1. The role of lubricants :

In the case of a piston compressor, for example, the main roles played by the lubricant are :

- to reduce the coefficient of friction between the mechanical parts which are in relative motion
- to reduce wear
- to ensure hermetic sealing between the piston and the liner by the creation and the maintenance of an oil film between the surfaces
- to participate in the thermal equilibrium of the whole compressor by ensuring rapid transport of the heat released in hot areas (i.e. the gas compression zone, or, to a lesser degree, in the crankshaft bearings...) towards the cooler zones.

...

Lubricants play a complex role in this system. To test their efficiency, there is only one absolute method : tests on a real compressor. The problem is that, depending on the type of compressor, (screw type, piston type, etc.) great differences exist in engineering design (geometry, metallurgy, ...) and as compressors are used in a vast range of applications, lubricants have to be adapted to extremely different operating conditions [1]. It is obvious that it is not possible to implement systematic tests on a "real life" scale. The first basic formulation phase means developing methods to simulate friction which enable :

- repeatable tests,
- to discriminate between lubricants,
- tests which are representative of the real mechanical systems
- rapid implementation.

These objectives are not very easy to achieve and require in-depth analysis of the problem as tribology - the science of friction and wear - is a multidisciplinary subject which covers mechanical, metallurgical, chemical and physico-chemical problems.

1.2. Lubricant test machines

There are a great many lubricant test machines for engine and industrial lubricants. In every case there are at least two mechanical parts which are in relative motion in this lubricant environment. Figure 1 shows some commonly used simple geometries. It is not easy to rank test machines as factors include the geometry of the samples (pin on disk, block on ring, four-balls...), the nature of the motion (sliding, rolling, oscillating...), the type of contact between the moving parts (contact on a point, on a line, on a surface...) and the complexity or purpose of the tests (test machines for gears, or specific test rigs for full-scale moving parts) [2].

Furthermore, for each test, there exists a range of factors depending on the metal from which the samples are made (steel, cast iron, aluminium, copper...), the thermal or metallurgical treatments that they undergo prior to tests (quench hardening, annealing, surface treatments...), the condition of surfaces and the state of their surfaces or their finishing (grinding, honing...).

Finally, for a given geometry and depending on sample type, test conditions can be modified (local pressure and average temperature of the contact, sliding or rolling speed), the lubrication method (continuous lubrication using new or regenerated oil, oil bath...) or the test environment (neutral or aggressive atmosphere, pressurised chamber...).

The field of mechanical tests on lubricants is complex and requires in-depth analysis of the problem as it is difficult to designate a priori a "miracle" test. Two approaches are possible :

- either to develop an extremely complete test protocol including metallurgies, temperatures, atmospheres and comparing them to results obtained from observing operations in "real life" conditions

- or to develop a set of simple and familiar tests (including, for example, the four-ball test), each of which is designed to measure a specific property of the lubricant being tested.

Experience shows that tribologists obtain excellent results using judiciously chosen combinations of these two approaches.

Simple tests enable the product to be compared to reference formulations or lubricants developed by competitors. Secondly, as they are familiar tests which are well known in term of repeatability and reproducibility, they are easy to interpret. Additionally, and often to make distinctions even more apparent, it is always interesting to use a rather more specific test, using a more complicated tribometer to simulate "true life" conditions in which lubricants are used at a given point in the machine. There is a balance to be kept as there is no point in making this test procedure over complicated, rendering it difficult to implement and the interpretation of the results rather more difficult.

2. DETERMINATION OF A LUBRICANT TEST METHOD

2.1. Results shown in bibliography

With the objective of decreasing major inertial efforts, for increasing the mechanical efficiency, many moving parts in compressors are made from aluminium alloys (for example, connecting-rod in piston type compressors). It has been known for many years that contact between steel or cast-iron and aluminium alloys is difficult to lubricate, particular by polyglycols [3, 4, 5, 6, 7]. A recent study has shown that polyolesters with modified chemical structures (mPOEs) reduce friction quite significantly between these metals. During this study, a severe test was developed on a pin and Vee-block FALEX machine fitted with different measurement instruments and using an silicium aluminium alloy (2024 T4) pin [8]. This test reflects results published in the literature. Furthermore, it was an efficient means of developing a range of mPOEs compatible with HFC-134a with good steel-aluminium anti-friction properties. The neutrality of HFC-134a in aluminium-steel friction on the FALEX pin and Vee-block machine was also observed [fig.2]. HFC-134a was brought into contact by "bubbling", which is a relatively common method in FALEX tests.

KOMATSUZAKI *et al.* [9, 10, 11] quite clearly show the lubricant effects of chlorine in CFCs. A steel or silicium aluminium alloy test bar rotates on a steel plane. The contact type is flat on flat. Friction is not lubricated, but the system is then placed in a hermetic chamber, into which, in sequence, is pumped air, HFC-134a (CH_2F CF_3), HCFC 22 ($CHClF_2$) and CFC 12 (CF_2Cl_2) [they are ranked in increasing order of chlorine in the molecules]. The system can change under the influence of different tribological parameters (pressure, temperature, sliding speed). In aluminium on steel friction, it can be observed that the behavior in the presence of HFC-134a is similar to the behavior in the presence of air : sample wear levels are high and 5 to 10 times greater than those observed using CFC 12. In the case of steel-steel friction, it has been clearly shown that the coefficient of friction is reduced by a factor of 3 to 5 if the chlorine content increases in the molecule. The chlorine present in CFC plays an active role in lubrication. Chlorine is an excellent extreme pressure element and KOMATSUZAKI *et al.* conclude that it is essential to add another EP agent to the lubricant to compensate for the lack of lubrication when changing from CFC 12 to HFC-134a.

In tests on real compressors, it has been shown that, depending on compressor production technology, an mPOE without an EP additive can sometimes be sufficient to lubricate the system correctly. However, these examples are quite rare and in practice it is most commonly essential to add an anti-wear or extreme pressure additive to the lubricant. This requirement is confirmed by the fact that, in most cases, compressor manufacturers use a lubricant qualification procedure which is based on tribological results obtained in laboratories. Test on real compressors are only implemented after lubricants have succeeded in simple mechanical tests. As simple mechanical tests are usually extremely severe, lubricants have to contain anti-wear or extreme pressure additives to obtain good results.

2.2. Test procedure

The procedure presented here was developed by considering the critical lubrication zones in a small piston type compressor, i.e. the connecting rod bearings and the piston-liner contact area. In the connecting rod bearings, the crankshaft and the piston pin are made either from steel or cast iron and the antagonistic metal is generally an aluminium alloy or a copper-based alloy (shell bearing). In small compressors, in which shaft are not usually fitted with shell bearings, there is a steel-aluminium alloy contact type which is more difficult to lubricate than the steel-copper alloy contact type. In the gas compression zone [piston-liner], the metals that are in contact are generally cast iron or steel/steel.

The bearing which is most difficult to lubricate is the small-end bearing due to the oscillation movement which prevents a continuous oil film from forming between the components. To simulate this type of friction, an automated PLINT-CAMERON alternative tribometer was selected [fig.3]. An aluminium alloy sample moves over a steel flat. The conditions of contact pressure, temperature and average sliding rate are close to reality (100 - 200 kg/cm^2 = 10 - 20 MPa, 120° C, 30 mm/s). As the tribometer is equipped with instruments, it can measure continuously the friction coefficient and wear and it is also possible to detect the presence (or not) of a friction-resistant film by the instantaneous measurement of the electrical resistance of the contact.

In every machine, some instabilities may appear. For example, in the case of shaft bearings, the shaft may be misaligned with its housing during a very short time. In the same way, pistons do not move in a perfectly rectilinear manner inside cylinders [fig.4]. This means that, locally, extremely high contact pressures are generated. Theoretical calculations of these elastic deformations (Hertz theorie) produce values in the order of 1 to 2 GPa [10000 - 20000 kg/cm^2]. This type of phenomenon occurs, for example, at top dead centre. To simulate these phenomena, a rapid high temperature wear test was selected using a four-ball machine.

Depending on the load applied, the wear diameter is measured after a ten minute test at 1200 rpm and 120° C. The table of figure 5 summarises the mechanical test conditions for these lubricants.

3. APPLICATION OF THE TEST PROCEDURE

3.1. Results

The procedure described above was applied to formulation, which exist or which are under development, and correlated in parallel with tests on real compressors. The procedure then enabled the rapid development of an effective anti-wear (AW) phosphorated additive. Today a range of grades ISO 22 to ISO 100 lubricants have been formulated to meet market requirements. We only present here the results concerning ISO 32 grade. The table in figure 6 summarises the results of the tests, executed using simulators and on real compressors. It may seem an odd idea to compare an ISO 68 mineral oil with synthetic mPOEs ISO 32 lubricants. However, at the working temperature of the compressor (110 - 120° C near the valves), the viscosities of ISO 68 mineral oil and mPOEs ISO 32 synthetic oil are approximately the same (i.e. 4 - 5 cSt), which is not the case at 40° C (temperature at which viscosity grades are defined). This is because the viscosity indices for mPOEs (120 - 130) are larger than those of mineral oils of the same ISO grade (40 -50).

Firstly, it should be noted that the results on products without additives reflect the published literature. The PAGs, as well as the mPOEs, do not achieve the same anti-wear levels as conventional mineral oils. We also observed that our tests on the simulator reflect the tests carried out simultaneously or a posteriori on real compressors - which confirms our choice.

This table also shows that it would be dangerous to use only one friction test. For example, PAGs give satisfactory results in four-ball machines whereas they are catastrophic in another tribological field (PLINT Aluminium/Steel). Furthermore, on the FALEX machine, mPOEs without additives would be at the same level as mineral oils, whereas, in operation and for other friction tests, this is not true. However, anti-wear mPOEs with additives have excellent performance levels in all simulations - levels which are higher than those of mineral oils. This result is confirmed by a test on a real compressor on which no wear at all was observed.

All the preceding results illustrate the fact that the interpretation of friction tests on simulators is sensitive and risky. In fact, it is always necessary to obtain additional tests enabling each product to be analysed through a large spectrum of tribological conditions.

3.2. The friction film

The detection of the friction film on the PLINT-CAMERON tribometer should be highlighted. In fact, figure 7 compares recordings of the contact resistance obtained for each type of lubricant and for the PLINT aluminium-steel test. It is clear that total wear recorded at the end of the test is virtually conditioned by the build-up of a stable thick film. The photographs shown in figure 8 display the surfaces in contact obtained after the test with mPOE alone and mPOE with anti-wear additives. The surface obtained with anti-wear additives appears to be much smoother and even. It appears to be coated in a regular way with a layer of products derived from the friction.

These solid films have been studied in depth [12, 13]. They are usually phosphor or sulphur based amorphous films with a normal thickness of approximately 1000 angström (0.1 microns). They adhere to surfaces in contact and greatly reduce friction between metal surfaces as their shear is extremely easy.

Some rapid analysis, using a scanning electron microscope (SEM) fitted with an X-ray emission analyser, were implemented on the friction surfaces obtained after tests on the PLINT machine [fig.9]. As published, this friction film contains quite significant quantities of phosphate.

Identical analyses carried out on wear particles obtained during the test on the PLINT machine with mineral oil reveals their composition. Basically, these particles contain aluminium, silicon and some iron picked up from the steel flat. Curiously, these particles are coated with sulphur. This element probably originates in the mineral base oil, where it is always present in low quantities (a very low quantity of sulphur is not able to corrode [copper alloys...]). From the results of these analyses, it would appear that sulphur reacts quite strongly with newly generated and extremely reactive surfaces such as wear particles, for example.

Additional analyses carried out on the friction surface of the balls, after four-ball tests with mineral oil, have also revealed traces of sulphur. This element which has always been known to be a good EP agent, is therefore one of the components of the friction film for the four-ball test. This means that by comparing the results from the analysis of PLINT and four-ball tests, it is possible to observe that, depending on test conditions, different elements react with the surfaces to form an anti-wear film. Sulphur acts in higher contact pressure areas than phosphorus. This result is one item of conventional formulation data. LAW and ROWE [14] give similar results for gearbox lubricants with phosphorus-sulphur additives. They observed that the greater the reactivity of the additives with surfaces, the greater the fretting wear, that was measured on an alternative tribometer ; conversely a decrease in wear is observed on the four-ball machine (continuous motion).

These examples show the need to possess a range of tests scanning a large range of tribological conditions so as to be able to measure the response of products, as additives react differently depending on test conditions.

4. CONCLUSION

Mechanical tests on lubricant are a major part of formulation. A major spectrum of friction tests on simulators is essential to enable "decomposition" of friction. A screening test close to true operating conditions would always be welcome but the test procedure should remain simple, efficient and rapid.

The test procedure developed by the ELF Research Center for the selection of lubricants used with HFC-134a refrigerant fluid is interesting. It covers a wide range of tribological conditions and enables, for example, the determination of specific friction conditions for which the various elements of an anti-wear formulation act. A range of anti-wear lubricants has been developed using these tests. The mPOE with anti-wear additive/ HCF 134a pair is an excellent replacement for mineral oil/CFC 12.

We discovered that a range of oils without additives can sometimes be sufficient depending on the technology used in the engineering design phase of the compressor. It would therefore appear to be interesting to consider lubricants as a component at the design phase and not as a product which has to be fitted to the final design.

REFERENCES

1 G.D. SHORT, "Synthetic lubricants and their refrigeration applications", LUBRICATION ENGINEERING, Journal of STLE, vol. 46, 4, p. 239 - 247, April 1990.

2 J. AYEL, D. FERRET, "Machines d'essais mécaniques des lubrifiants", Institut Français du Pétrole, ENSPM Documents, January 1990.

3 R.S. MONTGOMERY, "Chemical effects on wear in the lubrication of aluminium", WEAR 8, 1965, p. 289 - 302.

4 L.E. St PIERRE, R.S. OWENS, R.V. KLINT, "Chemical effects in the boundary lubrication of aluminium", WEAR 9, 1966, p. 160 - 168.

5 R.S. MONTGOMERY, L.H. GARRETT, "An electron-microscopic study of aluminium wear particles formed during sliding in the presence of polyglycols", WEAR 10, 1967, p. 310 - 312.

6 S. KITAICHI, S. SATO, R. ISHIDOYA, T. MACHIDA, "Tribological analysis of metal interface reactions in lubricant oil/CFC 12 and HFC 134a system", Proceedings of the 1990 USNC/IIR, PURDUE Refrigeration Conference, p. 153 - 162.

7 P. BRUSER, M. SMOLONG, "Studies in the wear of aluminium alloys and bronze alloys when lubricated with polyglycols", TRIBOLOGIE Antriebstechnik 27 (1988), n° 2, p. 53 - 56.

8 P. SANVI, N. GENET, F. ESPINOUX, G. BARDY, "Lubrication for HFC 134a compressors in home appliances", proceedings of the BALTIMORE internationale Conference on CFC and Halons Substitutes, december 1991.

9 S. KOMATSUZAKI, T. TOMOBE, Y. HON-MA, "Additive effects on lubricity and thermal stability of refrigerator oils", LUBRICATION ENGINEERING, Journal of ASLE, Volume 43, 1, p. 31 - 36, january 1987.

10 S. KOMATSUZAKI, Y. HOMMA, "Antiseizure and antiwear properties of lubricating oils under refrigerant gas environments", LUBRICATION ENGINEERING, Journal of STLE, Volume 47, 3, p. 193 - 198, March 1991.

11 S. KOMATSUZAKI, Y. HOMMA, K. KAWASHIMA, Y. ITOH, "Polyalkylene glycol as lubricant for HFC - 134a Compressors", LUBRICATION ENGINEERING, Journal of STLE, Volume 47, 12, p. 1018 - 1025, december 1991.

12 J.M. GEORGES, J.M. MARTIN, T. MATHIA, Ph. KAPSA, G. MEILLE, H. MONTES, "Mechanism of boundary lubrication with zinc dithiophosphate" Wear, vol. 53, 1, p. 9 - 34, 1979.

13 "Superficial physicochemical transformations and transfer films", vol. III, § 5-4, proceedings of the 4th EUROPEAN TRIBOLOGY CONGRESS, EUROTRIB 85, ECOLE CENTRALE DE LYON, ECULLY, FRANCE, septembre 1985.

14 D.A. LAW, C.N. ROWE, "Fretting wear with powertrain lubricants", LUBRICATION ENGINEERING, Journal of STLE, volume 43, 8, p. 616 - 622, August 1987.

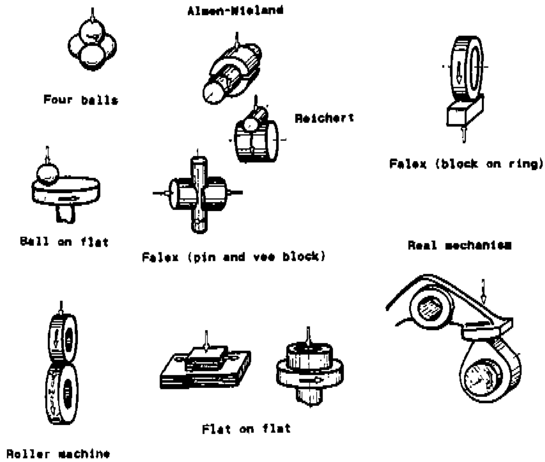
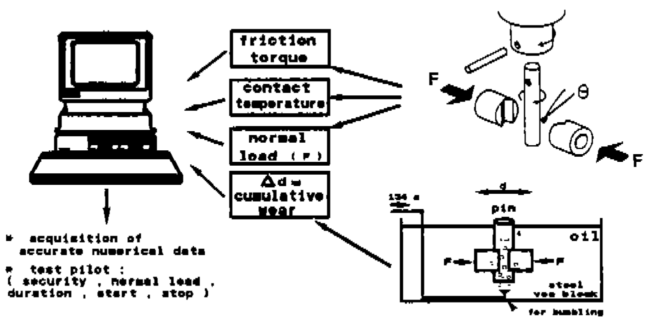


Fig.1 : Usual tribometers for testing lubricants



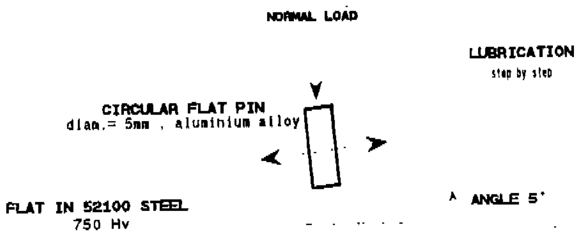
Total cumulative wear Δd (microns)	Notation
0 to 50	1
50 to 100	2
100 to 150	3
150 to 300	4
> 300	5

Wear notation in function of measurement

OIL \ TEST	Normal	Bubbling
* POE ISO 22	2.5	3
* POE ISO 32	2	2
* POE ISO 46	1.3	1
* POE ISO 68	1	1
* POE ISO 100	1	1

Mean of two tests (minimum)

Fig 2 : Influence of HFC-134a bubbling on aluminium (2024T4) / steel friction (automated FALEX pin and vee block)



ALTERNATIVE MOTION : frequency : 0.1 to 50 Hz
amplitude 1 to 15 mm

NORMAL LOAD : 0 to 250 N

TEMPERATURE : 20 to 400°C

Measurements during the test :
* friction coefficient
* cumulative wear
* electrical resistance of contact
(detection of a friction film)

Fig 3 : Plint - Cameron test .

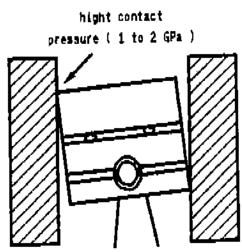


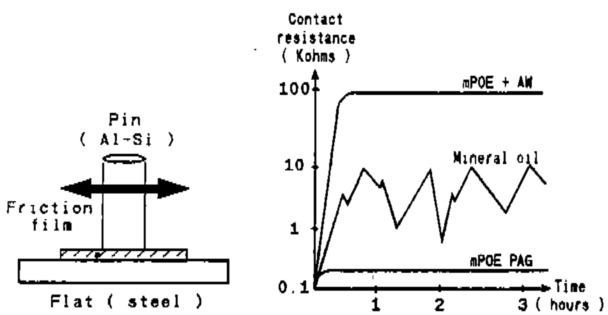
Fig 4 : Piston - liner contact .

	Plint (Al-Si / steel)	Falex (Al-Si / steel)	Falex (2024T4 / steel)	4 balls 20 (daN)	4 balls 40 (daN)	4 balls 60 (daN)
Contact pressure (MPa)	12	375	300	1670	2340	2700
Oil temperature (°C)	120	50 - 80 (near the contact)		120		
Contact temperature estimated (°C)	120	> 100		> 200		
Mean sliding Speed (cm/s)	30	100		460		
Lubrication mode	Fresh oil Step by step	Oil bath with or without bubbling		Oil bath		

Fig 5 : Test conditions .

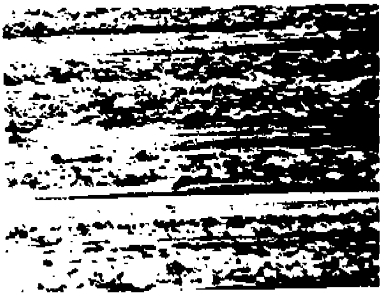
Test / Oil	Viscosity (Cst) 40°C	100°C	Wear scar diameter (mm) 4 balls 20 (daN)	40 (daN)	60 (daN)	Falex test (Al-Si pin and steel vee block) Test load : 150 Lbs Wear (microns)	Plint test Wear (microns)	friction film	Compressor 1 piston 450 hours high-pressure
MINERAL OIL ISO 68	69.3	7.3	0.44	0.83	1.76	79.2	24	+	+ CFC 12 : no wear
P A G ISO 32	32.5	7.3	0.39	0.52	0.68	9.1	162	- -	——
m POE ISO 32	32.6	5.9	0.52	0.62	2.00	20.0	248	- -	+ 134 A : important wear on piston and connecting rod
m POE + AW ISO 32	32.6	5.9	0.30	0.42	0.59	12.3	2	+ +	+ 134 A : no wear

Fig 6 : General results on simulators .

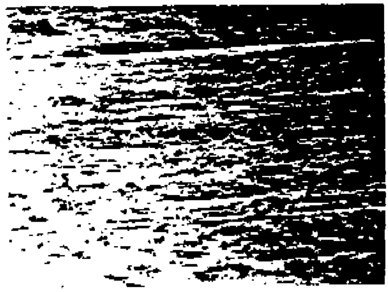


	PLINT TEST Cumulative wear (microns)
Mineral oil ISO 68	24
m POE ISO 32	248
PAG ISO 32	162
m POE + AW ISO 32	2

Fig 7 : Friction film , detection and correlation with cumulative wear obtained after PLINT test .



m POE ISO32



m POE ISO32 + AW

magnification 500

1 cm = 20 microns

⟷ : sliding direction

Fig 8 : Scanning electron microscope
(Observation of worn surfaces on steel flats
after PLINT test .)

		PLINT - CAMERON				4-BALLS
		m POE (ISO 32)		Mineral oil (ISO 68)		Mineral oil (ISO 68)
		normal	A W	wear track	wear particules	wear track
flat steel	Fe	93.1	94.5	91.0	1.8	97.2
flat steel	Cr	1.3	1.4	1.4	-	1.5
flat steel	Mn	0.7	0.6	0.6	-	0.6
pin alloy	Si	0.7	0.3	0.6	17.8	0.3
pin alloy	Al	4.2	2.1	6.4	76.0	0.3
	P	-	1.1	-	-	-
	S	-	-	-	4.4	0.1

Fig 9 : X-ray analyses on wear tracks
after PLINT and 4-balls tests .
(contents in weight %)
(we can't detect the light elements : C,N,O,...Na)