Lifetime Lubricated Engines using Triboreactive Materials

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ABSTRACT

By means of an analysis of future trends in engine oil specifications with the associated consequences for the functional properties performed by base oils and individual additives, the need and potential application of alternative fluids and triboactive materials or lubricious oxides will be displayed.

Oxidation resistance and low volatility represent key elements to assure long drains or lifetime lubrication in order to minimize or avoid manual or automatic top-ups.

The intrinsic properties of base oils and the additive package define the oxidation resistance and the related oxidative volatility. The overall engine oil consumption is also related to design (clearances, thermal stability of geometries, seals,....) and bore surface finishing and are not regarded here.

Lubricious oxides or triboactive materials and/or polar base oils substitute the EP and AW properties realized by the additives, thus enabling long drains and responding to "eco-tox" or "bio-no-tox" requirements as well as restrictions from the "chemical box".

1. DEVELOPMENT OF DRAINS

The drain intervals in passenger cars have increased in the last 30 years from ~3,000-5,000 km up to 50,000 km. The associated reduction in oil consumption and drained oil volume was compensated by much more higher prices for the formulations and a steady-state increase of the total vehicle fleet reaching today ~65% of the population in G7 countries. A drain of 50,000 km already can be interpreted as "lifetime" fill, since for many passenger car customers it means 5 years and more, but the OEMs wording is: "50,000 km or 2 years".

It is further important to now for the chemical and technical evaluation of the figure of 50.000 km, if top-ups are foreseen are not.

A drain of 50,000 km per se not defines for passenger cars a technical limit as it has been demonstrated by the RENAULT "ELLYPSE" demonstrator [1,2] seeking for a drain between 70,000 to 100,000 km.

Fleet operators, customers and end users request a life-time lubrication as perfect solution for their lube problems, so that the tribosystem or lube-site is for them unnoticeable. Such targets will require new type of formulations as well as alternative base fluids. Today intense work is for instance done with lubricants blended at the lowest tribological effective concentration of EP-/AW-additives (Phosphorus and sulfur!) possible and ash (Detergent capacity).

It is easy to recognize, that the transformation from fixed drain intervals via personalized drains to a life-time lubrication [3] cannot be provided from the lubricant chemistry alone. Here should be kept in mind,

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that the system approach describe a tribosystem. The strategic goal of the life-time lubrication (with or with out top-up?) can only be reached, if the design is material suited and the materials interact useful with the lubricant and not as in the past, that the lubricants solve afterwards unsuitable materials choices and design concepts.

In order to extend the oil-change intervals, methods must be employed to curtail the oil aging. Conventionally this is achieved by reducing the input of acidic products in the oil, minimizing the mechanical, thermal and oxidative stress on the lubrication fluid and increasing the aging resistance of the oil.

It has to be admitted, that the additional cost related to better performing lubricants are in any case inferior to design changes.The lubricant manufacturers have up to now kindly supplied and developed for such problems products and we all know the examples, in which lubricants have make afterwards materials and design concepts operational.

Table 1: Summary of commercial biodegradable engine oils

Product	$\eta_{40°C}$ **[mm²/s]**	$\eta_{100°C}$ **[mm²/s]**	**Visco-sity Index**	**Pour Point [°C]**	**HTHS [mPas]**	**NOACK [%]**	**Algae [mg/l]**	**Fish [mg/l]**	**OECD 301x [%]**
Titan GT1 0W20	46,5	8,9	160	-45	2,95	6	>1,000	>1,000	60
AMG Bio 10W30	47,8	9,53	193	-30				7,320	90
Greentec LS5W30	59,3	11,5	187	-39	4,0	5,5			68
BP Vistra 7000	86,9	14,0	167	-43	4,1	10,7	>50	>1,000	~80*
MOTUL 300V	69	12	169	-36					
Biomot LD 5W40	90,58	13,9	186	-48	4,68	7			
ELF HTX 822	111	17,4	184	-36	5,3	5			>60*

* CEC

2. INTRODUCTION OF ALTERNATIVE ENGINE OILS

Engine oils based on esters or polyglycols were only put in the past into operation as hydrocarbon-based ones didn't meet the more stringent specifications, as it could be seen in the second world war :

a. the US Air Force [4,5] used in P-38, P-47, P-51 und B-25 polyglycols (η_{100C} ~ 18.5 mm²/s) for soot deposits in the oil cooler and pourpoint reasons and

b. the Luftwaffe [6,7] used in all engines a blend of ester/ethylene oil (η_{100C} ~ 6.2 mm²/s) for resource, soot and pourpoint reasons

as well as

in the period of developments on "adiabatic engines" requiring polyolester oils with a thermal stability exceeding 300°C:

a. Adiabatics, Inc.	Polyolester [8,9] from Stauffer Chemicals and
b. ISUZU Co., Ltd.	Polyolester [10] from SHOWA SHELL Sekiyo Ltd,

using proven additive packages [11] from jet turbine oils, which are formulated to withstand 204-218°C.

These examples have always pushed the technical development of the hydrocarbon-based engine oils, so they could re-winning the previously lost business and market.

In the nineties and recently (see Table 1), some biodegradable engine oils based on esters or blends of esters with hydrocarbons appeared with no or a low market penetration. Especially the Titan GT 1 is the first bio-no-tox engine oils with an ACEA rating and conforms with the EC/1999/45 and some OEM specifications.

3. FUTURE TRENDS

The competition between hydrocarbons and alternative base oils is not yet technologically decided in favor for hydrocarbons or esters or polyglycols. In the past, the beneficial contribution of the additive technology can be illuminated by an increasing ability to support thermal loads. From the end of the sixties to now, the specific loading [12] had increased from ~35,000 kW/km/l² to 440,000 W/km/l² (kW power/km drain/liter of displacement), which will further increase by heavily supercharged diesel passenger car engines reaching 80 kW/l and more.

The following will illuminate some trends and the chemical key elements for long drains.

3.1 Chemical Box

The introduction of a "chemical box" will struggle the chemical freedom of formulations. The chemical box limits phosphorus (~800 ppm [P]), sulfur (< 0,3 wt.-% [S]), ash (<1,0 wt.-%) and/or volatility (<10% or < 13%) as general criteria. Additionally, the fragmentation of standardized oil specifications between Europe, Asia and US continues as wells as the diversification in OEM specs spreads more and more since they released engine designs requiring specific oil formulations.

Phosphorus and sulfur are direct related to the anti wear (AW) and extreme pressure (EP) properties.

3.2 Environmental Acceptable Lubricants

As displayed by the RENAULT demonstrator ELLYPSE and the FORD Model U, additional requirements may be in the future demanded, like

a. biodegradability and non-toxicity and/or

b. a content of renewables.

Figure 1 : FORD Model U and RENAULT „ELLYPSE“ using bio-no-tox or biobased engine oils

Some OEMs, like DaimlerChrysler with US 6,194,359 and RENAULT with FR 2 792 325 and FR 2 792 326, have begun to question, if the hydrocarbon technologies as well established products are still robust enough to fulfill all of these requirements or they may look after ester or polyglycol base oils with more intrinsic properties resulting in a lower treat level, which grant a durable application for the next decades with respect to the EC directive [13] 1999/45/EC regarding the symbol “N” labeling of preparations and US-DA [14] and US-EPA [15] policies.

Pure hydrocarbons it self can be US-FDA proof. The additive packages determine the eco-tox and/or bio-no-tox properties of hydrocarbon based formulation. It is obvious to substitute critical additives by others or new functional concepts.

3.3 Retention of Properties

The retention of all functional engine oil properties is the key issue to be solved for long drains or life-time lubrication beside oil consumption. They include the film forming properties as defined by viscosity “η” and pressure-viscosity coefficient “α” [16]. The oil aging according to Sequence VIB (ASTM D6202-02) for the fuel-efficiency covers approximately 6.500-8.000 km of driving.

High-performance additive packages define today the functional level of engine oils more than the hydrocarbon base oils, even both are important. Each additive owns an individual use time after which the functional active additive is no longer in the formulation, which is in major part first related to the boiling point or vapor pressure of the chemical.

The retention of tribological properties must be extended to greater than 50.000 km rising the question, if hydrocarbon base oils are suited for this?

Environmental agencies favor additional the fuel-economy retention as one environmental criteria.

3.3.1 EP-/AW Properties

The concentration of ZndttP [17] decreases linear by operation time and even the „new“ molybdenum-dithiodialkyl-phosphates and –carbamates [18,19,20] (Mo-dtP/dtc acting also as friction modifier) are consumed after ca. 5.000 km due to their low boiling temperature or because they participate to the oxidation protection of oils.

It would be desirable, the guarantee an AW/EP-retention by means of triboactive materials.

Regarding anti-wear resistance and extreme pressure properties as well as having the „chemical box“ in mind, alternative additives have to be identified [21] or triboactive materials to be applied for long-drains. Also polar base oil molecules, like polyglycols and some esters may act as substitute with the advantages, that the base oil with an “unlimited” concentration act now as AW/EP-additive and is quasi inconsumable.

It is also possible by means of other designs to skip the EP-requirement for 1,000-2,000 MPa of Hertzian contact pressures. This can be done by dry camless systems e.g. electromagnetic valve actuator. The remaining tribosystems of the crank shaft or the piston group operate below 250 MPa, thus requiring now EP-additives.

3.3.2 Viscosity improvers

Engine oils based on hydrocarbons use polymeric improvers for the viscosity index for multi-grade SAE rating. These VI improvers tend to shear and preferably to oxidize. They also tend to form deposits on the intake valves in direct injecting engines. PAO 6 to PAO 8 base oils not exceed VIs of 145. The question arises, if the VI improvers can be substituted by the intrinsically higher VI indices of saturated esters and polyglycols, thus allowing an improved viscosity retention?, because both exhibit VI indices above 150 and can reach 200 and more

3.3.3 Oxidation resistance

The ICOT test [22] using 27 ppm iron acetylacetonate as catalysor defines the oxidation resistance by three properties:

a. the viscosity increase (Δη <100%),

b. the increase in TAN and

c. the evaporation loss due to oxidation.

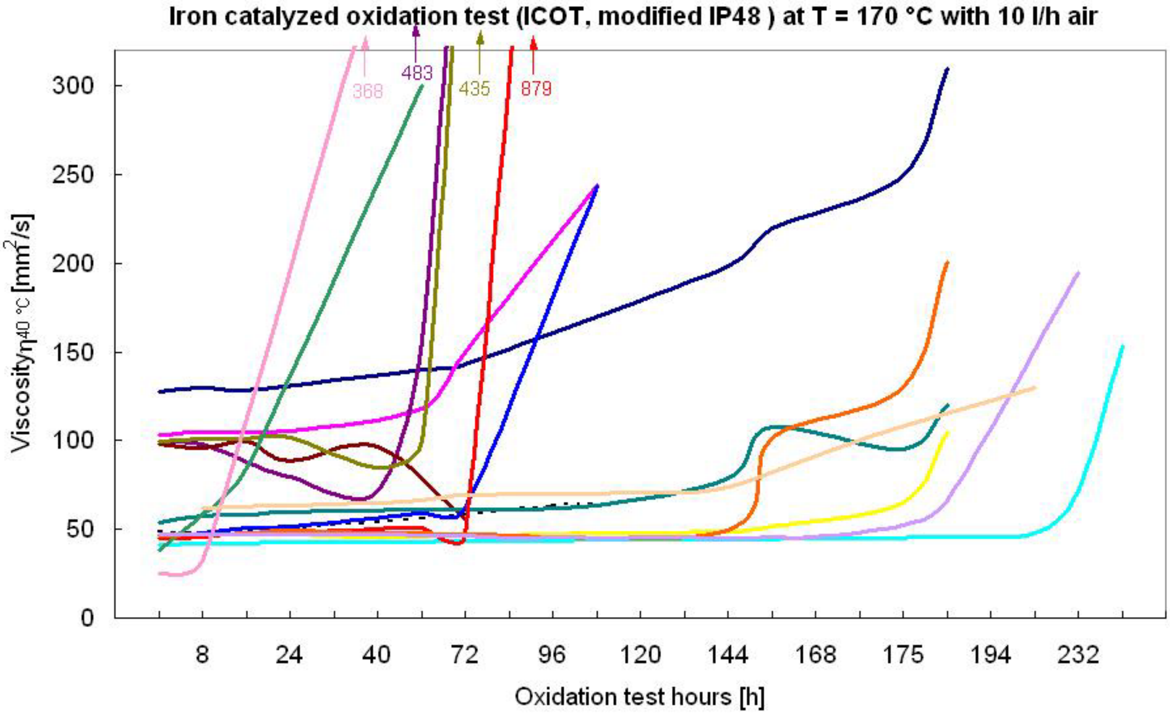

Figure 2 : Viscosity increase versus oxidation test time

The ICOT test indicates only the oxidative resistance and gives no hint about the AW/EP-retention of a formulation.

The Figure 2 displays the viscosity increase versus test time in the ICOT test adopted for engine oils (Base oils and ester, polyglycol as well as hydrocarbon formulations). For actual factory fill oils, one hour correspond to ~220-240 km of driving, which has to be validated for esters and polyglycols. The formulations with an ICOT life time between 150 and 200 hours respond additionally to “bio-no-tox” criteria, but are actual difficult to match with ICOT life times above >200 hours.

Jet oils (MIL-PRF-23699) have proven additive packages to prevent high-temperature oxidation. Ester and hydrocarbon based jet oil according to MIL-PRF-236999 are on sale. Mainly low viscosity tetraesters (pentaerythrit with C_5-C_7) are used as base oils. The ecotoxicological properties of these additives it self (see Table 2) times their treat rates conduct to formulations, even when using biodegradable esters, which require the labeling with symbol “N” and with other risk phrases.

The Figure 2 and the turbine oils illuminate, that the oxidation resistance of lubricants can be extended by the additives or intrinsic base oil properties to nearly lifetime operation, but this extension is today questionable with “bio-no-tox” criteria. It was shown with prototype engine oils, that oxidation resistance can be associated with low volatility versus time.

The question of oxidation resistance remain to the intrinsic behavior of base oil and additives and can not be transferred to materials.

3.3.4 Volatility

The evaporation of the additives and the base oils define the volatility of the engine oils and thus are one factor of the oil consumption [23]. The NOACK volatilities of base oils with 32 < ISO VG < 68 can be summarized as follows:

PAO 6-8	6,5-8,0%
Saturated, esters	3-6 %
Polyglycols	3-6 %

Table 2 : Eco-toxicological properties of jet oil additives

Substances	**WGK**	**Oral toxicity LD$_{50}$ [mg/kg]**	**Fish toxicity LC$_{50}$ [mg/l]**	**Algae toxicity EC$_{50}$ [mg/l]**	**Daphnia toxicity EC$_{50}$ [mg/l]**	**OECD 301x [%]**
EC/45/1999	-	>2.000	>100	>100	>100	≥60
1,2,3 Benzotriazol [<0,2%]	2	560	>100 LC$_0$	231	63-91	83 (302B)
Phenyl-α-Naphtylamine [1-5%]	2	>2.000	<1		<1	0
Benzenamine [15721-78-5, <2%]	3					
Tricresylphosphate [1330-78-5, 1-5%]	2	>2.000	4		5,6	80
Alkylated Diphenylamine [101-67-7, <1%]	2	>7.940	>1.000	>100	7,7	
Tri-isopropylated phenylphosphate [68937-41-7, <3%]	2	>5.000	1,6		2,4	

WGK= Water Hazard Class; 1= low hazard to waters; 2= hazard to water; 3= severe hazard to waters

The latest fully-synthetic SAE 0/5W-20/30 engine oils with NOACK (1 h) volatilities of greater 8% display the contribution of the additives, which increases by prolonging the NOACK test time to 3 h.

It would therefore be desirable, to be able to formulate low volatility oils by avoiding volatile additives and substituting their functional properties into the intrinsic ones of the base fluid, especially of esters and polyglycols.

3.3.5 Oil Consumption

In order to avoid manual or automatic top-ups in a long-drain or lifetime concepts, the volatile losses of base oil and additives, composed of

a. physical evaporation (NOACK at 250°C for 1h or 3h) and

b. oxidation fragments

have to be minimized by maximizing the oxidation stability and

c. the overall oil consumption

has to be reduced by proper engine design and manufacturing regarding valve shaft and turbocharger leakages or oil lubricated fuel pumps as well as to the liner surface topography [25,24] and dimensional stability (also thermal induced distortion) of the liner and piston group.

A passenger sedan with an oil fill volume of 5 liters can accept over 100.000 km an oil consumption of max. 2 liters, thus requiring a specific oil consumption of 0.02 liters/1,000 km, which is for away from actual state-of-the-art, especially, when liner wear took place. This figure is for today's engine challenging for the production line, even OEMs [25,26] have displayed this feasibility recently, because they intend to reduce the oil contribution to exhaust emissions and loading of particulate filter by oil ash.

4. OIL-FREE ENGINE

The demonstrators realized mainly by FORD [27,28], Cummins/ADIABATICS [29], DLR [30], RENAULT [31] and ISUZU [32] are acknowledge and the tribology is reviewed in [3].

The expression "oil-free" can imply several possible, different technical solutions:

a. Oil-free for the customer (i.e. life-time fill),

b. Oil-free operation (i.e. dry or unlubricated)

c. No use of a circulating pump system or

d. use of a liquid lubricant other than a hydrocarbon based engine oil.

One example for the option d.) is the "zero emission engine" [[33]] using steam in a Rankine cycle lubed by a water/polyglycol blend as crank case oil.

An unlubricated internal combustion engine is of interest, because it will be more compact in its basic construction (fewer parts), maintenance-free and will avoid some environmental problems related to oil leakage, oil burning (exhaust emissions) and drain (waste disposal, water and soil contamination,…).

It was shown for the piston ring, that candidate materials for dry running must present wear rates much smaller than 5 10^{-8} mm^3/Nm (independent from temperature and sliding speed!), in order to compete with liquid lubricated ones [3,[34]], where by the PxV-value (Pressure times sliding speed) must match those from hydrodynamic lubricated ones.

Another important object is the removal of the wear particle, which is done by the liquid and the filter. An unlubricated four cylinder (2,0 liter) engine will produce during 2,000 h roughly 2,000 mm^3 of wear debris/particles [34] (piston group, valve guide and cam).

The enormous improvement of the internal combustion engine is due mainly to the many brilliant and innovative inventions throughout the last 115 years. The lubrication has remained in principle unchanged. Liquid lubricants are essential in tribosystems

-to separate the mating surfaces for low friction and wear,

-to remove wear particles,

-to cool the surface and components and

-to avoid adhesive wear (mainly for metals)

In consequence, a liquid lubricant seems to be indispensable for low friction and fuel efficiency, heat transfer and removal of wear particles, but the wear resistance of the tribosystems may be achieved with triboactive materials or lubricious oxides. The oil formulation will thus not require AW-/EP-additives. The use of solid lubricants for the tribosystems didn´t succeed [35,36].

All of these considerations lead to the work of DaimlerBenz in the nineties on water-cooled, lifetime lubricated engines [37] using

-alternative liquid lubricants in a strategic lubrication concept [38,39]

and

-highly wear resistant sliding couples [40].

This joint materials and fluid based approach in a water cooled engines was recently continued by RENAULT [1,2,41,42] in the direction of using “bio-no-tox” oils.

In contrast to the area “engines with monolithic ceramics”, the OEMs reinforce today the tribological properties of components where it is needed by means of thermal spraying, even ceramic or cermet coatings.

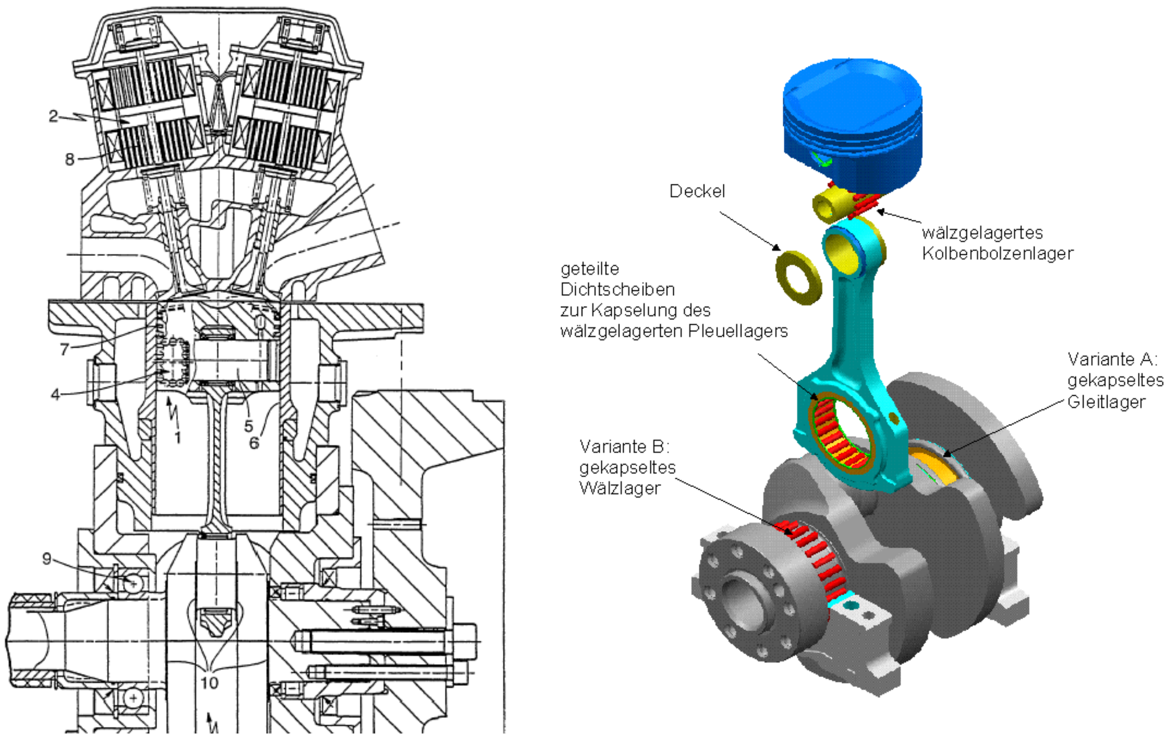

Figure 3 : „Oil-free“ or lifetime lubricated engine concept of DaimlerBenz [38,43] using carbon piston (Note: the dry electromagnetic valve actuation!)

5. TRIBOACTIVE MATERIALS/LUBRICIOUS OXIDES

A wear resistant coating is a very important consideration in mechanical design, since most failures of machine elements are a result of different wear mechanisms. Especially in the future the tribologically stressed machine elements will operate with a less amount of lubricant’s or with biologically fast degradable fluids with low additive content. Furthermore it is possible to have a “life time” lubricated machine with very large extended drain intervals or even dry sliding conditions. Therefore the tribological function of the lubricants or of some additives must be fulfilled by other lubrication mechanism or intrinsic materials properties [3]. The key problems are:

a. How to substitute the energy efficient shearing of a liquid film or monolayers between to surfaces?

b. Which alternative material based shearing mechanisms will be able to serve this function?

As pointed out earlier, no materials based concept appeared today, which showed under unlubricated conditions a coefficient of friction below 0,03 **in air** sliding up to 20 m/s in a temperature range up to 600°C [3,44]. The only one was related to the steam environment (400°C, 3 m/s) [45].

In consequence, the following is only focused on the wear resistance of sliding materials.

Lubricious oxides and triboactive materials appeared recently in scientific literature and display estimated functional properties by different approaches. There exists within the scientific community no official consensus about their meaning.

The term of "lubricious oxides" was created 1989 by Michael N. Gardos [46,47] as TiO_{2-x} as well as thematized by [48] and aim low wear with may be associated low dry coefficient of friction. The correct term for TiO_{2-x} is Magnéli-phases of titania, Ti_nO_{2n-1} with $4 \leq n \leq 9$, whereas TiO_{2-x} , with $x \leq 0{,}01$, describe "Wadsley"-defects.

The term "triboactive materials" appeared in Europe end of the nineties describing more a beneficial reaction between the surface and the lubricant or the ambient, thus indicating a more overall functional approach. So they cover any oxide, hydroxide or hydrate.

The estimated tribological benefits from these oxides attracted the attention of engine developers (For a review see [44]). The automotive industry investigate them in view of their wear resistance in combination with liquid lubrication and the aerospace industry more as wear resistant coatings under dry high-temperature friction. These efforts were focused on thermally sprayed coatings and coatings, which form by tribooxidation "lubricious oxides" or "triboreactive materials".

5.1 FORD

In contrast to previous work on ceramic engines, FORD published since 1997 some papers and patents related to understoichiometric and/or triboactive oxides [49] of the type Mey0 (Me= Ni, Fe, Cu). The defect or understoichiometry is more on the cation side for $FeO_{0,95-1,05}$, $NiO_{0,75-1,25}$, $CuO_{0,40-0,60}$ and $MoO_{2,5-3,2}$.

The benefits of these oxides, preferably deposited by means of thermal spraying, are the substitution of extreme pressure additives [19] as well as the reduction of sulfur and phosphorus containing compounds. Additionally, they reduce the friction forces on cylinder liners [50]. The tribological properties of the systems $Fe\text{-}Fe_xO$ or Ni-hex. BN are published in [51].

More suited are FeO and Fe_3O_4 in a matrix of a low alloyed steel [52] on AlSi7-10 or on cast iron. FORD seems to favor its own Fe/FeO coating and deposition process "Plasma Transfer Wire Arc" (PTWA) [53].

5.2 DaimlerChrysler AG

For life-time lubrication [43], DaimlerChrysler investigates „Lubricious Oxides" (LO) as coatings for tribosystems of internal combustion engines in order to avoid anti-wear (AW) and extreme pressure (EP) additives as well as viscosity index improvers. The LOs [40] consist of Magnéli-Phases of titanium dioxide ($\gamma\text{-}Ti_3O_5$, $Ti_{10}O_{19}$), of vanadium oxide ($\gamma\text{-}V_3O_5 \Rightarrow V_8O_{15}$) as well as of molybdenum and tungsten oxides ($W_{18}O_{49} \Rightarrow W_{40}O_{118}$), with general formula $(Ti,V)_nO_{2n-1}$ or $(Mo,W)_nO_{3n-1}$, with $3{,}4 \leq n \leq 10$, which can also be formed by means of tribooxidation.

The work [54] is focused on the phases $Ti_4O_7, \Rightarrow Ti_6O_{11}$ and TiO_2 deposited by atmospheric plasma spraying (APS) (Rotaplasma®). The thermal sprayed TiO_x-phases exhibit for ceramic a relatively low Vickers hardness HV between 8,5 and 11 GPa. As consequence, wear debris entering the lube system are in consequence less abrasive and the coatings don't require a too smooth surface or fine honing.

5.3 RENAULT SA

The metallurgy of Renault is complementary to that initiated by FORD and DaimlerChrysler and shares the strategy of "triboactive oxides" with the patent applications [41,55]:

a. Oxides with cation defects „Revêtements triboactifs à base d´oxydes métalliques présentant des défauts en cations métalliques",

$Ni_{1-y}O$, $Co_{1-y}O$, CrO_{2-x}, $FeO_{1,06-1,20}$, $Fe_{3-y}O_4$ and Mn_yO with $0,001<y<0,15$

and

b. Oxides with planar defects „Pièce mécanique de friction recouverte d´oxydes triboactifs stabilisés par des oligoéléments",

$(Ti,V)_nO_{2n-1}$ or $(Mo,W)_nO_{3n-1}$ with the «oligo elements» Ni, Al, Zr, Ni, Cr, Fe, Co, Ti, K, Mn, Nb < 3000 ppm and the mixture $Ti_{n-2}O_{2n-1}$+15% Fe_2O_3.

Especially the potential for high resistance against oxidation up to 1500°C of $Ti_{n-2}Cr_2O_{2n-1}$, with $6 \leq n \leq 9$, and the phase stability of the planar defects makes this system attractive for atmospheric and thermal spraying.

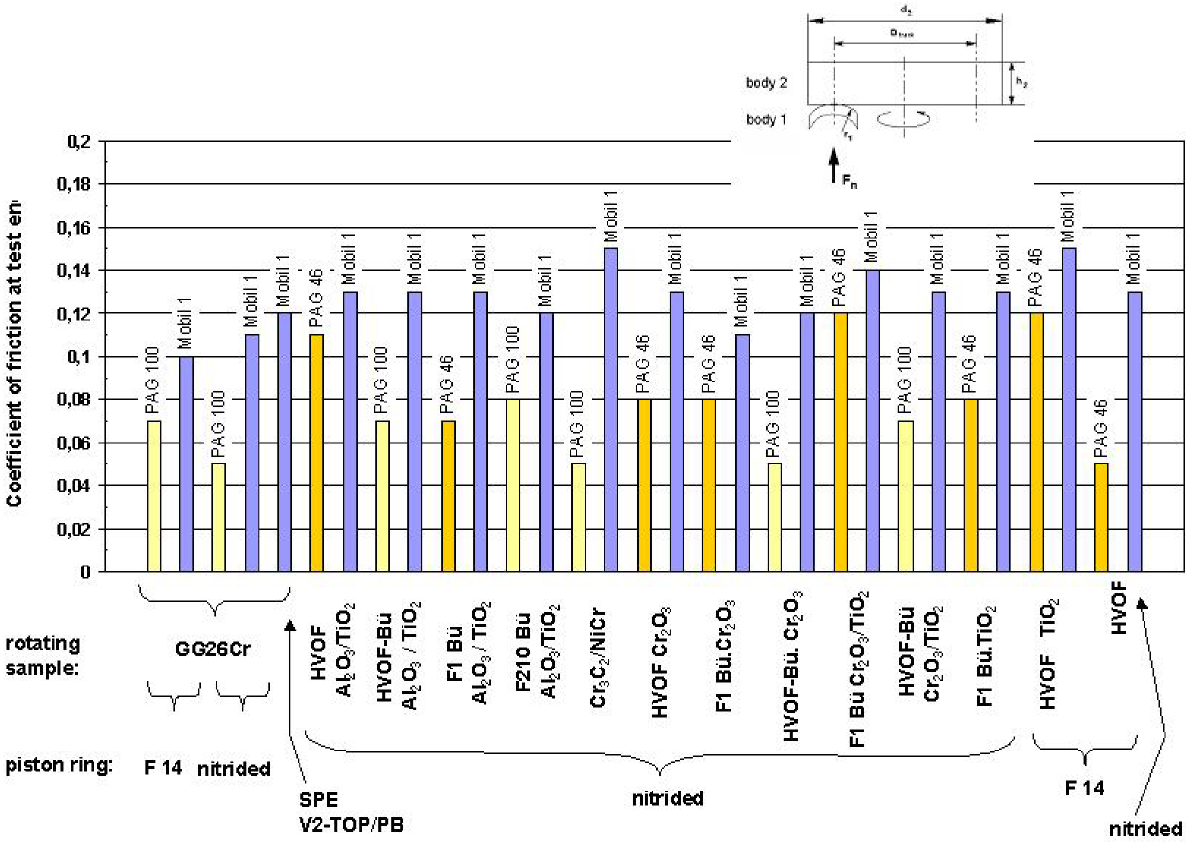

Figure 4 : Coefficients of friction under mixed/boundary lubrication of sliding couples (F_N= 50 N; v= 0,3 m/s; T= 170°C; s= 24 km) [56]

6. SOME TRIBOLOGICAL TEST RESULTS

The following results aim to give hints, whether the AW/EP- and frictional properties of additives can be substituted by materials and/or alternative base oils.

6.1 Friction Retention

The test procedure for determining the results shown in Figure 4 are presented elsewhere [57]. The ceramic coatings Cr_2O_3, Cr_2O_3/TiO_2-60/40, Cr_3C_2/NiCr-80/20, TiO_2, Al_2O_3/TiO_2-60/40 were thermally sprayed by means of APS (F1, F210) and HVOF (TopGun G). They need a peak roughness after finishing of $R_{pk} \leq 0{,}15$ µm. A grey cast iron with 3,15-3,55 wt.-% carbon (GGL26Cr, $R_{pk} \leq 0{,}6$ µm) is used as reference. It was necessary in some cases to reduce the surface finishing of the ceramic coatings to $R_{pk} <$ 0,06 µm. The "F14" and "nitrided" piston rings were supplied by FM Goetze [58] and the "SPE" (71,5(Ti,Mo)(C,N)+28,5Ni) from DANA Perfect Circle Sealed Power Europe.

(Ti,Mo)(C,N) is of interest, since on its surfaces "triboactive oxides", like Magnéli-phases of titania [59], are formed by tribooxidation.

The candidate engine oils were selected from two polyalkyleneglycols ((Diol with EO:PO = 1:1), VG46 (η_{100C} = 8,0 mm²/s; HTHS = 3,52 mPas) and VG100 (η_{100C} = 18,1 mm²/s; HTHS = 7,8 mPas)) and one factory filled MOBIL I SHC 10W-40 (η_{100C} = 14,5 mm²/s; HTHS = 4,0 mPas). The polyalkyleneglycols were formulated according to US 6,194,359, are free of polymers, Zn and Calcium, need no labeling with symbol „N", and contain only 600 ppm [P] and about 500 ppm [S].

Another advantage of polyglycols for military equipment is related to the low burning calorific values, which is roughly 60% of those known from hydrocarbons.

With MOBIL I the ceramic coatings didn't present low friction under mixed/boundary conditions with CoF of 0,1-0,15. In contrast, the polyalkykeneglycols have drawn a uniform picture of low friction, which is independent of the used liner material as ceramics and GG26Cr.

In conclusion, friction modifiers are not necessary using PAGs. A long friction retention is probably guaranted by the interaction between the polarity of the PAG base oils and the materials surfaces.

6.2 Extreme Pressure Properties

The SRV™ test method is well established in ASTM D5706, D5707 and D6425 as well as in DIN 51834, part 1 to 9. A procedure for the "Tribological Characterization of Piston Ring and Cylinder Liner Materials and Lubricants" is currently under development for validation in an OEM driven working group.

Cam systems normally don't exceed Hertzian contact pressures of 1,200 MPa with exceptions as for example the BMW Valvetronic [60] and the VW "pump injection system", which reach 2,000 MPa.

The prototype engine oils were prepared by FUCHS Petrolub, TOTAL (former ELF Oil) and Fragol in cooperation with BAM. The Hertzian contact pressures before occurrence of adhesive failure (Figure 5) of prototype oils based on 100% ester, blends of esters with hydrocarbons and polyglycols compete with high-end engine oils and overcome the limit of 2,000 MPa.

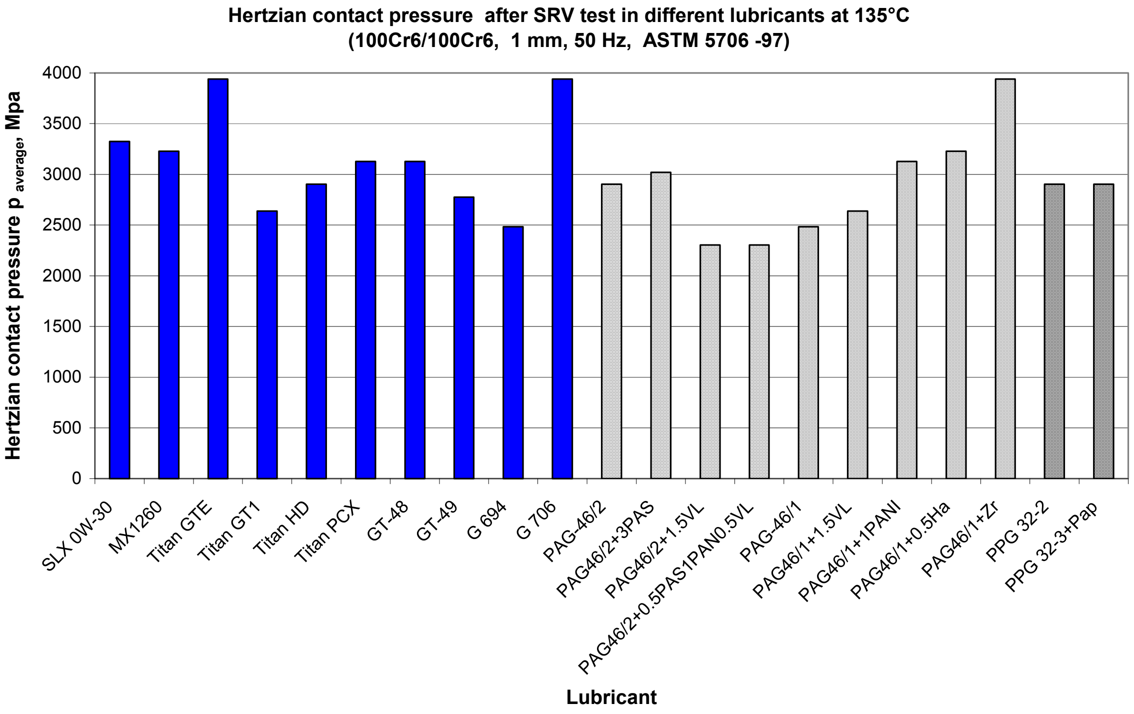

Figure 5 : Hertzian contact pressures calculated from the pass load using the SRV step load test according to ASTM D5706 (100Cr6H = AISI 52100)

6.3 Antiwear Properties

Normally, the highest contact pressures in the tribosystem “piston ring/liner” are related to the combustion pressure and depend on the shape of the mating ring surface. The anti-wear properties of the lubricants are normally predominant under mixed/ boundary lubrication. Under “oil-off” conditions, the sliding materials have to display additional anti-wear and anti-seizure properties, which are not regarded here. The Figure 6 presents the volumetric wear coefficients of ring and of liner simulating the top-dead-center using the SRV test equipment according to ASTM D6425-02.

The triboelements made of 100Cr6H (AISI 52100) exhibit under mixed/boundary lubrication with the prototype oils wear rates comparable to factory filled engine oils. The wear rates under mixed/boundary lubrication don´t depend on the HTHS viscosity. Especially the polyglycols seem to be tribologically sensitive to some antioxidation additives and/or base oil blends, which increase the wear rates. One answer to solve this effect would be the use of triboactive materials.

Figure 7 compares the wear response of piston rings coated with Ti_nO_{2n-1} and with molybdenum (MKP81A [58]; 67-77 wt.-% Mo, 0,5-2,0 wt.-% C, 16-24 wt.-% Ni, 3-7 wt.-% Cr) both sliding against a cast iron “GGL20HCN” with a carbon content of 3,65 wt.-%. For MKP81A/GGL20HCN couples the wear rates of cast iron liner material GGL20HCN depend significant on the used oils, whereas the wear rates of the cast iron liner material sliding against Ti_nO_{2n-1} coated ring are lower and additionally less sensitive to the type of oil. The Ti_nO_{2n-1} (APS) ring coating causes less wear at the GGL20HCN liner than the state-of-the-art Mo (MKP81A) coating. Overall the Ti_nO_{2n-1} ring coating displays wear rates comparable to molybdenum “MKP81A”. Figure 7 displays a potential to substitute the strategic material “molybdenum” as well as to avoid AW/EP-additives using Magnéli-phases of titania, because some oil formulations with low wear of the ring / liner system contain no AW/EP-additives.

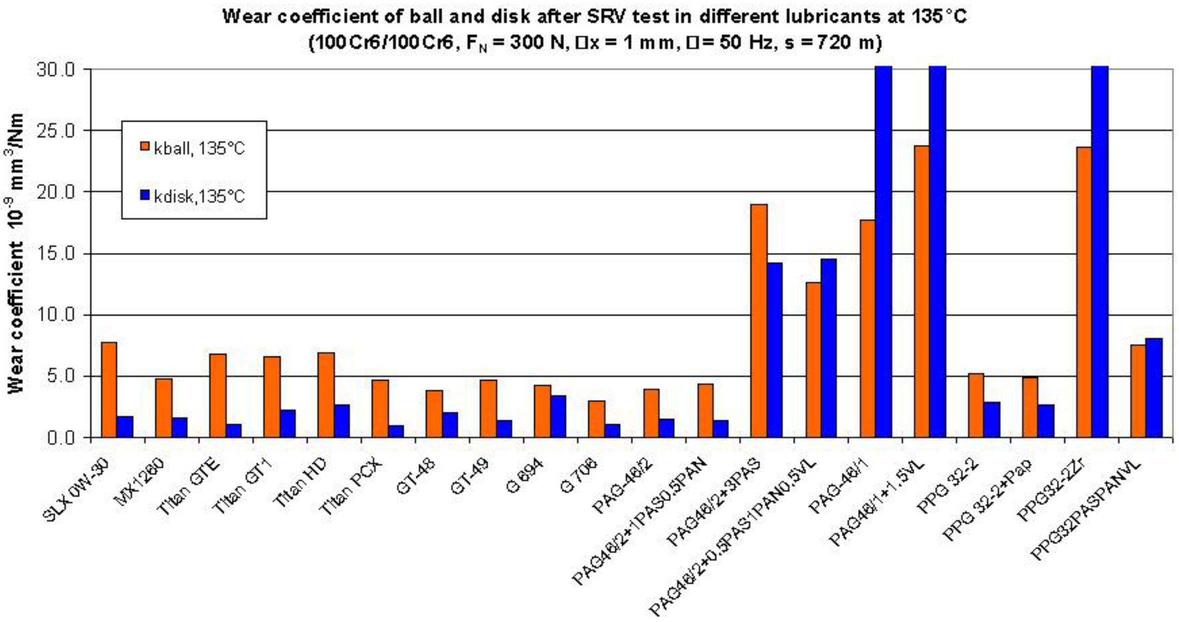

Figure 6 : Wear rates (coefficients) of ring and liner using the SRV according to ASTM D6425

To spray the TiO_2, Ti_6O_{11}, Ti_4O_7/Ti_5O_9 and Ti_3O_5 powders on AlMg alloy substrates an APS process with F210 torch was used. The surfaces were grinded and lapped to obtain C.L.A. (R_a) values below 0,1 µm.

Polyglycol PAG100 shows a better performance in terms of a significant reduced coefficient of friction. Slightly lower ring wear rates were measured with MOBIL I compared with the polyalkylenglycol PAG100. The lowest wear rate was achieved with the (Ti,Mo)(C,N)-28,5Ni piston ring in MOBIL I, which is nevertheless not so far away from wear coefficients of couples as nitrided ring sliding against Ti_nO_{2n-1} coated liner in PAG100 with wear coefficients in the order of 10^{-9} mm³/Nm. Additionally, for both GGL26Cr and Ti_nO_{2n-1} coated liners the PAG100 acts beneficial in reducing the wear rates associated with lower coefficients of frictions.

New classes of bio-no-tox lubricants as PAG 46/100 offer their potential for a significant reduction of coefficient of friction down to 0,05 under mixed/boundary conditions compared to those in the range between 0,1-0,14, measured with common factory filled engine oils. It was demonstrated by means of novel additive chemistry using hydrocarbon based oils that cof as low as 0,05 are feasible, but the retention capability of the cof has to be checked.

Figure 8 and Figure 9 summarize the coefficient of friction and wear rate of different stoichiometries of titania (TiO_x) liner coatings sliding against nitrided steel and against plasma sprayed TiMoCN/Ni piston rings under mixed/boundary conditions in Mobil 1 and in PAG100 using the test procedure described in [57]. GGL26Cr acts as reference liner material.

On the ring side, the lowest ring wear was achieved using the (Ti,Mo)(C,N)-28,5Ni ring coating sliding against GGL26Cr or Ti_nO_{2n-1} in MOBIL I, but the lowest coefficient of friction were achieved using nitrided or (Ti,Mo)(C,N)-28,5Ni rings in PAG.

The liner wear and coefficient of friction can be reduced lubricating with PAG or using the Ti,Mo)(C,N)-28,5Ni ring or Ti_nO_{2n-1} liner coating.

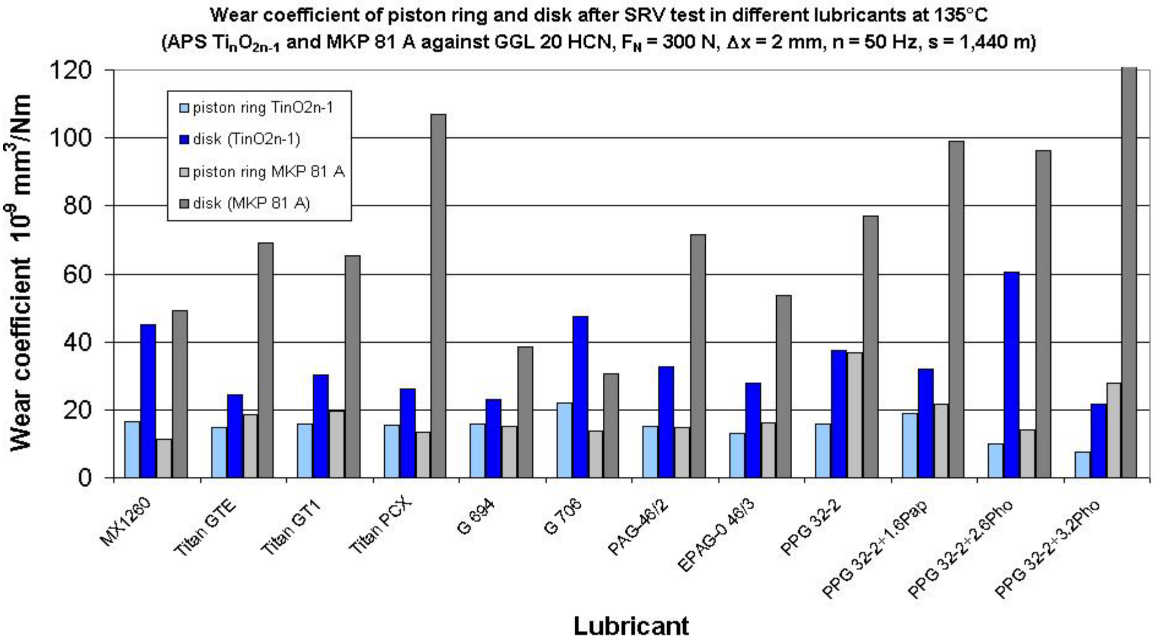

Figure 7 : Wear rates (coefficients) of liner and rings coated with APS Ti_nO_{2n-1} and APS Mo (MKP81A) using the SRV according to ASTM D6425

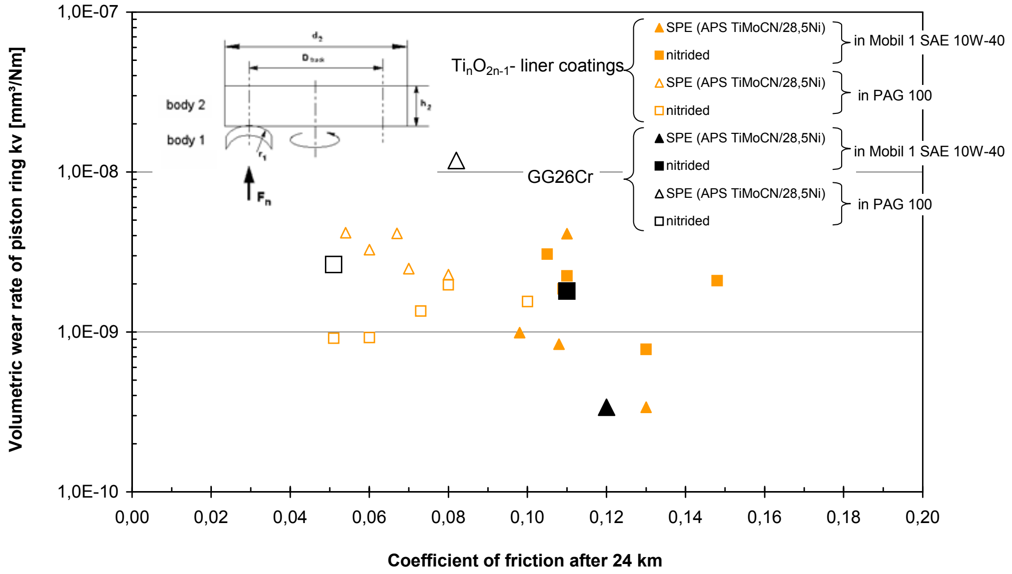

Figure 8 : Summarizing plot of “Coefficient of friction at test end” versus “Wear rate for piston ring” of a set of tribocouples in different media (F_N= 50 N ; v = 0,3 m/s ; T = 170°C ; s = 24 km)

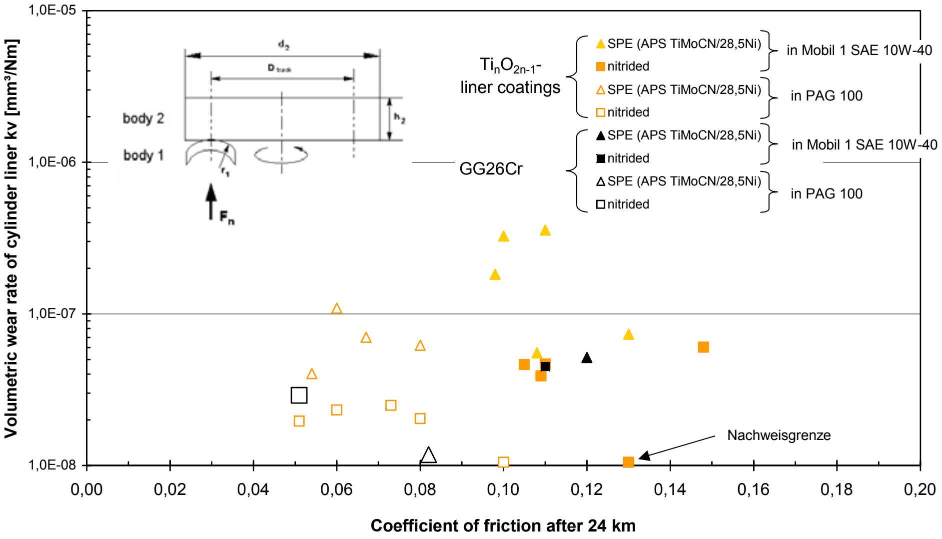

Figure 9 : Summarizing plot of "Coefficient of friction at test end" versus "Wear rate for liner" of a set of tribocouples in different media (F_N= 50 N ; v = 0,3 m/s ; T = 170°C ; s = 24 km)

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AVT-109
Specialist Meeting on the Control and Reduction of Wear in Military Platforms

Summary of Discussion Sessions

The following presents a summary of the discussion of papers presented in the various sessions of the workshop. Only questions where the authors provided transcripts of their answers are reported.

Session 2 – Reciprocating Engines and Lubrication Systems

Chair: Ernest Chin, Army Research Laboratory, United States

Paper MP-AVT-109-9

Dr. Jane Adams, AMSRD-ARL-WM-MD, USA

Q. What was the prime reason that polyglycol lubricants were abandoned after World War II?

Dr. M. Woydt, FIMRT, Germany

A. The main reasons were the price of polyglycols, compared to mineral oils at that time and the up and coming jet engine. Polyglycols compete today with synthetic hydrocarbons regarding base oil prices.