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TNO report

End-Report of Annex XX of the IEA/AMF of the IEA: 'DME as an Automotive Fuel II'

PART 1

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Summary

Technical Work

Di-Methyl Ether (DME) is an alternative fuel for CI engines. However, most conventional gasket and seal materials are not suitable for use with DME. Four promising elastomers, EPDM, IIR, Kalrez and HNBR, have been selected for further investigation. Results of tests show that EPDM without softeners and HNBR have some potential for use with DME. However, Kalrez is superior to those two.

DME does have poor lubricity performance. Sliding surfaces suffer from wear using DME. Investigation on wear has been done by examining worn fuel injection pump parts used with DME. This shows a relatively mild wear process, polishing and smoothening of the contact area. A wear measuring device, a Tribometer, has been modified and experiments have been carried out to measure wear using diesel or DME as medium between two contact surfaces. ‘Diamond Like Coating’ has been tested as an alternative for commonly used fuel injection pump part materials.

The influence of additives on lubricity and viscosity has been investigated by DTU (Danish Technological University). It appears that lubricity can be improved very well up to a level surpassing diesel fuel. It was however not possible to improve (increase) viscosity significant with reasonable amounts of additive. Because of this, it is will be difficult to use DME in conventional injection systems. This work is reported by DTU (Annex XX end-report, Part 2).

Workshops / newsletters

Information has been taken care of by the organisation of workshops and preparation of newsletters and brochures.

Workshops # 7, 8 and 9 were organised within this Annex. These were respectively in Plymouth, Michigan USA (June 2000), Växjö, Sweden (January 2001) and Paris, France (May 2001).

Two newsletters have been issued.

International DME Association (IDA) has been founded for continuation of information exchange and DME promotion.

Contents

1 Introduction

This Annex runs under the Implementing Agreement: Advanced Motor Fuels of the International Energy Agency (IEA). It can be considered as successor of Annex XIV 'DME as an Automotive Fuel' with TNO Automotive is as operating agent as well.

Recent research has shown that Dimethyl Ether is an excellent alternative to conventional diesel fuel. This means high efficiency combined with smoke-free combustion and low NOx emissions. However, despite the very promising possibilities of Dimethyl Ether as an automotive fuel, some elements require extra attention:

- Most elastomers are unsuitable for use with DME.
- Conventional fuel injection systems suffer from extreme wear using DME. This is caused by relatively low viscosity and poor lubricating properties of DME.

Those key-elements need to be improved significantly before DME can be used reliably in mass production engines.

The objectives of Annex XX are:

1. Offering technical solutions to wear and elastomer compatibility problems;
2. The development of a basis to launch DME projects with industrial involvement;
3. The co-ordination of the DME activities around the world through workshops;
4. The interest of the industrial and public interest in DME through newsletters.

To meet the objectives the Task is divided in two Subtasks:

1. Subtask 1: Research on DME wear and polymer compatibility.
2. Subtask 2: Project management, workshops and newsletters.

The first Subtask consists of:

- Selection and testing of a number of elastomers (Chapter 2)

- Examining used fuel pump parts on wear. (Chapter 3)

- Investigation on improvement of the lubricity and viscosity of DME through the use of additives. This work has been carried out and reported by DTU [1] (Annex XX end-report, Part 2)

The second Subtask is reported in Chapter 4.

2 Subtask 1: Elastomers

Most elastomers are not suitable for use with DME. Appendix A "Elastomer characteristics" shows a table with 17 ‘standard’ elastomers and their main reason of failure with DME. This table is made during a brainstorm session with specialists of plastic manufacturer Helvoet BV and DuPont Dow Elastomers. Based on their experience four elastomers have been selected from the list:

- EPDM (with and without softener)
- IIR
- Kalrez
- HNBR (fluor polymer)

For comparison, the four elastomers are rated (1=good, 4=poor):

Table 2.1: Rating of different elastomers

Material	Swell	Permeation	Wear	Low temp	High temp	Tensile strength	Price	Total
EPDM	2	1	4	2	4	4	1	**18**
IIR	2	4	3	1	2	2	1	**15**
Kalrez	1	1	2	4	1	3	4	**16**
HNBR	4	3	1	3	2	1	3	**17**

On this basis the four elastomers are rather equivalent, so further investigation was needed. They are investigated on different properties and detailed results are presented in Appendix A "Elastomer characteristics".

They have been investigated on following characteristics:

- Hardness;
- Tensile strength;
- Stretch at braking;
- Modulus at 100% stretch;
- Compression set.

Some of those characteristics have been tested after aging at high temperatures and after swelling. However, swell tests did not take place with DME, because of absence of proper affordable equipment. Diethyl Ether (DEE) is used instead.

With respect to deformation after compression set at 100°C, Kalrez seems to be worst. However, this deformation is acceptable for its function. IIR is unsuitable regarding the deformation during compression set at 150°C.

Regarding aging at 100°C temperature, all materials, seem to be suitable. At 150°C IIR is the only elastomer which is not appropriate.

With respect to swell followed by drying Kalrez has the best characteristics. The other materials suffer from considerable swell and are far worse than Kalrez. EPDM with softener suffers to much from extraction after drying and is therefore unsuitable. Seal rings made of this material will probably leak after removing DME followed by shrinking of the ring.

3 Subtask 1: Investigation on wear

3.1 Description of wear test equipment

The Tribology group of TNO Industrial Technology normally performs wear tests with a so-called 'Tribometer'. However, measurement of wear using quick evaporating fluids has not been possible so far. For that reason the Tribometer has been modified for the use of liquid DME. The Tribometer has been put into a pressure vessel. This vessel is filled with nitrogen at 7.5 bars of absolute pressure to keep the DME in liquid phase.

This work is descibed in detail in a separate report [2]. Appendix B "Pictures of Tribometer" shows pictures of the test rig.

The main working principle is shown in figure 3.1

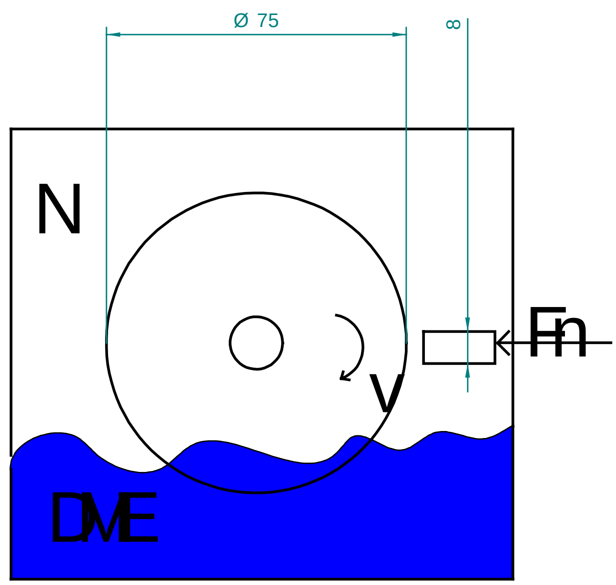


Figure 3.1: Main principle wear test

A 75-mm disc is rotating in one direction with a circumferential speed of 0.25 m/s ('v'). An 8-mm pin is pushed to the circumference of the disc with a 100-N normal force ('Fn').

Before starting of the test a low-volume test tank, in which the disc is rotating, is filled with liquid DME via a pick-up tube. When the test starts, the rotating disc scoops DME between pin and disc. During the tests Fn, Fw (tangential friction force) and linear displacement of pin are measured by data acquisition equipment. Coefficient of friction is calculated afterwards and is an indication for the quantity of wear.

3.2 Investigation on wear of components from fuel pump used for DME

In [2] investigation on several parts of a worn fuel pump used for DME applications are described. Two contact situations have been determined. From one situation profile and roughness measurements haven been carried out. The results of those measurements show a relatively mild wear process (polishing). Both contact materials show smoothening of the surface. No signs of severe scratching or scuffing are detected

For both cases the materials used in the pump are estimated, using SEM (Scanning electron microscopy), OES (Optical Emission Spectroscopy), light microscopy and roughness measurements.
In both situations the contact is between nitrocarburised or carbonitrided steel, probably 21MnCr5, and through hardened steel, probably 100Cr6.
With respect to the measurement results of the examined fuel pump several possible solutions can be proposed. Figure 3.2 shows some possible metal surface treatments.

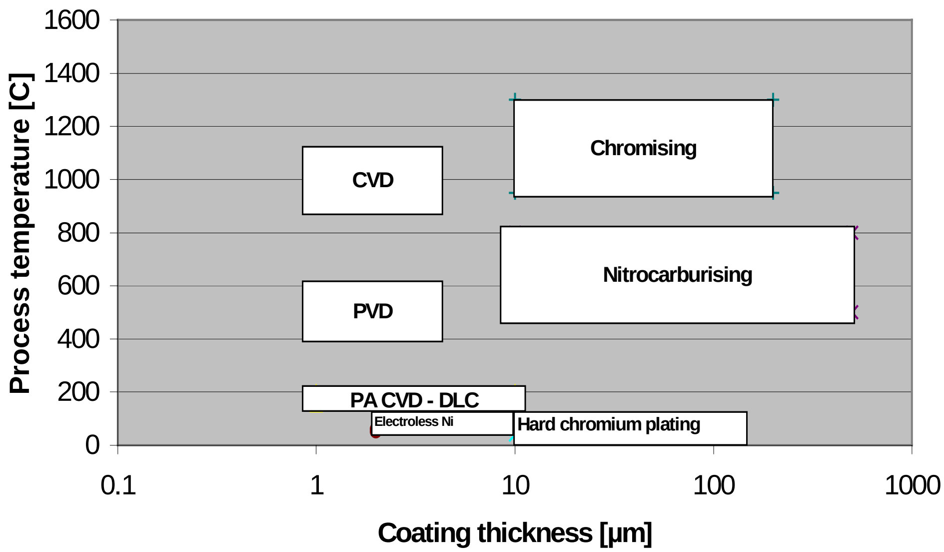


Figure 3.2: Surface treatments

However, those solutions are not always applicable keeping the original pump design and the original materials used in the pump in mind. Especially materials used in this application are limiting the amount of possibilities. The low tempering temperature of 100Cr6 (180°C) limits the amount of possibilities. All solutions need to be self-lubricating.

Possible solutions are:

- Hard layers applied in a plasma-assisted Chemical Vapour Deposition process (Diamond Like Carbon)
- Soft layers with solid lubricants (e.g. MoS_2)

However, soft layers have not been investigated because of the experimental character of the project and the expectation of a problematic adherence of the lubricant.

3.3 Results of wear measurements with DME

Three tests have been performed with different contact surfaces and materials as shown in table 3.3:

Tabel 3.3: Conditions wear test

Contact surface pin:	**Contact surface disc**	**Medium between pin and disc**	**Ambient pressure (bar)**	**Sliding distance (m)**	**DME temperature (°C)**
100Cr6 (60 HRc)	21MnCr5 + nitrocarburizing	DME	7.5	900	20-25
100Cr6 (60 HRc)	21MnCr5 + nitrocarburizing	Diesel (standard quality)	1	900	20-25
100Cr6 (60 HRc)	21MnCr5 + case hardening + DLC (about 2 micrometer thickness)	DME	7.5	900	20-25

The results are also presented in Figure 3.4

Further information about these tests is to be seen in appendix C.

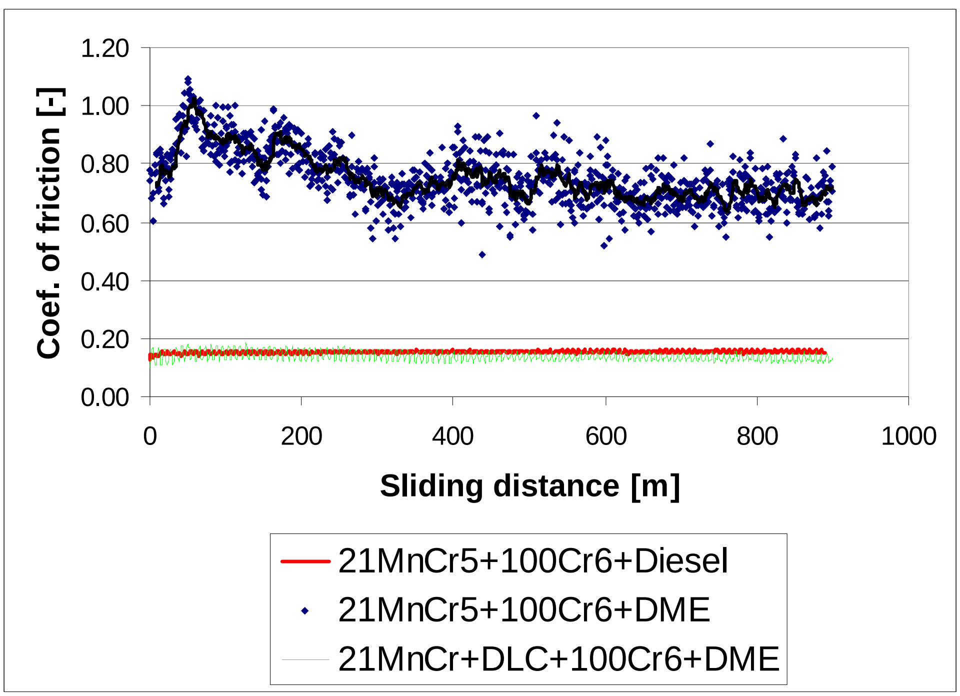


Figure 3.4: Coefficient of friction vs sliding distance for different materials and different media.

The results show a very large coefficient of friction using DME and conventional pump materials 21MnCr5 and 100Cr6. The coefficient of friction is not constant as well. This indicates an unstable process. This will probably cause relatively severe wear.

DLC (Dymond Like Carbon) coating and DME shows comparable results to conventional materials in Diesel: there was no visible wear.

Remarks:

- No linear wear/mass loss is measured;
- The stability of normal force is not very good (100+/-20N);
- It was difficult to get proper line contact between hard surfaces;
- The repeatability is not known.

4 Subtask 2: Workshops and Newsletters

Workshops

To co-ordinate the work in this Annex and to facilitate the exchange of information between participants and other interested parties, workshops were organised approximately every 6 month. This series of workshops succeeded the series of workshops organised in the previous Annex on DME (Annex XIV, last workshop in December 1999).

For Annex XX the workshops organised are (number 7, 8 and 9):
- Workshop #7: May 2000, at AVL NA, Plymouth MI, USA;
- Workshop #8: January 2001, Växjö kommun, Sweden;
- Workshop #9: May 2001, IEA, Paris, France.

All three workshops addressed a number of general issues:
- reporting the progress of the technical tasks;
- exchanging information on the DME activities of the companies present;
- discussions on how to co-ordinate and stimulate the worldwide activities on DME.

The exchange of information has been very useful for the participants. Therefore a need for continuation of this activity was present. At the beginning of 2001 a group of participants founded the International DME Association (IDA). Through IDA the information exchange on DME related subjects is and will be continued and possibly even intensified.

Newsletters

During Annex XIV as well as during Annex XX several newsletters covering the latest developments on DME as an automotive fuel and related subject were issued. These newsletters are available in pdf format from the TNO Automotive website (www.automotive.tno.nl search for DME newsletter).

At the end of Annex XIV there was a need for a DME leaflet summarising and clarifying all aspects of DME as an automotive fuel. Since the budget of Annex XIV did not have room for such an extra activity a group of participants separately funded the realisation and distribution of such a leaflet. A copy of this leaflet is added to this report for information purposes.

By concluding the activities of this Annex, also the publication of newsletters will stop. The International DME Association is obvious party to fill the gap.

5 Financial overview

5.1 Contributions

Table 5.1 gives an overview of the financial and in-kind contributions. There is some deviation in the original proposal (left columns) and the actual situation (right columns).

Funding contributions Original proposal	**(k-USD)**	**Funding contributions Actual situation**	**(k-USD)**
Contracting Parties		Contracting Parties	
Denmark	10	Denmark	10
Finland	10	Finland	10
France	10	France	10
Japan	10	Japan	10
Sweden	10	Sweden	10
US	10	US	10
Italy	10	Italy	10
Sponsors:		Sponsors:	
PSA	10	PSA	10?
IFP	10	Renault	10
Renault	10		
Total funding	100		80-90
In kind contributing parties:		In kind contributing parties:	
Renault	10	Renault	10
Helvoet	10	Helvoet	10
DuPont Dow Elastomers	10	DuPont Dow Elastomers	10
Haldor Topsoe	10	Haldor Topsoe	10
TNO	10	TNO	10
Total	150	Total	130

Table 2: The actual contributions compared to the original proposal, in k-USD

5.2 Costs

Table 5.2 shows a comparison between the originally planned costs and the expected costs (realisation is now 95%) . The numbers are excluding the in-kind contributions. From Table 5.2 it can be concluded, that there is some shortage in funding.

Original plan	(k-USD)	Actual and expected costs	(k-USD)
Technical University of Denmark (DTU)	10	Technical University of Denmark (DTU)	10
TNO (technical)	50	TNO (technical)	45
TNO		TNO	
operating agent	10	operating agent	20
workshop	23	workshop	20
newsletters	7	newsletters	7
Total costs	100		102
Income	100		80-90

Table 3: Project costs: Original plan versus expected realisation, in k-USD

6 Conclusions and recommendations

6.1 Conclusions

Subtask 1: Elastomers

Four selected elastomers were experimentally evaluated for the use with DME :
- Kalrez has the best characteristics.
- EPDM without softener and HNBR do not have optimum characteristics with regarding swell, but seem to have some potential. Especially HNBR is very wear resistant.
- EPDM with softener and IIR are not suitable for use with DME.

Subtask 1: Investigation on wear

Worn fuel pump parts used with DME were examined. The results show a relatively mild wear process (polishing) and the surfaces are smoothened. Investigation on used pump materials resulted in the choice for ‘Diamond Like Carbon’ (DLC) coating for better performance on wear.

A modified Tribometer was designed and built to do wear tests in liquid DME. Three tests have taken place, one with conventional materials in diesel, one with conventional materials in DME and one test with DLC coated material in DME.
Results show poor performance using conventional pump materials with DME. DLC coatings on conventional pump materials seem to have a good potential, because friction coefficient is almost the same as friction coefficient between conventional pump materials in diesel.

Subtask 1: *influence of additives on lubricity and viscosity*

This has been investigated by DTU (Danish Technological University).
Conclusions are:
- lubricity can be improved very well, even up to a level surpassing diesel fuel.
- viscosity cannot significantly be improved with reasonable amounts of additive.

Subtask 2: Workshops and newsletters

To exchange information between participants several workshops have been organised and some newsletters have been made. For continuation of these workshops and newsletters the International DME Association (IDA) has been founded.

6.2 Recommendations

Subtask 1: Elastomers

Kalrez is quite expensive compared to other elastomers. Besides, production techniques are complicated and material working up is done by only a small selection of companies. Other companies sell materials with equivalent properties. With respect to swell behaviour further investigation on other fluor polymers may lead to cheaper alternatives.

Recently a new type of VITON has been introduced. First impressions show higher swell than Kalrez, but considerable lower swell than EPDM and HNBR. Further investigation could be of interest.

Subtask 1: Investigation on wear

- Further optimising of the test rig is preferred.
- More experiments should be carried out. At least 3 experiments per material/medium combination should be performed.
- Investigation of DLC coating on the 100Cr6 material or both contact surfaces with DLC coating seems to be an interesting lead as well.

7 References

[1] I. M. Siveback: "End-Report of Annex XX of the IEA/AMF of the IEA: 'DME as an Automotive Fuel II Part 2", DTU report November 2001, project code MEK-ET-ES 2001-04

[2] E van der Heide, M Sc: "The effect of DME on wear of fuel pump parts", TNO report Div400.1101, 2000.

A Elastomer characteristics

Tabel A.1: Elastomers and main reason of failure on DME

Elastomer	**Main reason of failure on DME**
NR	ABD
SBR	ABD
NBR	AB?D?
Cr	?
IIR	?
EPDM	B
AU/EU	?
EAM	?
VMQ	?
FVMQ	?
PNR	?
FKM	?
ECO	?
ACM	?
HNBR	?
KALREZ	D
VITON ETP	?

The main criteria are:

A. Low swell;
B. Low permeation;
C. Low extractables;
D. Temperature range –40/120°C

Tabel A.2: Results of experiments on potential DME suitable elastomers

Material	EPDM*	EPDM**	IIR***	Kalrez	HNBR****
Hardness (Sh. A)	74	68	58	70	69
Tensile strength (MPa)	14.0	17.4	11.6	20.5	20.9
Stretch at breaking (%)	207	157	296	172	204
Modulus at 100% stretch (MPa)	4.3	8.2	2.7	8.9	8
Compression set 72h 100°C (%)	8	15	23	32	10
Compression set 24h 150°C (%)	16	24	43	25	24
Aging in air 72h 100°C					
Change in hardness (Sh. A)	+1	-1	+3	0	+1
Change in tensile strength (%)	+3.6	-9.8	-0.9	0	0
Change in stretch at breaking (%)	+14.0	-4.5	-0.3	+6.4	+1
Aging in air 24h 150°C					
Change in hardness (Sh. A)	+1	0	+16	-1	+1
Change in tensile strength (%)	+2.9	+3.4	-18.1	0	-1.9
Change in stretch at breaking (%)	+6.8	-6.4	-19.9	-1.7	-11.3
Swelling in DEE 48h 23°C					
Change in hardness (Sh. A)	-17	-30	-28	-7	-14
Change in weight (%)	+47.7	+44.0	+37.2	+1.4	+47.7
Change in volume (%)	+77.8	+70.5	+64.4	+4.0	+79.3
Swelling DEE 48h 23°C and immediate drying 24h 23°C					
Change in hardness (Sh. A)	0	+9	-5	-5	-2
Change in weight (%)	-0.3	-8.8	-2.6	+0.9	-0.1
Change in volume (%)	-0.2	-11.6	-2.1	+2.5	-0.8

* without softener, peroxide cured
** with softener, peroxide cured
*** (butyl) gas tight and peroxide cured
**** peroxide cured

B Pictures of Tribometer

Figure B.1: Overview of Tribometer

Figure B.2: Inside of Tribometer (Tank cover removed)

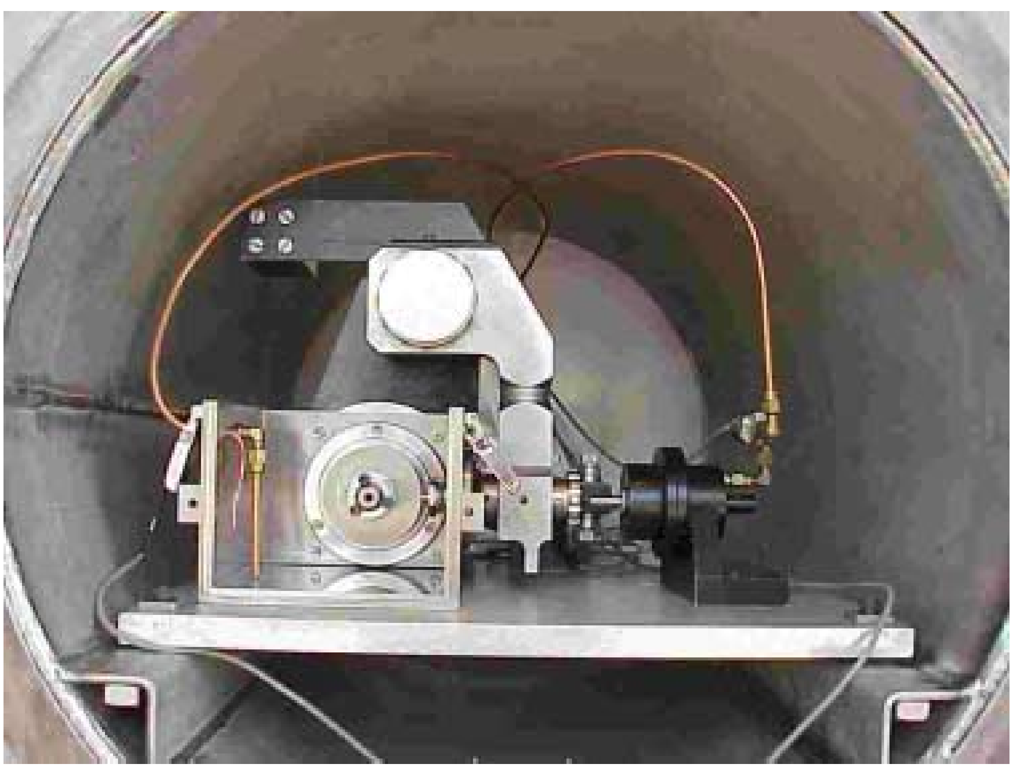
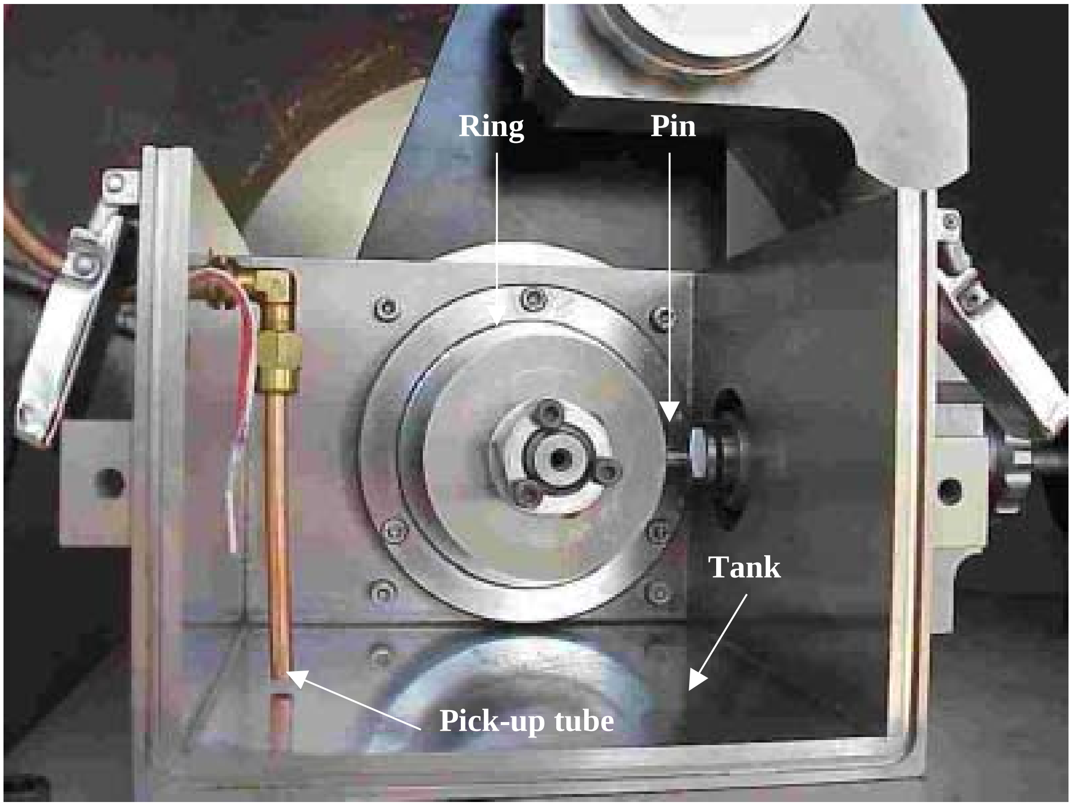


Figure B.3: Inside of Tribometer (Tank cover removed)



C Further information about wear test

23-05-2001

Nitrocarburized 21 MnCr 5 / 100Cr6 / DME

TEST CONDITIONS

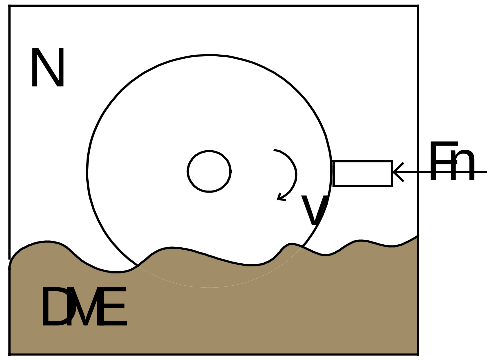
APPARATUS : TNO Tribometer

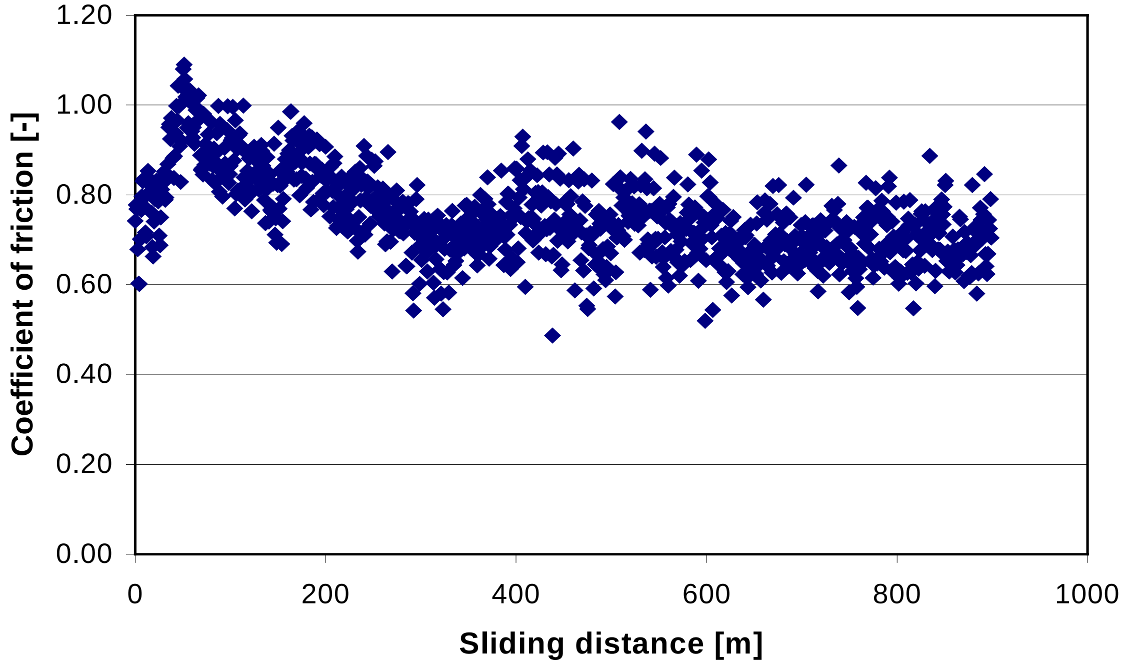
PIN : Hardened ball bearing steel 100Cr 6, AISI 51200
stationary : Cylinder ∅ 8 mm, grinded, roughness R_a = 0.1 µm.

RING : 21 MnCr 5, nitrocarburized (Philips Harderij)
rotating Dim. ∅ 75 x 13 mm, grinded, roughness R_a = 0.1 µm

LUBRICANT : None

PARAMETERS : Sliding speed v = 0.25 m/s
Normal force F_N = 100 N
Test duration = 60 min.
DME inlet pressure = 9 bar
Nitrogen pressure = 7.5 bar





23-05-2001

21 MnCr 5 + DLC / 100Cr6 / DME

TEST CONDITIONS

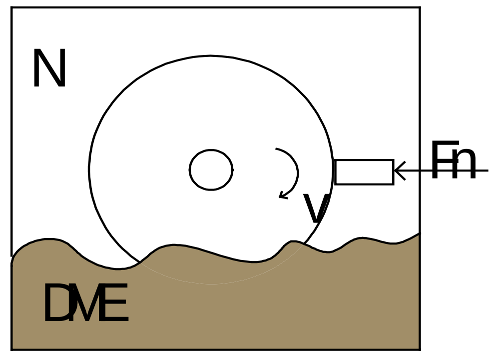
APPARATUS : TNO Tribometer

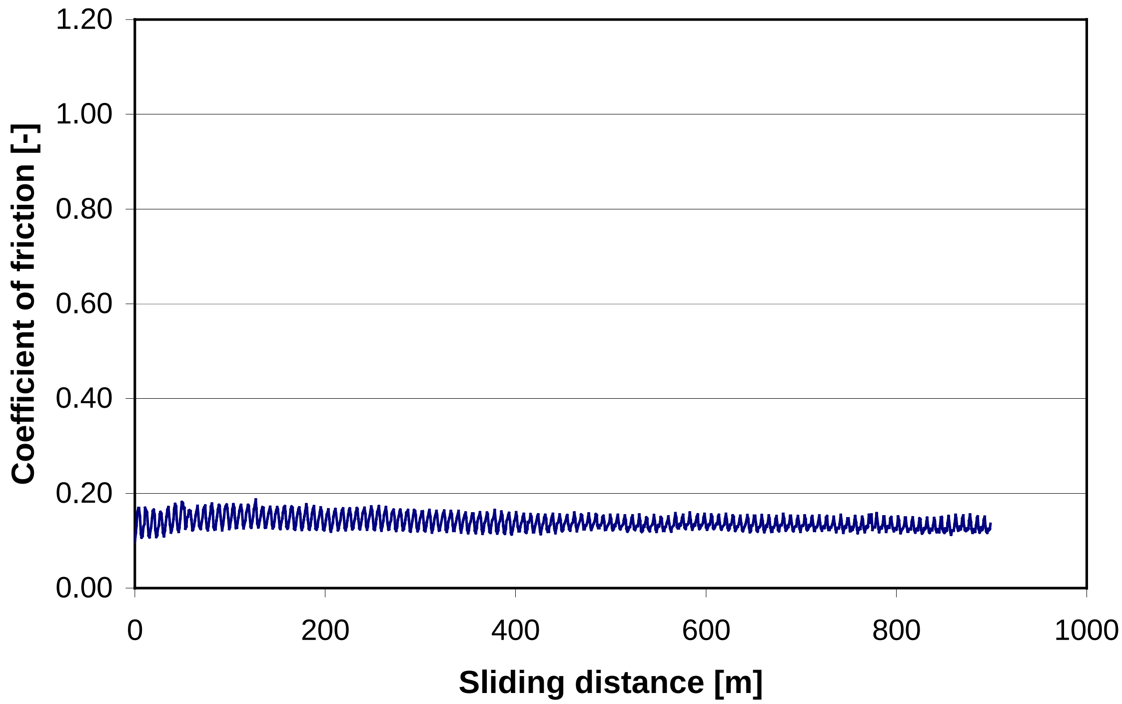
PIN : Hardened ball bearing steel 100Cr 6, AISI 51200
stationary : Cylinder ∅ 8 mm, grinded, roughness R_a = 0.1 µm.

RING : 21 MnCr 5, case hardened 0.6 – 0.9 mm (PhilipsHarderij)
rotating , grinded + DLC coating (Bekaert Dymonics)
Dim. ∅ 75 x 13 mm, roughness R_a = 0.1 µm

LUBRICANT : None

PARAMETERS : Sliding speed v = 0.25 m/s
Normal force F_N = 100 N
Test duration = 60 min.
DME inlet pressure = 9 bar
Nitrogen pressure = 7.5 bar





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23-05-2001

Nitrocarburized 21 MnCr 5 / 100Cr6 / Diesel oil

TEST CONDITIONS

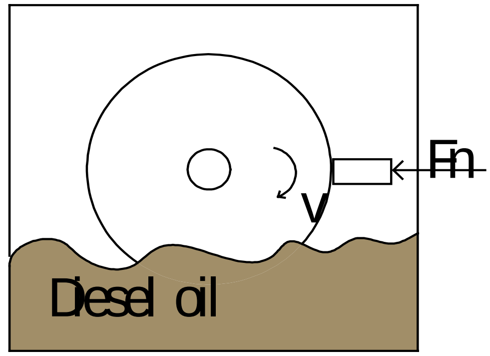
APPARATUS : TNO Tribometer

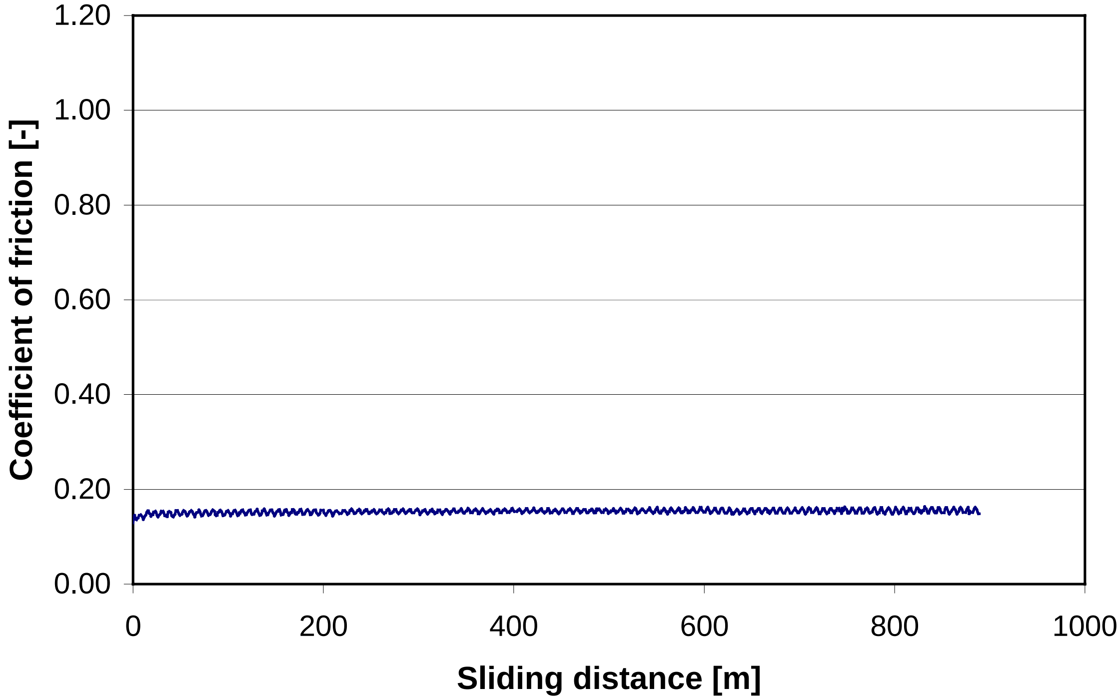
PIN : Hardened ball bearing steel 100Cr 6, AISI 51200
stationary : Cylinder ∅ 8 mm, grinded, roughness R_a = 0.1 µm.

RING : 21 MnCr 5, nitrocarburized (Philips Harderij)
rotating Dim. ∅ 75 x 13 mm, grinded, roughness R_a = 0.1
µm

LUBRICANT : None

PARAMETERS : Sliding speed v = 0.25 m/s
Normal force F_N = 100 N
Test duration = 60 min.





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