GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 9/29/80

Project Title: Fundamental Studies of Tribology as Related to the Automotive Fuel Economy

Project No: E-25-637

Project Director(s): Dr. S. Ramalingam, Dr. W.O. Winer

Sponsor: U.S. Department of Transportation, RSPA

Agreement Period: From 8/1/80 Until 7/31/83

Type Agreement: Contract No. DTRS5680-C-00015

Amount: $434,960 (Incrementally funded at $145,000 through 7/31/81)

Reports Required: Qtrly Progress, Phase, Final

Sponsor Contact Person(s):

<table>
<thead>
<tr>
<th>Technical Matters</th>
<th>Contractual Matters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russell Zub, DTS-323</td>
<td>Theodore R. Higgs, Jr.</td>
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<td>Department of Transportation</td>
<td>Department of Transportation, RSPA</td>
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<td>400 Seventh St. SW</td>
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<tr>
<td>Cambridge, MA 02142</td>
<td>Washington, D.C. 20590</td>
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<td>(617) 494-2056</td>
<td>(202) 426-2620</td>
</tr>
</tbody>
</table>

Defense Priority Rating: N/A

Assigned to: Mechanical Engineering (School/Laboratory)

COPIES TO:

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School/Laboratory Director
Dean/Director—EES
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EES Information Office
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Project Code (GTRI)
Other C.E. Smith
SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 1/16/84

Project No. E-25-637

Includes Subproject No.(s)

Project Director(s) Dr. Winer/Dr. Ramalingam

Sponsor U. S. Department of Transportation

Title Fundamental Studies of Tribology as Related to the Automotive Fuel Economy

Effective Completion Date: 9/30/82 (Performance) 9/30/82 (Reports)

Grant/Contract Closeout Actions Remaining:

☐ None
☐ Final Invoice or Final Fiscal Report
☒ Closing Documents
☒ Final Report of Inventions
☒ Govt. Property Inventory & Related Certificate
☐ Classified Material Certificate
☐ Other

Continues Project No. Continued by Project No.

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Form OCA 60:1028
20 March 1981

Ms. Helen Whitfield, DPB-50
Office of University Research
U.S. Department of Transportation
400 Seventh Street, S.W.
Washington, D.C. 20590

Subject: Deliverable Items 1 (first), 2 and 3
DOT DTRS 5680-C-00015

Dear Ms. Whitfield:

Attached are the above deliverable items. We apologize for the delay.

Sincerely yours,

S. Ramalingam
Professor and Principal Investigator

W. O. Winer
Professor and Principal Investigator

cc: with attachments
Mr. Russell Zub, DTS-323
Technical Monitor
Transportation Research Center
U. S. Department of Transportation
Kendall Square
Cambridge, Massachusetts 02142

Reports Coordinator
Support Services (2 copies)

S. P. Kezios, Director
School of Mechanical Engineering (1 copy)
Tasks I, II, III, IV will be completed in Phase 1 (the first year). Professor Ramalingam will be responsible for Tasks I and II on coating technology while Professor Winer will be responsible for Task III on engine oil rheology. Professor Winer will also coordinate Task IV, the preparation of the Phase I report.

The research engineer, S. Bair, will work with both Professors Ramalingam and Winer to assist in the design and construction of the experimental equipment on all three tasks. Four graduate students will be working with Professor Ramalingam and Professor Winer and Mr. Bair in the construction of the equipment and data gathering and analysis.

Approximate schedule:

Task I: Development of Coating Technique  
Completed by Mid-April 1981

Task II: Preliminary Coating Trials  
Completed by 30 August 1981

Task III: Shear Rheological Characterization of Motor Oils  
a) pressure viscosity:  
Completed mid-April 1981  
b) limiting shear stress:  
Completed by 30 August 1981

Task IV: Phase One Report  
Completed 30 September 1981
During this initial three months of the contract primary attention was directed towards securing graduate students and initiating the research. Because the final commitment was not available until after the beginning of the Fall Quarter, some difficulty was experienced in hiring graduate students. However, sufficient commitments were made to initiate the research.

TASK I: DEVELOPMENT OF COATING TECHNIQUES

The equipment was assembled for magnetron reactive sputtering and solid lubricant coating techniques. Samples of materials to be coated were acquired and preliminary trial coatings begun. Coating parameters are being evaluated to enhance coating rates. These evaluations shall continue during the next quarter and Task II, Preliminary Coating Tests, will begin during that time.

TASK III: SHEAR RHEOLOGICAL CHARACTERIZATION
OF LIQUID LUBRICANTS (MOTOR OILS)

The equipment was calibrated and lubricant samples acquired. The pressure viscosity measurements at three temperatures (40, 100, 150°C) were begun and will continue through the next quarter. The limiting shear stress measurements may begin during the latter part of the next quarter. Because of the difficulty of acquiring well defined fully formulated lubricants, 12 off-the-shelf representative engine oils were selected plus the reference oil being used in the ASTM Fuel Efficient Oil program. A copy of the list of these oils is attached. The suppliers have been written requesting generic information about these formulations.
<table>
<thead>
<tr>
<th>SAE GRADE</th>
<th>MANUFACTURER</th>
<th>NAME</th>
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<td>Fire and Ice</td>
<td>Gas Saving Formula</td>
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<td>GTX</td>
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<tr>
<td>HR-1</td>
<td>ASTM-FEO Program</td>
<td></td>
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</tr>
</tbody>
</table>
The attached set of mailing labels (plus four copies of list) make up the proposed Potential User List. Of those on this list, the following five will constitute the five professionals with whom we shall establish and maintain quarterly communication:

D. F. Hays, G.M. Research Labs
J. Mayer, Ford Motor Company
J. L. Palmer, Lubrizol
A. R. McMillan, GMC
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1 May 1981

Ms. Helen Whitfield, DPB-50
Office of University Research
U.S. Department of Transportation
400 Seventh Street, S.W.
Washington, D.C. 20590

Subject: Deliverable Items 1 (first)
DOT DTRS 5680-C-00015

Dear Ms. Whitfield:

Attached are the above deliverable items.

Sincerely yours,

S. J. Vajravelgam
Professor and Principal Investigator

W. O. Winer
Professor and Principal Investigator

cc: with attachments
Mr. Russell Zub, DTS-323
Technical Monitor
Transportation Research Center
U.S. Department of Transportation
Kendall Square
Cambridge, Massachusetts 02142

Reports Coordinator
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S. P. Kezios, Director
School of Mechanical Engineering (1 copy)
2nd QUARTERLY 
PROGRESS REPORT 
January - March 1981 
DOT DTRS 5680-C-00015 
THE ROLE OF TRIBOLOGY IN AUTOMOTIVE FUEL ECONOMY 

S. Ramalingam/W. O. Winer 
Principal Investigators 
School of Mechanical Engineering 
Georgia Institute of Technology 
Atlanta, Georgia 30332 

The research has been progressing satisfactorily and on schedule during the past quarter, and is expected to continue on schedule during the next quarter. 

TASK I: DEVELOPMENT OF COATING TECHNIQUES 

A sputtering facility consisting of a D.C. magnetron head, vacuum chamber, sputtering gas flow, mixing and composition control system has been designed, built and tested. This facility allows high rate sputtering of metal targets and reactive sputtering of metals in an argon-environment to produce hard compound coating. 

Through a series of trial runs, the optimal sputtering conditions for metal sputtering and hard compound sputtering have been identified. In the present system magnetron sputtering (magnetic field assisted sputtering) can be carried out at pressures as low as 0.5 μm of Hg. This pressure is two orders of magnitude lower than conventional sputtering and allows the production of well-adherent coatings (coating adhesion is vital to tribological coatings). Low pressure sputter coating also minimizes the occlusion of sputtering gas (argon). Dense coatings are produced. 

Argon and nitrogen flow rates necessary for the reproducible deposition of titanium nitride have been identified. Golden yellow, stoichiometric titanium nitride coating are now being produced routinely. 

To assess the utility of hard coatings (TiN) in non-ferrous automotive castings such as pistons, test blocks of aluminum, magnesium and titanium alloys have been sputter coated with titanium nitride. Sliding contact wear tests (LFW-I) have been carried out and wear coefficients determined. The results obtained are summarized in a paper to be presented in July 1981 in Brussels [IPAT 81 International Conference sponsored by the European Physical Society, Metals Society (London) and the Welding Institute (London)]. The paper has been accepted for publication in a forthcoming issue of Thin Solid Films.
Briefly, the test results obtained show that well-adherent thin coats (5 μm or less in thickness) offered excellent wear protection to non-ferrous alloys. At each hertzian contact stress level, full wear protection is obtained only above a film thickness threshold of the order of 1.5 to 2 μm. Wear resistance is improved by several orders of magnitude (wear coefficients measured are tabulated in the paper). A copy of the paper is attached to this progress report.

The LFW-1 wear tests are low speed tests. To carry out medium and higher speed sliding tests (conditions comparable to those experienced by piston skirts), LFW-6 test specimens are being fabricated. These tests are due to be carried out in the next program period.

While hard coat adhesion is easily obtained with non-ferrous materials, significant problems are encountered in producing well-adherent coatings on hardened steels (valve train components are hardened irons and steels). Chemical surface treatments (prior to sputter coating) have been found to overcome the adhesion problems. Early tests in rolling hertzian contact tests at up to 150 ksi have been successful. A summary of test results (LFW-6 tests) will become available at the end of the next program period.

Techniques for DC sputtering of dichalcogenide soft coats have been developed. Soft coats have been found to have a limited life. Coating adhesion problems that do not appear to be surmountable by chemical surface conditioning are encountered. Radio frequency magnetron sputtering is essential. Authority to procure an RF power supply is being sought from the DOT program monitor. (Budget contains provision for this equipment and funds have been approved. According to DOT contract, authorization is necessary for equipment procurement.) It is expected that well-adherent soft coats can be produced on ferrous and non-ferrous test bodies by RF sputtering.

A torsion and a bend test have been conceived for the reliable measurement of coating to substrate bond strength. This test scheme does not have the ambiguities of the peel or scratch tests. Test results obtained will be summarized in the report for the next program period.

SUMMARY

Hard coat techniques for the protection of ferrous and non-ferrous automotive and other alloys have been developed. Though satisfactory soft coats can be produced for friction control, coating-to-substrate adhesion problems (as expected) are being encountered. Authority is hence sought to procure an RF power supply for which funding has been approved on this DOT contract.
TASK III: SHEAR RHEOLOGICAL CHARACTERIZATION
OF LIQUID LUBRICANT (MOTOR OILS)

The engine oil rheology program's first major task has been nearly completed. That task was the measurement of the viscosity of 13 commercial engine oils vs. a function of temperature (40, 100, 150°C) and pressure (1 atm to 600 MPa) at low shear stress (< 60 Pa). Measurements on 11 of the 13 oils are complete and the remaining two are underway. The data of viscosity and pressure viscosity coefficients have all been reduced and the interpretation of the significance of these data is underway.

The responses to the producer inquiry as to generic composition of the oils have been received from six of the eight oil producers. Followups are underway on the remaining two.

The measurement of traction/friction behavior of the 13 engine oils has begun and will continue through the next two quarters. These measurements are made in a unique tribotester that permits a wide range of load, speeds (rolling and sliding) and temperature be imposed on the lubricant. These conditions will simulate the behavior various engine components so that the energy dissipation of the lubricant in the engine can be assessed. Film thickness measurements are also being made in the same device which permit the estimation of the high shear rate viscosity of the lubricant.
The light-weight non-ferrous alloys (titanium, aluminum and magnesium alloys) used in aerospace applications are prone to severe wear in small-displacement and large-displacement un lubricated contacts. Few metallurgical means are available for the surface protection of this class of materials. Deposition of hard compounds by sputtering provides a simple means of protecting such surfaces. Hard coating and tribological studies of coated samples were therefore carried out. The results obtained are presented in this paper. It is shown that magnetron-sputtered TiN hard coatings do provide the required wear protection.

1. INTRODUCTION

Non-ferrous alloys of aluminum, magnesium and titanium are light-weight materials. Further, the precipitation-hardenable alloys of aluminum and titanium possess high strength-to-weight ratios. They also exhibit excellent fracture toughnesses. These characteristics have led to the wide use of aluminum, titanium and magnesium alloys in aerospace applications.

These non-ferrous alloys are soft. In their bare form, in sliding contact without lubrication, the light-weight alloys are prone to severe adhesive and abrasive wear. Scuffing and galling occur readily. Surface protection through surface treatments is essential if these alloys are to be used efficiently in applications where boundary-lubricated or un lubricated contact with a counterface is unavoidable. Protection is also necessary in fretting environments.

Metallurgy of these alloys, however, does not allow the use of routine surface treatments that are common for iron and steel alloys (surface and case-hardening treatments). Treatments involving high temperatures are also not possible for aluminum and magnesium alloys since they melt at moderate temperatures. Precipitation hardening, commonly used to improve the yield strength and fracture toughness, also involves treatment temperatures only some 100–200°C above room temperature. Surface treatments involving elevated temperatures are therefore not suitable for improving the friction and wear properties of non-ferrous alloys.

The tribological properties, however, can be improved greatly by replacing the surface layers of these alloys with other materials. Conversion coatings and anodization are examples. Deposition of thin coatings is yet another way of altering surface properties. A wide range of materials can be deposited without the limitations inherent in conversion coatings and anodization. Deposition of thin coatings at room temperature or low temperatures will preserve the strength and fracture properties and at the same time will provide much better friction and wear properties.

Earlier studies carried out on 6061 aluminum alloys have demonstrated that thin hard coatings of TiN are useful for improving the wear properties of lightweight alloys. The present study was undertaken to assess whether the same hard coating techniques are also useful for improving the wear resistances of other aluminum alloys as well as those magnesium and titanium alloys.

2. RATIONALE FOR THE CHOICE OF COATING PROCESS AND COATING MATERIAL

Reactive magnetron-sputtered coatings of TiN have been used to protect the non-ferrous alloy surfaces. The process and material selection were based on the considerations outlined below.

Soft coatings of metals such as lead have been used to overcome the friction and wear problems encountered with non-ferrous alloys. Soft films, however, wear gradually and the protection is eventually lost. The endurance life of soft films is a function of the operating environments but is finite. However, this is not the case with hard coatings.

In a sliding contact between a soft base material of hardness $H_b$ and a harder counterface of hardness $H_c$, the rate of wear of the soft material depends on the hardness ratio $H_c / H_b$. Un lubricated wear tests by Kruschov have shown that very rapid wear of the soft base material occurs when the $H_c / H_b$ ratio is of the order of 1.5 and above. Wear is light when the ratio is of the order of 0.72–1.15. Similar results have been reported by Richardson: this has led Halling to suggest that an $H_c / H_b$ ratio of 0.4 is essential to make the wear rate of the soft substrate negligible. This implies that a hard coating with a hardness some 2.5 times that of the counterface will yield wear protection to the base material (the substrate). Wear is now restricted to the hard counterface. Since the coating “will not wear”, thick coatings are not necessary.

If the counterface is a steel, since the maximum counterface hardness in engineering use commonly lies in the Vickers hardness range 600–800 kgf mm$^2$ (for the hardened steel counterface), coatings with Vickers hardnesses of 1500–2000 kgf mm$^2$ are sufficient for the total wear protection of non-ferrous substrates. Hard compounds of refractory metals (WC, TiC, TiN etc.) meet these requirements. The hard coatings promise indefinite wear life. An adequate coating hardness is a necessary condition.

Hard coatings are not usually used with soft substrates since differential strains at the coating–substrate interface can cause film failure. To offset this risk, when hard layers are used on softer substrates for wear protection, they are generally thick (of the order of 1 mm or more when case hardening, plasma spraying etc. are used) provided that hard coatings can be deposited without geometric defects. This is not a
MAGNETRON SPUTTERING OF NON-FERROUS ALLOYS

Theoretical requirement. The thin hard coating can be treated as a Griffith solid. High fracture stresses and fracture (tensile) strains must then be expected. The thin coating may be treated as a compliant coating. Ideally, the coating should have the same elastic properties as the substrate, but this is impossible. When the coating is well bonded, the violation of this requirement is not very serious. As close a match as possible is desirable. Thin hard coatings satisfactorily bonded to the substrate thus meet most of the requirements necessary and sufficient to provide wear protection.

The use of thin hard coatings precludes large temperature gradients across them and limits the propensity of the coating to debond. The other characteristic of importance here is the product $E\alpha$ where $E$ is Young’s modulus and $\alpha$ is the coefficient of thermal expansion. Thin coatings of hard metal compounds with small $E\alpha$ products are thus preferred for the wear protection of non-ferrous alloys.

Nearly all the hard compounds of refractory metals (WC, W2C, TiC, TiN, HfC, HfN, ZrC etc.) meet the hardness requirements. The product $E\alpha$ considerations favor titanium, hafnium and zirconium compounds, in that order. The final choice among these will have to be based on factors related to the choice of deposition process and the ease of coating deposition.

The substrate temperature permissible during hard coating restricts the allowable coating processes. Plasma-assisted coating is essential to obtain the required coating-to-substrate bond strength. Vacuum sputtering processes are the candidates. R.f. and d.c. sputtering can meet the requirements. Ion plating cannot be used because of the uncontrolled temperature rise and the possibility of gas (argon) occlusion during film deposition. Reactive ion plating also requires close control of the ion-plating atmosphere to produce the required stoichiometry.

The film thickness required lies in the range 1-10 $\mu$m. The coating rates feasible with r.f. and conventional d.c. sputtering are low. Magnetron sputtering is preferred; this process also permits reactive sputtering with inexpensive metallic targets. The availability of titanium and zirconium in plate and sheet form makes titanium and zirconium compounds the prime hard coating candidates. Titanium is a better “getter” than zirconium and is preferred for sputter coating in a cleaner vacuum.

In the reactive sputtering of titanium to produce TiC and TiN, the use of Ar-hydrocarbon and Ar-N$_2$ environments is essential. Nitrogen is a more reactive gas in the plasma environment. Concurrent synthesis and deposition of TiN are fairly easy. The use of N$_2$ also avoids the risk of hydride formation. Well-bonded coatings are routinely produced by reactive magnetron sputtering. Thin hard coatings of TiN were therefore selected and deposited with magnetron sputtering in this study to assess the ability of TiN to protect aluminum, magnesium and titanium alloys from wear.

3. EXPERIMENTAL MATERIALS AND METHODS

Test samples 10.16 mm x 15.75 mm x 6.35 mm suitable for friction and wear measurements in a Faville-LeVally Alpha model LFW-1 wear tester were machined from rolled plates of 2024-T351 aluminum and Ti-6Al-4V. Magnesium samples were machined from magnesium alloy castings (Mg-4.25Zn-1.25rare earths-0.5Zr). Surfaces to be coated were prepared by wet grinding in a metallographic polishing
Fresh 600 grit SiC was used to produce a standard initial surface roughness in all test samples. The wet ground samples were repeatedly washed in distilled water and acetone and were then dried with a blast of N₂. Cleaned specimens were placed in the sputter-coating chamber with minimal delay.

The TiN coating was deposited by operating a d.c. magnetron coating system in the reactive sputtering mode. An Ar–N₂ atmosphere was used. The hard coatings were deposited at an operating pressure of 0.09–0.15 Pa. By varying the deposition time (coating rate, 120 nm min⁻¹), films ranging in thickness between 1 and 4.5 μm were produced. The system used is the same as that used in an earlier work. To obtain the required coating-to-substrate bond strength, the test samples were sputter cleaned initially at a pressure of 2.7 Pa for 5 min. A movable shutter was used to prevent target contamination during sputter cleaning. The reactive sputtering conditions (operating voltage, cathode current density, gas mixture composition, flow rate etc.) used in the present work were identical with those reported earlier. Using these conditions, hard coatings (of Vickers hardness 1900 kg mm⁻²) are routinely produced. The golden-yellow films produced exhibit lattice parameters within 1°–2° of the theoretical value. From lattice parameter and X-ray diffraction studies the films were judged to be stoichiometric or nearly so. For stoichiometry measurements, Rutherford backscattering studies are preferred and are in progress.

Friction and wear studies were conducted on a Faville–LaVally Alpha model LFW-1 test machine using procedures given in the ASTM Standard. All tests were carried out at a sliding speed of 0.13 m s⁻¹. An unformulated paraffinic mineral oil of viscosity 26 mm² s⁻¹ at room temperature was used in the tests. Test rings hardened to a Rockwell C hardness of 61–63 with a surface finish of 0.4 μm (r.m.s.) were used. A typical test sliding distance for hard-coated specimens was 550 m. Tests on uncoated samples were terminated when the volume of wear was excessive. Figure 1 shows the dimensions of wear scars produced on bare samples when the tests were terminated.

Tests on aluminum, titanium and magnesium alloys were carried out at maximum initial hertzian pressures (block-on-ring test geometry; nominal line contact) equal to 0.62 of the calculated yield strength. Yield strengths were...
calculated by measuring the indentation hardness and using the well-known relation

\[
\text{yield strength} = 3 \times \text{indentation hardness}
\]

Calculations and friction and wear observations show that the elastohydrodynamic lubrication load-carrying component of the lubricant film was insignificant. New test rings and fresh oil were used in each test. Test conditions used with the three hard contact substrate materials are shown in Tables I and II.

**TABLE I**
WEAR TEST CONDITIONS AND RESULTS ON 2024-T351 ALUMINUM TEST SPECIMENS

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<th>Parameter</th>
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<td>0.19, 0.16</td>
</tr>
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</tr>
<tr>
<td>Ring mass loss (mg)</td>
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</tr>
<tr>
<td>Block wear coefficient ( k \times 10^6 )</td>
<td>10.2</td>
<td>3.57</td>
</tr>
<tr>
<td>Ring wear coefficient ( k \times 10^6 )</td>
<td>( \leq 10^2 )</td>
<td>7.38</td>
</tr>
<tr>
<td>Sliding distance (m)</td>
<td>330</td>
<td>550</td>
</tr>
</tbody>
</table>

\* The coefficient of friction values quoted are the time-averaged values for the beginning and end of the tests.

\* A negative loss indicates that the ring gained mass.

\* For coated specimens a Vickers hardness of 2200 kg mm^-2 for TiN was used.

**TABLE II**
WEAR TEST CONDITIONS AND RESULTS ON CAST MAGNESIUM ALLOY (OF COMPOSITION Mg 4.25Zn 1.25
RARE EARTHS -0.5Zr)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncoated</th>
<th>TiN coated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3.6 pm</td>
</tr>
<tr>
<td>Load (kN m^-1)</td>
<td>23.3</td>
<td>23.3</td>
</tr>
<tr>
<td>Hertzian pressure (MN m^-2)</td>
<td>133.8</td>
<td>182.0</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>0.21, 0.20</td>
<td>0.24, 0.20</td>
</tr>
<tr>
<td>Block weight loss (mg)</td>
<td>7.52</td>
<td>11.15</td>
</tr>
<tr>
<td>Ring weight loss (mg)</td>
<td>-0.36</td>
<td>0.00</td>
</tr>
<tr>
<td>Block wear coefficient ( k \times 10^6 )</td>
<td>71.4</td>
<td>56.0</td>
</tr>
<tr>
<td>Ring wear coefficient ( k \times 10^6 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sliding distance (m)</td>
<td>231</td>
<td>231</td>
</tr>
</tbody>
</table>

\* See Table I.

5. TEST RESULTS AND DISCUSSION

Friction and wear test data are presented in Tables I–III for the coated and uncoated test samples. As mentioned earlier, three different film thicknesses were used for the aluminum alloy substrates. In addition to the standard maximum hertzian pressure (which is equal to 0.62 of the yield strength) normally used, a
second set of tests were carried out at a hertzian pressure of 0.85 of the yield strength for the cast magnesium alloys (Table II).

### TABLE III

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncoated</th>
<th>TiN-coated 3.6 μm coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (kN m⁻¹)</td>
<td>283.3</td>
<td>283.3</td>
</tr>
<tr>
<td>Hertzian pressure (MN m⁻¹)</td>
<td>650.2</td>
<td>650.2</td>
</tr>
<tr>
<td>Coefficient of friction *</td>
<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>Block mass loss (mg)</td>
<td>5.15</td>
<td>0.12</td>
</tr>
<tr>
<td>Ring mass loss (mg)</td>
<td>0.43</td>
<td>1.61</td>
</tr>
<tr>
<td>Block wear coefficient * k (× 10⁹)</td>
<td>1000</td>
<td>1.44</td>
</tr>
<tr>
<td>Ring wear coefficient * k (× 10⁹)</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>Sliding distance (m)</td>
<td>2</td>
<td>550</td>
</tr>
</tbody>
</table>

* See Table I.

The test results presented show that TiN coatings not less than 3.6 μm thick reduce the wear rate of 2024 aluminum alloys by approximately two orders of magnitude. The wear protection afforded to titanium is more spectacular. Titanium is known to gall and wear severely in sliding contact. The mass loss in the bare titanium alloy test in only 2 m of sliding is 5.15 g whereas the mass loss of TiN-protected sample is negligible, i.e. wear debris is transferred to the counterface. The reduction in the wear coefficient is more than three orders of magnitude when a thin 3.6 μm TiN hard coating is used to protect titanium alloys.

For the cast magnesium alloy, the 3.6 μm thick hard coating is sufficient to obtain wear resistance at maximum contact stresses equal to 0.62 of the yield strength. The higher contact stress tests indicate a gain in wear resistance, but not total wear protection. Apparently a thicker hard coating is essential. This observation is similar to that with a thin coating (1 μm) on aluminum.

### 6. SUMMARIZING REMARKS AND CONCLUSIONS

Light-weight non-ferrous alloys commonly used in aerospace applications are prone to severe wear in sliding contact. Theoretical considerations suggest that improvements in wear resistance are possible with thin hard coatings. Magnetron-sputtered hard coatings of TiN may provide the required wear resistance.

Sliding wear tests carried out with hard coatings 1–4.5 μm thick show that TiN films 3.6 μm thick are sufficient to reduce the wear rate to negligibly small levels provided that the contact stress does not exceed 0.62 of the yield strength.

All three alloys of interest in aerospace applications can be protected with TiN hard coatings. The rationale for the use of hard coatings to improve the wear resistance of soft materials, outlined in Section 2, is confirmed.

The absence of debonding demonstrates that well-bonded TiN hard coatings can be produced by reactive magnetron sputtering. Coefficient of friction measurements show that coating-to-substrate shear strengths in excess of 27 MPa, 48 MPa and 95 MPa can be produced in magnesium, aluminum and titanium substrates respectively. Commonly, the contact stress under boundary-lubricated
sliding contact conditions rarely exceeds 20 MPa. The bond strength required is obtained easily.

ACKNOWLEDGMENTS

The authors thank Richard Marks, Pratt and Whitney, Mississauga, Ontario, Canada, for the provision of the magnesium alloy test samples. We thank Mrs. J. Van Hook for careful manuscript preparation.

The results reported here were obtained in the course of a tribology research program funded by the U.S. Department of Transportation under Contract DTRS5680-C-00015 (Mr. Russell Zub, Project Monitor, Transportation Systems Center, Cambridge, MA).

REFERENCES

This draft phase report summarizes the accomplishments in the first ten months of the first phase of the program entitled: "Fundamental Studies in Tribology as Related to Automotive Fuel Economy".

Work schedule for the first phase requires under Task I: (a) development of coating techniques, (b) preliminary coating trials, and (c) screening for tribological behavior. Under Task II the schedule calls for high pressure shear rheological studies of motor oils. Theoretical work on mechanics of thin film function and wear of automotive tribosystems are called for in Task III.

In the following pages of the draft phase report, the work accomplished in Tasks I and II are summarized. Coating system and technology have been developed. Coating trials are underway. Non-ferrous and ferrous materials of interest for automotive application have been coated successfully. Shear rheological and traction studies have been carried out on motor oils. This phase report is a concise summary and will serve as the basis for a detailed Phase Report due on 31 July 1981. It will, in addition, contain results obtained in the program period June and July 1981.
TASK I: DEVELOPMENT OF COATING TECHNIQUES

A sputtering facility for high rate deposition of metals and hard compounds has been developed and tested. It has been used to deposit thin layers of hard and soft compounds to modify friction and wear characteristics of tribological pairs. Friction and wear tests have been carried out on coated ferrous and non-ferrous test samples.

The coating process developed to modify the friction and wear characteristics of tribological pairs and the tribological test results obtained are presented in the following sections of this part of the progress report.

a. Coating System

The coating system developed consists of four principal sub-systems. It is designed to facilitate metallic coating at high rates (magnetron sputtering) as well as coating of hard material compounds such as TiN. The latter requires reactive sputtering. Suitable provisions have therefore been made for atmosphere control.

The principal sub-systems developed are:

a) a vacuum plant
b) a high rate sputtering head
c) a sputtering atmosphere control system, and
d) a power supply.

The vacuum plant developed consists, basically of a CVC 14" vacuum system suitably modified for the present needs. A vacuum chamber defined by a 12 inch diameter x 12 inch high Pyrex cylinder, a top
plate and a base plate is used. The vacuum chamber can be evacuated to pressures less than $10^{-5}$ torr with a four inch diffusion pump and a 5.6 CFM Mechanical pump. The system is equipped with a four inch gate valve and two roughing valves for vacuum sequencing and to control ambient pressure during sputtering. The system is equipped with a bleed valve to bring the vacuum chamber to atmospheric pressure for specimen loading and unloading.

The top plate of the vacuum chamber carries the sputtering head and is electrically insulated from it with the insulator ring. It also carries a sputtering pressure monitoring gage, a shutter control, and a gas inlet. The base plate of the system contains a number of electrical and instrumentation feed-throughs.

The specimens to be coated are carried on a platform connected to a high voltage feed-through to facilitate specimen cleaning by sputtering. A ground shield serves to limit the plasma generated during sputter cleaning from acting on the back streaming molecules. A shutter serves to shield the coating target from the contaminating species during the cleaning.

The sputtering head developed is a cylindrical structure with four ALNICO ring magnets and a HICOREX magnet. The ring magnets, the pole pieces and the HICOREX magnet define a circularly symmetric magnetic field needed for high rate magnetron sputtering. The magnet assembly is positioned on the atmospheric side of the cathode carrier while the metallurgically bonded coating target is carried on the vacuum side. The magnet assembly and the cathode carrier are mounted on a cathode
ring and enclosed in a water-cooled casing.

Water introduced through a 1/4 inch steel tube is routed through the pole piece to cool the rear surface of the cathode carrier. Following circulation, water is drained through an opening in the PVC case. Water cooling and metallurgical bonding of the target are essential to remove the large power dissipated (up to 1.8 kW) at the cathode surface during high rate sputtering.

An appropriately configured anode is positioned close to the cathode. The anode geometry and the position with respect to the cathode have been empirically optimized. The close coupling between the magnetic field B and the electric field E, is the key factor in permitting successful reactive sputtering to produce golden yellow TiN at high deposition rates.

Consistent and reproducible reactive sputtering of hard compounds requires higher sputtering voltages than those available in commercial magnetron sputtering systems. Therefore a new system had to be designed, built and tested to meet the needs of tribological coatings.

The two-inch sputtering head developed is a key component of the sputtering system. This newly designed system has been tested at a total cathode current of over two amperes. Coating at 900 volts with a cathode current of two amperes represents a 1.8 kW sputtering system. Under typical sputtering pressures of 0.5 to 1.5 millitorr, power dissipation density at the cathode surface is then 90 watts per cm² (which is among the highest attained anywhere). The cathode current density in this magnetic field-assisted system is three orders of magnitude (1000 times) higher than that in conventional DC sputtering systems.
The operating voltage of 300 to 1000 volts, is also much lower than the 2.5 to 10 kV typical in conventional sputtering systems. High sputter coating rates are hence obtained.

The sputtering atmosphere control system developed requires flexibility. In the present instance, two types of gaseous atmospheres are necessary: (a) a low pressure argon environment for high rate sputtering of metals and alloys, and (b) a low pressure argon-nitrogen environment to synthesize and deposit hard compounds (reactive sputtering). The integrated gas control system developed meets both these needs.

The gases dispensed from the tanks at pressures of 5 psia are dried in molecular sieve drying columns and metered through needle valves into an oxygen trap. The dry gases mixed in the trap emerge oxygen-free and are admitted into the vacuum chamber through a gas inlet.

Typically, the argon flow rate is 5 SCCM during glow discharge cleaning. During sputter coating, the total gas flow rate through the system is about 4 SCCM, or as needed. In course of reactive sputtering, the argon flow rate is 2 SCCM, while the nitrogen flow rate is 2.5 SCCM (Values found empirically to yield golden yellow, TiN films). To obtain these specific flow rates, two needle valves are used. Two separate mass flow rate meters are used to control the sputtering atmosphere.

Two power supplies are used in conjunction with the sputtering system. The first one, a CVC Model LC-301, is a high reactance, variable voltage DC supply rated at 300 ma (continuous duty) at 5 kV (maximum voltage). The second one is a high current (2.5 amp) low voltage
(1000 V max) power supply, Hippotronics MODEL 801-2500, equipped with a high speed shut-off to protect the solid state rectifiers in the system.

The CVC power supply is typical of that in commercial use for conventional DC sputtering. It was used in this program solely for glow discharge cleaning prior to coating.

The main supply in commercial high rate deposition systems are also high reactance power supplies (usually limited to 800 volts). High reactance is considered to be essential for the protection of the supply system during arcing transients and sputter target flaking during high rate sputtering. When high reactance transformers are not a part of the power supply, a saturable core reactor is used to limit the cathode current during various instabilities.

Instead of these usually high cost power supplies, an off-the-shelf power supply (Hippotronics Model 8100-2500) was used in this program. To obtain system stability, a low resistance, high current inductor connected in series with the sputtering head was used. The 30-ohm, 1.25 amp. inductors used (5H) are fully able to suppress all but the most severe arcing transients. System could be operated routinely, once stability is attained, for longer than one hour at a time, fully unattended.

b. Coating Practice

In a typical sputtering run, the components to be coated are washed with water and detergent followed by ultrasonic cleaning in acetone. They are withdrawn from the acetone bath, dried with a blast
of nitrogen and placed on the specimen carrier plate of the sputtering chamber. Once the substrates (specimens) to be coated are placed in the vacuum chamber, the chamber is rough-pumped to a pressure between 50 and 100 millitorr. Roughing valve is then closed and dry nitrogen admitted into the vacuum chamber to a pressure to 5 torr. The vacuum chamber is pumped again to better than 100 millitorr. It is back filled with dry argon to 5 torr and evacuated again to a residual pressure of 50 millitorr.

On reaching 50 millitorr, the diffusion pump is used to evacuate the system to its limiting pressure (approximately $10^{-6}$ torr). This pumping sequence is followed to desorb as much of the contaminating vapor species (mostly water vapor) as is possible.

After approximately five minutes at limiting pressure, argon gas is admitted into the system and the gate valve is adjusted to obtain a steady chamber pressure of 20 millitorr. A negative potential between 2 and 2.5 kV is applied to the substrate and the substrate is glow-discharge cleaned. Glow discharge cleaning is carried out for 15 minutes. Power dissipation during glow discharge cleaning (100 to 125 watts) is sufficiently low to preclude large temperature rise during cleaning (heating up to 100 to 150°C is desirable to desorb water vapor from surfaces to be coated).

Following glow discharge cleaning, argon flow is reduced to 2 SCCM and the high vacuum valve is readjusted to maintain the chamber pressure at 2 to 5 millitorr. With the shutter still in position, a negative potential is applied to the sputtering cathode (with the specimen at ground potential) and the voltage raised until a stable,
low current magnetron discharge is initiated. The pressure is then dropped to between 1 and 2 millitorr and cathode current raised to between 500 and 600 ma.

As the contaminant gases are sputtered away from the target, the initial pink-violet discharge changes color to an intense blue. Once the intense blue is obtained (due to titanium sputtering), the shutter is rotated out of position and titanium deposited on the substrate for up to two minutes (maximum cathode current during this phase is 1000 ma). Nitrogen gas is then admitted into the system (flow rate of 2.5 SCCM) and high vacuum valve readjusted to maintain the pressure between 0.5 and 1.2 millitorr.

On the admission of nitrogen, due to its inefficient sputtering, system current drops by approximately 55%. Sputtering pressure and voltage are then adjusted to raise the system current to 1000 ma. Under these conditions, Titanium is sputtered off the target at a rate greater than that possible for nitrogen to condense on its surface. TiN synthesis in the vapor phase ensues to yield golden-yellow nitride.

If golden-yellow TiN is essential it is absolutely necessary to operate the system at high cathode currents, low pressures and high voltages. In the course of this program, it has been found that the best TiN films are produced with the present system at the following operating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>System voltage</td>
<td>925 to 950 V</td>
</tr>
<tr>
<td>Cathode current</td>
<td>1000 to 1200 ma</td>
</tr>
<tr>
<td>System Pressure</td>
<td>1.75 to 2.25 millitorr</td>
</tr>
</tbody>
</table>
Typically a coating run is for 30 to 60 minutes. Following the coating, nitrogen flow is cut-off and the system left in place to 'cool down' for 30 minutes. After shutting argon flow and isolating the vacuum chamber from the pumping system, air is bled into the system and top plate removed to take the coated specimens out of the coating system.

Principal heating during coating is due to the condensation of the TiN on the substrate surface. There is some secondary heating due to 'electron leak' from the vicinity of the central pole piece. Measurement of specimen surface temperature immediately following the cessation of coating shows that surface temperatures do not exceed 375F.

c. Coating System Operating Characteristics

While metallic coatings are easily produced at a variety of coating conditions, coatings of hard compounds (with specific stoichiometry) require particular combinations of operating voltages, coating pressures and atmospheres. These factors were recognized during system design. System developed hence permitted desired hard coatings to be deposited routinely. Typical operating conditions necessary to produce needed wear-resistant coatings are shown in the previous section.
As expected from plasma coating theory, coating rate increased with decreasing coating pressures. Coating rate also increased with sputtering power. Some typical experimental results obtained are shown in Figure I.C.1.

In magnetron sputtering, the coating flux is obtained from a planar, extended, non-homogeneous source. Thickness of the coating produced is a function of axial and radial distance from the center of the cathode. To assess coating uniformity, test samples were coated at various radial locations (axial distance was maintained constant), and thickness produced measured. The results obtained are shown in Figure I.C.2.

A theoretical model has been developed to predict the expected coating thickness distribution. It was assumed that the strength of the source is proportional to the transverse field strength of the electron trap used in magnetron sputtering. The transverse field strength of the magnetic field used in the system was measured with a Hall probe assembly and used to calculate the expected coating thickness distribution. Measured values and expected values are in good agreement as may be seen from Figure I.C.2. Coating characteristics of magnetron sputtering systems are found to depend on magnetic field design (for electron trap).

d. Characterization of Wear-resistant Coatings

Micro-hardness measurements and x-ray diffraction techniques were used to characterize coatings deposited. Micro-hardness measurements on taper-sectioned test samples showed that coatings with
Figure 1.C.1 Coating Rate as Function of Operating Pressure and Consumed Power.
Figure 1.C.2  Calculated Thickness versus Measured Thickness

Measured Strength of the Horizontal Component of the Applied Magnetic Field as Function of Radial Distance on Target Surface.
hardnesses greater than $H_v 2000$ are routinely produced by reactive sputtering of titanium (to produce TiN). Titanium nitride, a defect compound, can possess a range of stoichiometries. Distinct colors are associated with specific ranges of stoichiometry, golden-yellow being that of the perfect compound. This was obtained routinely.

Since in sputtering, non-equilibrium structures are usually produced and the films deposited are under stress, x-ray analysis is not an unambiguous indicator of film stoichiometry. Additional x-ray analysis problems are introduced by preferred texture in coatings. Despite these difficulties, x-ray analysis suggests that the films produced are titanium nitride compounds. Expected x-ray peaks and those observed are listed in Table I.D.1. The data obtained is taken to indicate TiN film deposition. Supporting evidence is provided by microhardness and color data.

Films produced do possess substantial tensile residual stresses. By measuring the "bowing" of coated stainless steel foils, the residual stresses have been determined to be of the order of $200 \times 10^3$ psi (when coated on steel substrates). These large residual stresses can lead to adhesion problems in tribological applications. Hence tests are now in progress to lower the residual stresses.

e. Tribological Evaluation of Coatings Produced

To assess the utility of hard coatings (TiN) in non-ferrous automotive castings such as pistons, test blocks of aluminum, and magnesium alloys have been sputter coated with titanium nitride. Sliding contact wear tests (LFW-1) have been carried out and wear
Table I.D.1

X-Ray Diffraction Peaks of TiN (ASTM Data)

<table>
<thead>
<tr>
<th>Reflection Plane</th>
<th>Spacing (d(\text{A}))</th>
<th>Peak at* (2\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h) (k) (l)</td>
<td>(2\theta)</td>
<td>(2\theta)</td>
</tr>
<tr>
<td>1 1 1</td>
<td>2.4480</td>
<td>36.68°</td>
</tr>
<tr>
<td>2 0 0</td>
<td>2.1200</td>
<td>42.61°</td>
</tr>
<tr>
<td>2 2 0</td>
<td>1.4991</td>
<td>61.84°</td>
</tr>
<tr>
<td>3 1 1</td>
<td>1.2784</td>
<td>74.46°</td>
</tr>
</tbody>
</table>

*With Ni-filtered CuK\(\alpha\) radiation.

X-Ray Diffraction Peaks Attributable to the Coating

<p>| Peak Observed at (2\theta) | Spacing* (d(\text{A})) |
|-----------------------------|----------------|------------------|
| 36.4°                       | 2.4685         |</p>
<table>
<thead>
<tr>
<th>42.4°</th>
<th>2.1321</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.76</td>
<td>1.2699</td>
</tr>
</tbody>
</table>

*Computed values correspond to observed \(2\theta\) values.
Table I.D.2. LFW-6 Test Results*

<table>
<thead>
<tr>
<th>Material</th>
<th>Friction Coefficient μ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RPM 200</td>
</tr>
<tr>
<td>Steel (AISI 1214)</td>
<td>0.098</td>
</tr>
<tr>
<td>Steel (AISI 1018)</td>
<td>0.146</td>
</tr>
<tr>
<td>Cast Iron (As Received)</td>
<td>0.112</td>
</tr>
</tbody>
</table>

*Test duration 30 minutes
Test surface and the counter faces were TiN coated. Coatings survived all the tests. All tests were carried out with n-hexadecane. Fluid used is not a lubricant.
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Film Thickness</th>
<th>Cord Length</th>
<th>Total Deflection</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>h: (μ in)</td>
<td>2L: (in)</td>
<td>f: (in)</td>
</tr>
<tr>
<td>A</td>
<td>81</td>
<td>1.478</td>
<td>0.0995</td>
</tr>
<tr>
<td>B</td>
<td>43</td>
<td>1.515</td>
<td>0.082</td>
</tr>
</tbody>
</table>

Measured Deflection of Stainless Steel Shim Stock after Nitride Sputtering.

Configuration of Stainless Steel Shim Stock after Nitride Sputtering.

\[ \sigma_1 = \frac{E}{3L^2} \left( \frac{(H - h_1)^2}{\Delta h_1} \right) \left( \frac{\Delta f}{\Delta h} \right)_1 = 0.2076 \times 10^6 \text{ psi} \]

Young's modulus of TiN is \(29 \times 10^6\) psi. Thus, elastic strains of \(0.2076/29 \times 100\%\) are expected, \(\varepsilon = 0.7157\%\).
coefficients determined. The results obtained are summarized in a paper to be presented in July 1981 in Brussels [IPAT 81 International Conference sponsored by the European Physical Society, Metals Society (London) and the Welding Institute (London)]. The paper has been accepted for publication in a forthcoming issue of Thin Solid Films.

Briefly, the test results obtained show that well-adherent thin coats (5 μm or less in thickness) offered excellent wear protection to non-ferrous alloys. At each hertzian contact stress level, full wear protection is obtained only above a film thickness threshold of the order of 1.5 to 2 μm. Wear resistance is improved by several orders of magnitude (wear coefficients measured are tabulated in the paper). A copy of the paper is attached to this progress report.

The LFW-1 wear tests are low speed, high stress friction and wear tests. To assess, medium and high speed friction characteristics, LFW-6 test specimens (pure sliding) have been fabricated and coated. One cast iron and two types of annealed steels have been used to fabricate test samples. Coated and tested samples exhibit wear protection due to the hard coating. Friction test results are summarized in Table I.C.I. The results obtained suggest that wear protection can be afforded to such automotive components as cam shafts, tappets, etc., made of cast iron (preliminary test results). Additional and more extensive test program is now under way and the results will be reported in the annual report. While hard coat adhesion is easily obtained with non-ferrous materials, significant problems are encountered in producing well-adherent coatings on hardened steels.
(valve train components are hardened irons and steels). Chemical surface treatments (prior to sputter coating) have been found to overcome the adhesion problems. Early tests in rolling hertzian contact tests at up to 150 ksi have been successful. A summary of test results (LFW-6 tests) will be reported in the final report of the first year's work of the present program.

Techniques for DC sputtering of dichalcogenide soft coats have been developed. Soft coats have been found to have a limited life. Coating adhesion problems that do not appear to be surmountable by chemical surface conditioning are encountered. Radio frequency magnetron sputtering is essential. A RF power supply is presently on order. Additional work with soft coats awaits the delivery of the RF sputtering power supply.

f. Work in Progress

Tribological pairs found in automotive engines and transmission systems require substantial wear life. By hard and soft coating, wear life and wear-in characteristics can be improved to attain better economy. To preserve these characteristics, the coatings deposited must be well-bonded to the substrate. Retention of improved tribological characteristics depends critically on coating-to-substrate bond strength.

Quantitative bond strength tests are not available. 'Peel' tests subject coatings to plastic bonding. Measured quantities contain non-quantifiable contributions due to plastic bending of coating. Stress state in "scratch" tests is not determinable. Hence both these tests are not satisfactory as quantitative film-to-substrate bond strength tests.
By coating substrates and monitoring the film during stressing, substrate stress at film debonding can be determined. Elastic displacements in the substrate and coating will have to be the same just before film debonding. Equality of displacements at the coating-substrate interface and elastic modulii, then allow the interface shear strength \( \tau^* \) to be determined.

For tribological coatings to be successful, \( \tau^* \) must exceed \( \tau \) the shear stress on the coating surface during frictional contact. The quantity \( \tau \) is given by \( (\mu\sigma_n) \) where \( \mu \) is the friction coefficient and \( \sigma_n \) is the normal stress. Thus a knowledge of \( \tau^* \) and \( \mu \) allows, films failure normal stress \( \sigma_n^* \) to be calculated. Design contact stress \( \sigma_n \) cannot exceed \( \sigma_n^* \) to preclude film failure.

Tensile and torsion test samples are being coated to determine the film bond strength \( \tau^* \). The results obtained will be reported in the annual report.

The LFW-1 wear tests on TiN coated non-ferrous test samples show that bond shear strengths in excess of 27 and 48 MPa are obtained easily when magnesium and aluminum test samples are magnetron sputtered. In practice the normal stress in boundary lubricated sliding pairs does not exceed 15 MPa. Bond strengths obtained are thus sufficient to withstand friction coefficients \( \mu \geq 1 \). Similar data is being gathered presently for coated bodies of cast iron and steel (soft and hard).

Series of LFW-1 and LFW-6 tests are also in progress to determine the friction and wear characteristics of coated C.I and steel samples (soft and hard).
g. **Summary**

Task I is directed at establishing viable coating techniques applicable to non-ferrous and ferrous automotive components (pistons, piston rings, cams, tappets, gear train and valve train components, etc.) in order to lower the frictional dissipations, enhance wear-in and to lower wear rates. Magnetron sputtering technique has been chosen as a viable technology (This technology is now in use in G.M., and has been used by Borg-Warner for automotive and transmission applications).

A coating system has been developed and tested. Friction and wear tests have been carried out on selected non-ferrous materials. It has been demonstrated that significant modifications in tribological properties are possible and are obtained without difficulty. Preliminary tests have been carried out on a cast iron and two steels (both in the annealed condition).

Additional tribological studies and film-to-substrate bond strength studies are now in progress. Further development of soft coat techniques are also being pursued.
The light-weight non-ferrous alloys (titanium, aluminum and magnesium alloys) used in aerospace applications are prone to severe wear in small-displacement and large-displacement unlubricated contacts. Few metallurgical means are available for the surface protection of this class of materials. Deposition of hard compounds by sputtering provides a simple means of protecting such surfaces. Hard coating and tribological studies of coated samples were therefore carried out. The results obtained are presented in this paper. It is shown that magnetron-sputtered TiN hard coatings do provide the required wear protection.

1. INTRODUCTION

Non-ferrous alloys of aluminum, magnesium and titanium are light-weight materials. Further, the precipitation-hardenable alloys of aluminum and titanium possess high strength-to-weight ratios. They also exhibit excellent fracture toughnesses. These characteristics have led to the wide use of aluminum, titanium and magnesium alloys in aerospace applications.

These non-ferrous alloys are soft. In their bare form, in sliding contact without lubrication, the light-weight alloys are prone to severe adhesive and abrasive wear. Scuffing and galling occur readily. Surface protection through surface treatments is essential if these alloys are to be used efficiently in applications where boundary-lubricated or unlubricated contact with a counterface is unavoidable. Protection is also necessary in fretting environments.

Metallurgy of these alloys, however, does not allow the use of routine surface treatments that are common for iron and steel alloys (surface and case-hardening treatments). Treatments involving high temperatures are also not possible for aluminum and magnesium alloys since they melt at moderate temperatures. Precipitation hardening, commonly used to improve the yield strength and fracture toughness, also involves treatment temperatures only some 100–200 °C above room temperature. Surface treatments involving elevated temperatures are therefore not suitable for improving the friction and wear properties of non-ferrous alloys.

The tribological properties, however, can be improved greatly by replacing the surface layers of these alloys with other materials. Conversion coatings and anodization are examples. Deposition of thin coatings is yet another way of altering surface properties. A wide range of materials can be deposited without the limitations inherent in conversion coatings and anodization. Deposition of thin coatings at room temperature or low temperatures will preserve the strength and fracture properties and at the same time will provide much better friction and wear properties.

Earlier studies carried out on 6061 aluminum alloys have demonstrated that thin hard coatings of TiN are useful for improving the wear properties of lightweight alloys. The present study was undertaken to assess whether the same hard coating techniques are also useful for improving the wear resistances of other aluminum alloys as well as those magnesium and titanium alloys.

2. RATIONALE FOR THE CHOICE OF COATING PROCESS AND COATING MATERIAL

Reactive magnetron-sputtered coatings of TiN have been used to protect the non-ferrous alloy surfaces. The process and material selection were based on the considerations outlined below.

Soft coatings of metals such as lead have been used to overcome the friction and wear problems encountered with non-ferrous alloys. Soft films, however, wear gradually and the protection is eventually lost. The endurance life of soft films is a function of the operating environment but is finite. However, this is not the case with hard coatings.

In a sliding contact between a soft base material of hardness \( H_s \), and a harder counterface of hardness \( H_c \), the rate of wear of the soft material depends on the hardness ratio \( H_c / H_s \). Unlubricated wear tests by Kruschov have shown that very rapid wear of the soft base material occurs when the \( H_c / H_s \) ratio is of the order of 1.5 and above. Wear is light when the ratio is of the order of 0.72-1.15. Similar results have been reported by Richardson: this has led Halling to suggest that an \( H_c / H_s \) ratio of 0.4 is essential to make the wear rate of the soft substrate negligible. This implies that a hard coating with a hardness some 2.5 times that of the counterface will yield wear protection to the base material (the substrate). Wear is now restricted to the hard counterface. Since the coating "will not wear", thick coatings are not necessary.

If the counterface is a steel, since the maximum counterface hardness in engineering use commonly lies in the Vickers hardness range 600-800 kgf mm\(^{-2}\) (for the hardened steel counterface), coatings with Vickers hardnesses of 1500-2000 kgf mm\(^{-2}\) are sufficient for the total wear protection of non-ferrous substrates. Hard compounds of refractory metals (WC, TiC, TiN etc.) meet these requirements. The hard coatings promise indefinite wear life. An adequate coating hardness is a necessary condition.

Hard coatings are not usually used with soft substrates since differential strains at the coating-substrate interface can cause film failure. To offset this risk, when hard layers are used on softer substrates for wear protection, they are generally thick (of the order of 1 mm or more when case hardening, plasma spraying etc. are used) provided that hard coatings can be deposited without geometric defects. This is not a
theoretical requirement. The thin hard coating can be treated as a Griffith solid. High fracture stresses and fracture (tensile) strains must then be expected. The thin coating may be treated as a compliant coating. Ideally, the coating should have the same elastic properties as the substrate, but this is impossible. When the coating is well bonded, the violation of this requirement is not very serious. As close a match as possible is desirable. Thin hard coatings satisfactorily bonded to the substrate thus meet most of the requirements necessary and sufficient to provide wear protection.

The use of thin hard coatings precludes large temperature gradients across them and limits the propensity of the coating to debond. The other characteristic of importance here is the product $E\varepsilon$ where $E$ is Young's modulus and $\varepsilon$ is the coefficient of thermal expansion. Thin coatings of hard metal compounds with small $E\varepsilon$ products are thus preferred for the wear protection of non-ferrous alloys.

Nearly all the hard compounds of refractory metals (WC, W2C, TiC, TiN, HfN, ZrC etc.) meet the hardness requirements. The product $E\varepsilon$ considerations favor titanium, hafnium and zirconium compounds, in that order. The final choice among these will have to be based on factors related to the choice of deposition process and the ease of coating deposition.

The substrate temperature permissible during hard coating restricts the allowable coating processes. Plasma-assisted coating is essential to obtain the required coating-to-substrate bond strength. Vacuum sputtering processes are the candidates. R.f. and d.c. sputtering can meet the requirements. Ion plating cannot be used because of the uncontrolled temperature rise and the possibility of gas (argon) occlusion during film deposition. Reactive ion plating also requires close control of the ion-plating atmosphere to produce the required stoichiometry.

The film thickness required lies in the range 1-10 $\mu$m. The coating rates feasible with r.f. and conventional d.c. sputtering are low. Magnetron sputtering is preferred; this process also permits reactive sputtering with inexpensive metallic targets. The availability of titanium and zirconium in plate and sheet form makes titanium and zirconium compounds the prime hard coating candidates. Titanium is a better "getter" than zirconium and is preferred for sputter coating in a cleaner vacuum.

In the reactive sputtering of titanium to produce TiC and TiN, the use of Ar-hydrocarbon and Ar-N$_2$ environments is essential. Nitrogen is a more reactive gas in the plasma environment. Concurrent synthesis and deposition of TiN is fairly easy. The use of N$_2$ also avoids the risk of hydride formation. Well-bonded coatings are routinely produced by reactive magnetron sputtering. Thin hard coatings of TiN were therefore selected and deposited with magnetron sputtering in this study to assess the ability of TiN to protect aluminum, magnesium and titanium alloys from wear.

3. EXPERIMENTAL MATERIALS AND METHODS

Test samples 10.16 mm x 15.75 mm x 6.35 mm suitable for friction and wear measurements in a Faville-LeVally Alpha model LFW-1 wear tester were machined from rolled plates of 2024-T351 aluminum and Ti-6Al-4V. Magnesium samples were machined from magnesium alloy castings (Mg-4.25Zn-1.25 rare earths-0.5Zr). Surfaces to be coated were prepared by wet grinding in a metallographic polishing
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calculated by measuring the indentation hardness and using the well-known relation

\[ \text{yield strength} = 3 \times \text{indentation hardness} \]

Calculations and friction and wear observations show that the elastohydrodynamic lubrication load-carrying component of the lubricant film was insignificant. New test rings and fresh oil were used in each test. Test conditions used with the three hard contact substrate materials are shown in Tables I and II.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coated</th>
<th>1.5 µm</th>
<th>3.6 µm</th>
<th>4.5 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (kN m(^{-1}))</td>
<td>63.0</td>
<td>63.0</td>
<td>63.0</td>
<td>63.0</td>
</tr>
<tr>
<td>Hertzian pressure (MN m(^{-1}))</td>
<td>257.2</td>
<td>257.2</td>
<td>257.2</td>
<td>257.2</td>
</tr>
<tr>
<td>Coefficient of friction (^{*})</td>
<td>0.16 (\pm) 0.02</td>
<td>0.15 (\pm) 0.016</td>
<td>0.19 (\pm) 0.016</td>
<td>0.18 (\pm) 0.016</td>
</tr>
<tr>
<td>Block mass loss (mg)</td>
<td>30</td>
<td>14.9</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>Ring mass loss (mg)</td>
<td>0.44</td>
<td>0.89</td>
<td>1.84</td>
<td>2.52</td>
</tr>
<tr>
<td>Block wear coefficient (k \times 10^{6})</td>
<td>0.21</td>
<td>0.20</td>
<td>0.24 (\pm) 0.20</td>
<td>0.27 (\pm) 0.18</td>
</tr>
<tr>
<td>Ring wear coefficient (k \times 10^{6})</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>Sliding distance (mm)</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

\(^{*}\) The coefficient of friction values quoted are the time-averaged values for the beginning and end of the tests.

\(^{*}\) A negative loss indicates that the ring gained mass.

\(^*\) For coated specimens a Vickers hardness of 22100 for TSN was used.

Friction and wear test data are presented in Tables I-III for the coated and uncoated test samples. As mentioned earlier, three different film thicknesses were used for the aluminum alloy substrates. In addition to the standard maximum hertzian pressure (which is equal to 0.62 of the yield strength) normally used, a
unit. Fresh 600 grit SiC was used to produce a standard initial surface roughness in all test samples. The wet ground samples were repeatedly washed in distilled water and acetone and were then dried with a blast of \( N_2 \). Cleared specimens were placed in the sputter-coating chamber with minimal delay.

The TiN coating was deposited by operating a d.c. magnetron coating system in the reactive sputtering mode. An Ar–\( N_2 \) atmosphere was used. The hard coatings were deposited at an operating pressure of 0.09–0.15 Pa. By varying the deposition time (coating rate, 120 nm min\(^{-1}\)), films ranging in thickness between 1 and 4.5 \( \mu m \) were produced. The system used is the same as that used in an earlier work\(^1\). To obtain the required coating-to-substrate bond strength, the test samples were sputter cleaned initially at a pressure of 2.7 Pa for 5 min. A movable shutter was used to prevent target contamination during sputter cleaning. The reactive sputtering conditions (operating voltage, cathode current density, gas mixture composition, flow rate etc.) used in the present work were identical with those reported earlier\(^9\). Using these conditions, hard coatings (of Vickers hardness 1900 kgf mm\(^{-2}\)) are routinely produced. The golden-yellow films produced exhibit lattice parameters within \( \pm 2\% \) of the theoretical value. From lattice parameter and X-ray diffraction studies, the films were judged to be stoichiometric or nearly so. For stoichiometry measurements, Rutherford backscattering studies are preferred and are in progress.

4. Evaluation of Friction and Wear Characteristics

Friction and wear studies were conducted on a Faiville-LaVally Alpha model LFW-1 test machine using procedures given in the ASTM Standard\(^10\). All tests were carried out at a sliding speed of 0.13 m s\(^{-1}\). An unformulated paraffinic mineral oil of viscosity 26 mm\(^2\) s\(^{-1}\) at room temperature was used in the tests. Test rings hardened to a Rockwell C hardness of 61–63 with a surface finish of 0.4 \( \mu m \) (r.m.s.) were used. A typical test sliding distance for hard-coated specimens was 550 m. Tests on uncoated samples were terminated when the volume of wear was excessive. Figure 1 shows the dimensions of wear scars produced on bare samples when the tests were terminated.

![Figure 1](image-url)

**Fig 1.** Surface profiles of wear scars for (a) TiN-coated magnesium (upper profile) for a sliding distance of 550 m and uncoated magnesium (lower profile) for a sliding distance of 231 m (load. 23.3 kN m\(^{-1}\)) and (b) TiN-coated titanium (upper profile) for a sliding distance of 550 m and uncoated titanium (lower profile) for a sliding distance of 2 m (load. 23.3 kN m\(^{-1}\)).

Tests on aluminum, titanium and magnesium alloys were carried out at maximum initial hertzian pressures (block-on-ring test geometry; nominal line contact) equal to 0.62 of the calculated yield strength. Yield strengths were
second set of tests were carried out at a hertzian pressure of 0.85 of the yield strength for the cast magnesium alloys (Table II).

**TABLE III**
WEAR TEST CONDITIONS AND RESULTS ON Ti 6Al-4V

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncoated</th>
<th>TiN 3.6 μm coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (kN/m)</td>
<td>283.3</td>
<td>283.3</td>
</tr>
<tr>
<td>Hertzian pressure (MN m⁻¹)</td>
<td>680.2</td>
<td>680.2</td>
</tr>
<tr>
<td>Coefficient of friction x 10⁻²</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>Block mass loss (g)</td>
<td>5.15</td>
<td>-</td>
</tr>
<tr>
<td>Ring mass loss (rpm)</td>
<td>0.47</td>
<td>1.61</td>
</tr>
<tr>
<td>Block wear coefficient (10⁻⁶ m⁻¹)</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>Ring wear coefficient (10⁻⁶ m⁻¹)</td>
<td>1150</td>
<td>1.44</td>
</tr>
<tr>
<td>Sliding distance (m)</td>
<td>2</td>
<td>550</td>
</tr>
</tbody>
</table>

* * See Table I

The test results presented show that TiN coatings not less than 3.6 μm thick reduce the wear rate of 2024 aluminum alloys by approximately two orders of magnitude. The wear protection afforded to titanium is more spectacular. Titanium is known to gall and wear severely in sliding contact. The mass loss in the bare titanium alloy test in only 2 m of sliding is 5.15 g whereas the mass loss of TiN-protected sample is negative, i.e., wear debris is transferred to the counterface. The reduction in the wear coefficient is more than three orders of magnitude when a thin 3.6 μm TiN hard coating is used to protect titanium alloys.

For the cast magnesium alloy, the 3.6 μm thick hard coating is sufficient to obtain wear resistance at maximum contact stresses equal to 0.62 of the yield strength. The higher contact stress tests indicate a gain in wear resistance, but not total wear protection. Apparently a thicker hard coating is essential. This observation is similar to that with a thin coating (1 μm) on aluminum.

6. SUMMARIZING REMARKS AND CONCLUSIONS

Light-weight non-ferrous alloys commonly used in aerospace applications are prone to severe wear in sliding contact. Theoretical considerations suggest that improvements in wear resistance are possible with thin hard coatings. Magnetron-sputtered hard coatings of TiN may provide the required wear resistance.

Sliding wear tests carried out with hard coatings 1-4.5 μm thick show that TiN films 3.6 μm thick are sufficient to reduce the wear rate to negligibly small levels provided that the contact stress does not exceed 0.62 of the yield strength.

All three alloys of interest in aerospace applications can be protected with TiN hard coatings. The rationale for the use of hard coatings to improve the wear resistance of soft materials, outlined in Section 2, is confirmed.

The absence of debonding demonstrates that well-bonded TiN hard coatings can be produced by reactive magnetron sputtering. Coefficient of friction measurements show that coating-to-substrate shear strengths in excess of 27 MPa, 48 MPa and 95 MPa can be produced in magnesium, aluminum and titanium substrates respectively. Commonly, the contact stress under boundary-lubricated
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sliding contact conditions rarely exceeds 20 MPa. The bond strength required is obtained easily.

ACKNOWLEDGMENTS

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REFERENCES

5. R. C. D. Richardson, The wear of metals by relatively soft abrasives. Wear, 44 (1978) 245
7. D. Scott, The assessment of wear-resistant coatings for arduous conditions of rolling contact. Wear 28 (1975) 125
TASK II: SHEAR RHEOLOGICAL CHARACTERIZATION OF LIQUID LUBRICANTS (MOTOR OILS)

Although tribosystems are necessary for the function of automotive systems, contact friction is a significant source of energy loss which reduces automotive fuel economy. The objective of the rheology portion of this phase of tribology studies was to measure the shear rheological properties of a group of automotive engine lubricants to determine the affect of lubricant composition on traction (friction) in concentrated contacts. Concentrated contacts occur in automotive systems at cams, gears and rolling element bearings. Traction drive mechanisms which are frequently discussed as future transmissions, also rely on concentrated contacts. To some degree lubricant behavior in concentrated contacts is indicative of its expected behavior in the ring-cylinder contact and in the high shear rate conditions of journal bearings.

The authors have shown [ref. 1,2] that the traction in concentrated contacts can be predicted by their limiting shear stress model using three primary rheological properties of the lubricant — the low shear stress viscosity, the limiting elastic shear modulus, and the limiting shear stress. Of these the limiting elastic shear modulus is important only for small shear strains of the film (less than three percent). Since practical systems quickly develop much greater strains than this, only the low shear viscosity and limiting stress are important for the evaluation of traction in automobile engines.

The low shear viscosity can be measured in a high pressure falling body viscometer (ref. [1]) and the limiting shear stress for comparison purposes can be obtained from concentrated contact traction
(shear stress) measurements (ref. [3]) in the form of the property averaged over a range of pressures. These measurements have been made for twelve commercial motor oils, the ASTM High Reference oil, and a pair of unformulated base oils and a pair of blends of polyalkylmethacrylate polymer (PAMA) and one base oil.

In addition, film thickness measurements were made for all samples to assess whether or not the traction measurements were made under full film conditions. These film thickness measurements allowed the calculation of an effective contact inlet viscosity and the subsequent comparison with measured low stress viscosity. This effective inlet viscosity is the high shear rate viscosity which can be expected to be indicative of the high shear rate viscosity important to journal bearing performance. The difference between the kinematic viscosity and the high shear viscosity is a function of the polymer type and concentration.

**FLUID SAMPLES**

Twelve commercial automotive engine oils typical of those in common use were obtained from service stations and auto parts retail stores. Descriptions provided by the manufacturer are listed in Appendix 1. They include five oils formulated for fuel economy, six SAE 10W-40 grades, three 10W-30 grades, and one each of 20W-50, 30, and 5W-20 grades. One is of synthetic base stock. The others are of refined petroleum base.

Also included in all tests run on the commercial oils was ASTM
High Reference Oil (HR) because this oil has been proposed as a standard for comparison in the ASTM Fuel Efficient Oil Program.

Two unformulated base oils and two blends of one of the base oils with two polyalkylmethacrylate polymers of different molecular weight were included in most tests to assess the effectiveness of V.I. improver alone. They are also described in Appendix 1.

EXPERIMENTAL EQUIPMENT

Viscometer

The viscometer used for these studies is shown in Figure 1. It is of the falling body type. The sinker is made of a magnetic material and translates through a thin brass sleeve plugged at one end and sealed at the other by an isolating piston to separate the sample from the pressurizing medium (Diester). Shearing of the sample occurs between the sinker and the sleeve inside diameter. The sleeve is housed in a non-magnetic vessel which is surrounded by a linear variable differential transformer.

The pressure of the medium (up to 0.66 Pa) is generated in an external pressure intensifier and measured with a precision Heise bourdon tube gauge. The viscometer is enclosed in an air-oven for temperature control (25-230°C) and is inverted to initiate a fall of the sinker. For a further description and additional results, see (ref. [4]).
**EHD Simulator**

The concentrated contact simulator is shown in Figure 2. The contact geometry is that of a crowned roller against a flat disk. The ellipticity of the contact can be varied from approximately 0.3 to 3 by varying the crown radius. All the data in this report are for an ellipticity ratio of 2.5 to 3. The disk is sapphire and the roller hardened 52100 steel.

The disk and roller are both driven through timing belts by a single variable speed motor. Therefore, the relative rotational speeds of the two surfaces are fixed by the timing gears. The rotational speeds are determined by a photo-optical tachometer on the drive motor shaft. The rolling speed or entrainment velocity is varied by the drive motor speed while the slip velocity, and hence the slide-roll ratio, is varied stepwise by the timing gears and continuously (± 0.07 about a mean) by the radial position of the roller contact on the disk. (The slide-roll ratio is defined as the difference between the velocities of the two surfaces divided by the average of the two surface velocities.)

The continuous variation of slide-roll ratio is accomplished through the slide-roll micrometer which moves the roller support along a linear bearing in a direction perpendicular to the disk rotational axis thereby varying the radial position of the contact on the disk. This causes the surface velocity of the disk at the contact to vary, hence varying the slide-roll ratio. The slide-roll ratio micrometer has a multi-turn potentiometer attached which results in an electrical
voltage proportional to the slide-roll ratio to facilitate recording the traction slide-roll ratio curve.

The side slip at the contact can also be varied through the side slip micrometer which moves the center of disk rotation perpendicular to the axis of roller rotation. If the axes of rotation of the disk and roller intersect, the side-slip is zero. The side-slip angle ($\theta$) has a significant influence on the traction in the low slide-roll ratio range (less than approximately $|0.03|$). All the data reported here was taken with zero slide slip.

The contact load is applied by a dead weight hung on the disk axis through a thrust bearing to prevent the weight from rotating. The weight is supported by the concentrated contact. The horizontal position of the disk axis is maintained at the drive gear by a ball bearing which is free to move axially and from above the disk by a flexible frame which resists the torque and motion along the roller axis of rotation. The horizontal position is laterally restrained in the direction of contact traction by the side-slip micrometer with a piezoelectric force transducer link to measure the contact traction. The piezoelectric traction transducer is very stiff (1 GN/m), has a flat frequency response to 10 kHz, and a force resolution of 0.01 N. The signals from this traction transducer and the slide-roll ratio transducer are connected to the y and x axis respectively of an x-y recorder to record the traction slide-roll ratio curve.

The disk, roller and roller support carriage are all in an enclosure to permit bulk temperature variation and measurement. The enclosure acts as a reservoir for liquid lubricants. The liquid
lubricant sample required is less than 5 cm$^3$.

The major simulator operating variable ranges are: hertz pressures to 2 GPa (depending on surface materials), rolling or entrainment velocity to $V = 3$ m/s, and bulk temperature from room temperature to 120°C.

Because of the high mechanical stiffness of the simulator and the good transient response of the traction transducer, small geometric irregularities in the system which cause small variations in the contact load and kinematics result in traction fluctuations. These are particularly apparent at low slide-roll ratio where the traction dependence on slide-roll ratio is very pronounced near zero slide-roll ratio. Those fluctuations resulting from kinematic variations tend to be eliminated as slide-roll ratio increases and traction becomes less dependent on slide-roll ratio. Those fluctuations, due to cam action of the disk or roller, will continue to be observed at higher slide-roll ratio.

Because of the flexibility of the device it is suitable for simulating a wide variety of tribosystems. For a further description and additional results, see ref. [3,5].

RESULTS

High Pressure Viscosity Measurements

In order to determine the low shear stress rheology of the lubricant samples their viscosity was measured as a function of pressure at the usual temperatures of 40°C, 100°C, and 150°C. (The two base oils and two blends were measured over a greater temperature range.) These data are shown in Figures 3-14 and tabulated for the motor oils in Table 1.
Figures 6 and 7 each contain data for two oils of the same grade and manufacturer but of differing formulation (i.e., standard versus fuel economy). No appreciable difference was found in the low shear rheology of these pairs. Oils S-7 and M-3 exhibited large increases in viscosity with time at low temperature (40°C) and moderate pressures (207 and 276 MPa respectively). This behavior has been observed before and is probably due to a solid phase separating from the oil. It is not likely to affect the short-time high shear stress rheology of the oil in a lubricated contact.

The conventional pressure viscosity coefficient, \( \alpha_{OT} \), and the reciprocal asymptotic isoviscous pressure coefficient, \( \alpha_1 \), are tabulated and defined for the motor oils in Table 2 and the base oils and polymer-base oil blends in Table 3.

**Traction Measurements**

The elastohydrodynamic traction (average lubricant shear stress for the full-film case) of all samples was measured in the simulator shown in Figure 2. In all cases the configuration was that of a sapphire disk on a hardened crowned steel roller.

Initial experiments were run with oil S-5 to finalize the technique for the traction program. A spherical roller which had been finished with #600 carbide paper was loaded to a peak Hertz pressure of \( P_H = 1.4 \) GPa and contact aspect ratio of one. The results are shown in Figure 15a for two consecutive runs as traction coefficient TC versus temperature for slide-roll ratios of \( \Sigma = 0.05 \) and 2.0. Measurements were taken in order of increasing temperature. The increase in TC with
temperature suggests that the lubrication mode is not full film but rather that as the temperature rises and the lubricant film diminishes, a greater share of the load and the traction is shared by the surface asperities. In fact, a "running in" effect can be seen in the first run where the traction level dropped for the measurement following the 70°C measurement whereas previous measurements showed successive increases in traction. This "running in" is carried over to Run 2 of Figure 15a where the traction curve is very much changed from Run 1. The calculated minimum film thickness for 80°C is 0.052 μm.

In Figure 15b, the same measurements were made for the roller after refinishing with 3/0 emery polishing paper and again for diamond lapping of the roller. The diamond lapping appears to reduce the affects of asperity interaction. It was decided to use a higher aspect ratio roller for the traction program to increase repeatability and reduce the peak Hertz pressure to that more characteristic of automotive practice.

The traction program for the thirteen motor oils consisted of loading a polished roller against an optically smooth disk to give a contact with an ellipticity ratio of $K = 3$ (minor axis in the direction of rolling) and a peak Hertzian pressure of 0.74 GPa (107,000 psi). The side-slip angle was set at zero and the sample and enclosure brought to temperature. With the rolling (average) velocity at $V = 1.0$ m/s, a slide-roll ratio range of $-0.08 < \Sigma < 0.06$ was scanned and the traction recorded. See Figure 16 for an example of the data as received from an x-y plotter. The drive pulleys were changed to result in a slide-roll
ratio of $\Sigma = 0.9$. The traction was recorded for $\Sigma = 0.9$ and -0.9 and the difference divided by 2 to arrive at an average traction. The traction coefficients for the thirteen motor oils are graphically presented in Figures 17-20. The traction is higher for $\Sigma = 0.9$ than for $\Sigma = 0.05$ in all cases indicating that the fluid behavior is primarily viscous at the high shear rates. The traction decreases with increased temperature (as is expected from limiting shear strength measurements of similar materials.) except for oils Ref. S-1, and S-6 at low temperatures. It is believed (Ref. [3]) that this is due to the oil film becoming very thick, allowing the pressure distribution to spread into the inlet and lower the peak fluid pressure.

In addition, the traction behavior of the two base oils R620-15 and R620-16, and two polymer-oil blends, R620-15 + PL4521 and PL4523, was measured for an aspect ratio of 2.5, peak Hertz pressure of $P_H = 1.0$ GPa, and temperature of $T = 26^\circ C$. As is expected from limiting shear stress measurements [6] the four percent addition of the methacrylate polymer reduces the traction coefficient of the R620-15 (Figure 21).

**Film Thickness Measurements**

Optical interferometry was used to measure lubricant film thickness during the operation of the simulator. A microscope with a through the lens light source was focussed on the contact (Figure 1). A narrow band pass filter (Wratan 72B) with a dominant wavelength $\lambda = 605$ nm was used between the tungsten lamp and microscope. An
aspect ratio of $K = 2.5$ was used, resulting in a Hertz pressure of $P_H = 0.80 \text{ GPa}$ from a load, $w = 25\text{N}$, identical to that of the traction measurements. Nearly pure rolling ($\Sigma = 0$) was obtained by removing the drive belt from the roller and allowing the roller to be driven by the disk. From the methods of Ref. [7] the minimum film thickness under these conditions was calculated to be within six percent of that during the traction measurements.

With this interference technique, changes in thickness of the film are viewed as alternate light and dark fringes appearing in the contact. The film thickness where a bright fringe occurs is

$$h_+ = \frac{\lambda}{2\zeta} \left(n + \frac{\Delta \phi}{2\pi} \right), \quad n = 0,1,2,\ldots$$

and where a dark fringe occurs is

$$h_- = \frac{\lambda}{2\zeta} \left(n + \frac{\Delta \phi}{2\pi} - \frac{1}{2} \right), \quad n = 0,1,2,\ldots$$

Where $\Delta \phi$ is the phase change due to roughness of the roller surface and $n$ is the fringe order. The fluid refractive index, $\zeta$, was taken to be 1.5 in all cases. This leaves $\Delta \phi$ to be calibrated for the particular system.

For the seventeen fluid samples, rolling speed was increased until a light or dark fringe was observed in the center of the contact. The speed and fringe order was noted. For the thirteen motor oils the fringes were noted when possible for minimum film thickness.

The system calibration was done with oil S-6 and is shown in Figure 22. A plot of fringe order ($n - 1/2$ for dark fringes) versus
$V^{0.67}$ yields a straight line whose intercept is

$$\frac{2 \Theta h}{\lambda} - \frac{\Delta \phi}{2\pi} = -0.42 .$$

Since at $V = 0$, $h = 0$,

$$\frac{\Delta \phi}{2\pi} = 0.42 .$$

Film thicknesses were observed at 25C, 50C, and 75C and are plotted for all samples in Figures 23-39. The open symbols represent bright fringe values and the solid symbols represent dark fringe values. Also plotted are film thickness predictions from the relations [5],

$$h_c = 2.69 R_x U^{0.67} G^{0.53} W^{0.067} (1 - 0.61 e^{-0.73 K})$$

$$h_m = 3.63 R_x U^{0.68} G^{0.49} W^{0.073} (1 - e^{0.68 K})$$

for central and minimum thickness respectively. Where

$$W = \frac{W}{E R_x^2}$$

$$U = \frac{U}{E R_x}$$

$$G = \alpha E$$

$$\frac{1}{E} = \frac{1}{2} \left( \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \right)$$
$E_1, E_2, \nu_1$ and $\nu_2$ are moduli of elasticity and Poisson's ratio for the disk and roller and $R_x$ is the roller radius in the direction of motion. The pressure-viscosity data measured and presented in this report were used in these calculations.

For oils S-6, M-5, Ref., R620-15, and R620-16 which are known to contain no polymer V.I. improver the agreement between measured and predicted film thickness is satisfactory. For other materials the viscosity data predicts higher values than those measured. In particular, the measured film thickness for R620-15 + PL4523 ($2 \times 10^6$ M.W. PAMA) is one-third of the predicted value. For the experimental blends (R620-15 + PL4521 and R620-15 + PL4523) the film thickness predicted from base oil properties is also plotted and the measured values lie between each pair of predicted curves.

From these plots it could be suggested that the rheological properties that determine the film thickness (i.e., $\mu_o$ and $\alpha$ in the high shear inlet region of the concentrated contact) for the polymer-oil blend are reduced from the values measured for the blend at low shear stress to those more representative of the base oil. Since the pressure-viscosity coefficient of the base oil is nearly the same as the blend it can be assumed that $\alpha$ does not change and the viscosity is responsible for the reduced film thickness. Therefore an effective viscosity, $\mu_{EFF}$, can be calculated from the film thickness data and the film thickness relations. These are tabulated in Table 4 and plotted against low shear rate viscosity for the oil with and without polymer in Figures 40 and 41 respectively.
CONCLUSIONS

Rheological measurements for phase I of the tribology studies consisted of pressure-viscosity, EHD traction (average lubricant shear stress in a concentrated contact), and EHD film thickness for thirteen motor oils and four well characterized experimental oils.

Pressure-viscosity measurement does not distinguish standard motor oils from fuel-economy formulated oils, even between oils of the same grade and manufacturer (Figures 6 and 7). It does however separate these samples by SAE grade if all motor oil data is plotted in one figure. This has been done in Figure 42. This generalized pressure-viscosity data may be useful for the prediction of EHD film thickness and therefore the design of automotive tribosystems and the specification of automotive lubricants.

No trend could be found which separated the traction characteristics of mileage formulated motor oils and standard oils, even between those of the same SAE grade and manufacturer (Figures 18c and 19a).

It is seen in Figure 43 that the traction behavior of the group of six SAE 10W-40 and three SAE 10-30 motor oils is a characteristic of the grade. If all motor oil traction data is plotted by viscosity grade, Figure 44 results. The ASTM High Reference oil and the 20W-50 generated the highest traction while the 5W-20 provided the lowest traction coefficient of the group.

It was seen that for the experimental oils of Figure 21 that a polymer V.I. improver can reduce the full film traction of the base oil to which it is added. It is believed then that the average
lubricant shear stress (full film traction) is determined by the base oil type and the presence of polymer V.I. improver.

Of course these full-film traction and rheology measurements do not evaluate the effect of friction modifiers on the mixed regime of lubrication and it is suggested that the next phase include a mixed film traction program.

Film thicknesses measured by interferometry agree well with those calculated from pressure-viscosity data using the Hamrock and Dowson equations [5] for the motor oils containing no polymer V.I. improver. However, the polymer thickened oils displayed a lower than predicted film thickness which can be related to a reduced effective inlet viscosity (Table 4). The film thickness measurements on the experimental oils confirmed the effect of polymer V.I. improver on effective viscosity.
REFERENCES


### Table 1. High Pressure Viscosities

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\( p_1 = 338 \text{ MPa} \)  \( p_2 = 548 \text{ MPa} \)  \( p_3 = 279 \text{ MPa} \)  \( p_4 = 517 \text{ MPa} \)  \( p_5 = 534 \text{ MPa} \)  \( p_6 = 538 \text{ MPa} \)  \( p_7 = 524 \text{ MPa} \)

- Sinker would not move at this pressure.
- Viscosity increasing with time.

Sinker would not move at this pressure. Viscosity increasing with time.
Table 2. Pressure Viscosity Coefficients for Thirteen Motor Oils

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Pressure-Viscosity Coefficient [GPa]^{-1}

\[
\alpha_{OT} = \left[ \frac{d}{dp} \ln \mu \right]_{T,p=0}
\]

\[
\alpha_{*OT} = \left[ \int_{0}^{\infty} \frac{\mu(0)}{\mu(p)} dp \right]_{T,p=\infty}^{-1}
\]
Table 3. Pressure-Viscosity Coefficients of Two Base Oils and Two Polymer-Base Oil Blends

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\[
\alpha_{OT} = \left. \frac{d\ln \mu}{dp} \right|_{T,p = 0}
\]

\[
\alpha^*_T = \left[ \int_0^{\mu(\infty)} \frac{\mu(T,p = 0)}{\mu(T,p)} dp \right]^{-1}
\]
Table 4. Effective Inlet Viscosity from Film Thickness Measurements Compared to Low Shear Viscosity

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<th>( \mu_o ) Low Shear Viscosity</th>
<th>( \mu_{\text{EFF}} ) Effective Viscosity 1 m/s</th>
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\[
(\frac{c}{2} \Delta \phi - \frac{h}{2\pi})
\]
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APPENDIX

LUBRICANT SAMPLE INFORMATION
### Mileage - Viscosity
#### Motor Oils

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<th>Comments</th>
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<td>10W-40</td>
<td>Gas saving formula</td>
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<td>Cam 2 Mileage</td>
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<td>Cam 2</td>
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<td>10W-40</td>
<td>Graphite</td>
<td>Atlantic Richfield Company</td>
<td>ARCO Graphite</td>
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<td>Deluxe</td>
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</table>
March 24, 1981

Ward O. Winer
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Dear Ward,

I recently received your request for information regarding oils included in your Tribology study being conducted under government contract. As reference oil chairman of the ASTM Task Force on Fuel Efficient Engine Oils, I can supply descriptive data for HR reference oil.

- **Name** - ASTM High Reference Oil (HR)
- **Base Oil** - 60/40 Solvent 150/Solvent 600
- **VI** - None
- **Friction Modifier** - None
- **DI Package** - API SF Quality
- **Finished Oil Analysis**
  - **Viscosity** - 9.5 cSt @ 210°F
  - **Zn** - 0.13 Wt.%
  - **Mg** - 0.13 Wt.%
- **Viscosity Grade** - SAE 20W30

I trust this information meets your needs and I look forward to receiving a copy of the contract reports.

Very truly yours,

GORDON R. FARNSWORTH

/ jzs

Reply to: Gordon R. Farnsworth
Exxon Chemical Company
P. O. Box 536
Linden, N. J. 07036
January 19, 1981

Professor Ward O. Winer  
Engineering Consultant  
1025 Mountain Creek Trail, NW  
Atlanta, Georgia 30328

Dear Ward:

The following information is available on sample OS No. 52287, the ASTM 5-Car FE Test High Reference Oil:

Kinematic Viscosity, cSt

<table>
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<tr>
<th>Temperature</th>
<th>Viscosity, cSt</th>
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</thead>
<tbody>
<tr>
<td>@ 40°C</td>
<td>75.42</td>
</tr>
<tr>
<td>@ 100°C</td>
<td>9.55</td>
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</table>

Elemental Analysis (by Emission Spectroscopy)

<table>
<thead>
<tr>
<th>Element</th>
<th>% Presence</th>
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<tbody>
<tr>
<td>Zn</td>
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<tr>
<td>P</td>
<td>0.125</td>
</tr>
<tr>
<td>Si</td>
<td>0.0012</td>
</tr>
<tr>
<td>B</td>
<td>0.10</td>
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<tr>
<td>Na</td>
<td>0.0005</td>
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<tr>
<td>Mg</td>
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</table>

We hope your studies with this oil are successful. We would, of course, be interested in your results and how they compare to vehicle data generated at Lubrizol. If I can be of any further assistance please let me know.

Very truly yours,

Brian M. O'Connor

BMO/cao
Professor Ward O. Winer  
Engineering Consultant  
1025 Mountain Creek Trail, NW  
Atlanta, Georgia 30328

Dear Ward:

Under separate cover we are sending you one pint of OS#52655, the current batch of ASTM Reference Oil, HR-2. This is as per our conversation at last month's SAE meeting.

Very truly yours,

W. B. Chamberlin

WBC/bj
May 8, 1981

Mr. Ward O. Winer
Georgia Institute of Technology
Atlanta, Georgia 30332

Dear Mr. Winer:

In response to your letters of 2/24 and 5/1, below are the requested items of information. I am sorry about the delay in responding.

Product: GTX 20w/50 motor oil (and all other GTX grades; note GTX 10w/30 is friction modified with a proprietary soluble compound).

Base oil: High VI solvent refined neutral parafinic

VI: Most production is with non-dispersant Olefin Co-polymer

% weight of neat polymer is approximately 1% in 20w/50

Average molecular weight is approximately 60,000 (by membrane osmometry); approximately 50,000 by gel permeation chromatography

Some production is with a dispersant Poly methacrylate

% weight of neat polymer is approximately 1% in 20w/50

Average molecular weight is approximately 150,000 by osmometry; approximately 125,000 by gel permeation chromatography

Please note that we cannot be certain of these % weight, and molecular weight since we do not produce the polymers ourselves. As a more general description, we pick VI improvers for 0 shear loss in the L-38 10 hour test; ASTM FISST loss is about 5% or less.
D-I: alkyl ZDDP, Calcium Sulfonate, ashless dispersants and antioxidants. SF/CC, CCMC approximately 5% of neat undiluted additives

FM: No (except GTX 10w/30)

We have been doing much research on the role of rheology on fuel economy. A joint SAE paper is due to be presented at the June '81 SAE meeting in Detroit. I cannot supply you a copy at this time, since it represents a joint project with other entities. It should be of considerable interest as background to your studies. The SAE paper number is 810800.

Regards,

Richard G. Tittel
Technical Coordinator

T-297
March 20, 1981

Prof. Ward O. Winer  
Georgia Institute of Technology  
Atlanta, Georgia 30332  

Dear Professor Winer:

Thank you for your inquiry concerning Texaco Havoline Motor Oil. In selecting Texaco motor oil for your studies we suggest you use Havoline Supreme 10W-40 which is our fuel efficient API-SF motor oil. It is formulated with all solvent neutral mineral oils, an olefin-copolymer VI improver and a DI package containing succinimide dispersant, calcium sulfonate detergent, alkyl zinc dithiophosphate. In addition, the oil contains an oil soluble friction modifier. Attached are typical inspection tests obtained on Havoline Supreme 10W-40.

We will be interested in the results of your study. Please advise if we can be of any further help in this matter.

Very truly yours,

RGL-bt

Attachment
Prof. Ward O. Winer  
Attachment  
March 20, 1981

HAVOLINE SUPREME 10W-40

**Typical Tests**

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Value</th>
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<tr>
<td>Gravity, °API</td>
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<tr>
<td>Flash, COC, °F</td>
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<tr>
<td>Kin Vis., cSt at 40°C</td>
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<td>100°C</td>
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<tr>
<td>CCS Vis., cP, -18°C</td>
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<tr>
<td>Pour Pt., °F</td>
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<tr>
<td>Ca, %</td>
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<tr>
<td>P, %</td>
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<td>Zn, %</td>
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<td>N, %</td>
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May 21, 1981

Dr. Ward Winer  
School of Mechanical Engineering  
Georgia Institute of Technology  
Atlanta, GA 30332

Dear Ward:

It has been quite a while since I've seen you, but it was good to get your letter about the "Role of Tribology in Automotive Fuel Economy", which was forwarded to me by Frank Didot. Since Jim Lauer left Sun in 1978, I have been involved in engine oil development, currently working in Technical Service for customers.

Your project looks very interesting, and I would appreciate receiving any information generated by the work. In turn, I am supplying in the attached table the data you requested on the oil sample that we supplied to you.

If I can be of any further assistance, contact me at (215) 447-1847.

Best regards,

Mel Peterkin  
Technical Service Engineer  
MEP:ldw

Attachment

cc: Mr. F. E. Didot  
Mr. G. G. Kroninger  
Mr. L. E. Slagle  
CTF
CAM2 MILEAGE

Base Oil Information:

100% mineral oil ~160 N Solvent Refined

VI Package:

Styrene-ester copolymer
Avg. mol. wt. of 328,000 wt. avg.
98,000 number avg.
Used at ~ 2 wt. %

D-I Package:

SF/CB Calcium Chemistry Detergent-Antioxidant at ~ 5%

Friction Modifier: Soluble Organic Phosphate

Other:

10W-30 SAE Viscosity Grade
SF/CB API Service Grade
Viscosity Index 170
Total Base Number (D664) 5.5
Total Acid Number (D664) 2.2
Viscosity cP/-18°C 1800
Viscosity, cSt/100°C 11.3
Pour Point, °C -33
Zinc, % Wt. 0.16
Phosphorus, % Wt. 0.20
Sulfated Ash, % Wt. 0.94

MEP:1dw
5/21/81
March 27, 1981

Professor Ward O. Winer
Georgia Institute of Technology
School of Mechanical Engineering
Atlanta, Georgia 30332

Dear Professor Winer:

We wish you well in your study on the "Role of Tribology in Automotive Fuel Economy" being conducted under contract to the U.S. Department of Transportation. The inclusion of several Quaker State motor oils in your studies is most complimentary. The general compositional information you requested and typical physical properties for the products are given in the attached table. In addition, we have also attached Quaker State Technical Information Bulletin T-1001F which contains additional descriptive information on Quaker State Motor Oils. Quaker State Sterling Motor Oil is a premium quality fuel economy oil that contains a special oil soluble friction modifier that provides outstanding fuel economy benefits. Both Quaker State DeLuxe Motor Oil, SAE 10W/40 and Super Blend Motor Oil, SAE 10W/30 meet the proposed ASTM fuel economy test requirements for a fuel economy oil. This, was accomplished without the use of a specific friction modifier additive by careful selection of the additive components used in the products with respect to their frictional characteristic's.

We trust that the material provided will be of value to the program and look forward to reviewing the results of your studies when they are published.

Very truly yours,

QUAKER STATE OIL REFINING CORP.
Research Center

John A. Lundquist,
Associate Director of
Research and Development

JAL/rls
Attach.
<table>
<thead>
<tr>
<th>Quaker State Motor Oils</th>
<th>Quaker State Motor Oils</th>
<th>Quaker State Motor Oils</th>
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<td><strong>Sterling Motor Oil</strong></td>
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<td>10W/40 SF-SE</td>
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<td>Select cuts of refined oil from Pennsylvania Grade Crude Oil Multifunctional Dispersant Type Zinc Dialkyldithiophosphates Overbased Sulfonates Ashless Dispersants Ashless Inhibitors Plus Other Additives</td>
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<td>0.99 0.95 0.95 0.80</td>
<td>0.99 0.95 0.95 0.80</td>
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</table>

*Y Index Improver than used in Quaker State DeLuxe and Super Blend motor oils.
QUAKER STATE MOTOR OILS
(Types and Compounding)

QUAKER STATE STERLING MOTOR OIL
SAE 10W-40 HD

Quaker State Sterling Motor Oil is blended from a select cut of base oil plus the following additives:

- Pour Depressant
- Anti-foam Agent
- Oxidation Inhibitors
- Corrosion Inhibitors
- Rust Inhibitors
- Anti-wear and Anti-scuff
- Detergent and Dispersant
- Viscosity Index Improver
- Friction Modifier

Base oil, as used in this Quaker State bulletin, refers to the motor oil refined from crude oil before any additives are used.

Sterling is an advanced motor oil designed to provide greater fuel economy and permit extended drain intervals.

Sterling Motor Oil meets the following designations and specifications:

1. For API Service Designations SF, SE
2. All current automobile manufacturers’ specifications

QUAKER STATE DELUXE MOTOR OIL
SAE 10W-40 HD and 20W-50 HD

Quaker State DeLuxe Motor Oil is formulated from scientifically selected base oils, plus the following additives:

- Pour Depressant
- Anti-foam Agent
- Oxidation Inhibitors
- Corrosion Inhibitors
- Rust Inhibitors
- Anti-wear and Anti-scuff
- Detergent and Dispersant
- Viscosity Index Improver

DeLuxe Motor Oil meets the following specifications and designations:

1. For API Service Designation SF, SE, and SD
2. All current automobile manufacturers’ specifications
3. The SAE 10W-40 product meets proposed ASTM fuel economy tests.

QUAKER STATE SUPER BLEND MOTOR OIL
SAE 5W-20 HD, 10W-30 HD and 20W-40 HD

Quaker State Super Blend Motor Oil is basically similar to DeLuxe in formulation. Super Blend meets the following specifications and designations:

1. For API Service Designation SF, SE, SD, and CC.
2. All current automobile manufacturers’ specifications.
4. The SAE 10W-30 product meets proposed ASTM fuel economy tests.

QUAKER STATE HD MOTOR OIL
SAE 10W, 20W-20, 30, 40, and 50

Quaker State HD Motor Oil is formulated from scientifically selected base oils, plus the following additives:

- Pour Depressant
- Anti-foam Agent
- Oxidation Inhibitors
- Corrosion Inhibitors
- Rust Inhibitors
- Anti-wear and Anti-scuff
- Detergent and Dispersant

Quaker State HD Motor Oil meets the following specifications and designations:

1. For API Service Designation SF, SE, SD, and CC
2. All current automobile manufacturers’ specifications
4. Mack EO-H
5. Detroit Diesel
6. Cummins Diesel (Non-turbocharged)
7. International Harvester

(continued on other side)
QUAKER STATE RACING MOTOR OIL
SAE 30 HD, 40 HD, 50 HD, and 20W-50 HD

Quaker State Racing Motor Oil contains the same types of additives as HD Motor Oil.

However, Quaker State Racing Motor Oil contains a much higher treatment of anti-foam additives, and a considerably higher content of anti-wear and anti-scuff additives. This extra treatment has been found to be highly beneficial in engines operated under full throttle, especially at engine RPMs over 4000.

Quaker State Racing Motor Oil meets the following specifications and designations:
1. For API Service Designation SF, SE, SD, and CC
2. All current automobile manufacturers’ specifications

QUAKER STATE HDX UNIVERSAL FLEET MOTOR OIL
SAE 10W, 20W-20, 30, 40, and 15W-40

Quaker State HDX Universal Fleet Motor Oil is especially formulated to meet the requirements of API Service Designation CD and U.S. Military Specification MIL-L-2104C.

HDX is formulated from scientifically selected base oils, plus the latest proven additives.

HDX contains a very high content of special detergent and dispersant additives especially designed for the requirements of heavy duty Diesel engines, and particularly those which have to be operated on poor grades of Diesel Fuel (high sulfur and/or high aromatic hydrocarbon content, or high endpoint distillation range).

HDX is also suitable for use in severe duty gasoline engines where unusual operating conditions cause heavy crankcase contamination with blowby residues.

HDX meets the following specifications and designations:
1. For API Service Designation SF, SE, CD, and CC
3. Caterpillar TO-2
4. Cummins
5. Detroit Diesel
6. International Harvester
7. Mack EO-J
8. Detroit Diesel Allison Division C-2/C-3 - SAE 10W and 30 Grades
9. Certified to meet automobile manufacturers’ specifications
10. Recommended where Series 3 type oils are required

QUAKER STATE HDX EO-K MOTOR OIL
SAE 15W-40

Quaker State HDX EO-K Motor Oil is blended from scientifically selected base stocks and additives to provide outstanding protection in today’s heavy duty engines. This product is designed specifically to exceed Mack EO-K requirements. It can, however, be used in other heavy duty Diesel engines and in gasoline engines.

HDX EO-K meets the following specifications and designations:
1. For API Service Designation SF, SE, CD, and CC
2. Mack EO-K
3. Mack EO-J
4. Cummins
5. International Harvester
6. Caterpillar
7. Certified to meet Automobile Manufacturers’ Specifications
8. Recommended where Series 3 type oils are required.

QUAKER STATE REGULAR MOTOR OIL
SAE 20W-20 and 30

Quaker State Regular Motor Oil is formulated from scientifically selected base oils, plus the following additives:

- Pour Depressant
- Oxidation Inhibitors
- Corrosion Inhibitors
- Anti-wear and Anti-scuff
- Detergent and Dispersant

Quaker State Regular Motor Oil meets only the requirements of API Service Designation SC. Regular motor oil should only be used in car engines built before 1968.

Produced in U.S.A.
March 16, 1981

Dr. Ward O. Winer
Professor
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Dear Dr. Winer:

Your letter addressed to J. G. Valdez has been passed onto me for response. I will attempt to supply as much information as I can to you within the limits of propriety and my own knowledge.

One of the factors involved in motor oil technology is, of course, the fact that the additive suppliers mix the various components in proprietary fashion to give us the performance requirements we desire. On that basis, it is quite difficult to identify in any detail what the DI package of any motor oil is. I can certainly identify VI package and to some extent friction modifiers.

Pennzoil is a multi-location, multi-base stock company and so it is difficult to identify any specific base oil composition. We also use more than one DI and VI package combination at our various locations. In general, it is our policy to establish performance targets which the additive suppliers are requested to meet.

The attached table gives what information I have available at this time on our formulations. Since you note only the SAE 10W-40 grade in your tabulation of products, I am sending information only on that grade.

If you have any further questions, please feel free to contact me.

Sincerely yours,

S. E. Swedberg, Manager
Product Development
Automotive Products
Pennzoil Multi-Vis
SAE 10W-40
Saves Gasoline

<table>
<thead>
<tr>
<th>Location Code</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Oil Composition</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid Continent Solvent Refined Base Oil (27.0 cst at 40°C)</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid Continent Solvent Refined Base Oil (29.0 cst at 40°C)</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Pennsylvania HF Base Oil (27.0 cst at 40°C)</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td><strong>VI Improver (As solid, Wt. %)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non Dispersant OCP (SSI=20)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>DI Package (Wt. %)</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SF Performance Level</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
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<tr>
<td><strong>Friction Modifier</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soluble material consisting of one or more of the following:</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Fatty acid esters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfurized fatty acid esters</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
March 30, 1981

Professor Ward O. Winer
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

Dear Professor Winer:

This replies to your February 24, 1981 letter requesting information on our large volume branded passenger car engine oil, Shell FIRE & ICE® 10W/40 Motor Oil.

The HVI base oils used in blending FIRE & ICE 10W/40 Motor Oil are manufactured primarily from domestic Mid-Continent crude sources used in combination with small but significant quantities of foreign crudes. Processing includes solvent extraction and hydro-finishing. A proper ratio of HVI 100 and HVI 250 is used to provide viscosities meeting the SAE 10W specification at -18°C and the SAE 40 specification at 100°C.

SHELLVIS® 40, a styrene/olefin-based hydrocarbon co-polymer manufactured by Shell Chemical Company, is used as the VI improver. This solid, oil-soluble polymer is used in optimum concentration to meet 10W/40 viscosity classifications with the combination of base oils noted.

A proprietary Shell DI (detergent-inhibitor) additive system is used in combination with SHELLVIS 40. Treatment is near the 10 percent level common for API SF quality automotive oils. It encompasses a calcium overbased detergent and a conventional ashless dispersant for engine deposit control, antiwear additives as required to meet API SF standards, a pour point depressant and an antifoam agent. 0.15%w zinc as dialkyl zinc dithiophosphate is used for antiwear performance and a proprietary oil-soluble friction modifier is used for fuel efficiency.

Test results show that Shell FIRE & ICE 10W/40 Motor Oil comfortably meets all API SF quality requirements and the proposed ASTM test requirements for energy conserving oils.
Typical chemical and physical properties for the finished oil are given in Attachment 1.

Hopefully, this information will be satisfactory for your needs.

Sincerely,

/ S. A. Herbert, Manager
Lubricants Department

SAH/sgf
Attachment
SHELL FIRE & ICE MOTOR OIL 10W-40

SUMMARY OF BENCH TEST RESULTS

Finished Oil Characteristics

1. Gravity, °API (ASTM D-287)  
   | 29.2 |

2. Flash Point, °F (ASTM D-92)  
   | 400 |

3. Pour Point, °F (ASTM D-97)  
   | -25 |

4. Foaming, ml (ASTM D-892)  
   | Tend/Stab, Sequence 1, 2, 3 | 0/0, 15/0, 0/0 |

5. Viscosity, cP at -18°C (ASTM D-2602)  
   | 2250 |

   cSt at 40°C (ASTM D-445)  
   | 80.0 |

   cSt at 100°C (ASTM D-445)  
   | 13.9 |

6. Viscosity Index (ASTM D-2270)  
   | 180 |

7. Total Base No. (ASTM D-664)  
   | 7.3 |

8. Total Acid No. (ASTM D-664)  
   | 3.1 |

9. Sulfated Ash, %, (ASTM D-874)  
   | 1.08 |

10. Analyses for identifiable elements, wt.%.
    | Mg NIL | Ca 0.26 | Ba NIL | P 0.14 | Zn 0.15 |
    | N 0.03 | S 0.34 |
March 25, 1981

Dr. Ward O. Winer  
School of Mechanical Engineering  
Georgia Institute of Technology  
Atlanta, Georgia 30332

Dear Dr. Winer:

Your recent letter asked that we provide the composition of our SAE 10W-40 ARCOgraphite motor oil in terms suitable for describing the product in a technical publication such as an SAE paper. We can release information of this type to the extent that the oil contains an all mineral oil base oil composition. In addition, the oil does contain graphite as a colloidal friction modifier. We trust that this information along with any physical or chemical data you may generate on the sample you use for testing will suffice to define the oil in a publication.

Very truly yours,

ARCO Petroleum Products Company

D. L. DeVries  
Engine Oils Research and Development

DLD: sjv
March 18, 1981

File: 311.1
Proj: 182-10

Dr. Ward O. Winer
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Dear Dr. Winer:

In response to your inquiry of February 24, 1981, we offer the following. Mobil 1 5W-20 employs a fully synthetic base stock which is mostly SHF made from the polymerization of olefins. An ester is also included as an elastomer seal swell agent. Because these synthetic base stocks have an inherently high viscosity index, the SAE 5W-20 multigrade viscosity characteristics are obtained with no polymeric VI improver in the formulation.

The additive system in Mobil 1 was developed specifically for optimum response with the synthetic base fluids and contains metallic detergents, ashless dispersant and alkyl zinc dithiophosphate. The physical and chemical properties of Mobil 1 5W-20 are summarized below.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity</td>
<td></td>
</tr>
<tr>
<td>@ 100°C (212°F), cSt</td>
<td>6.7</td>
</tr>
<tr>
<td>@ 40°C (104°F), cSt</td>
<td>36.9</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>140</td>
</tr>
<tr>
<td>CCS Viscosity @ 0°F (-17.8°C), P</td>
<td>11</td>
</tr>
<tr>
<td>Flash Point, °C (°F)</td>
<td>238 (460)</td>
</tr>
<tr>
<td>Pour Point, °C (°F)</td>
<td>-65 (-85)</td>
</tr>
<tr>
<td>TBN (D2896)</td>
<td>6.2</td>
</tr>
<tr>
<td>Sulfated Ash, % Wt.</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcium, % Wt.</td>
<td>0.21</td>
</tr>
<tr>
<td>Zinc, % Wt.</td>
<td>0.13</td>
</tr>
<tr>
<td>Phosphorus, % Wt.</td>
<td>0.12</td>
</tr>
</tbody>
</table>

We trust this information is helpful and are glad to be of assistance.

Very truly yours,

H. V. Lowther, Manager
Engine & Power Train Lubricants
**DESCRIPTION OF EXPERIMENTAL FLUIDS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>R-620-15</th>
</tr>
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<tbody>
<tr>
<td>Source</td>
<td>Sun Oil Company</td>
</tr>
<tr>
<td>Type</td>
<td>Naphthenic Base Oil</td>
</tr>
<tr>
<td>Properties</td>
<td></td>
</tr>
<tr>
<td>Viscosity at 37.8°C, mm²/s</td>
<td>24.1</td>
</tr>
<tr>
<td>Viscosity at 98.9°C, mm²/s</td>
<td>3.75</td>
</tr>
<tr>
<td>Viscosity Index (ASTM D-2270)</td>
<td>-13</td>
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<tr>
<td>Flash Point, C</td>
<td>157°</td>
</tr>
<tr>
<td>Pour Point, C</td>
<td>-43</td>
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<tr>
<td>Density at 20°C, Kg/m³</td>
<td>915.7</td>
</tr>
<tr>
<td>Average Molecular Weight</td>
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</table>

<table>
<thead>
<tr>
<th>Symbol</th>
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</thead>
<tbody>
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<td>Source</td>
<td>Sun Oil Company</td>
</tr>
<tr>
<td>Type</td>
<td>Naphthenic Base Oil</td>
</tr>
<tr>
<td>Properties</td>
<td></td>
</tr>
<tr>
<td>Kinematic Viscosity at 37.8°C mm²/s</td>
<td>114</td>
</tr>
<tr>
<td>Kinematic Viscosity at 98.9°C mm²/s</td>
<td>8.1</td>
</tr>
<tr>
<td>Density at 20°C kg/m³</td>
<td>930</td>
</tr>
<tr>
<td>Average Molecular Weight</td>
<td>357</td>
</tr>
</tbody>
</table>
Symbol: PL4521, PL4523
Source: Rohm and Haas Company
Type: Polyalkylmethacrylate
(Polymer additive used in solution in R620-15, 4.0% polymer by weight)

The chemical composition of each is the same. They differ only in molecular weight and are supplied in a carrier oil similar to R620-15

<table>
<thead>
<tr>
<th>Properties</th>
<th>PL4521</th>
<th>PL4523</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Weight:</td>
<td>36.1%</td>
<td>19.0%</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$560 \times 10^3$</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Average Molecular Weight:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PHASE REPORT
DOT DTRS 5680-C-00015

FUNDAMENTAL STUDIES IN TRIBOLOGY AS RELATED TO AUTOMOTIVE FUEL ECONOMY

Co-Principal Investigators:
S. Ramalingam, Professor
W. O. Winer, Professor

Prepared for:
Transportation Research Center
U.S. Department of Transportation
Kendall Square
Cambridge, Massachusetts 02142

Project Co-ordinator:
Russel Zub (DTS-323)

July, 1981
GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
SCHOOL OF MECHANICAL ENGINEERING
ATLANTA, GEORGIA 30332

1981
Fundamental Studies in
Tribology as Related to Automotive Fuel Economy

Georgia Institute of Technology
Atlanta, Georgia 30332

Principal Investigators:
S. Ramalingam & W. O. Winer

Project Monitor:
Russel Zub, DTS-323
PHASE REPORT: Phase I
1 September 1980 to 28 July 1981

GEORGIA INSTITUTE OF TECHNOLOGY
(DTRS 5680-C-00015)

PRINCIPAL INVESTIGATORS
S. Ramalingam
W. O. Winer

DOT PROJECT MONITOR
Russel Zub (ITS-323)
Transportation Research Center
Cambridge, Massachusetts

SUMMARY

This phase report summarizes the accomplishments in the first eleven months of the first phase of the program entitled: "Fundamental Studies in Tribology as Related to Automotive Fuel Economy".

Work schedule for the first phase shown on overleaf requires under Task I:

(a) development of coating techniques,
(b) preliminary coating trials, and
(c) screening for tribological behavior.

Under Task II the schedule calls for high pressure shear rheological studies of motor oils. Theoretical work on mechanics of thin film function and wear of automotive tribosystems are called for in Task III.

In the following pages of the first phase report, the work accomplished in Tasks I and II are summarized. Coating system and technology have been developed. Coating trials are underway. Nonferrous and ferrous materials of interest for automotive application have been coated successfully. Shear rheological and traction studies have been carried out on motor oils.

This phase report presents a summary of the work accomplished in phase I covering the period 1 September 1980 to 28 July 1981.

S. Ramalingam
Principal Investigator

W. O. Winer
Principal Investigator

29 July 1981
## TASK SUMMARY

<table>
<thead>
<tr>
<th>Task Description</th>
<th>7/80</th>
<th>7/81</th>
<th>7/82</th>
<th>7/83</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.a Development of coating techniques</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>b Preliminary coating trials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c Screening for tribological behavior</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d Identification of promising coating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 2.a High pressure shear rheology (motor oils)                    |      |      |      |      |
| b High pressure shear rheology (gear oils)                       |      |      |      |      |
| c High shear high temperature characterization at near atmospheric pressure |      |      |      |      |
| d Shear characterization of solid lubricants                      |      |      |      |      |

| 3 Characterization of the mechanics of thin film friction and wear of automotive tribo-systems |      |      |      |      |

**Report and Review**

- 0
- 0
- 0
TASK I: DEVELOPMENT OF COATING TECHNIQUES

A sputtering facility for high rate deposition of metals and hard compounds has been developed and tested. It has been used to deposit thin layers of hard and soft compounds to modify friction and wear characteristics of tribological pairs. Friction and wear tests have been carried out on coated ferrous and non-ferrous test samples.

The coating process developed to modify the friction and wear characteristics of tribological pairs and the tribological test results obtained are presented in the following sections of this part of the progress report.

a. Coating System

The coating system developed consists of four principal sub-systems. It is designed to facilitate metallic coating at high rates (magnetron sputtering) as well as coating of hard material compounds such as TiN. The latter requires reactive sputtering. Suitable provisions have therefore been made for atmosphere control.

The principal sub-systems developed are:

a) a vacuum plant
b) a high rate sputtering head
c) a sputtering atmosphere control system, and
d) a power supply.

The vacuum plant developed consists, basically of a CVC 14" vacuum system suitably modified for the present needs. A vacuum chamber defined by a 12 inch diameter x 12 inch high Pyrex cylinder, a top
plate and a base plate is used. The vacuum chamber can be evacuated to pressures less than $10^{-5}$ torr with a four inch diffusion pump and a 5.6 CFM Mechanical pump. The system is equipped with a four inch gate valve and two roughing valves for vacuum sequencing and to control ambient pressure during sputtering. The system is equipped with a bleed valve to bring the vacuum chamber to atmospheric pressure for specimen loading and unloading. Vacuum plant is shown in Figure 1.a.1.

The top plate of the vacuum chamber carries the sputtering head and is electrically insulated from it with the insulator ring. It also carries a sputtering pressure monitoring gage, a shutter control, and a gas inlet. The base plate of the system contains a number of electrical and instrumentation feed-throughs (See Figure 1.a.2).

The specimens to be coated are carried on a platform connected to a high voltage feed-through to facilitate specimen cleaning by sputtering. A ground shield serves to limit the plasma generated during sputter cleaning from acting on the back streaming molecules. A shutter serves to shield the coating target from the contaminating species during the cleaning.

The sputtering head developed is a cylindrical structure with four ALNICO ring magnets and a HICOREX magnet. The ring magnets, the pole pieces and the HICOREX magnet define a circularly symmetric magnetic field needed for high rate magnetron sputtering. The magnet assembly is positioned on the atmospheric side of the cathode carrier while the metallurgically bonded coating target is carried on the vacuum side. The magnet assembly and the cathode carrier are mounted on a cathode
1. Vacuum Chamber
2. Top Plate
3. Sputtering Head
4. Pyrex Cylinder
5. Base Plate
6. Vacuum Chamber Leak Valve
7. Roughing Valve - Mechanical Pump
8. High Vacuum, Gate Valve
9. Diffusion Pump Roughing Valve
10. Diffusion Pump
11. Two-Stage Mechanical Pump.

FIGURE 1.a.1 SCHEMATIC ILLUSTRATION OF VACUUM PLANT
1. Sputtering Head
2. Shutter Control Handle
3. Sputtering Gas Inlet
4. Sputtering Pressure Monitoring Gage
5. Sputtering Head Insulator
6. Vacuum Chamber Top Plate
7. Sputtering Target
8. Test Specimens (Coating Substrates)
9. Pyrex Bell Jar (Cylinder)
10. Ground Shield for Sputter Cleaning
11. Manifold to Pumping System
12. Shutter

FIGURE 1.a.2  INTERNAL CONFIGURATION OF THE VACUUM CHAMBER FOR SPUTTERING
ring and enclosed in a water-cooled casing.

Water introduced through a 1/4 inch steel tube is routed through the pole piece to cool the rear surface of the cathode carrier. Following circulation, water is drained through an opening in the PVC case. Water cooling and metallurgical bonding of the target are essential to remove the large power dissipated (up to 1.8 kW) at the cathode surface during high rate sputtering.

An appropriately configured anode is positioned close to the cathode. The anode geometry and the position with respect to the cathode have been empirically optimized. The close coupling between the magnetic field B and the electric field E, is the key factor in permitting successful reactive sputtering to produce golden yellow TiN at high deposition rates.

Consistent and reproducible reactive sputtering of hard compounds requires higher sputtering voltages than those available in commercial magnetron sputtering systems. Therefore a new system had to be designed, built and tested to meet the needs of tribological coatings.

The two-inch sputtering head developed is a key component of the sputtering system. This newly designed system has been tested at a total cathode current of over two amperes. Coating at 900 volts with a cathode current of two amperes represents a 1.8 kW sputtering system. Under typical sputtering pressures of 0.5 to 1.5 millitorr, power dissipation density at the cathode surface is then 90 watts per cm$^2$ (which is among the highest attained anywhere). The cathode current density in this magnetic field-assisted system is three orders of magnitude (1000 times) higher than that in conventional DC sputtering systems.
The operating voltage of 300 to 1000 volts, is also much lower than the 2.5 to 10 kV typical in conventional sputtering systems. High sputter coating rates are hence obtained.

The sputtering atmosphere control system developed requires flexibility. In the present instance, two types of gaseous atmospheres are necessary: (a) a low pressure argon environment for high rate sputtering of metals and alloys, and (b) a low pressure argon-nitrogen environment to synthesize and deposit hard compounds (reactive sputtering). The integrated gas control system developed meets both these needs.

The gases dispensed from the tanks at pressures of 5 psia are dried in molecular sieve drying columns and metered through needle valves into an oxygen trap. The dry gases mixed in the trap emerge oxygen-free and are admitted into the vacuum chamber through a gas inlet.

Typically, the argon flow rate is 5 SCCM during glow discharge cleaning. During sputter coating, the total gas flow rate through the system is about 4 SCCM, or as needed. In course of reactive sputtering, the argon flow rate is 2 SCCM, while the nitrogen flow rate is 2.5 SCCM (Values found empirically to yield golden yellow, TiN films). To obtain these specific flow rates, two needle valves are used. Two separate mass flow rate meters are used to control the sputtering atmosphere. Gas control manifold is shown in Figure 1.a.3.

Two power supplies are used in conjunction with the sputtering system. The first one, a CVC Model LC-301, is a high reactance, variable voltage DC supply rated at 300 ma (continuous duty) at 5 kV (maximum voltage). The second one is a high current (2.5 amp) low voltage
1. Argon Tank
2. Nitrogen Tank
3. High Pressure Valve
4. Pressure Regulator
5. Gas Flow Cut-Off Valve
6. Drying Column
7. Flow Rate Indicator
8. Metering, Needle Valve
9. Oxygen Trap
10. Vacuum Chamber

FIGURE 1.a.3 SCHEMATIC ILLUSTRATION OF GAS CONTROL MANIFOLD
(1000 V max) power supply, Hippotronics MODEL 801-2500, equipped with a high speed shut-off to protect the solid state rectifiers in the system.

The CVC power supply is typical of that in commercial use for conventional DC sputtering. It was used in this program solely for glow discharge cleaning prior to coating.

The main supply in commercial high rate deposition systems are also high reactance power supplies (usually limited to 800 volts). High reactance is considered to be essential for the protection of the supply system during arcing transients and sputter target flaking during high rate sputtering. When high reactance transformers are not a part of the power supply, a saturable core reactor is used to limit the cathode current during various instabilities.

Instead of these usually high cost power supplies, an off-the-shelf power supply (Hippotronics Model 8100-2500) was used in this program. To obtain system stability, a low resistance, high current inductor connected in series with the sputtering head was used. The 30-ohm, 1.25 amp. inductors used (5H) are fully able to suppress all but the most severe arcing transients. System could be operated routinely, once stability is attained, for longer than one hour at a time, fully unattended.

b. Coating Practice

In a typical sputtering run, the components to be coated are washed with water and detergent followed by ultrasonic cleaning in acetone. They are withdrawn from the acetone bath, dried with a blast
of nitrogen and placed on the specimen carrier plate of the sputtering chamber. Once the substrates (specimens) to be coated are placed in the vacuum chamber, the chamber is rough-pumped to a pressure between 50 and 100 millitorr. Roughing valve is then closed and dry nitrogen admitted into the vacuum chamber to a pressure to 5 torr. The vacuum chamber is pumped again to better than 100 millitorr. It is back filled with dry argon to 5 torr and evacuated again to a residual pressure of 50 millitorr.

On reaching 50 millitorr, the diffusion pump is used to evacuate the system to its limiting pressure (approximately $10^{-6}$ torr). This pumping sequence is followed to desorb as much of the contaminating vapor species (mostly water vapor) as is possible.

After approximately five minutes at limiting pressure, argon gas is admitted into the system and the gate valve is adjusted to obtain a steady chamber pressure of 20 millitorr. A negative potential between 2 and 2.5 kV is applied to the substrate and the substrate is glow-discharge cleaned. Glow discharge cleaning is carried out for 15 minutes. Power dissipation during glow discharge cleaning (100 to 125 watts) is sufficiently low to preclude large temperature rise during cleaning (heating up to 100 to 150°C is desirable to desorb water vapor from surfaces to be coated).

Following glow discharge cleaning, argon flow is reduced to 2 SCCM and the high vacuum valve is readjusted to maintain the chamber pressure at 2 to 5 millitorr. With the shutter still in position, a negative potential is applied to the sputtering cathode (with the specimen at ground potential) and the voltage raised until a stable,
low current magnetron discharge is initiated. The pressure is then dropped to between 1 and 2 millitorr and cathode current raised to between 500 and 600 ma.

As the contaminant gases are sputtered away from the target, the initial pink-violet discharge changes color to an intense blue. Once the intense blue is obtained (due to titanium sputtering), the shutter is rotated out of position and titanium deposited on the substrate for up to two minutes (maximum cathode current during this phase is 1000 ma). Nitrogen gas is then admitted into the system (flow rate of 2.5 SCCM) and high vacuum valve readjusted to maintain the pressure between 0.5 and 1.2 millitorr.

On the admission of nitrogen, due to its inefficient sputtering, system current drops by approximately 55%. Sputtering pressure and voltage are then adjusted to raise the system current to 1000 ma. Under these conditions, Titanium is sputtered off the target at a rate greater than that possible for nitrogen to condense on its surface. TiN synthesis in the vapor phase ensues to yield golden-yellow nitride.

If golden-yellow TiN is essential it is absolutely necessary to operate the system at high cathode currents, low pressures and high voltages. In the course of this program, it has been found that the best TiN films are produced with the present system at the following operating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>System voltage</td>
<td>925 to 950 V</td>
</tr>
<tr>
<td>Cathode current</td>
<td>1000 to 1200 ma</td>
</tr>
<tr>
<td>System Pressure</td>
<td>1.75 to 2.25 millitorr</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Substrate-Cathode Distance</td>
<td>4.5 to 6 cm</td>
</tr>
<tr>
<td>Argon flow rate</td>
<td>2 SCCM</td>
</tr>
<tr>
<td>Nitrogen flow rate</td>
<td>2.5 SCCM</td>
</tr>
<tr>
<td>Magnetic Field strength on the cathode surface</td>
<td>1200 Gauss</td>
</tr>
<tr>
<td>(other pole)</td>
<td></td>
</tr>
<tr>
<td>Cathode diameter</td>
<td>5 cm (nominal 2 inches)</td>
</tr>
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</table>

Typically a coating run is for 30 to 60 minutes. Following the coating, nitrogen flow is cut-off and the system left in place to 'cool down' for 30 minutes. After shutting argon flow and isolating the vacuum chamber from the pumping system, air is bled into the system and top plate removed to take the coated specimens out of the coating system.

Principal heating during coating is due to the condensation of the TiN on the substrate surface. There is some secondary heating due to 'electron leak' from the vicinity of the central pole piece. Measurement of specimen surface temperature immediately following the cessation of coating shows that surface temperatures do not exceed 375°F.

### c. Coating System Operating Characteristics

While metallic coatings are easily produced at a variety of coating conditions, coatings of hard compounds (with specific stoichiometry) require particular combinations of operating voltages, coating pressures and atmospheres. These factors were recognized during system design. System developed hence permitted desired hard coatings to be deposited routinely. Typical operating conditions necessary to produce needed wear-resistant coatings are shown in the previous section.
As expected from plasma coating theory, coating rate increased with decreasing coating pressures. Coating rate also increased with sputtering power. Some typical experimental results obtained are shown in Figure I.C.1.

In magnetron sputtering, the coating flux is obtained from a planar, extended, non-homogeneous source. Thickness of the coating produced is a function of axial and radial distance from the center of the cathode. To assess coating uniformity, test samples were coated at various radial locations (axial distance was maintained constant), and thickness produced measured. The results obtained are shown in Figure I.C.2.

A theoretical model has been developed to predict the expected coating thickness distribution. It was assumed that the strength of the source is proportional to the transverse field strength of the electron trap used in magnetron sputtering. The transverse field strength of the magnetic field used in the system was measured with a Hall probe assembly and used to calculate the expected coating thickness distribution. Measured values and expected values are in good agreement as may be seen from Figure I.C.2. Coating characteristics of magnetron sputtering systems are found to depend on magnetic field design (for electron trap).

d. Characterization of Wear-resistant Coatings

Micro-hardness measurements and x-ray diffraction techniques were used to characterize coatings deposited. Micro-hardness measurements on taper-sectioned test samples showed that coatings with
Figure 1. Coating Rate as Function of Operating Pressure and Consumed Power.
Measured Strength of the Horizontal Component of the Applied Magnetic Field as Function of Radial Distance on Target Surface.

Figure 1.C.2 Calculated Thickness versus Measured Thickness
hardnesses greater than $H_v \geq 2000$ are routinely produced by reactive sputtering of titanium (to produce TiN). Titanium nitride, a defect compound, can possess a range of stoichiometries. Distinct colors are associated with specific ranges of stoichiometry, golden-yellow being that of the perfect compound. This was obtained routinely.

Since in sputtering, non-equilibrium structures are usually produced and the films deposited are under stress, x-ray analysis is not an unambiguous indicator of film stoichiometry. Additional x-ray analysis problems are introduced by preferred texture in coatings. Despite these difficulties, x-ray analysis suggests that the films produced are titanium nitride compounds. Expected x-ray peaks and those observed are listed in Table 1.D.1. The data obtained is taken to indicate TiN film deposition. Supporting evidence is provided by microhardness and color data.

Films produced do possess substantial tensile residual stresses. By measuring the "bowing" of coated stainless steel foils, the residual stresses have been determined to be of the order of $200 \times 10^3$ psi (when coated on steel substrates). These large residual stresses can lead to adhesion problems in tribological applications. Hence tests are now in progress to lower the residual stresses.

e. Tribological Evaluation of Coatings Produced

To assess the utility of hard coatings (TiN) in non-ferrous automotive castings such as pistons, test blocks of aluminum, and magnesium alloys have been sputter coated with titanium nitride. Sliding contact wear tests (LFW-1) have been carried out and wear
Table I.D.1

X-Ray Diffraction Peaks of TiN (ASTM Data)

<table>
<thead>
<tr>
<th>Reflection Plane</th>
<th>Spacing ( d(\text{Å}) )</th>
<th>Peak at* ( 2\theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (h; k; l) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1 1</td>
<td>2.4480</td>
<td>36.68°</td>
</tr>
<tr>
<td>2 0 0</td>
<td>2.1200</td>
<td>42.61°</td>
</tr>
<tr>
<td>2 2 0</td>
<td>1.4991</td>
<td>61.84°</td>
</tr>
<tr>
<td>3 1 1</td>
<td>1.2784</td>
<td>74.46°</td>
</tr>
</tbody>
</table>

*With Ni-filtered CuK\( \alpha \) radiation.

X-Ray Diffraction Peaks Attributable to the Coating

<table>
<thead>
<tr>
<th>Peak Observed at ( 2\theta )</th>
<th>Spacing* ( d(\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.4°</td>
<td>2.4685</td>
</tr>
<tr>
<td>42.4°</td>
<td>2.1321</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>74.76</td>
<td>1.2699</td>
</tr>
</tbody>
</table>

*Computed values correspond to observed \( 2\theta \) values.
Table 1.D.2. LFN-6 Test Results*

<table>
<thead>
<tr>
<th>Material</th>
<th>Friction Coefficient $\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>Steel (AISI 1214)</td>
<td>0.088</td>
</tr>
<tr>
<td>Steel (AISI 1018)</td>
<td>0.146</td>
</tr>
<tr>
<td>Cast Iron (As Received)</td>
<td>0.112</td>
</tr>
</tbody>
</table>

*Test duration 30 minutes

Test surface and the counter faces were TiN coated. Coatings survived all the tests. All tests were carried out with n-hexadecane. Fluid used is not a lubricant.
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Film Thickness h: (μ in)</th>
<th>Cord Length 2L: (in)</th>
<th>Total Deflection f: (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>81</td>
<td>1.478</td>
<td>0.0995</td>
</tr>
<tr>
<td>B</td>
<td>43</td>
<td>1.515</td>
<td>0.082</td>
</tr>
</tbody>
</table>

Measured Deflection of Stainless Steel Shim Stock after Nitride Sputtering.

Configuration of Stainless Steel Shim Stock after Nitride Sputtering.

\[
\sigma_1 = \frac{E}{3L^2} \left( \frac{(H-h_2)^2}{\Delta h_1} \right) \left( \frac{\Delta f}{\Delta h_1} \right) = 0.2076 \times 10^6 \text{ psi}
\]

Young’s modulus of TiN is 29x10^6 psi. Thus, elastic strains of 0.2076/29 x 100% are expected, ε = 0.7157%.
coefficients determined. The results obtained are summarized in a paper to be presented in July 1981 in Brussels [IPAT 81 International Conference sponsored by the European Physical Society, Metals Society (London) and the Welding Institute (London)]. The paper has been accepted for publication in a forthcoming issue of Thin Solid Films.

Briefly, the test results obtained show that well-adherent thin coats (5 μm or less in thickness) offered excellent wear protection to non-ferrous alloys. At each hertzian contact stress level, full wear protection is obtained only above a film thickness threshold of the order of 1.5 to 2 μm. Wear resistance is improved by several orders of magnitude (wear coefficients measured are tabulated in the paper). A copy of the paper is attached to this progress report.

The LFW-1 wear tests (see Figure 1.e.1 for test geometry) are low speed, high stress friction and wear tests. To assess medium and high speed friction characteristics, LFW-6 test specimens (see Figure 1.e.2 for test geometry) (pure sliding) have been fabricated and coated. One cast iron and two types of annealed steels have been used to fabricate test samples. Coated and tested samples exhibit wear protection due to the hard coating. Friction test results are summarized in Table I.D.1. The results obtained suggest that wear protection can be afforded to such automotive components as cam shafts, tappets, etc., made of cast iron (preliminary test results). Additional and more extensive test program is now underway and the results will be reported in the second annual report. While hard coat adhesion is easily obtained with non-ferrous materials, significant problems are
MAXIMUM LOAD 630 LBS
FRICTION LOAD INDICATOR
TEST BLOCK CYLINDRICAL SEATED FOR UNIFORM LOAD DISTRIBUTION OVER ENTIRE LINE CONTACT AREA
FRICTION FORCE AT LINE OF CONTACT DIRECTLY TRANSMITTED TO LOAD PICK UP
TEST RING
FRICITION LOAD PICK UP

Figure 1.e.1 Functional Diagram of Alpha LFW-1 Testing Machine
Figure 1.e.2  Standard (sliding) and special (rolling) mode attachments for the Faville No. 6 Friction and Wear Tester. LFW-6 Test Geometry
encountered in producing well-adherent coatings on hardened steels (valve train components are hardened irons and steels). Chemical surface treatments (prior to sputter coating) have been found to overcome the adhesion problems. Early tests in rolling hertzian contact tests (see Figure 1.e.2) at up to 150 ksi have been successful. Additional LFW-6 tests on a variety of automotive alloys (sliding contact and rolling contact tests) are now in progress and are scheduled to be completed by 30 December 1981. A summary of test results obtained will be reported fully in Phase II final report.

f. Soft Coats

Techniques for D.C. sputtering of dichalcogenide soft coats have been developed. Preliminary tests (LFW-6 type) show that soft coats have a limited life. Coating adhesion problems are also encountered that do not appear to be surmountable by chemical surface conditioning prior to coating.

Previous work on chalcogenide coatings (MoS$_2$, for example) have always used RF sputtering to obtain well-bonded coatings. It would appear that RF sputtering may in fact be essential.

This coating problem was expected and, as a part of phase I, a budget provision was made to procure a RF power supply. A 1.6 kw, "Plasmaloc" power supply has been procured (Delivered 17 July 1981). The system has been integrated with the existing coating system and has been rendered operational. Capability for RF sputtering now exists and soft coat activity has been reactivated at 125 kHz.

Test data obtained with RF sputtered soft coat films will be reported in the semi-annual report due on 30 December 1981.
g. Work in Progress

Tribological pairs found in automotive engines and transmission systems require substantial wear life. By hard and soft coating, wear life and wear-in characteristics can be improved to attain better economy. To preserve these characteristics, the coatings deposited must be well-bonded to the substrate. Retention of improved tribological characteristics depends critically on coating-to-substrate bond strength.

Quantitative bond strength tests are not available. 'Peel' tests subject coatings to plastic bending. Measured quantities contain non-quantifiable contributions due to plastic bending of coating. Stress state in "scratch" tests is not determinable. Hence both these tests are not satisfactory as quantitative film-to-substrate bond strength tests.

By coating substrates and monitoring the film during stressing, substrate stress at film debonding can be determined. Elastic displacements in the substrate and coating will have to be the same just before film debonding. Equality of displacements at the coating-substrate interface and elastic modulii, then allow the interface shear strength $\tau^*$ to be determined.

The interface shear strength $\tau^*$ determined experimentally are shown Tables 1.e.1 and 1.e.2. A steel metal strip 1/2" x 4" of thickness $d$ (variable) was coated with a film of thickness $t$. The coated composite of thickness $(d + t)$ was bent to a specified radius $R$ (variable) to subject the coating-substrate interface to a shear stress $\tau$ given by
Table 1.e.l. Bend tests for coating adhesion

1) Without sputtering cleaning:

a) Matrix: Aluminum \( G_m \) = 3.8 \( \times \) 10\(^6\) psi
   Coated film: Titanium \( E_f \) = 15 \( \times \) 10\(^6\) psi

<table>
<thead>
<tr>
<th>d(in)</th>
<th>( \tau_{max} ) (psi)</th>
<th>t (in)</th>
<th>2.6 ( \mu )m</th>
<th>3.9 ( \mu )m</th>
<th>5.2 ( \mu )m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.012</td>
<td>1.0</td>
<td>5,000</td>
<td>6,120</td>
<td>7,070</td>
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<tr>
<td></td>
<td>0.5</td>
<td>9,950</td>
<td>12,180</td>
<td>14,070</td>
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<tr>
<td>0.040</td>
<td>1.0</td>
<td>9,020</td>
<td>11,050</td>
<td>12,760</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>17,760</td>
<td>21,760*</td>
<td>25,120*</td>
<td></td>
</tr>
</tbody>
</table>

*coated film debonded

b) Matrix: Stainless Steel \( G_m \) = 10.6 \( \times \) 10\(^6\) psi
   Coated film: Titanium \( E_f \) = 15 \( \times \) 10\(^6\) psi

<table>
<thead>
<tr>
<th>d(in)</th>
<th>( \tau_{max} ) (psi)</th>
<th>t (in)</th>
<th>3.1 ( \mu )m</th>
<th>4.1 ( \mu )m</th>
<th>5.1 ( \mu )m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>3.2</td>
<td>---</td>
<td>6,680</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>---</td>
<td>---</td>
<td>9,510*</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>2.25</td>
<td>8,230</td>
<td>9,470*</td>
<td>10,560*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.375</td>
<td>13,400*</td>
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<td></td>
</tr>
</tbody>
</table>

*coated film debonded
Table 1.e.2. Bend tests for coating adhesion

1) With sputtering cleaning:

a) Matrix: Stainless Steel \( G_M = 10.6 \times 10^6 \) psi  
Coated film: Titanium \( E_f = 15 \times 10^6 \) psi

<table>
<thead>
<tr>
<th>d(in)</th>
<th>( \tau_{o \text{ max}} ) (psi)</th>
<th>t</th>
<th>5 ( \mu \text{m} )</th>
<th>5 ( \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>1.0</td>
<td>18,050</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>23,880</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>33,980</td>
<td>43,870</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>65,440</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

b) Matrix: Aluminum  
Coated film: TiN \( G_M = 3.8 \times 10^6 \) psi  \( E_f = 29 \times 10^6 \) psi

<table>
<thead>
<tr>
<th>d(in)</th>
<th>( \tau_{o \text{ max}} ) (psi)</th>
<th>t</th>
<th>3 ( \mu \text{m} )</th>
<th>4 ( \mu \text{m} )</th>
<th>5 ( \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.040</td>
<td>0.5</td>
<td>26,530</td>
<td>30,640</td>
<td>34,250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>---</td>
<td>30,640</td>
<td>34,250</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>---</td>
<td>66,440</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

c) Matrix = Stainless Steel  
Coated film: TiN \( G_M = 10.6 \times 10^6 \) psi  \( E_f = 29 \times 10^6 \) psi

<table>
<thead>
<tr>
<th>d(in)</th>
<th>( \tau_{o \text{ max}} ) (psi)</th>
<th>t</th>
<th>3 ( \mu \text{m} )</th>
<th>4 ( \mu \text{m} )</th>
<th>5 ( \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>0.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>63,470</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>122,240</td>
</tr>
</tbody>
</table>

NOTE: None of the films failed in these tests.
\[ \tau = \frac{0.6d}{(R + 0.4d)} \sqrt{\frac{t \cdot G_M E_f}{d}} \]

where \( G_M \) is the shear modulus of the substrate and \( E_f \) is the Young's modulus of the coating.

If, as a consequence of bending the film did not peel off, the coating to substrate shear strength is clearly larger than \( \tau \). Substrate thickness \( d \), coating thickness \( t \) and bend radius \( R \) were varied to raise \( \tau \) till the film peeled off. Aluminum and stainless steel substrates were used.

Test results obtained show that coatings deposited on well-cleaned substrates yield coating to substrate bond strengths in excess of 20,000 psi (138 MPa) for Ti coating on aluminum, 60,000 psi (413 MPa) for TiN on aluminum, 65,000 psi (448 MPa) for Ti on stainless steel and 120,000 (827 MPa) psi for TiN on stainless steel. Well-bonded coatings are thus producible with the coating techniques developed.

For tribological coatings to be successful, \( \tau^* \) must exceed \( \tau \) the shear stress on the coating surface during frictional contact. The quantity \( \tau \) is given by \( (\mu \sigma_n) \) where \( \mu \) is the friction coefficient and \( \sigma_n \) is the normal stress. Thus a knowledge of \( \tau^* \) and \( \mu \) allows, films failure normal stress \( \sigma_n^* \) to be calculated. Design contact stress \( \sigma_n \) cannot exceed \( \sigma_n^* \) to preclude film failure.

The LFW-1 wear tests on TiN coated non-ferrous test samples show that bond shear strengths in excess of 27 and 48 MPa are obtained easily when magnesium and aluminum test samples are magnetron sputtered.
In practice the normal stress in boundary lubricated sliding pairs does not exceed 15 MPa. Bond strengths obtained are thus sufficient to withstand friction coefficients $\mu > 1$. Similar data is being gathered presently for coated bodies of cast iron and steel (soft and hard).

h. Summary

Task I is directed at establishing viable coating techniques applicable to non-ferrous and ferrous automotive components (pistons, piston rings, cams, tappets, gear train and valve train components, etc.) in order to lower the frictional dissipations, enhance wear-in and to lower wear rates. Magnetron sputtering technique has been chosen as a viable technology (This technology is now in use in G.M., and has been used by Borg-Warner for automotive and transmission applications).

A coating system has been developed and tested. Friction and wear tests have been carried out on selected non-ferrous materials. It has been demonstrated that significant modifications in tribological properties are possible and are obtained without difficulty. Preliminary tests have been carried out on a cast iron and two steels (both in the annealed condition).

Additional tribological studies and film-to-substrate bond strength studies are now in progress. Further development of soft coat techniques are also being pursued.
MAGNETRON SPUTTERING OF NON-FERROUS AEROSPACE ALLOYS FOR WEAR PROTECTION

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School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

The light-weight non-ferrous alloys (titanium, aluminum and magnesium alloys) used in aerospace applications are prone to severe wear in small-displacement and large-displacement unlubricated contacts. Few metallurgical means are available for the surface protection of this class of materials. Deposition of hard compounds by sputtering provides a simple means of protecting such surfaces. Hard coating and tribological studies on coated samples were therefore carried out. The results obtained are presented in this paper. It is shown that magnetron-sputtered TiN hard coatings do provide the required wear protection.

1. INTRODUCTION

Non-ferrous alloys of aluminum, magnesium and titanium are light-weight materials. Further, the precipitation-hardenable alloys of aluminum and titanium possess high strength-to-weight ratios. They also exhibit excellent fracture toughnesses. These characteristics have led to the wide use of aluminum, titanium and magnesium alloys in aerospace applications.

These non-ferrous alloys are soft. In their bare form, in sliding contact without lubrication, the light-weight alloys are prone to severe adhesive and abrasive wear. Scuffing and galling occur readily. Surface protection through surface treatments is essential if these alloys are to be used efficiently in applications where boundary-lubricated or unlubricated contact with a counterface is unavoidable. Protection is also necessary in fretting environments.

Metallurgy of these alloys, however, does not allow the use of routine surface treatments that are common for iron and steel alloys (surface and case-hardening treatments). Treatments involving high temperatures are also not possible for aluminum and magnesium alloys since they melt at moderate temperatures. Precipitation hardening, commonly used to improve the yield strength and fracture toughness, also involves treatment temperatures only some 100 – 200 °C above room temperature. Surface treatments involving elevated temperatures are therefore not suitable for improving the friction and wear properties of non-ferrous alloys.

The tribological properties, however, can be improved greatly by replacing the surface layers of these alloys with other materials. Conversion coatings and anodization are examples. Deposition of thin coatings is yet another way of altering surface properties. A wide range of materials can be deposited without the limitations inherent in conversion coatings and anodization. Deposition of thin coatings at room temperature or low temperatures will preserve the strength and fracture properties and at the same time will provide much better friction and wear properties.

Earlier studies carried out on 6061 aluminum alloys have demonstrated that thin hard coatings of TiN are useful for improving the wear properties of lightweight alloys. The present study was undertaken to assess whether the same hard coating techniques are also useful for improving the wear resistances of other aluminum alloys as well as those magnesium and titanium alloys.

2. RATIONALE FOR THE CHOICE OF COATING PROCESS AND COATING MATERIAL

Reactive magnetron-sputtered coatings of TiN have been used to protect the non-ferrous alloy surfaces. The process and material selection were based on the considerations outlined below.

Soft coatings of metals such as lead have been used to overcome the friction and wear problems encountered with non-ferrous alloys. Soft films, however, wear gradually and the protection is eventually lost. The endurance life of soft films is a function of the operating environments but is finite. However, this is not the case with hard coatings.

In a sliding contact between a soft base material of hardness $H_s$ and a harder counterface of hardness $H_c$, the rate of wear of the soft material depends on the hardness ratio $H_s/H_c$. Un lubricated wear tests by Kruschov have shown that rapid wear of the soft base material occurs when the $H_s/H_c$ ratio is of the order of 1.5 and above. Wear is light when the ratio is of the order of 0.72 to 1.15. Similar results have been reported by Richardson: this has led Halling to suggest that an $H_s/H_c$ ratio of 0.4 is essential to make the wear rate of the soft substrate negligible. This implies that a hard coating with a hardness some 2.5 times that of the counterface will yield wear protection to the base material (the substrate). Wear is now restricted to the hard counterface. Since the coating "will not wear", thick coatings are not necessary.

If the counterface is a steel, since the maximum counterface hardness in engineering use commonly lies in the Vickers hardness range 600-800 kgf mm$^{-2}$ for the hardened steel counterfaces, coatings with Vickers hardnesses of 1500-2000 kgf mm$^{-2}$ are sufficient for the total wear protection of non-ferrous substrates. Hard compounds of refractory metals (WC, TiC, TiN etc.) meet these requirements. The hard coatings promise indefinite wear life. An adequate coating hardness is a necessary condition.

Hard coatings are not usually used with soft substrates since differential strains at the coating-substrate interface can cause film failure. To offset this risk, when hard layers are used on softer substrates for wear protection, they are generally thick (of the order of 1 mm or more when case hardening, plasma spraying etc. are used) provided that hard coatings can be deposited without geometric defects. This is not a
theoretical requirement. The thin hard coating can be treated as a Griffith solid. High fracture stresses and fracture (tensile) strains must then be expected. The thin coating may be treated as a compliant coating. Ideally, the coating should have the same elastic properties as the substrate, but this is impossible. When the coating is well bonded, the violation of this requirement is not very serious. As close a match as possible is desirable. Thin hard coatings—satisfactorily bonded to the substrate—meet most of the requirements necessary and sufficient to provide wear protection.

The use of thin hard coatings precludes large temperature gradients across them and limits the propensity of the coating to debond. The other characteristic of importance here is the product $E\alpha$ where $E$ is Young's modulus and $\alpha$ is the coefficient of thermal expansion. Thin coatings of hard metal compounds with small $E\alpha$ products are thus preferred for the wear protection of non-ferrous alloys.

Nearly all the hard compounds of refractory metals (WC, W$_2$C, TiC, TiN, HfC, HfN, ZrC, etc.) meet the hardness requirements. The product $E\alpha$ is considered in choosing titanium, hafnium and zirconium compounds, in that order. The final choice among these will have to be based on factors related to the choice of deposition process and the ease of coating deposition.

The substrate temperature permissible during hard coating restricts the allowable coating processes. Plasma-assisted coating is essential to obtain the required coating-to-substrate bond strength. Vacuum sputtering processes are the candidates. R.f. and d.c. sputtering can meet the requirements. Ion plating cannot be used because of the uncontrolled temperature rise and the possibility of gas target occlusion during film deposition. Reactive ion plating also requires close control of the ion-plating atmosphere to produce the required stoichiometry.

The film thickness required lies in the range 1-10 $\mu$m. The coating rates feasible with r.f. and conventional d.c. sputtering are low. Magnetron sputtering is preferred. This process also permits reactive sputtering with inexpensive metallic targets. The availability of titanium and zirconium in plate and sheet form makes titanium and zirconium compounds the prime hard coating candidates. Titanium is a better "getter" than zirconium and is preferred for sputter coating in a cleaner vacuum.

In the reactive sputtering of titanium to produce TiC and TiN, the use of Ar-hydrocarbon and Ar-$N_2$ environments is essential. Nitrogen is a more reactive gas in the plasma environment. Concurrent synthesis and deposition of TiN are fairly easy. The use of $N_2$ also avoids the risk of hydride formation. Well-bonded coatings are routinely produced by reactive magnetron sputtering. Thin hard coatings of TiN were therefore selected and deposited with magnetron sputtering in this study to assess the ability of TiN to protect aluminum, magnesium and titanium alloys from wear.

3. EXPERIMENTAL MATERIALS AND METHODS

Test samples 10.16 mm x 15.75 mm x 6.35 mm suitable for friction and wear measurements in a Faville-LeVally Alpha model LFW-I wear tester were machined from rolled plates of 2024-T351 aluminum and Ti-6Al-4V. Magnesium samples were machined from magnesium alloy castings (Mg-4.25Zn-1.25 rare earths-0.5Zr). Surfaces to be coated were prepared by wet grinding in a metallographic polishing...
calculated by measuring the indentation hardness and using the well-known relation

yield strength = 3 x indentation hardness

Calculations and friction and wear observations show that the elastohydrodynamic lubrication load-carrying component of the lubricant film was insignificant. New test rings and fresh oil were used in each test. Test conditions used with the three hard contact substrate materials are shown in Tables I and II.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>WEAR TEST CONDITIONS AND RESULTS ON ALUMINUM ALLOY MATERI ALS.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
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<tr>
<td>Load (kN m⁻¹)</td>
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<tr>
<td>Hertzian pressure (MN m⁻²)</td>
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</tr>
<tr>
<td>Coefficient of friction</td>
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<tr>
<td>Block wear coefficient (μm)</td>
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<tr>
<td>Ring wear coefficient (μm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Sliding distance (m)</td>
<td>23</td>
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</tbody>
</table>

*The coefficients of friction values quoted are the time-averaged values for the beginning and end of the test.

**A negative loss indicates that the ring gained mass.

The uncoated specimen has a hardness of 100 HRA; for TiN coated, all HRA was used.

TABLE II | WEAR TEST CONDITIONS AND RESULTS ON LUBRICANT MATERIALS DETERMINED AT 570 °C. |
<table>
<thead>
<tr>
<th></th>
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<tr>
<td>Parameter</td>
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<td>Coefficient of friction</td>
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<td>Ring wear coefficient (μm)</td>
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<tr>
<td>Sliding distance (m)</td>
<td>550</td>
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</tbody>
</table>

** See Table I

5. TEST RESULTS AND DISCUSSION

Friction and wear test data are presented in Tables I-Ill for the coated and uncoated test samples. As mentioned earlier, three different film thicknesses were used for the aluminum alloy substrates. In addition to the standard maximum hertzian pressure which is equal to 0.62 of the yield strength, normally used, a
unit. Fresh 600 grit SiC was used to produce a standard initial surface roughness in all test samples. The wet ground samples were repeatedly washed in distilled water and acetone and were then dried with a blast of \( \text{N}_2 \). Cleaned specimens were placed in the sputter-coating chamber with minimal delay.

The TiN coating was deposited by operating a d.c. magnetron coating system in the reactive sputtering mode. An Ar-\( \text{N}_2 \) atmosphere was used. The hard coatings were deposited at an operating pressure of 0.09-0.15 Pa. By varying the deposition time (coating rate 120 nm min\(^{-1} \)), films ranging in thickness between 1 and 4.5 \( \mu \)m were produced. The system used is the same as that used in an earlier work\(^1\). To obtain the required coating-to-substrate bond strength, the test samples were sputter cleaned initially at a pressure of 2.7 Pa for 5 min. A movable shutter was used to prevent target contamination during sputter cleaning. The reactive sputtering conditions (operating voltage, cathode current density, gas mixture composition, flow rate etc.) used in the present work were identical with those reported earlier\(^6\). Using these conditions, hard coatings (of Vickers hardness 1900 kgf mm\(^{-2} \)) are routinely produced. The golden-yellow films produced exhibit lattice parameters within 1% of the theoretical value. From lattice parameter and X-ray diffraction studies, the films were judged to be stoichiometric or nearly so. For stoichiometry measurements, Rutherford backscattering studies are preferred and are in progress.

4. EVALUATION OF FRICTION AND WEAR CHARACTERISTICS

Friction and wear studies were conducted on a Fawley-LaVally, Alpha model LFW-1 test machine using procedures given in the ASTM Standard\(^{10} \). All tests were carried out at a sliding speed of 13 m s\(^{-1} \). An unformulated paraffinic mineral oil of viscosity 26 mm\(^2\) s\(^{-1} \) at room temperature was used in the tests. Test rings hardened to a Rockwell C hardness of 61-63 with a surface finish of 0.4 \( \mu \)m tr.m.s. were used. A typical test sliding distance for hard-coated specimens was 550 m. Tests on uncoated samples were terminated when the volume of wear was excessive. Figure 1 shows the dimensions of wear scars produced on bare samples when the tests were terminated.

![Fig 1. Surface profile of wear scars for (a) TiN-coated magnesium upper profile for a sliding distance of 550 m and uncoated magnesium lower profile for a sliding distance of 231 m load, 23.5 kN m\(^{-1} \) and (b) TiN-coated titanium upper profile for a sliding distance of 550 m and uncoated titanium lower profile for a sliding distance of 2 m load, \( V = 1.3 \text{kN m}^{-1} \).](image)

Tests on aluminum, titanium and magnesium alloys were carried out at maximum initial hertzian pressures (block-on-ring test geometry; nominal line contact equal to 0.62 of the calculated yield strength. Yield strengths were
second set of tests were carried out at a hertzian pressure of 0.55 of the yield strength for the cast magnesium alloys (Table III).

<table>
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<tr>
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<th>TiN-coated</th>
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<tr>
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<td>Coefficient of friction</td>
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<td>Block mass loss (g)</td>
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<td>Ring mass loss (g)</td>
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<td>Sliding distance (m)</td>
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</table>

*See Table I*

The test results presented show that TiN coatings not less than 3.6 µm thick reduce the wear rate of 2024 aluminum alloys by approximately two orders of magnitude. The wear protection afforded to titanium is more spectacular. Titanium is known to gall and wear severely in sliding contact. The mass loss in the bare titanium alloy test in only 2 m of sliding is 5.15 g whereas the mass loss of TiN-protected sample is negative, i.e., wear debris is transferred to the counterface. The reduction in the wear coefficient is more than three orders of magnitude when a thin 3.6 µm TiN hard coating is used to protect titanium alloys.

For the cast magnesium alloy, the 3.6 µm thick hard coating is sufficient to obtain wear resistance at maximum contact stresses equal to 0.62 of the yield strength. The higher contact stress tests indicate a gain in wear resistance but not total wear protection. Apparently a thicker hard coating is essential. This observation is similar to that with a thin coating (1 µm) on aluminum.

6. SUMMARIZING REMARKS AND CONCLUSIONS

Light-weight non-ferrous alloys commonly used in aerospace applications are prone to severe wear in sliding contact. Theoretical considerations suggest that improvements in wear resistance are possible with thin hard coatings. Magnetron-sputtered hard coatings of TiN may provide the required wear resistance.

Sliding wear tests carried out with hard coatings 1-4.5 µm thick show that TiN films 3.6 µm thick are sufficient to reduce the wear rate to negligibly small levels provided that the contact stress does not exceed 0.62 of the yield strength.

All three alloys of interest in aerospace applications can be protected with TiN hard coatings. The rationale for the use of hard coatings to improve the wear resistance of soft materials, outlined in Section 2, is confirmed.

The absence of debonding demonstrates that well-bonded TiN hard coatings can be produced by reactive magnetron sputtering. Coefficient of friction measurements show that coating-to-substrate shear strengths in excess of 27 MPa, 48 MPa and 95 MPa can be produced in magnesium, aluminum and titanium substrates respectively. Commonly, the contact stress under boundary-lubricated
MAGNETRON SPUTTERING OF NON-FERROUS ALLOYS

sliding contact conditions rarely exceeds 20 MPa. The bond strength required is obtained easily.

ACKNOWLEDGMENTS

The authors thank Richard Marks, Pratt and Whitney, Mississauga, Ontario, Canada, for the provision of the magnesium alloy test samples. We thank Mrs. J. Van Hook for careful manuscript preparation.

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REFERENCES

TASK II: SHEAR RHEOLOGICAL CHARACTERIZATION OF LIQUID LUBRICANTS (MOTOR OILS)

Although tribosystems are necessary for the function of automotive systems, contact friction is a significant source of energy loss which reduces automotive fuel economy. The objective of the rheology portion of this phase of tribology studies was to measure the shear rheological properties of a group of automotive engine lubricants to determine the affect of lubricant composition on traction (friction) in concentrated contacts. Concentrated contacts occur in automotive systems at cams, gears and rolling element bearings. Traction drive mechanisms which are frequently discussed as future transmissions, also rely on concentrated contacts. To some degree lubricant behavior in concentrated contacts is indicative of its expected behavior in the ring-cylinder contact and in the high shear rate conditions of journal bearings.

The authors have shown [ref. 1,2] that the traction in concentrated contacts can be predicted by their limiting shear stress model using three primary rheological properties of the lubricant — the low shear stress viscosity, the limiting elastic shear modulus, and the limiting shear stress. Of these the limiting elastic shear modulus is important only for small shear strains of the film (less than three percent). Since practical systems quickly develop much greater strains than this, only the low shear viscosity and limiting stress are important for the evaluation of traction in automobile engines.

The low shear viscosity can be measured in a high pressure falling body viscometer (ref. [1]) and the limiting shear stress for comparison purposes can be obtained from concentrated contact traction
(shear stress) measurements (ref. [3]) in the form of the property averaged over a range of pressures. These measurements have been made for twelve commercial motor oils, the ASTM High Reference oil, and a pair of unformulated base oils and a pair of blends of polyalkyl-mythacrylate polymer (PAMA) and one base oil.

In addition, film thickness measurements were made for all samples to assess whether or not the traction measurements were made under full film conditions. These film thickness measurements allowed the calculation of an effective contact inlet viscosity and the subsequent comparison with measured low stress viscosity. This effective inlet viscosity is the high shear rate viscosity which can be expected to be indicative of the high shear rate viscosity important to journal bearing performance. The difference between the kinematic viscosity and the high shear viscosity is a function of the polymer type and concentration.

**FLUID SAMPLES**

Twelve commercial automotive engine oils typical of those in common use were obtained from service stations and auto parts retail stores. Descriptions provided by the manufacturer are listed in Appendix 1. They include five oils formulated for fuel economy, six SAE 10W-40 grades, three 10W-30 grades, and one each of 20W-50, 30, and 5W-20 grades. One is of synthetic base stock. The others are of refined petroleum base.

Also included in all tests run on the commercial oils was ASTM
High Reference Oil (HR) because this oil has been proposed as a standard for comparison in the ASTM Fuel Efficient Oil Program.

Two unformulated base oils and two blends of one of the base oils with two polyalkylmethacrylate polymers of different molecular weight were included in most tests to assess the effectiveness of V.I. improver alone. They are also described in Appendix 1.

EXPERIMENTAL EQUIPMENT

Viscometer

The viscometer used for these studies is shown in Figure 1. It is of the falling body type. The sinker is made of a magnetic material and translates through a thin brass sleeve plugged at one end and sealed at the other by an isolating piston to separate the sample from the pressurizing medium (Diester). Shearing of the sample occurs between the sinker and the sleeve inside diameter. The sleeve is housed in a non-magnetic vessel which is surrounded by a linear variable differential transformer.

The pressure of the medium (up to 0.66 Pa) is generated in an external pressure intensifier and measured with a precision Heise bourdon tube gauge. The viscometer is enclosed in an air-oven for temperature control (25-230°C) and is inverted to initiate a fall of the sinker. For a further description and additional results, see (ref. [4]).
**EHD Simulator**

The concentrated contact simulator is shown in Figure 2. The contact geometry is that of a crowned roller against a flat disk. The ellipticity of the contact can be varied from approximately 0.3 to 3 by varying the crown radius. All the data in this report are for an ellipticity ratio of 2.5 to 3. The disk is sapphire and the roller hardened 52100 steel.

The disk and roller are both driven through timing belts by a single variable speed motor. Therefore, the relative rotational speeds of the two surfaces are fixed by the timing gears. The rotational speeds are determined by a photo-optical tachometer on the drive motor shaft. The rolling speed or entrainment velocity is varied by the drive motor speed while the slip velocity, and hence the slide-roll ratio, is varied stepwise by the timing gears and continuously (± 0.07 about a mean) by the radial position of the roller contact on the disk. (The slide-roll ratio is defined as the difference between the velocities of the two surfaces divided by the average of the two surface velocities.)

The continuous variation of slide-roll ratio is accomplished through the slide-roll micrometer which moves the roller support along a linear bearing in a direction perpendicular to the disk rotational axis thereby varying the radial position of the contact on the disk. This causes the surface velocity of the disk at the contact to vary, hence varying the slide-roll ratio. The slide-roll ratio micrometer has a multi-turn potentiometer attached which results in an electrical
voltage proportional to the slide-roll ratio to facilitate recording the traction slide-roll ratio curve.

The side slip at the contact can also be varied through the side slip micrometer which moves the center of disk rotation perpendicular to the axis of roller rotation. If the axes of rotation of the disk and roller intersect, the side-slip is zero. The side-slip angle (θ) has a significant influence on the traction in the low slide-roll ratio range (less than approximately |0.05|). All the data reported here was taken with zero slide slip.

The contact load is applied by a dead weight hung on the disk axis through a thrust bearing to prevent the weight from rotating. The weight is supported by the concentrated contact. The horizontal position of the disk axis is maintained at the drive gear by a ball bearing which is free to move axially and from above the disk by a flexible frame which resists the torque and motion along the roller axis of rotation. The horizontal position is laterally restrained in the direction of contact traction by the side-slip micrometer with a piezoelectric force transducer link to measure the contact traction. The piezoelectric traction transducer is very stiff (1 GPa/m), has a flat frequency response to 10 kHz, and a force resolution of 0.01 N. The signals from this traction transducer and the slide-roll ratio transducer are connected to the y and x axis respectively of an x-y recorder to record the traction slide-roll ratio curve.

The disk, roller and roller support carriage are all in an enclosure to permit bulk temperature variation and measurement. The enclosure acts as a reservoir for liquid lubricants. The liquid
The lubricant sample required is less than 5 cm$^3$.

The major simulator operating variable ranges are: hertz pressures to 2 GPa (depending on surface materials), rolling or entrainment velocity to $V = 3$ m/s, and bulk temperature from room temperature to 120°C.

Because of the high mechanical stiffness of the simulator and the good transient response of the traction transducer, small geometric irregularities in the system which cause small variations in the contact load and kinematics result in traction fluctuations. These are particularly apparent at low slide-roll ratio where the traction dependence on slide-roll ratio is very pronounced near zero slide-roll ratio. Those fluctuations resulting from kinematic variations tend to be eliminated as slide-roll ratio increases and traction becomes less dependent on slide-roll ratio. Those fluctuations, due to cam action of the disk or roller, will continue to be observed at higher slide-roll ratio.

Because of the flexibility of the device it is suitable for simulating a wide variety of tribosystems. For a further description and additional results, see ref. [3,5].

RESULTS

High Pressure Viscosity Measurements

In order to determine the low shear stress rheology of the lubricant samples their viscosity was measured as a function of pressure at the usual temperatures of 40°C, 100°C, and 150°C. (The two base oils and two blends were measured over a greater temperature range.) These data are shown in Figures 3-14 and tabulated for the motor oils in Table 1.
temperature suggests that the lubrication mode is not full film but rather that as the temperature rises and the lubricant film diminishes, a greater share of the load and the traction is shared by the surface asperities. In fact, a "running in" effect can be seen in the first run where the traction level dropped for the measurement following the 70°C measurement whereas previous measurements showed successive increases in traction. This "running in" is carried over to Run 2 of Figure 15a where the traction curve is very much changed from Run 1. The calculated minimum film thickness for 80°C is 0.052 μm.

In Figure 15b, the same measurements were made for the roller after refinishing with 3/0 emery polishing paper and again for diamond lapping of the roller. The diamond lapping appears to reduce the affects of asperity interaction. It was decided to use a higher aspect ratio roller for the traction program to increase repeatability and reduce the peak Hertz pressure to that more characteristic of automotive practice.

The traction program for the thirteen motor oils consisted of loading a polished roller against an optically smooth disk to give a contact with an ellipticity ratio of K = 3 (minor axis in the direction of rolling) and a peak Hertzian pressure of 0.74 GPa (107,000 psi). The side-slip angle was set at zero and the sample and enclosure brought to temperature. With the rolling (average) velocity at $V = 1.0 \text{ m/s}$, a slide-roll ratio range of $-0.08 < E < 0.06$ was scanned and the traction recorded. See Figure 16 for an example of the data as received from an x-y plotter. The drive pulleys were changed to result in a slide-roll
ratio of $\Sigma = 0.9$. The traction was recorded for $\Sigma = 0.9$ and -0.9 and the difference divided by 2 to arrive at an average traction. The traction coefficients for the thirteen motor oils are graphically presented in Figures 17-20. The traction is higher for $\Sigma = 0.9$ than for $\Sigma = 0.05$ in all cases indicating that the fluid behavior is primarily viscous at the high shear rates. The traction decreases with increased temperature (as is expected from limiting shear strength measurements of similar materials.) except for oils Ref. S-1, and S-6 at low temperatures. It is believed (Ref. [3]) that this is due to the oil film becoming very thick, allowing the pressure distribution to spread into the inlet and lower the peak fluid pressure.

In addition, the traction behavior of the two base oils R620-15 and R620-16, and two polymer-oil blends, R620-15 + PL4521 and PL4523, was measured for an aspect ratio of 2.5, peak Hertz pressure of $P_H = 1.0 \, \text{GPa}$, and temperature of $T = 26^\circ\text{C}$. As is expected from limiting shear stress measurements [6] the four percent addition of the methacrylate polymer reduces the traction coefficient of the R620-15 (Figure 21).

**Film Thickness Measurements**

Optical interferometry was used to measure lubricant film thickness during the operation of the simulator. A microscope with a through the lens light source was focussed on the contact (Figure 1). A narrow band pass filter (Wratan 72B) with a dominant wavelength $\lambda = 605 \, \text{nm}$ was used between the tungsten lamp and microscope. An
aspect ratio of $K = 2.5$ was used, resulting in a Hertz pressure of $P_H = 0.80$ GPa from a load, $w = 25N$, identical to that of the traction measurements. Nearly pure rolling ($\gamma = 0$) was obtained by removing the drive belt from the roller and allowing the roller to be driven by the disk. From the methods of Ref. [7] the minimum film thickness under these conditions was calculated to be within six percent of that during the traction measurements.

With this interference technique, changes in thickness of the film are viewed as alternate light and dark fringes appearing in the contact. The film thickness where a bright fringe occurs is

$$h_+ = \frac{\lambda}{2\pi} \left( n + \frac{\Delta \phi}{2\pi} \right), \quad n = 0, 1, 2, \ldots$$

and where a dark fringe occurs is

$$h_- = \frac{\lambda}{2\pi} \left( n + \frac{\Delta \phi}{2\pi} - \frac{1}{2} \right), \quad n = 0, 1, 2, \ldots$$

Where $\Delta \phi$ is the phase change due to roughness of the roller surface and $n$ is the fringe order. The fluid refractive index, $\xi$, was taken to be 1.5 in all cases. This leaves $\Delta \phi$ to be calibrated for the particular system.

For the seventeen fluid samples, rolling speed was increased until a light or dark fringe was observed in the center of the contact. The speed and fringe order was noted. For the thirteen motor oils the fringes were noted when possible for minimum film thickness.

The system calibration was done with oil S-6 and is shown in Figure 22. A plot of fringe order ($n - 1/2$ for dark fringes) versus
\( V^{-0.67} \) yields a straight line whose intercept is

\[
\frac{2\pi h}{\lambda} - \frac{\xi}{2\pi} = -0.42
\]

Since at \( V = 0, h = 0 \),

\[
\frac{\xi}{2\pi} = 0.42
\]

Film thicknesses were observed at 25C, 50C, and 75C and are plotted for all samples in Figures 23-39. The open symbols represent bright fringe values and the solid symbols represent dark fringe values. Also plotted are film thickness predictions from the relations [5],

\[
h_c = 2.69 R_x V^{0.67} C^{0.53} W^{-0.067} (1 - 0.61 e^{-0.73K})
\]

\[
h_m = 3.63 R_x V^{0.68} C^{0.49} W^{-0.073} (1 - e^{-0.68K})
\]

for central and minimum thickness respectively. Where

\[
W = \frac{\nu}{ER_x}
\]

\[
U = \frac{\nu_0 V}{ER_x}
\]

\[
G = \alpha E
\]

\[
\frac{1}{E} = \frac{1}{2} \left( \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right)
\]
$E_1, E_2, \nu_1$ and $\nu_2$ are moduli of elasticity and Poisson's ratio for the disk and roller and $R_x$ is the roller radius in the direction of motion. The pressure-viscosity data measured and presented in this report were used in these calculations.

For oils S-6, M-5, Ref., R620-15, and R620-16 which are known to contain no polymer V.I. improver the agreement between measured and predicted film thickness is satisfactory. For other materials the viscosity data predicts higher values than those measured. In particular, the measured film thickness for R620-15 + PL4523 ($2 \times 10^6$ M.W. PAMA) is one-third of the predicted value. For the experimental blends (R620-15 + PL4521 and R620-15 + PL4523) the film thickness predicted from base oil properties is also plotted and the measured values lie between each pair of predicted curves.

From these plots it could be suggested that the rheological properties that determine the film thickness (i.e., $\nu_o$ and $\alpha$ in the high shear inlet region of the concentrated contact) for the polymer-oil blend are reduced from the values measured for the blend at low shear stress to those more representative of the base oil. Since the pressure-viscosity coefficient of the base oil is nearly the same as the blend it can be assumed that $\alpha$ does not change and the viscosity is responsible for the reduced film thickness. Therefore an effective viscosity, $\nu_{\text{eff}}$, can be calculated from the film thickness data and the film thickness relations. These are tabulated in Table 4 and plotted against low shear rate viscosity for the oil with and without polymer in Figures 40 and 41 respectively.
CONCLUSIONS

Rheological measurements for phase I of the tribology studies consisted of pressure-viscosity, EHD traction (average lubricant shear stress in a concentrated contact), and EHD film thickness for thirteen motor oils and four well characterized experimental oils.

Pressure-viscosity measurement does not distinguish standard motor oils from fuel-economy formulated oils, even between oils of the same grade and manufacturer (Figures 6 and 7). It does however separate these samples by SAE grade if all motor oil data is plotted in one figure. This has been done in Figure 42. This generalized pressure-viscosity data may be useful for the prediction of EHD film thickness and therefore the design of automotive tribosystems and the specification of automotive lubricants.

No trend could be found which separated the traction characteristics of mileage formulated motor oils and standard oils, even between those of the same SAE grade and manufacturer (Figures 18c and 19a).

It is seen in Figure 43 that the traction behavior of the group of six SAE 10W-40 and three SAE 10-30 motor oils is a characteristic of the grade. If all motor oil traction data is plotted by viscosity grade, Figure 44 results. The ASTM High Reference oil and the 20W-50 generated the highest traction while the 5W-20 provided the lowest traction coefficient of the group.

It was seen that for the experimental oils of Figure 21 that a polymer V.I. improver can reduce the full film traction of the base oil to which it is added. It is believed then that the average
lubricant shear stress (full film traction) is determined by the base oil type and the presence of polymer V.I. improver.

Of course these full-film traction and rheology measurements do not evaluate the effect of friction modifiers on the mixed regime of lubrication and it is suggested that the next phase include a mixed film traction program.

Film thicknesses measured by interferometry agree well with those calculated from pressure-viscosity data using the Hamrock and Dowson equations [5] for the motor oils containing no polymer V.I. improver. However, the polymer thickened oils displayed a lower than predicted film thickness which can be related to a reduced effective inlet viscosity (Table 4). The film thickness measurements on the experimental oils confirmed the effect of polymer V.I. improver on effective viscosity.
REFERENCES


Table 1. High Pressure Viscosities

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<th>S-1</th>
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- b: Sinker would not move at this pressure.
- c: Viscosity increasing with time.
- d: P = 338 MPa
- e: P = 548 MPa
- f: P = 617 MPa
- g: P = 554 MPa
- h: P = 485 MPa
- i: P = 574 MPa
### Table 2. Pressure Viscosity Coefficients for Thirteen Motor Oils

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<th>T[°C]</th>
<th>Oil</th>
<th>S-1</th>
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<th>S-3</th>
<th>S-4</th>
<th>S-5</th>
<th>S-6</th>
<th>S-7</th>
<th>M-1</th>
<th>M-2</th>
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**Pressure-Viscosity Coefficient \([\text{GPa}^{-1}]\)**

\[
\alpha_{0T} = \left[ \frac{d}{dp} \left( \tau \ln \nu \right) \right]_{T,p = 0}
\]

\[
\alpha_{0T}^* = \left[ \int_0^\infty \frac{\nu(0)}{\nu(p)} dp \right]^{-1}_{T,p = \infty}
\]
Table 3. Pressure-Viscosity Coefficients of Two Base Oils and Two Polymer-Base Oil Blends

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<th>Fluid</th>
<th>T/C</th>
<th>$\alpha_{OT}$</th>
<th>$\alpha^*_T$</th>
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$\alpha_{OT} = \left. \frac{d \ln \nu}{dp} \right|_{T,p = 0}$

$\alpha^*_T = \left[ \int_0^{p_{\infty}} \frac{\nu(T,p = 0)}{\nu(T,p)} dp \right]^{-1}$
## Table 4. Effective Inlet Viscosity from Film Thickness Measurements Compared to Low Shear Viscosity

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<th>$\nu_0$ Low Shear Viscosity (m/s)</th>
<th>$\nu_{\text{EFF}}$ Effective Viscosity 1 m/s</th>
<th>$\nu_0$ Low Shear Viscosity (m/s)</th>
<th>$\nu_{\text{EFF}}$ Effective Viscosity 1 m/s</th>
<th>$\nu_0$ Low Shear Viscosity (m/s)</th>
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Roller Finish: 3/0 Paper

Diamond Lapped

Fluid: S-5

$K = 1.0, P_h = 1.4 \text{ GPa}$

- $\Sigma = 2.0$
- $\Sigma = 0.05$

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\[
\left( \frac{2 \xi_h - \Delta \phi}{2 \pi} \right)
\]
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Figure 30. Measured and Predicted Film Thickness for Oil S-7.
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Figure 33. Measured and Predicted Film Thickness for Oil M-3.
Figure 34. Measured and Predicted Film Thickness for Oil M-4.
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APPENDIX

LUBRICANT SAMPLE INFORMATION
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<th>Comments</th>
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<td>Fire and Ice</td>
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<td>10W-40</td>
<td>Energy Saving</td>
<td>Quaker State Oil Refining Company</td>
<td>Sterling</td>
</tr>
<tr>
<td>S-5</td>
<td>10W-20W-30</td>
<td></td>
<td>Quaker State Oil Refining Company</td>
<td>Super Blend</td>
</tr>
<tr>
<td>S-6</td>
<td>30</td>
<td></td>
<td>Quaker State Oil Refining Company</td>
<td>HD Oil</td>
</tr>
<tr>
<td>M-5</td>
<td>5W-20</td>
<td>Synthetic</td>
<td>Mobil Oil Corporation</td>
<td>Mobil 1</td>
</tr>
<tr>
<td>S-7</td>
<td>10W-40</td>
<td></td>
<td>Pennzoil Company</td>
<td>Multi-Vis</td>
</tr>
<tr>
<td>REF.</td>
<td>HR-1</td>
<td></td>
<td>ASTM-1450 Program</td>
<td></td>
</tr>
</tbody>
</table>
March 24, 1981

Dear Ward,

I recently received your request for information regarding oils included in your Tribology study being conducted under government contract. As reference oil chairman of the ASTM Task Force on Fuel Efficient Engine Oils, I can supply descriptive data for HR reference oil.

- **Name** - ASTM High Reference Oil (HR)
- **Base Oil** - 60/40 Solvent 150/Solvent 600
- **VI** - None
- **Friction Modifier** - None
- **DI Package** - API SF Quality
- **Finished Oil Analysis**
  - Viscosity - 9.5 cSt @ 210°F
  - Zn - 0.13 Wt.%
  - Mg - 0.13 Wt.%
- **Viscosity Grade** - SAE 20W30

I trust this information meets your needs and I look forward to receiving a copy of the contract reports.

Very truly yours,

GORDON R. FARNSWORTH

Ward O. Winer
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

GORDON R. FARNSWORTH
January 19, 1981

Professor Ward O. Winer
Engineering Consultant
1025 Mountain Creek Trail, NW
Atlanta, Georgia 30328

Dear Ward:

The following information is available on sample OS No. 52287, the ASTM 5-Car FE Test High Reference Oil:

Kinematic Viscosity, cSt

\[
\begin{align*}
@ 40{}^\circ C & : 75.43 \\
@ 100{}^\circ C & : 9.55 
\end{align*}
\]

Elemental Analysis (by Emission Spectroscopy)

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.147</td>
</tr>
<tr>
<td>P</td>
<td>0.125</td>
</tr>
<tr>
<td>Si</td>
<td>0.0012</td>
</tr>
<tr>
<td>B</td>
<td>0.10</td>
</tr>
<tr>
<td>Na</td>
<td>0.0005</td>
</tr>
<tr>
<td>Mg</td>
<td>0.137</td>
</tr>
</tbody>
</table>

We hope your studies with this oil are successful. We would, of course, be interested in your results and how they compare to vehicle data generated at Lubrizol. If I can be of any further assistance please let me know.

Very truly yours,

Brian M. O'Connor

BMO/cao
Professor Ward O. Winer  
Engineering Consultant  
1025 Mountain Creek Trail, NW  
Atlanta, Georgia 30328  

Dear Ward:

Under separate cover we are sending you one pint of OS#52655, the current batch of ASTM Reference Oil, HR-2. This is as per our conversation at last month's SAE meeting.

Very truly yours,

W. B. Chamberlin

WBC /bj
May 8, 1981

Mr. Ward O. Winer
Georgia Institute of Technology
Atlanta, Georgia 30332

Dear Mr. Winer:

In response to your letters of 2/24 and 5/1, below are the requested items of information. I am sorry about the delay in responding.

**Product:** GTX 20w/50 motor oil (and all other GTX grades; note GTX 10w/30 is friction modified with a proprietary soluble compound).

**Base oil:** High VI solvent refined neutral parafinic

**VI:** Most production is with non-dispersant Olefin Co-polymer

- % weight of neat polymer is approximately 1% in 20w/50
- Average molecular weight is approximately 60,000 (by membrane osmometry); approximately 50,000 by gel permeation chromatography
- Some production is with a dispersant Poly methacrylate

- % weight of neat polymer is approximately 1% in 20w/50
- Average molecular weight is approximately 150,000 by osmometry; approximately 125,000 by gel permeation chromatography

Please note that we cannot be certain of these % weight, and molecular weight since we do not produce the polymers ourselves. As a more general description, we pick VI improvers for 0 shear loss in the L-38 10 hour test; ASTM FISST loss is about 5% or less.
D-I: alkyl ZDDP, Calcium Sulfonate, ashless dispersants and antioxidants. SF/CC, CCMC approximately 5% of neat undiluted additives

FM: No (except GTX 10w/30)

We have been doing much research on the role of rheology on fuel economy. A joint SAE paper is due to be presented at the June '81 SAE meeting in Detroit. I cannot supply you a copy at this time, since it represents a joint project with other entities. It should be of considerable interest as background to your studies. The SAE paper number is 810800.

Regards,

Richard G. Tittel
Technical Coordinator
March 20, 1981

Prof. Ward O. Winer
Georgia Institute of Technology
Atlanta, Georgia 30332

Dear Professor Winer:

Thank you for your inquiry concerning Texaco Havoline Motor Oil. In selecting Texaco motor oil for your studies we suggest you use Havoline Supreme 10W-40 which is our fuel efficient API-SF motor oil. It is formulated with all solvent neutral mineral oils, an olefin-copolymer VI improver and a DI package containing succinimide dispersant, calcium sulfonate detergent, alkyl zinc dithiophosphate. In addition, the oil contains an oil soluble friction modifier. Attached are typical inspection tests obtained on Havoline Supreme 10W-40.

We will be interested in the results of your study. Please advise if we can be of any further help in this matter.

Very truly yours,

RGL-bt

Attachment
HAVOLINE SUPREME 10W-40

Typical Tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, °API</td>
<td>32.0</td>
</tr>
<tr>
<td>Flash, COC, °F</td>
<td>420</td>
</tr>
<tr>
<td>Kin Vis., cSt at 40°C</td>
<td>85.4</td>
</tr>
<tr>
<td></td>
<td>13.13</td>
</tr>
<tr>
<td>CCS Vis., cP, -18°C</td>
<td>2430</td>
</tr>
<tr>
<td>Pour Pt., °F</td>
<td>-20</td>
</tr>
<tr>
<td>Ca, %</td>
<td>0.24</td>
</tr>
<tr>
<td>P, %</td>
<td>0.14</td>
</tr>
<tr>
<td>Zn, %</td>
<td>0.15</td>
</tr>
<tr>
<td>N, %</td>
<td>0.10</td>
</tr>
</tbody>
</table>
May 21, 1981

Dr. Ward Winer
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

Dear Ward:

It has been quite a while since I’ve seen you, but it was good to get your letter about the "Role of Tribology in Automotive Fuel Economy", which was forwarded to me by Frank Didot. Since Jim Lauer left Sun in 1978, I have been involved in engine oil development, currently working in Technical Service for customers.

Your project looks very interesting, and I would appreciate receiving any information generated by the work. In turn, I am supplying in the attached table the data you requested on the oil sample that we supplied to you.

If I can be of any further assistance, contact me at (215) 447-1847.

Best regards,

Mel Peterkin
Technical Service Engineer

MEP:1dw

Attachment

cc: Mr. F. E. Didot
Mr. G. G. Kroninger
Mr. L. E. Slagle
CTF

CTF
Base Oil Information:

100% mineral oil ~160 N Solvent Refined

VI Package:

Styrene-ester copolymer
Avg. mol. wt. of 328,000 wt. avg.
98,000 number avg.
Used at ~2 wt.%

D-I Package:

SF/CB Calcium Chemistry Detergent-Antioxidant at ~5%

Friction Modifier: Soluble Organic Phosphate

Other:

10W-30 SAE Viscosity Grade
SF/CB API Service Grade
Viscosity Index 170
Total Base Number (D664) 5.5
Total Acid Number (D664) 2.2
Viscosity cP/-18°C 1800
Viscosity, cSt/100°C 11.3
Pour Point, °C -33
Zinc, % Wt. 0.16
Phosphorus, % Wt. 0.20
Sulfated Ash, % Wt. 0.94

MEP: ldw
5/21/81
Professor Ward O. Winer
Georgia Institute of Technology
School of Mechanical Engineering
Atlanta, Georgia 30332

Dear Professor Winer:

We wish you well in your study on the "Role of Tribology in Automotive Fuel Economy" being conducted under contract to the U.S. Department of Transportation. The inclusion of several Quaker State motor oils in your studies is most complimentary. The general compositional information you requested and typical physical properties for the products are given in the attached table. In addition, we have also attached Quaker State Technical Information Bulletin T-1001F which contains additional descriptive information on Quaker State Motor Oils. Quaker State Sterling Motor Oil is a premium quality fuel economy oil that contains a special oil soluble friction modifier that provides outstanding fuel economy benefits. Both Quaker State Deluxe Motor Oil, SAE 10W/40 and Super Blend Motor Oil, SAE 10W/30 meet the proposed ASTM fuel economy test requirements for a fuel economy oil. This was accomplished without the use of a specific friction modifier additive by careful selection of the additive components used in the products with respect to their frictional characteristic's.

We trust that the material provided will be of value to the program and look forward to reviewing the results of your studies when they are published.

Very truly yours,

QUAKER STATE OIL REFINING CORP.
Research Center

John A. Lundquist,
Associate Director of
Research and Development

JAL/rls
Attach.
<table>
<thead>
<tr>
<th>Product</th>
<th>Quaker State Sterling Motor Oil</th>
<th>Quaker State Deluxe Motor Oil</th>
<th>Quaker State Super Blend Motor Oil</th>
<th>Quaker State HD Motor Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE Grade</td>
<td>10W/40</td>
<td>10W/40</td>
<td>10W/30</td>
<td>30</td>
</tr>
<tr>
<td>API Service Designation</td>
<td>SF-SE</td>
<td>SF-SE-SD</td>
<td>SF-SE-SD-CC</td>
<td>SF-SE-SD-CC</td>
</tr>
</tbody>
</table>

### General Description

- **Base Oil**: Select cuts of refined oil from Pennsylvania Grade Crude Oil
- **Viscosity Index Improver**: Multifunctional
- **Dispersant Type**: Zinc Dialkyldithiophosphates
- **Detergent/Inhibitor Package**: Overbased Sulfonates, Ashless Dispersants, Ashless Inhibitors, Plus Other Additives
- **Friction Modifier Additive**: Oil Soluble Type

### Typical Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Quaker State Sterling Motor Oil</th>
<th>Quaker State Deluxe Motor Oil</th>
<th>Quaker State Super Blend Motor Oil</th>
<th>Quaker State HD Motor Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, °API</td>
<td>29.5</td>
<td>30.5</td>
<td>30.4</td>
<td>28.0</td>
</tr>
<tr>
<td>Viscosity @ 210°F., SUS</td>
<td>77.1</td>
<td>77.6</td>
<td>62.2</td>
<td>67.9</td>
</tr>
<tr>
<td>Apparent Viscosity (CCS) @ 0°F., cP 20°F.</td>
<td>2250</td>
<td>2350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash Point, CDC, °F.</td>
<td>420</td>
<td>405</td>
<td>405</td>
<td>430</td>
</tr>
<tr>
<td>Total Base No.</td>
<td>7.7</td>
<td>6.7</td>
<td>6.6</td>
<td>6.5</td>
</tr>
<tr>
<td>Sulfated Ash, wt. %</td>
<td>0.99</td>
<td>0.95</td>
<td>0.95</td>
<td>0.80</td>
</tr>
</tbody>
</table>

* Different type of Viscosity Index Improver than used in Quaker State Deluxe and Super Blend motor oils.

Research Center
March 1981
QUAKER STATE STERLING MOTOR OIL
SAE 10W-40 HD

Quaker State Sterling Motor Oil is blended from a select cut of base oil plus the following additives:

- Pour Depressant
- Anti-foam Agent
- Oxidation Inhibitors
- Corrosion Inhibitors
- Rust Inhibitors
- Anti-wear and Anti-scuff
- Detergent and Dispersant
- Viscosity Index Improver
- Friction Modifier

Base oil, as used in this Quaker State bulletin, refers to the motor oil refined from crude oil before any additives are used.

Sterling is an advanced motor oil designed to provide greater fuel economy and permit extended drain intervals.

Sterling Motor Oil meets the following designations and specifications:

1. For API Service Designation SF, SE
2. All current automobile manufacturers' specifications

QUAKER STATE DELUXE MOTOR OIL
SAE 10W-40 HD and 20W-50 HD

Quaker State DeLuxe Motor Oil is formulated from scientifically selected base oils, plus the following additives:

- Pour Depressant
- Anti-foam Agent
- Oxidation Inhibitors
- Corrosion Inhibitors
- Rust Inhibitors
- Anti-wear and Anti-scuff
- Detergent and Dispersant
- Viscosity Index Improver

DeLuxe Motor Oil meets the following specifications and designations:

1. For API Service Designation SF, SE, SD
2. All current automobile manufacturers' specifications
3. The SAE 10W-40 product meets proposed ASTM fuel economy tests.

QUAKER STATE SUPER BLEND MOTOR OIL
SAE 5W-20 HD, 10W-30 HD and 20W-40 HD

Quaker State Super Blend Motor Oil is basically similar to DeLuxe in formulation. Super Blend meets the following specifications and designations:

1. For API Service Designation SF, SE, SD, and CC
2. All current automobile manufacturers' specifications
3. Any U.S. Military Specification MIL-L-46152
4. The SAE 10W-30 product meets proposed ASTM fuel economy tests.

QUAKER STATE HD MOTOR OIL
SAE 10W, 20W-20, 30, 40, and 50

Quaker State HD Motor Oil is formulated from scientifically selected base oils, plus the following additives:

- Pour Depressant
- Anti-foam Agent
- Oxidation Inhibitors
- Corrosion Inhibitors
- Rust Inhibitors
- Anti-wear and Anti-scuff
- Detergent and Dispersant

DeLuxe Motor Oil meets the following specifications and designations:

1. For API Service Designation SF, SE, SD, and CC
2. All current automobile manufacturers' specifications
3. Any U.S. Military Specification MIL-L-46152
4. The SAE 10W-30 product meets proposed ASTM fuel economy tests.
5. Mack EO-H
6. Detroit Diesel
7. Cummins Diesel (Non-turbocharged)
8. International Harvester

(continued on other side)
QUAKER STATE RACING MOTOR OIL
SAE 30 HD, 40 HD, 50 HD, and 20W-50 HD

Quaker State Racing Motor Oil contains the same types of additives as HD Motor Oil.

However, Quaker State Racing Motor Oil contains a much higher treatment of anti-foam additives, and a considerably higher content of anti-wear and anti-scuff additives. This extra treatment has been found to be highly beneficial in engines operated under full throttle, especially at engine RPMs over 4000.

Quaker State Racing Motor Oil meets the following specifications and designations:

1. For API Service Designation SF, SE, SD, and CC
2. All current automobile manufacturers' specifications

QUAKER STATE HDX UNIVERSAL FLEET MOTOR OIL
SAE 10W, 20W-20, 30, 40, and 15W-40

Quaker State HDX Universal Fleet Motor Oil is especially formulated to meet the requirements of API Service Designation CD and U.S. Military Specification MIL-L-2104C.

HDX is formulated from scientifically selected base oils, plus the latest proven additives.

HDX contains a very high content of special detergent and dispersant additives especially designed for the requirements of heavy duty Diesel engines, and particularly those which have to be operated on poor grades of Diesel Fuel (high sulfur and/or high aromatic hydrocarbon content, or high endpoint distillation range).

HDX is also suitable for use in severe duty gasoline engines where unusual operating conditions cause heavy crankcase contamination with blowby residues.

HDX meets the following specifications and designations:

1. For API Service Designation SF, SE, CD, and CC
3. Caterpillar TO-2
4. Cummins
5. Detroit Diesel
6. International Harvester
7. Mack EO-J
8. Detroit Diesel Allison Division C-2/C-3 - SAE 10W and 30 Grades
9. Certified to meet automobile manufacturers' specifications
10. Recommended where Series 3 type oils are required

QUAKER STATE HDX EO-K MOTOR OIL
SAE 15W-40

Quaker State HDX EO-K Motor Oil is blended from scientifically selected base stocks and additives to provide outstanding protection in today's heavy duty engines. This product is designed specifically to exceed Mack EO-K requirements. It can, however, be used in other heavy duty Diesel engines and in gasoline engines.

HDX EO-K meets the following specifications and designations:

1. For API Service Designation SF, SE, CD, and CC
2. Mack EO-K
3. Mack EO-J
4. Cummins
5. International Harvester
6. Caterpillar
7. Certified to meet Automobile Manufacturers' Specifications
8. Recommended where Series 3 type oils are required

QUAKER STATE REGULAR MOTOR OIL
SAE 20W-20 and 30

Quaker State Regular Motor Oil is formulated from scientifically selected base oils, plus the following additives:

Pour Depressant
Oxidation Inhibitors
Corrosion Inhibitors
Anti-wear and Anti-scuff
Detergent and Dispersant

Quaker State Regular Motor Oil meets only the requirements of API Service Designation SC. Regular motor oil should only be used in car engines built before 1968.

Produced in U.S.A.
March 16, 1981

Dr. Ward O. Winer  
Professor  
School of Mechanical Engineering  
Georgia Institute of Technology  
Atlanta, Georgia  30332

Dear Dr. Winer:

Your letter addressed to J. G. Valdez has been passed onto me for response. I will attempt to supply as much information as I can to you within the limits of propriety and my own knowledge.

One of the factors involved in motor oil technology is, of course, the fact that the additive suppliers mix the various components in proprietary fashion to give us the performance requirements we desire. On that basis, it is quite difficult to identify in any detail what the DI package of any motor oil is. I can certainly identify VI package and to some extent friction modifiers.

Pennzoil is a multi-location, multi-base stock company and so it is difficult to identify any specific base oil composition. We also use more than one DI and VI package combination at our various locations. In general, it is our policy to establish performance targets which the additive suppliers are requested to meet.

The attached table gives what information I have available at this time on our formulations. Since you note only the SAE 10W-40 grade in your tabulation of products, I am sending information only on that grade.

If you have any further questions, please feel free to contact me.

Sincerely yours,

S. E. Swedberg, Manager  
Product Development  
Automotive Products  

S/Sc  
attachments  

a division of PENNZOIL COMPANY
Pennzoil Multi-Vis  
SAE 10W-40  
Saves Gasoline

<table>
<thead>
<tr>
<th>Location Code</th>
<th>A</th>
<th>B</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td><strong>Base Oil Composition</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid Continent Solvent Refined Base Oil (27.0 cst at 40°C)</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid Continent Solvent Refined Base Oil (29.0 cst at 40°C)</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Pennsylvania HF Base Oil (27.0 cst at 40°C)</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td><strong>VI Improver (As solid, Wt. %)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non Dispersant OCP (SSI=20)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>DI Package (Wt. %)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF Performance Level</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td><strong>Friction Modifier</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soluble material consisting of one or more of the following:</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Fatty acid esters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfurized fatty acid esters</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
March 30, 1981

Professor Ward O. Winer  
School of Mechanical Engineering  
Georgia Institute of Technology  
Atlanta, GA 30332

Dear Professor Winer:

This reply to your February 24, 1981 letter requesting information on our large volume branded passenger car engine oil, Shell FIRE & ICE 10W/40 Motor Oil.

The HVI base oils used in blending FIRE & ICE 10W/40 Motor Oil are manufactured primarily from domestic Mid-Continent crude sources used in combination with small but significant quantities of foreign crudes. Processing includes solvent extraction and hydro-finishing. A proper ratio of HVI 100 and HVI 250 is used to provide viscosities meeting the SAE 10W specification at -18°C and the SAE 40 specification at 100°C.

SHELLVIS® 40, a styrene/olefin-based hydrocarbon co-polymer manufactured by Shell Chemical Company, is used as the VI improver. This solid, oil-soluble polymer is used in optimum concentration to meet 10W/40 viscosity classifications with the combination of base oils noted.

A proprietary Shell DI (detergent-inhibitor) additive system is used in combination with SHELLVIS 40. Treatment is near the 10 percent level common for API SF quality automotive oils. It encompasses a calcium overbased detergent and a conventional ashless dispersant for engine deposit control, antiwear additives as required to meet API SF standards, a pour point depressant and an antifoam agent. 0.15%w zinc as dialkyl zinc dithiophosphate is used for antiwear performance and a proprietary oil-soluble friction modifier is used for fuel efficiency.

Test results show that Shell FIRE & ICE 10W/40 Motor Oil comfortably meets all API SF quality requirements and the proposed ASTM test requirements for energy conserving oils.
Typical chemical and physical properties for the finished oil are given in Attachment 1.

Hopefully, this information will be satisfactory for your needs.

Sincerely,

S. 'A. Herbert, Manager
Lubricants Department

SAH/sgf
Attachment
# SHELL FIRE & ICE MOTOR OIL 10W-40

## SUMMARY OF BENCH TEST RESULTS

### Finished Oil Characteristics

1. **Gravity, °API (ASTM D-287)**  
   
2. **Flash Point, °F (ASTM D-92)**  
   400

3. **Pour Point, °F (ASTM D-97)**  
   -25

4. **Foaming, ml (ASTM D-892)**  
   Tend/Stab, Sequence 1, 2, 3  
   0/0, 15/0, 0/0

5. **Viscosity, cP at -18°C (ASTM D-2602)**  
   2250

   cSt at 40°C (ASTM D-445)  
   80.0

   cSt at 100°C (ASTM D-445)  
   13.9

6. **Viscosity Index (ASTM D-2270)**  
   180

7. **Total Base No. (ASTM D-664)**  
   7.3

8. **Total Acid No. (ASTM D-664)**  
   3.1

9. **Sulfated Ash, %, (ASTM D-874)**  
   1.08

10. **Analyses for identifiable elements, wt.%**  
    - Mo NIL  
    - Ca 0.26  
    - Ba NIL  
    - P 0.14  
    - Zn 0.15  
    - N 0.03  
    - S 0.34
March 25, 1981

Dr. Ward O. Winer  
School of Mechanical Engineering  
Georgia Institute of Technology  
Atlanta, Georgia 30332

Dear Dr. Winer;

Your recent letter asked that we provide the composition of our SAE 10W-40 ARCOgraphite motor oil in terms suitable for describing the product in a technical publication such as an SAE paper. We can release information of this type to the extent that the oil contains an all mineral oil base oil composition. In addition, the oil does contain graphite as a colloidal friction modifier. We trust that this information along with any physical or chemical data you may generate on the sample you use for testing will suffice to define the oil in a publication.

Very truly yours,

ARCO Petroleum Products Company

D. L. DeVries  
Engine Oils Research and Development

DLD: sjv
March 18, 1981
File: 311.1
Proj: 182-10

Dr. Ward O. Winer
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Dear Dr. Winer:

In response to your inquiry of February 24, 1981, we offer the following. Mobil 1 5W-20 employs a fully synthetic base stock which is mostly SHF made from the polymerization of olefins. An ester is also included as an elastomer seal swell agent. Because these synthetic base stocks have an inherently high viscosity index, the SAE 5W-20 multigrade viscosity characteristics are obtained with no polymeric VI improver in the formulation.

The additive system in Mobil 1 was developed specifically for optimum response with the synthetic base fluids and contains metallic detergents, ashless dispersant and alkyl zinc dithiophosphate. The physical and chemical properties of Mobil 1 5W-20 are summarized below.

<table>
<thead>
<tr>
<th>Tests</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity</td>
<td></td>
</tr>
<tr>
<td>@ 100°C (212°F), cSt</td>
<td>6.7</td>
</tr>
<tr>
<td>@ 40°C (104°F), cSt</td>
<td>36.9</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>140</td>
</tr>
<tr>
<td>CCS Viscosity @ 0°F (-17.8°C), P</td>
<td>11</td>
</tr>
<tr>
<td>Flash Point, °C(°F)</td>
<td>238 (460)</td>
</tr>
<tr>
<td>Pour Point, °C (°F)</td>
<td>-65 (-85)</td>
</tr>
<tr>
<td>TBN (D2896)</td>
<td>6.2</td>
</tr>
<tr>
<td>Sulfated Ash, % Wt.</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcium, % Wt.</td>
<td>0.21</td>
</tr>
<tr>
<td>Zinc, % Wt.</td>
<td>0.13</td>
</tr>
<tr>
<td>Phosphorus, % Wt.</td>
<td>0.12</td>
</tr>
</tbody>
</table>

We trust this information is helpful and are glad to be of assistance.

Very truly yours,

H. V. Lowther, Manager
Engine & Power Train Lubricants

CDLack/jpa
DESCRIPTION OF EXPERIMENTAL FLUIDS

Symbol: R-620-15
Source: Sun Oil Company
Type: Naphthenic Base Oil
Properties:
- Viscosity at 37.8°C, mm²/s: 24.1
- Viscosity at 98.9°C, mm²/s: 3.73
- Viscosity Index (ASTM D-2270): -13
- Flash Point, °C: 157
- Pour Point, °C: -43
- Density at 20°C, kg/m³: 915.7
- Average Molecular Weight: 305

Symbol: R620-16
Source: Sun Oil Company
Type: Naphthenic Base Oil
Properties:
- Kinematic Viscosity at 37.8°C mm²/s: 114
- Kinematic Viscosity at 98.9°C mm²/s: 8.1
- Density at 20°C kg/m³: 930
- Average Molecular Weight: 357
**Symbol:** PL4521, PL4523  

**Source:** Rohm and Haas Company  

**Type:** Polyalkylmethacrylate  
(Polymer additive used in solution in R620-15, 4.0% polymer by weight)  

The chemical composition of each is the same. They differ only in molecular weight and are supplied in a carrier oil similar to R620-15.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PL4521</th>
<th>PL4523</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Weight:</td>
<td>36.1%</td>
<td>19.0%</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$560 \times 10^3$</td>
<td>$2 \times 10^6$</td>
</tr>
</tbody>
</table>