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             AN INVESTIGATION OF THE EFFECTS OF OXYGEN AND WATER VAPOR ON TH--ETC(U)
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Battelle
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Report

AFOSR-76-3051

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⑨ FINAL ANNUAL REPORT

on

⑥ AN INVESTIGATION OF THE EFFECTS
OF OXYGEN AND WATER VAPOR ON THE
COMPRESSIVE STRENGTH OF BOUNDARY
FILMS ON IRON SUBSTRATES

to

DEPARTMENT OF THE AIR FORCE
OFFICE OF SCIENTIFIC RESEARCH

⑪ 5 August 5, 1977

⑬ 32p.

by

⑩ W. R. Bucknor, E. J. Drauglis,
and D. K. Snediker

⑮ AF-AFOSR-3951-76 ⑯ 2303 ⑰ A2

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ABSTRACT

The purpose of this program is to determine the effects of O_2 and H_2O on boundary film formation by studying a model system consisting of 2-ethylhexyl sebecate and tricresyl phosphate (TCP) on ARMCO iron surfaces. This report deals with the first year, wherein, film compressive strength measurements, supported by ellipsometry, were used to study the behavior of these reactants as a function of time and temperature in a laboratory atmosphere. For films formed out of the pure ester, two transitions in compressive strength and film thickness were observed at 93 C and 180 C. The rate of change of film compressive strength of TCP-ester solutions decreases with temperature to 100–120 C after which the rate increases. For the pure ester, the rate of formation of a mechanically significant film is low until temperatures >120 C are reached. Under all conditions of temperature, mechanically significant films form relatively slow -- of the order of minutes -- from the TCP solution. Water, adsorbed or dissolved, appears to play a significant role in the formation and degradation of these films. A working hypothesis in terms of the hydrolysis of the ester to form sebacic acid at temperatures around 100 C is presented. Ellipsometric data suggest that the high temperature loss of compressive strength in those films is due to the onset of rapid substrate oxidation, perhaps accompanied by decomposition of the surface-bound organic species.

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SUMMARY

The purpose of this program is to study the effects of O_2 and
H_2O on the compressive strength of boundary films on iron surfaces and
to correlate these effects with the fundamental physicochemical phenomena
responsible for the formation and degradation of such films.

In the first year of the program, baseline experiments aimed
at determining the behavior of boundary-film reactants on well-characterized
iron surfaces were performed. ARMCO iron was selected as a substrate
material and 2-ethylhexyl sebecate and tricresyl phosphate as reactants.
Compressive strength measurements and ellipsometric measurements were
taken at various temperatures. Both kinetic and static data were obtained.

Compressive-strength measurements were made by means of Battelle's
Columbus Laboratories (BCL) film-penetration apparatus, in which a stylus
is used to measure the compressive strength of a film in a microscopically
small area. Two basic kinds of rupture-pressure studies were carried out.

(1) Study of short-term film strength of 2-ethylhexyl
     sebecate (E-105) and E-105 + 5 volume percent TCP
     films on ARMCO iron as a function of temperature
     from room temperature to 204 C.

(2)   Study of the time-dependent behavior of E-105 and
E-105 + 5 volume percent TCP films on ARMCO iron
at temperatures from 24 C to 150 C.

The static experiments yielded a bimodal distribution of film
strengths; that is, the films have a low-strength component and a high-
strength component. Two transitions were found; the first at about 93 C,
at which temperature the high-strength component grows apparently at the
expense of the low-strength component. The high-strength component fails
at about 180 C.

Ellipsometric measurements of film thickness as a function of
temperature also showed these transitions. It was concluded tentatively
that the first transition was essentially the hydrolysis of the diester
and the chemisorption of sebacic acid or the monoester. The second
transition represents a desorption of the film caused by breaking chemisorp-
tion bonds. As yet, no firm conclusions can be drawn on the role of TCP
in stabilizing the films.

Study of the time-dependent behavior of the compressive strength
of films formed from E-105 and E-105 + TCP yielded some interesting obser-
vations. With both the pure E-105 and the TCP solution, major changes
in the rate of change in film strength take place at temperatures in the
100 to 120 C range. This observation strongly suggests the influence of
dissolved or chemisorbed water on the process of film formation. Another
interesting observation is the relatively low rate at which mechanically
significant films form from TCP solutions. The formation of compressively
strong films takes on the order of minutes, even at temperatures as high
as 150 C.

INTRODUCTION

Although most machine elements operate in the boundary regime of lubrication and boundary lubrication determines the useful life of such elements, comparatively little attention has been paid to the elucidation of fundamental boundary-lubrication mechanisms. Nearly all of the research performed has been concerned with specific applications and has been performed mostly on poorly characterized lubricants and bearing materials. Even so, much progress has been made in the past decade in the study of the chemistry and physics of the interaction of antiwear additives, base oils, and various metals. A beginning of a fundamental understanding of the formation and decomposition of boundary films has resulted from these studies. The mechanisms of reaction of common boundary-lubricant additives are well understood, at least qualitatively. Moreover, progress is being made on understanding the role of the base oil in the formation of boundary-lubricating films. However, much work remains to be done before the physical chemistry of these films is sufficiently understood to provide useful information to the formulator of new lubricants for boundary-lubricated systems.

One conspicuous factor that has not been studied extensively is the effect of oxygen and water on the formation and destruction of effective boundary films. Some progress has been made in determining the effects of O_2 by such workers as Buckley[1], Fein[2], and Begelinger[3]. However, the role of H_2O in boundary lubrication is much less understood. Little research has been performed on the combined effects of water and oxygen on boundary lubrication. Schatzberg has worked on the effects of O_2 and H_2O in sliding wear[4], and Beerbower[5] has described boundary-film formation involving stearic acid and hydrated iron oxide.

Another gap in the knowledge of boundary-lubricating processes is the role of the properties--metallurgical structure and chemical composition--of the substrate. Matveevskiy[6] and Rebinder[7] have contributed strongly in this area, but much of their research has been performed with relatively severe 4-ball, pin-on-disk or practical machine element tests. This type of work cannot answer basic questions concerning the manner in which the antiwear species compete with O_2 in surface reactions; on the

_____ _____

(1) References are listed in the back of text on Page 29.

role of active sites such as inclusions, dislocations, and carbides; on
the role of hydrated oxide species; and on the role of alloy constituents
in boundary-film formation.

The answers to such questions are urgently needed for the ultimate
elucidation of the mechanisms of boundary-film dynamics. No single approach
will provide these answers. A variety of experimental techniques must be
applied to well-characterized systems. Last year, a program aimed at eluci-
dating the effects of O_2 and H_2O on boundary-lubricant films was started.
The approach taken in this program was to study a fundamental mechanical
property of thin films--the compressive rupture strength. This involves
the use of a sharply pointed stylus to penetrate films which have been
formed on hard surfaces. Provision is made for loading the stylus over
a large load range. Film rupture is detected by electrical continuity.
Details of the apparatus are given in Reference 8. In the past year, this
apparatus was used to study films formed from a pure diester and a diester
containing tricresyl phosphate at a given range of temperatures and time.
In addition, some work on the thermal degradation of rubbed films was
performed by an optical technique--ellipsometry.

The results of the rupture-strength measurements are described
herein and an effort is made to correlate these results with the ellipso-
metric data.

BACKGROUND

The original plan for the first year of the program called for baseline experiments, the purpose of which was to determine the behavior of boundary-film reactants on pure iron surfaces and to select model systems for subsequent study. Specifically, the principal outputs of the first year of research were to be an understanding of the oxidation of pure iron in the presence of various quantities of H_2O vapor and O_2, studies on the kinetics of the formation of boundary films, and identification of a model system for intensive studies in the second and third years of the program. To data, most of these goals have been met, although some redirection has been made out of practical necessity.

Originally, it was planned to use single-crystal iron as a substrate. However, this proved impractical and too expensive because of the need for a large number of specimens. Therefore, ARMCO iron was selected a   substrate material. Specimens approximately 0.60 cm thick w   from a 4 cm-diameter bar. After some experimentation, a polish   cleaning technique which produced a clean, wetting surface was developed.

After due consideration, the ester E-105 (diethylhexyl sebacate) was selected as the base fluid. This ester was chosen because it is readily available in a highly purified form, is reactive, and is used as the base fluid in practical jet-engine-lubricant formulations. It was also decided to study one additive TCP (tricresyl phosphate), a widely used antiwear additive.

Rupture-strength measurements were performed by means of BCL's film penetration apparatus, and ellipsometric studies of film degradation were also conducted.

EXPERIMENTAL DETAILS

The first phase of this research has made use of two methods for characterizing surface films on pure iron substrates. The principal tool for characterizing these films is a special instrument that measures the compressive strength of a surface film by determining the load (stress) required to rupture the film. The second method, ellipsometry, was employed in order to allow the determination of changes in film thickness. All experiments were carried out in laboratory air with the relative humidity ranging from 40 percent to 70 percent. These methods, along with the detailed experimental methodology are discussed below.

Compressive-Strength Measurements

The apparatus used in these experiments is an advanced version of that described in Reference 8. Figure 1 shows the essential details of the apparatus. The flat specimen rests on a heated stage. The stage can be moved kinematically in the x and y directions by means of micrometer drives. A stylus is loaded against the specimen plate. The load is applied by a deadweight system directly onto the stylus which is supported by a precision ball-bearing pivot and lever arm seen in the left background of Figure 1. Load release is accomplished by a micrometer level system. In the early work, the apparatus was limited to 100 grams load on the stylus. Modifications were made, however, to allow operation at loads up to 250 grams. The increased capacity was used primarily for the time-dependent studies.

The primary instrumentation is an electrical-continuity system for observing the onset of metallic contact between the stylus and the plate. Both low voltage ac and dc systems were explored for this task. However, because of minute thickness of the boundary films, premature electrical contact resulting from some type of dielectric breakdown of the film loomed as a significant problem. The most successful approach involved the attachment of mating thermocouple lead wires to the test stylus and the plate to measure the induced thermoelectric voltage as metal-to-metal contact occurred. The total voltage imposed across the stylus/plate interface was of the order of 1 mV. The styli were made of hardened steel with a polished spherical tip having a radius of 0.0051 cm.
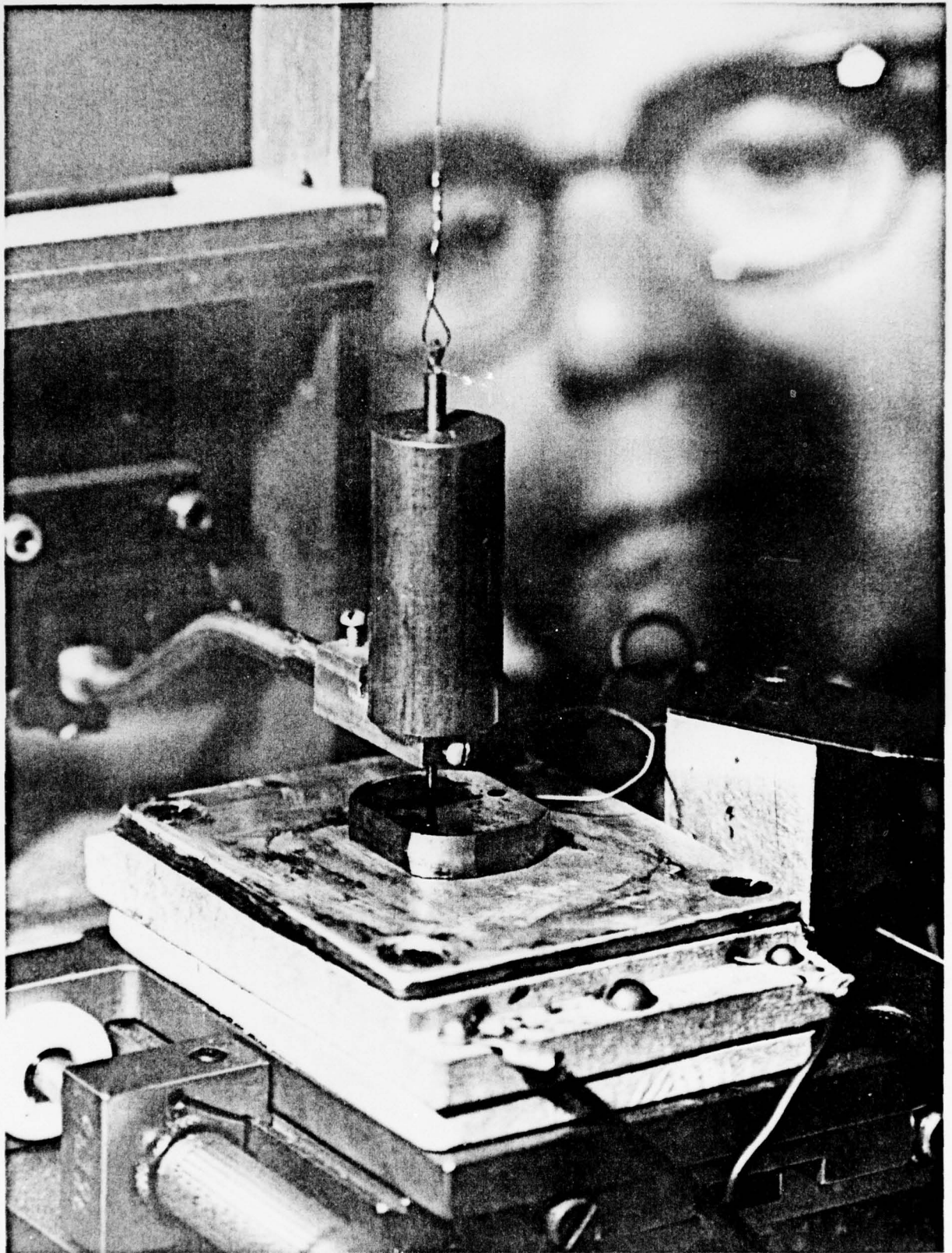
FIGURE 1. DETAIL OF THE APPARATUS USED IN THE DETERMINATION
OF THE COMPRESSIVE STRENGTH OF SURFACE FILMS

All styli were first cleaned by tumbling in Al_2O_3 and then cleaned thoroughly with deionized H_2O and absolute ethyl alcohol. The styli were 100 percent microscopically inspected to ensure a tip radius of 0.0051 cm, a spherical geometry, and good surface finish.

The rupture-pressure determinations on thin surface films were used in two kinds of experiments: rupture pressure as a function of temperature and as a function of time.

In the temperature studies, a polished 4.5 cm-diameter disk of ARMCO iron was positioned in the apparatus and a room ambient temperature measurement made on the bare surface (that is, no ester present). A standard procedure was employed, whereby ten rupture pressures were determined at ten different, randomly chosen locations. A thick film of ester or ester + 5 volume percent TCP was placed on the entire plate surface and a second series of measurements were made at room temperature. The temperature was then increased in ~30 C increments, equilibrating temperature and taking measurements at each level. As the ester began to evaporate at the higher temperatures, it was replenished in order to maintain a thick liquid film over the entire plate at all times. The heating rate was adjusted such that each heating cycle took 15 minutes.

A similar approach was used in the time studies. Here, the experiments were carried out at a constant temperature. The specimen was quickly brought to a given temperature and the rupture-pressure determined at fixed intervals. Again, the practice of taking ten readings at ten different locations on the plate was employed.

The data may be reduced in several ways. Each series of rupture-strength determinations produces a distribution of rupture strengths that is generally not random. Thus, a simple average or median value frequently has little meaning. It is most fruitful to express the results of the temperature studies as population distributions. These distributions (see Figures 4 and 5) involve the number of measured film ruptures in a given load interval as a function of the various intervals. In order to establish the rates at which the films changed compressive strength, it was necessary to reduce the complex rupture-pressure distributions described above to a more simple figure of merit. Since the apparatus had been modified to a capacity of 250 grams, the number of rupture-pressure determinations beyond the capacity of the apparatus was significantly

reduced. This made a simple average a reasonably good representation of the film strength at a given time. In order to minimize the effects of the very large pressure values occasionally obtained, the highest and the lowest values were discarded before the average was taken.

Ellipsometry Measurements

Ellipsometry is an optical technique in which changes in the state of polarized light upon reflection from a specimen are used to obtain information about the optical properties of clean solid surfaces or of films in contact with such surfaces. The technique is concerned with the measurement of two quantities: Δ, the change in relative phase between the component of polarized light in the plane of incidence and the component perpendicular to the plane of incidence; and ψ, a function of the change in the relative amplitudes of the two components. From measured values of Δ and ψ, one can calculate the index of refraction, absorption coefficient, and thickness of an adsorbed film. Figure 2 shows the essential features of an ellipsometer and Figure 3 is a photograph of the instrument used in the present project, a Gaertner Model L119.

In the rupture-strength measurements, the boundary film under study is always covered with a layer of bulk fluid. Because of the unavailability of a suitable sample cell and sufficient E-105, it was not possible to perform ellipsometric measurements on such films. Instead, the degradation of rubbed films was studied. Films were prepared by depositing about 0.5 ml of the ester on a standard ARMCO iron flat (as used in the rupture-strength measurements) and allowing the fluid to spread until it covered the entire specimen. Upon completion of the spreading, most of the excess fluid was wicked off with Xerox 8R25 cotton* and 50 rubs were performed with fresh cotton. Measurements of Δ and ψ showed that a film of E-105 having a thickness of about 50A and an index of refraction of about 1.44 was usually produced by this technique.

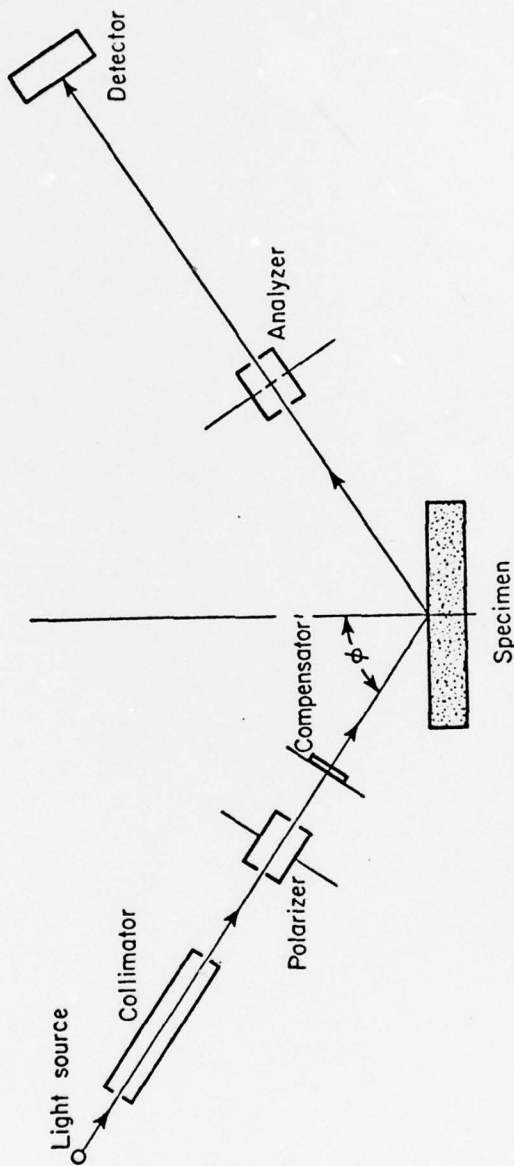* Solvent extracted cotton used to clean selenium-coated xerography drums.

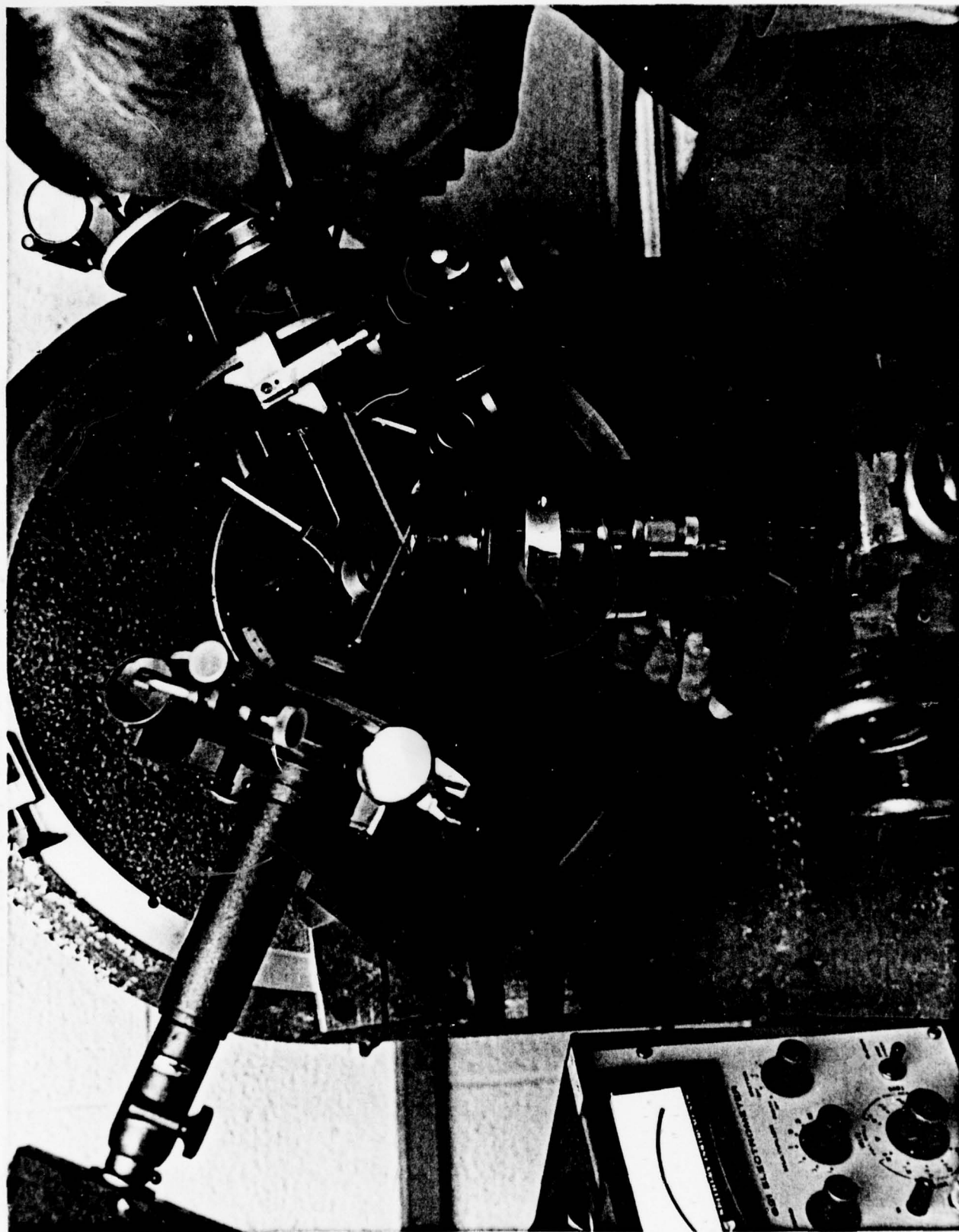FIGURE 2. SCHEMATIC DRAWING OF THE ELLIPSOMETER

FIGURE 3. A VIEW OF THE ELLIPSOMETER, SHOWING THE INCIDENT BEAM ON THE RIGHT, THE REFLECTED BEAM ON THE LEFT, AND THE SPECIMEN PLATE IN THE CENTER
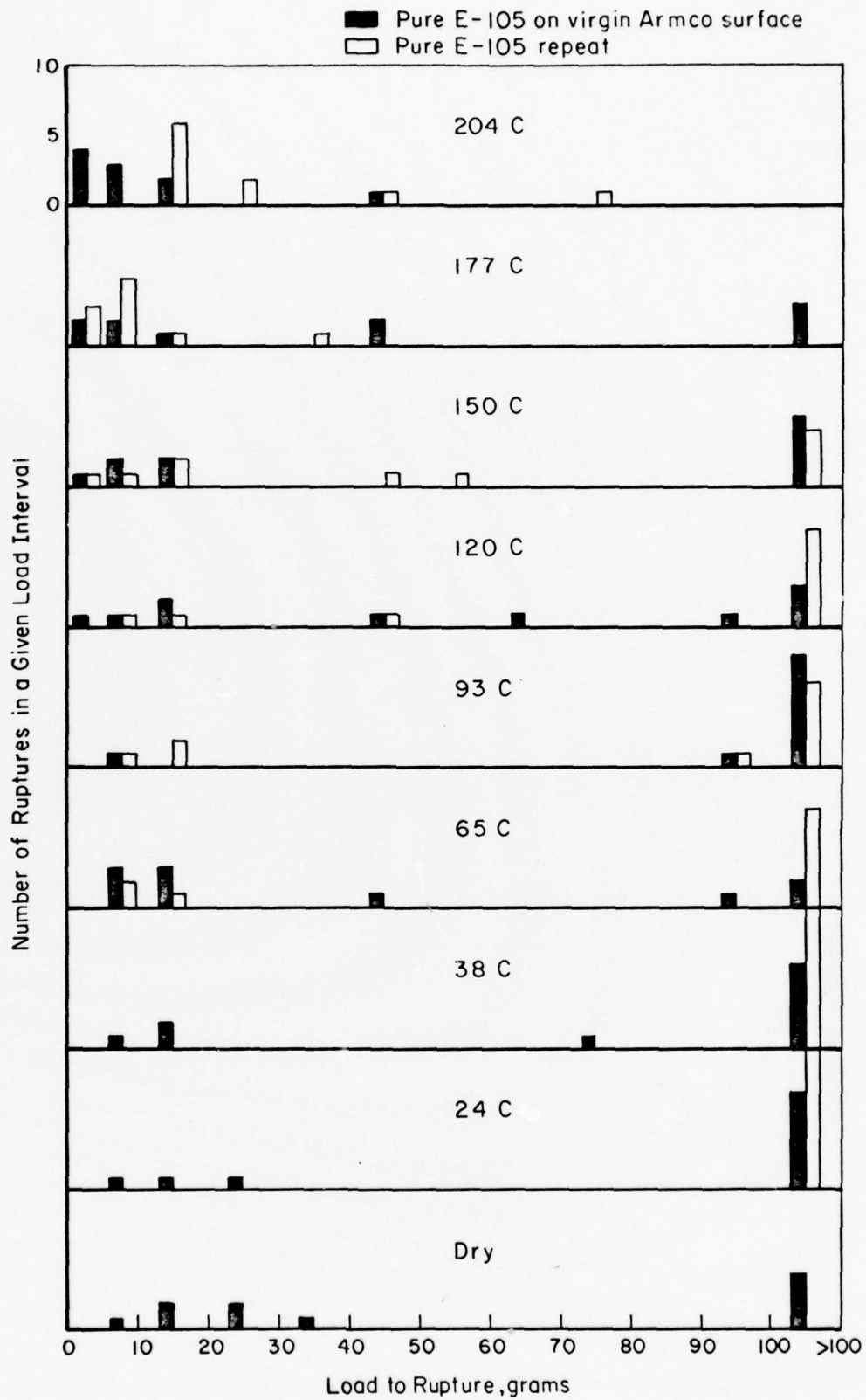
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FIGURE 4. DISTRIBUTION OF LOADS-TO-RUPTURE FOR FILMS FORMED FROM PURE E-105 ON ARMCO IRON AS A FUNCTION OF TEMPERATURE
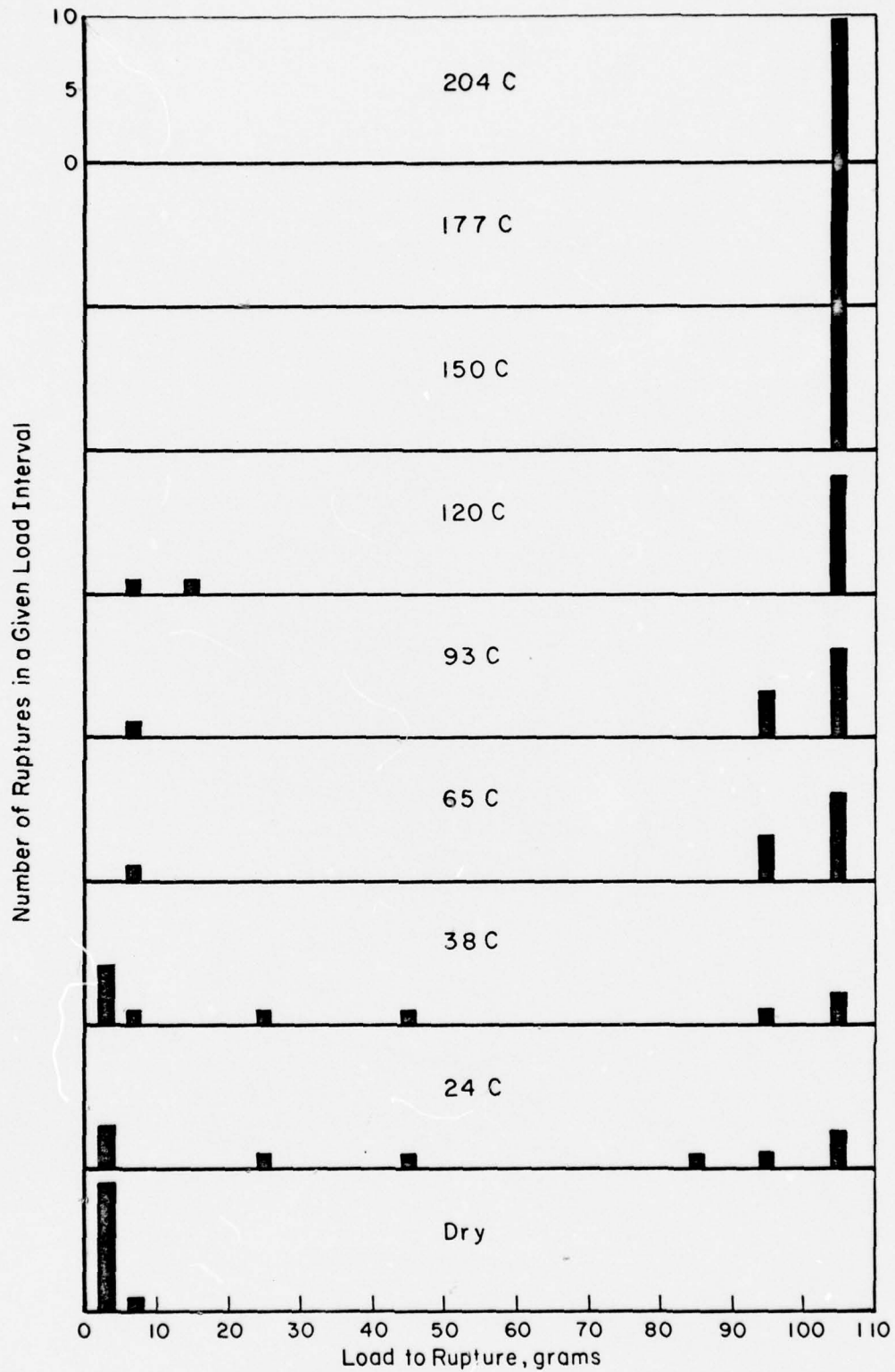
FIGURE 5. DISTRIBUTION OF LOADS-TO-RUPTURE FOR FILMS FORMED FROM
E-105 CONTAINING 5 VOLUME PERCENT TCP ON ARMCO IRON AS
A FUNCTION OF TEMPERATURE

Two types of experiments were performed. In the first, a specimen prepared as described above was heated slowly from room temperature to approximately 200 C and Δ and ψ were measured at intervals. In the second, the specimen was placed on a stage that had been preheated to a desired temperature and changes in Δ and ψ with time were followed. The measured values of Δ and ψ were used to calculate film thickness and index of refraction by means of a Fortran IV program devised by F. L. McCrackin at the National Bureau of Standards and modified at BCL to run on a Hewlett-Packard HP-2100 minicomputer.

Materials

In all of the experiments described in this report, the substrate material was ARMCO iron. This material has the following properties.

- Composition:

C	Mn	P	S	Si	Fe
.015	.028	.005	.025	.003	Bal.

- Tensile Strength: 42,000 psi

- Rockwell Hardness: B40-50

- Modulus of Elasticity: 30×10^{6} psi .

After extensive experimentation with various finishing and cleaning techniques, including sputter etching, the following procedure was found to yield the most consistent and reproducible surfaces.

(1) Cut from bar stock and surface grind both sides flat.

(2) Wet polish on metallographic papers through 600 grit.

(3) Diamond lap.

(4) Store in dessicator (air) until just before experiment.

(5) Just prior to experiment, polish to a high mirror
finish with a deionized water slurry of Linde-B
on a Buehler microcloth wheel.

(6) Rinse: Tap H_2O

Deionized H_2O

Absolute CH_3CH_2OH

Air Dry: Filtered laboratory air at low flow rate.

(7) Conduct a dry rupture-pressure experiment. The
specimen was refinished if the average rupture
pressure of the surface film (oxides, adsorbed H_2O,
etc.) exceeded 10 grams.

(8) Immediately coat with liquid reactants.

The liquid reactants used in these experiments were a diester
of relatively high purity -- 99 percent 2-ethylhexyl sebecate (E-105,
1 percent probably monoester) and technical-grade *tricresyl phosphate*
(TCP). The technical grade TCP contained essentially 25 percent each of
the four isomers with two other components at the 2 percent level.

EXPERIMENTAL RESULTS

Compressive Strength as a
Function of Temperature

Figure 4 shows a typical series of distributions for pure E-105 on ARMCO iron for the various temperature levels. The solid bars represent the first series carried out on a fresh surface, while the open bars show the data obtained for a repeat on the same surface. (That is, after the measurements were made at 204 C in the initial series, the specimen was cooled to room temperature and the series repeated with the addition of fresh E-105, but without cleaning the surface.)

Note the bimodality of the distribution of film strengths. In the initial series, this bimodality is fairly temperature independent (except for some anomalous behavior at 66 to 121 C) up to 177 C. Between 177 and 204 C, the film dramaticaly loses strength and the high strength component collapses. Returning to room temperature restores the strength of the film (yellow bars). Catastrophic loss of strength again occurs in the temperature range 149 to 177 C. It may be significant that the boiling point of ethylhexyl alcohol, one of the products of the hydrolysis of E-105, is 185 C.

Figure 5 shows a similar series of rupture-pressure distributions for E-105 ester to which 5 volume percent tricresyl phosphate has been added. Here, the high-strength component grows in as the temperature increases, and no collapse at higher temperatures is observed. A repeat with the same reactants (steel and solution) shows at all temperatures essentially the same data as that obtained over 149 to 204 C range.

Compressive Strength
as a Function of Time

An extensive series of experiments to determine the rate of film growth at constant temperature were conducted using both pure E-105 and E-105 + TCP 5 volume percent solution as in the studies of compressive strength as a function of temperature. In these experiments, the compressive strength (or rupture strength) of the surface films was measured as a function of time at constant tempeature levels from 80 C to 150 C. The massive

quantity of data obtained has been reduced in two forms: rupture-load
distributions as a function of time, and simple average rupture load as
a function of time. Figures 6 and 7 show typical average load to rupture
as a function of time for the pure E-105 on ARMCO steel at 107 C and 121 C,
respectively. Figure 8 shows the rupture-load distributions as a function
of time for an experiment carried out at 121 C. At 107 C, the pure
reactant showed little propensity to develop a compressively strong film.
The distributions at this temperature (not shown) show all of the loads
to rupture in the 0 to 10-gram range. At 121 C, the distribution begins
to show the bimodality characteristic of the formation of a high-strength
film component, after approximately 120 minutes. After approximately 170
minutes, an equilibrium condition appears to be reached and the film does
not change significantly in its compressive strength (referring to
Figure 4 which shows the rupture-strength distributions as a function of
temperature, note that an increase in temperature, say of 50 C, has a
greater effect on film strength than does time and constant temperature).

Figures 9 and 10 show typical average rupture pressure as a func-
tion of time for the reaction of the E-105 + 5 volume percent TCP solution
with ARMCO iron. The constant temperature levels are 121 C and 150 C,
respectively. Figure 11 shows the distribution of rupture pressures
as a function of time at 121 C. This distribution is fairly typical of
the distributions obtained over the entire temperature range. As one might
expect, E-105 + TCP solution forms strong surface films much more rapidly
than the pure E-105 solvent. Once formed, the films have a greater average
strength, as seen in the relative dominance of the components at over
200 grams rupture strength. It is surprising to note, however, that on
the basis of the compressive strength alone, TCP-derived films grow
somewhat slowly. Many of the "functional scenarios" of the mechanism of
TCP as an antiwear agent invoke rapid reaction of this species, or a
derivative thereof, with a surface in a region of relatively high temper-
ature. Our data suggest that either TCP reacts much more rapidly in a
region of extreme surface distress, or that its beneficial in situ effects
are based more upon a soaking effect than on instantaneous reaction.
Experience with TCP in ball bearings tends to support the latter.

If the slopes of curves such as those in Figures 6, 7, 9, 10
are determined by linear approximation, it is possible to arrive at an
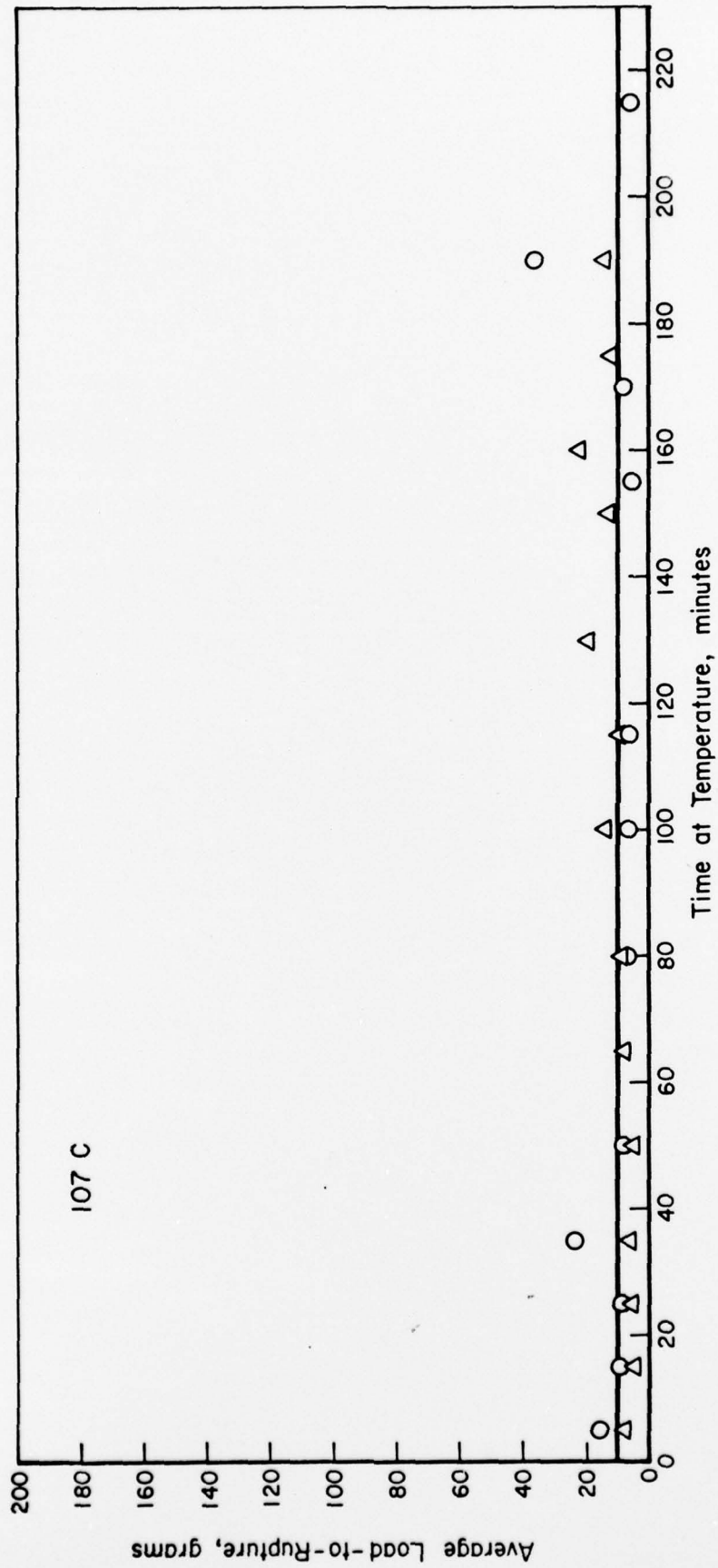estimate of the rate of formation of a film in terms of grams rupture

FIGURE 6. AVERAGE LOAD-TO-RUPTURE AS A FUNCTION OF TIME FOR PURE E-105 ON ARMCO IRON AT 107 C
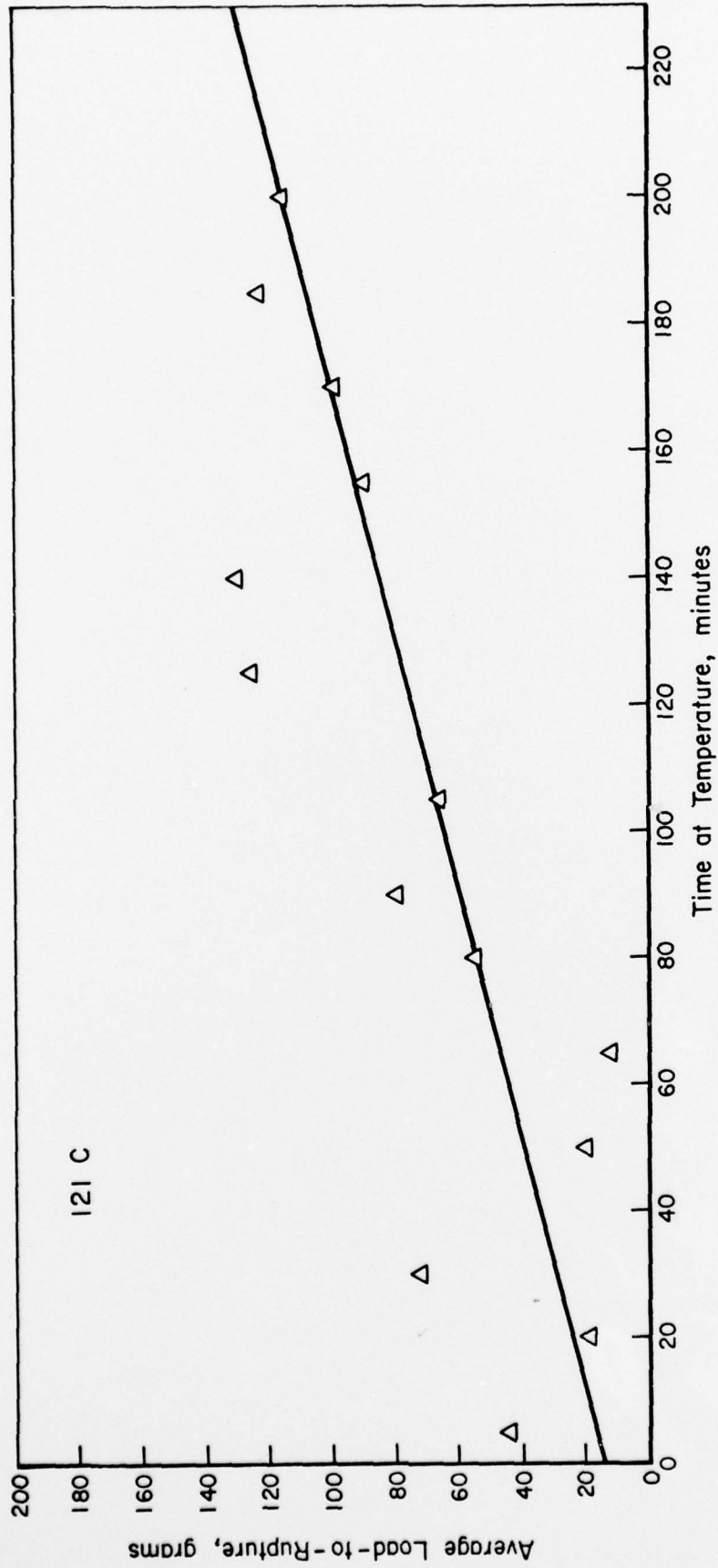
FIGURE 7. AVERAGE LOAD-TO-RUPTURE AS A FUNCTION OF TIME FOR PURE E-105 ON ARMCO IRON AT 121 C
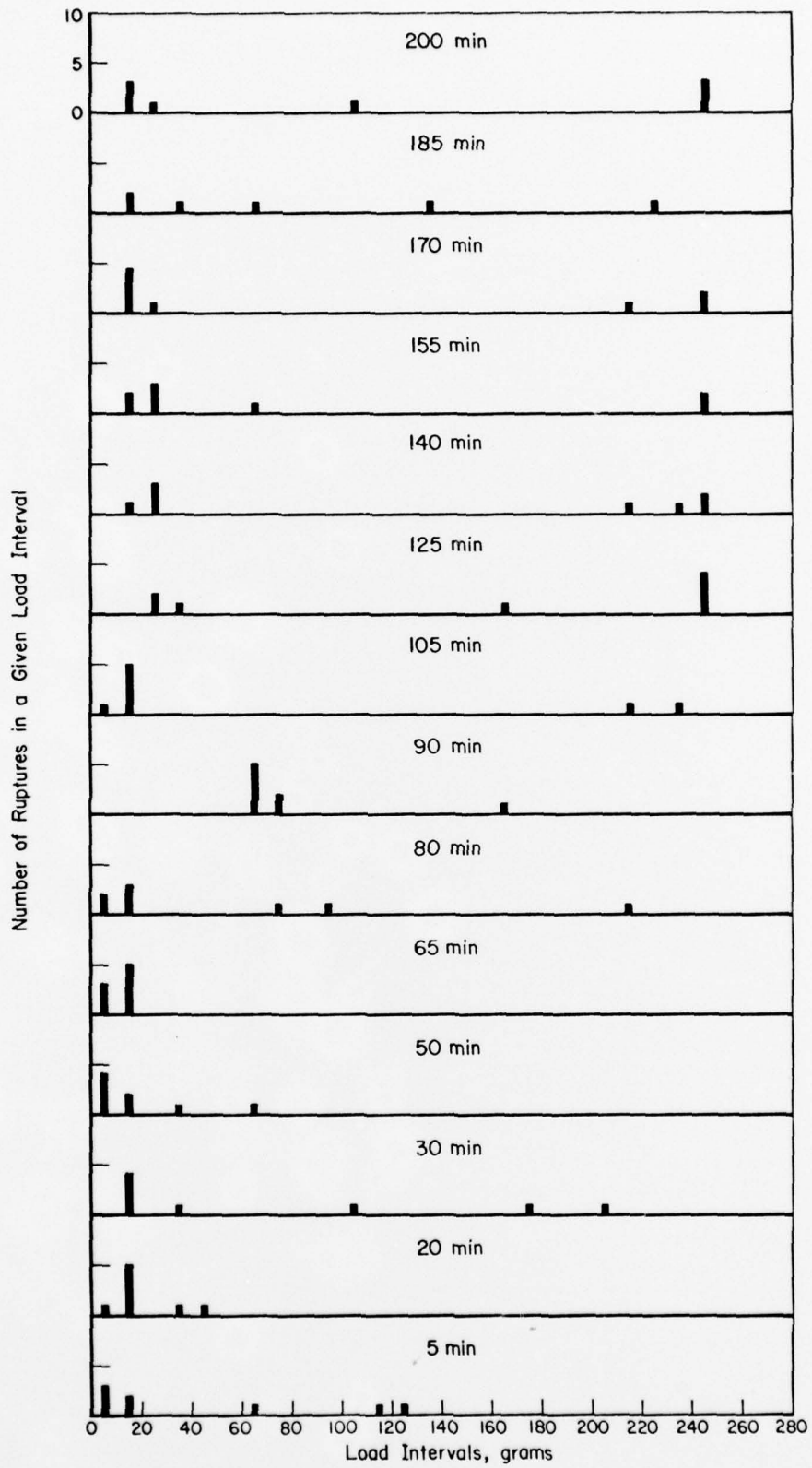
FIGURE 8. RUPTURE LOAD DISTRIBUTIONS AS A FUNCTION OF
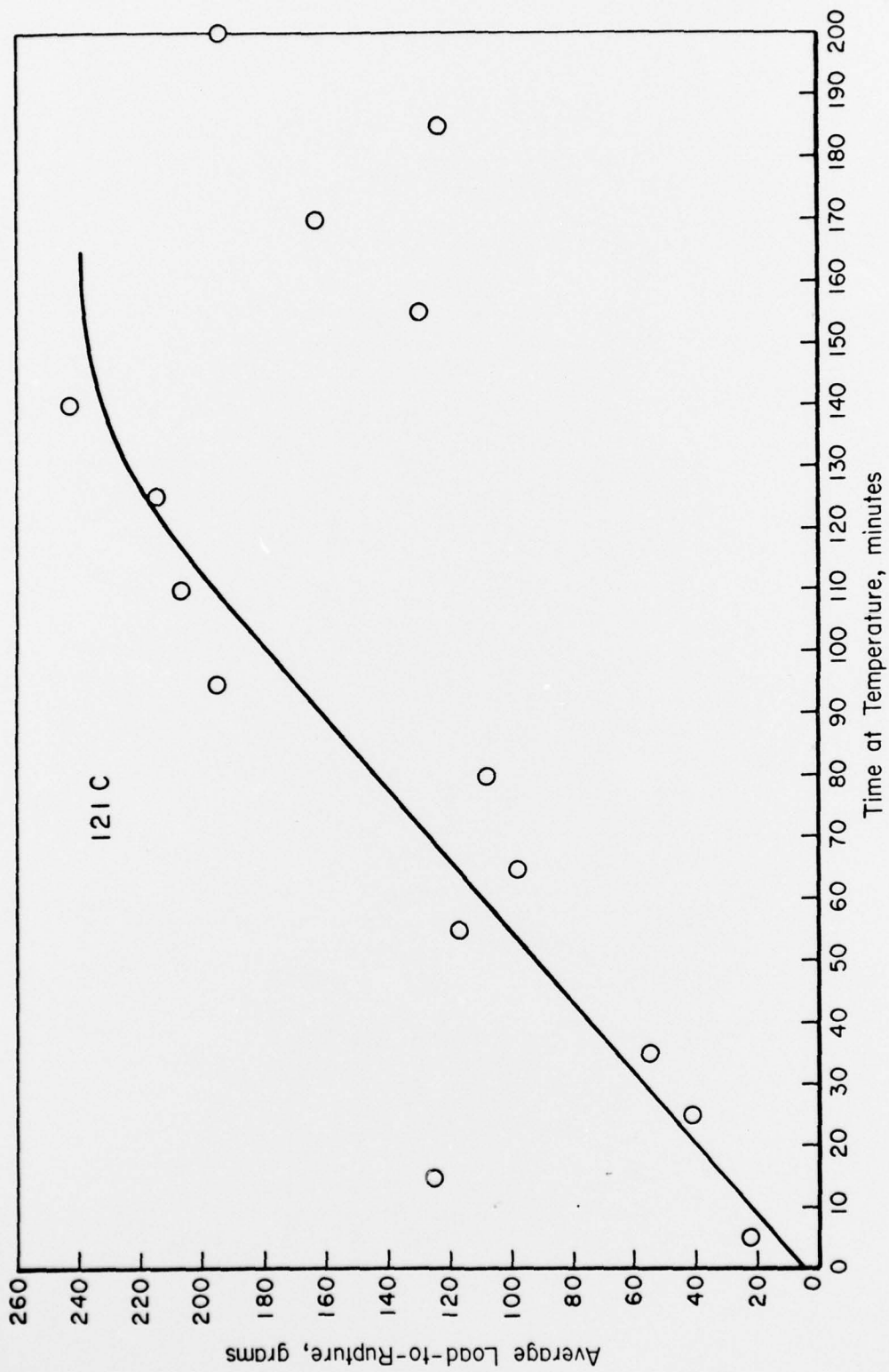TIME FOR PURE E-105 ON ARMCO IRON AT 121 C

FIGURE 9.   AVERAGE LOAD-TO-RUPTURE AS A FUNCTION OF TIME FOR A 5 VOLUME PERCENT SOLUTION OF TCP
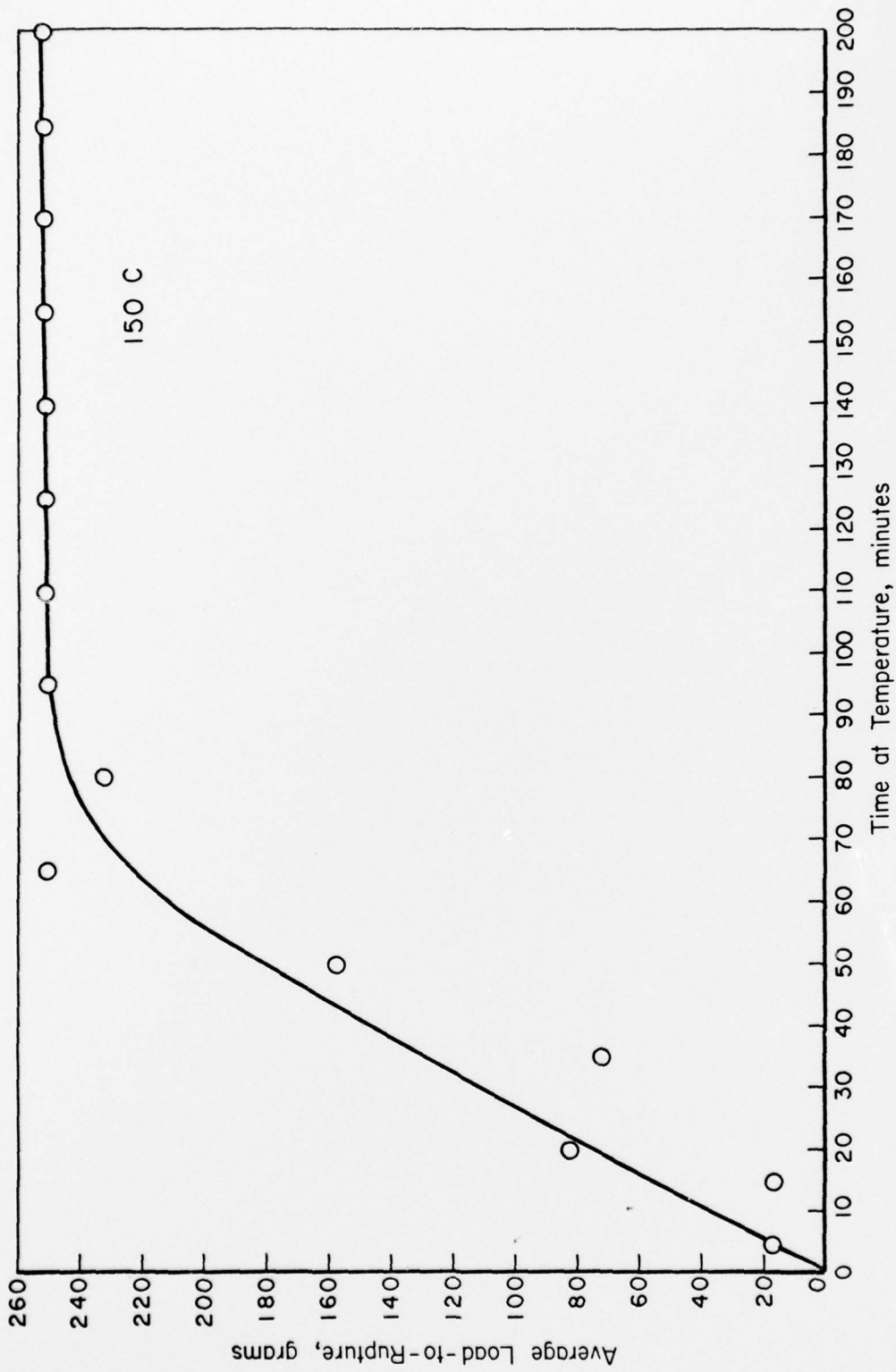IN E-105 AT 121 C

FIGURE 10. AVERAGE LOAD-TO-RUPTURE AS A FUNCTION OF TIME FOR A 5 VOLUME PERCENT SOLUTION OF TCP IN E-105 AT 150 C
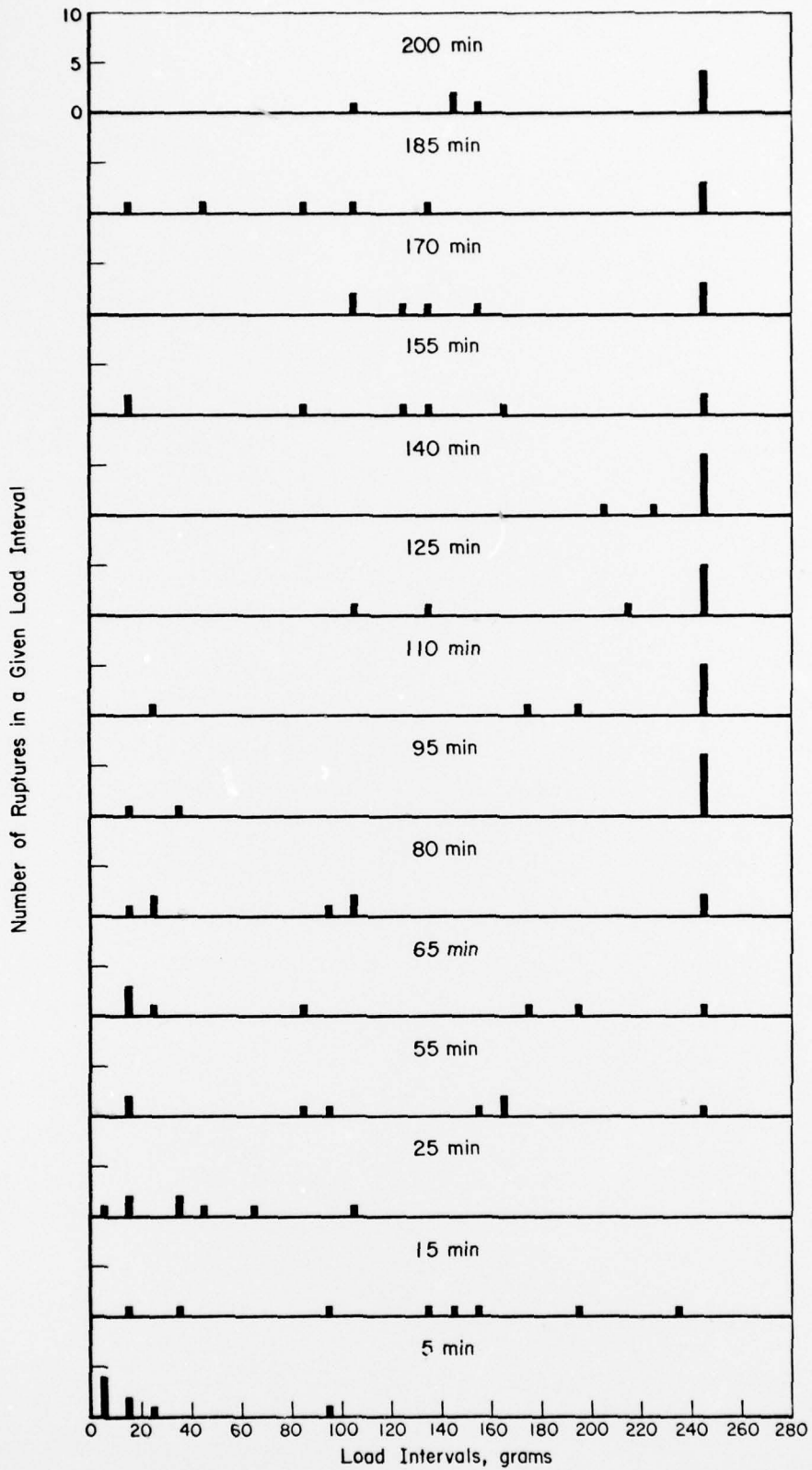
FIGURE 11.   RUPTURE LOAD DISTRIBUTIONS AS A FUNCTION OF
             TIME FOR A 5 VOLUME PERCENT SOLUTION OF TCP
             in E-105 AT 121 C

strength per unit time at temperature. Figure 12 shows a series of curves representing the rate of change in rupture strength as a function of temperature for the reaction of pure E-105 on ARMCO iron and the E-105 + 5 volume percent TCP solution on ARMCO iron. From these curves, it can be seen immediately that the solution forms stronger films at lower temperatures. The pure ester does not begin to form films of any mechanical consequence until temperatures on the order of 120 C are reached. The transformation rate for the solution shows a curious (and reproducible) minimum in the region around 100 C. The data for upper curve (inverse triangles) was taken in a relative humidity of ~40 percent. The lower (upright triangles) was taken a few months later in a relative humidity of 57 to 70 percent. This suggests that dissolved or adsorbed water may play an important role in the film-formation process. Hydrolysis of the ester into ethylhexyl alcohol and decanoic acid or competition for active surface sites may be indicated.

Ellipsometric Experiments

Oxidation of ARMCO Iron

In order to check the apparatus and obtain data on the nature of the oxide coating on the substrate material, an experiment was performed in which a standard specimen was heated in ambient air (relative humidity = 28 percent) at 191 C and changes in Δ and Ψ with time were followed. Initial measurements indicated that about 50A of iron oxide was present. Upon heating, the specimen oxidized very slowly, as indicated by measurements of Δ and Ψ. After 5-1/2 hours, an additional 225A of oxide film had grown and the experiment was discontinued.

Film Degradation

A rubbed film of E-105 on a standard ARMCO flat was prepared by the technique described earlier. The specimen was heated from room temperature (19 C) to 204 C, and Δ and ψ were measured at intervals. Up to about 71 C, no changes in either Δ and ψ were observed. Between 71 C and 93 C, a rapid increase in Δ occurred, indicating that a decrease in film thickness had occurred. Calculations showed the thickness of the
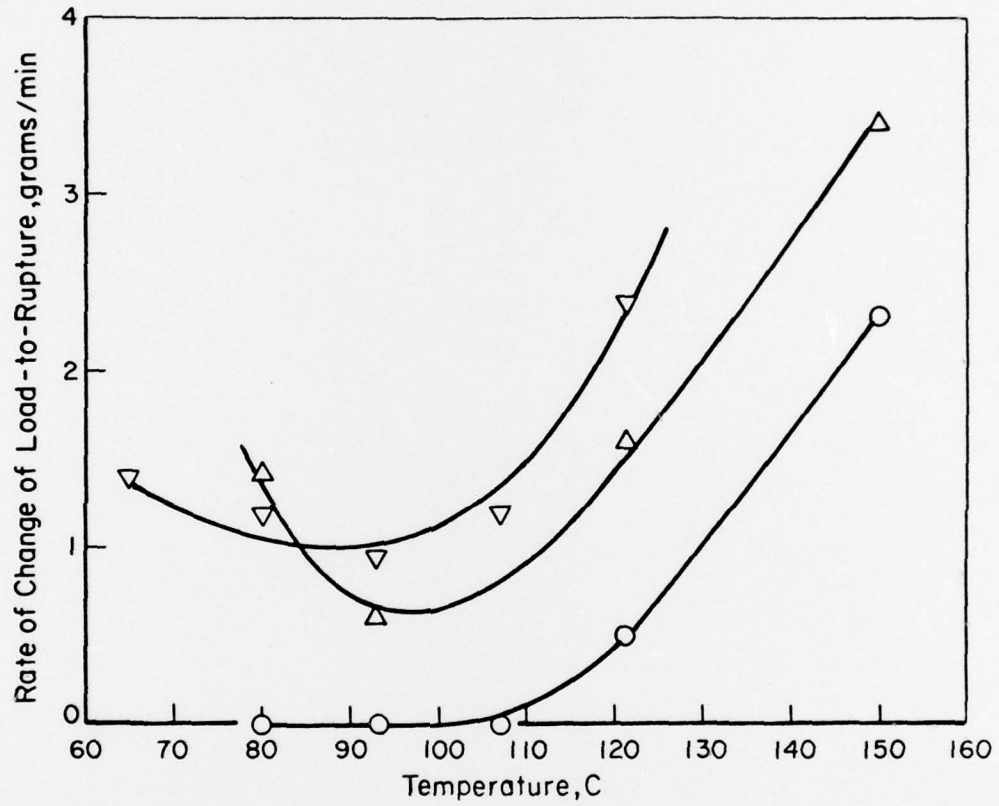
FIGURE 12. RATE OF CHANGE OF THE LOAD-TO-RUPTURE AS A FUNCTION OF TEMPERATURE FOR FILMS FORMED FROM PURE E-105 (CIRCLES) AND A 5 VOLUME PERCENT SOLUTION OF TCP IN E-105 (TRIANGLES)

remaining film to be about 25A. Between 93 C and 149 C, no further changes
were observed. At 149 C, Δ began decreasing. This indicated the onset
of oxidation and very probably chemical reaction of the residual film with
the substrage and further degradation of the film.

In the second experiment, a film specimen was prepared in the
standard manner and put on a stage which had been preheated to 100 C.
Rapid increase in Δ was observed for the first 10 minutes of heating,
indicating a thinning of the film. After this period, no further changes
in Δ or ψ were observed eventhough the heating was continued an additional
2 hour period. Calculations showed that about 25A of film remained.

DISCUSSION

Although insufficient data are available to draw definitive conclusions as to the nature of the interactions between the lubricant E-105 and the substrate material, sufficient information is available to formulate a working hypothesis to guide the research for the time remaining in the first year of the program. This hypothesis is as follows. Two transitions seem to occur in E-105 films as they are heated -- the first at about 93 C and the second at about 177 C. As previously mentioned, since the first transition occurs near the boiling point of water, it is probable that the transition represents the hydrolysis of the diester into ethylhexyl alcohol and either sebacic acid or the monoester of sebacic acid and ethylhexyl alcohol. The ellipsometric data indicate a drastic thinning of the film at around 93 C. A thinner film could have a lower compressive strength. Then, as the system is heated further, the remaining fragments of the diester react chemically with the iron-iron oxide substrate to form a tough, chemisorbed film. The primary bonding of this film to the iron-iron oxide substrate would be through the formation of chemical bonds between an oxygen atom of a carboxyl group of *sebacic acid* (or its ester) and an iron atom. This type of film would be constituted of a monolayer which could be anywhere from 5A (if all the molecular chains are parallel to the substrate) to over 50A thick if the molecules are more or less perpendicular. At 177 C, a further transition takes place in which the film drastically loses strength. This transition probably represents a thermal degradation of the film brought about by the rupture of the C-O-Fe bonds and the oxidation of the substrate.

Many questions remain in the further development of the above working hypothesis. For example, what is the role of the TCP? Does it form an integral part of the structure of the film? Or is its role merely to catalyze the reaction between the E-105, H_2O, and the iron substrate? Perhaps it may even be the principal component of the boundary film, as suggested by the classic work of Klaus[9] and our high-temperature static data obtained at BCL. This latter possibility is somewhat unlikely because inorganic films of the type postulated by Klaus would not be expected to decompose at temperatures as low as 177 C. Thus, it is more probable that the film is primarily organic with some stabilization by TCP fragments.

Furthermore, why does the rate curve for the TCP solution show a characteristic, and reproducible, minimum around 100 C? This minimum, along with the fact that the pure ester does not begin to significantly interact with the surface until a temperature of about 120 C is reached, strongly suggest that water, adsorbed or dissolved, plays an important role in the formation of mechanically significant films.

Much more research is needed to clarify the above points.

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     121 Volume III, June, 1976.

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
AFOSR-TR- 77- 0999		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
AN INVESTIGATION OF THE EFFECTS OF OXYGEN AND WATER VAPOR ON THE COMPRESSIVE STRENGTH OF BOUNDARY FILMS ON IRON SUBSTRATES	Interim
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
W. R. Bucknor, E. J. Drauglis, and D. K. Snediker	AFOSR-76-3051

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Battelle Memorial Institute 505 King Avenue Columbus, Ohio 43201	2303/A2, 61102F

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Air Force Office of Scientific Research/NC Bldg 410, Bolling AFB Washington, D. C. 20332	August 1977
	13. NUMBER OF PAGES
	31

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this program is to determine the effects of O_2 and H_2O on boundary film formation by studying a model system consisting of 2-ethylhexyl sebecate and tricresyl phosphate (TCP) on ARMCO iron surfaces. This report deals with the first year, wherein, film compressive strength measurements, supported by ellipsometry, were used to study the behavior of these reactants as a function of time and temperature in a laboratory atmosphere. For films formed out of the pure ester, two transitions in compressive strength and film thickness were observed at 93 C and 180 C. The rate of change of film

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

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20. ABSTRACT (Continued)

compressive strength of TCP-ester solutions decreases with temperature of
100-120 C after which the rate increases. For the pure ester, the rate of
formation of a mechanically significant film is low until temperatures
>120 C are reached. Under all conditions of temperature, mechanically
significant films form relatively slow -- of the order of minutes -- from
the TCP solution. Water, adsorbed or dissolved, appears to play a signifi-
cant role in the formation and degradation of these films. A working
hypothesis in terms of the hydrolysis of the ester to form sebacic acid at
temperatures around 100 C is presented. Ellipsometric data suggest that the
high temperature loss of compressive strength in those films is due to the
onset of rapid substrate oxidation, perhaps accompanied by decomposition of
the surface-bound organic species.