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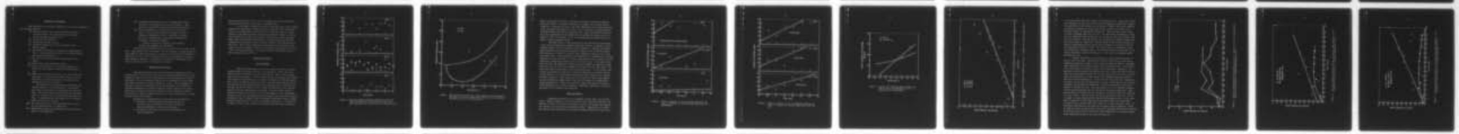

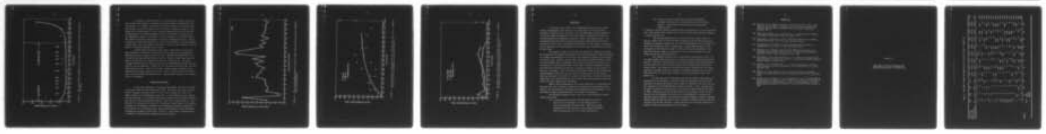

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AN INVESTIGATION OF THE EFFECTS OF OXYGEN AND WATER VAPOR ON THE COMPRESSIVE FILM STRENGTH OF BOUNDARY FILMS ON IRON SUBSTRATES — PART II,

to

DEPARTMENT OF THE AIR FORCE
OFFICE OF SCIENTIFIC RESEARCH

August 8, 1978

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by

(10) E. J. Drauglis, J. W. Kissel
~~and~~ D. K. Snediker

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SUMMARY

The objectives of this program are to study the effect of O_2 and H_2O on the compressive strength of boundary lubricant films on iron surfaces and to correlate these effects with the basic physical and chemical phenomena responsible for the formation and stabilization of the films and the converse phenomena of degradation and dissolution. The work described in this report is for the second year of a 3-year AFOSR program.

In the first year of the program, basic experiments at ambient relative humidity were performed on films formed from the diester, di-2-ethylhexyl sebacate (E-105), and solutions of the antiwear additive tricresyl phosphate (TCP) on highly polished ARMCO iron substrates. Compressive strength measurements and optical measurements were made on these films at various temperatures ranging from 20 to 204 C. Compressive strength measurements were made by means of a unique film penetration apparatus developed and constructed at Battelle's Columbus Laboratories (BCL). In this apparatus, an accurately controlled load is imposed on a fine spherically tipped stylus until the collapse of the film is detected by electrical continuity.

Both static and kinetic measurements were made of film strengths of E-105 and E-105 + TCP solutions. In the static measurements (performed at temperatures ranging from 20 to 204 C), it was found that the films have a low-strength component and a high-strength component and that a kind of phase transition occurs at about 93 C at which the high-strength component grows at the expense of the low-strength component. The high-strength component decomposes at about 180 C. Ellipsometric measurements over the same temperature range confirmed the existence of these transitions. The kinetic measurements showed that major changes in the rate of change in film strength occur in the temperature range 100 to 120 C.

In the second year of the program, the film penetration apparatus was modified to permit repeatable, routine measurements under controlled atmospheres. The apparatus was modified such that the rate of load application is now automatic and reproducible. A new electric continuity circuit was constructed which removed subjectivity from the identification of the "rupture point".

Experiments carried out in dry and wet air environments indicate that the presence of H_2O has a strong retarding effect on the formation of strong boundary films from both pure ester and TCP solutions. The reaction rates were observed to increase sharply at temperatures above 105 – 110 C.

Experiments carried out in dry and wet argon environments indicate that O_2 is essential to the formation of compressively strong films. Weak films found in argon gained strength with exposure to air.

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INTRODUCTION

Most lubricated machine elements operate, at least in part, in the boundary regime in which very thin films having properties significantly different from bulk fluids, are responsible for the effectiveness of the lubrication and the service life of the lubricated element. These critical boundary films are formed by complex physical and chemical interactions between a solid (usually metal) machine element, the lubrication fluid, and the ambient atmosphere. In the past decade, significant advances have been made in gaining an understanding of the chemistry of the interaction of many different types of additives, base oils, and various metal substrates.(1-7)* However, relatively little effort has been expended on the study of the effects of ambient atmosphere on the formation and stabilization of boundary films. In particular, the most common and reactive substances found in the atmosphere, O_2 and H_2O, have been sadly neglected. In recent years, only Buckley(1), Fein(2), and Begelinger and DeGee(3) have made significant advances in our understanding of the role of O_2 in the formation of boundary lubricant films. However, much less work has been performed on the role of H_2O and almost no research has been performed on the combined effects of H_2O and O_2. The small amount of work performed on these substances indicates that their effects on lubricant films are large. However, the precise elucidation of the basic interactions occurring among H_2O, O_2, the lubricant, and the substrate requies much more research on well-characterized substrates and well-defined lubricating fluids.

About 2 years ago, a research program was initiated at BCL aimed at answering some of the basic questions relating to the role of H_2O and O_2 in lubricant films. The approach taken in this program was to study a fundamental mechanical property of the films — the compressive rupture strength. Well-characterized, well-purified lubricants and additives and well-characterized substrates were used. Rupture strength measurements were made on a unique film-penetration apparatus developed at BCL(8). This apparatus is so constructed that a stylus may be incrementally loaded over a wide load range until film rupture detected by electrical continuity occurs. In the first 2 years of the program, films formed from a diester, di-2-ethylhexyl sebacate, and the solutions of tricresyl phosphate in the diester were studied. In addition to the film

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* References are listed on page 28.

rupture strength measurements, ellipsometry and external reflection infrared spectroscopy were performed. In all experiments, the substrate was highly polished ARMCO iron. In the following sections, a more detailed description of the work performed in the first 2 years of the program is presented.

EXPERIMENTAL METHODS

Static compressive strength, the primary boundary film characterization parameter used in this research, was measured using a modified version of the apparatus described in Reference 8. This phase of the research was devoted to the time- and temperature-dependent behavior of boundary films formed from 2-ethyl hexyl sebacate and tricresyl phosphate in the presence or absence of O_2 and H_2O. The apparatus, the reagents, and the techniques used are described in detail in the following sections.

Apparatus

The apparatus used in this study is an advanced version of that referred to above. Figure 1 shows the essential details of the apparatus. A flat specimen (the substrate) rests on a heated stage. This stage can be moved kinematically in the x-y direction by means of micrometer drives and air-tight feed-throughs (multiple O-ring type) through a vacuum ring. A .0051-cm-radius stylus is loaded against the specimen plate by means of a mechanical release and dash-pot system. As the stylus drops onto the surface, the load is slowly transferred from a load cell to the stylus tip at a reproducible rate of ~5 g/sec up to a total of 130 grams. Film rupture is detected electrically. The stylus-substrate interface is a part of an electrical circuit that imposes a voltage of 1.6 across that interface and automatically trips at a preset resistance of 20 ohms. This trip load is automatically registered for readout. The constant application of load and the film rupture detection circuit eliminates two sources of experimental uncertainty associated with the old apparatus — constancy and smoothness at load application and reproducible identification of the point of film rupture. Reproducibility and drift of the electronic components involved were found to produce less than 1 percent variation in readings taken over many hours.

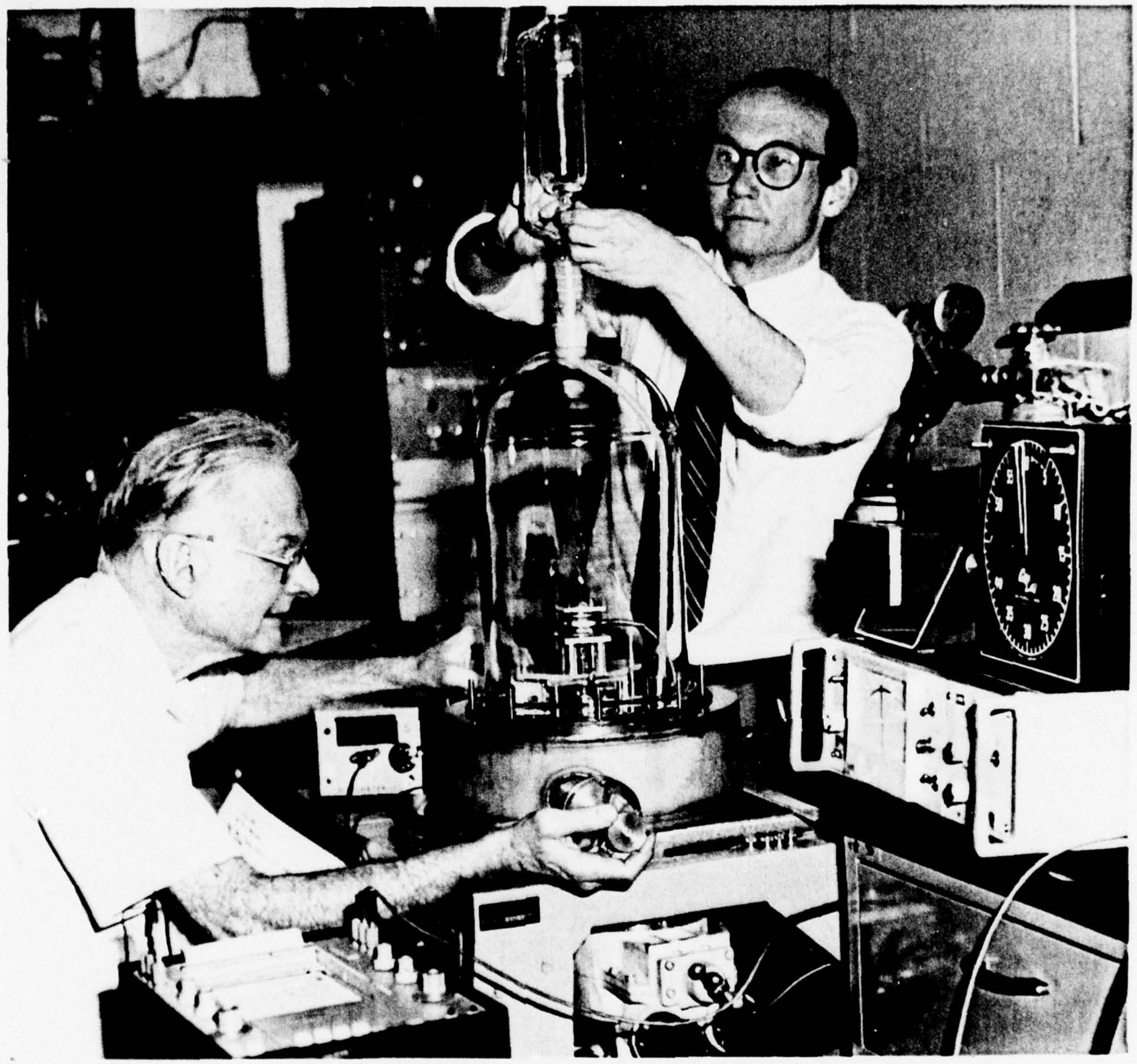

FIGURE 1. OVERALL VIEW OF THE APPARATUS USED TO DETERMINE THE COMPRESSIVE STRENGTH OF BOUNDARY FILMS

The entire apparatus is enclosed in a vacuum chamber, as shown in Figure 2. The chamber is provided with feed-throughs for mechanical motion; load raising and release; electrical signals; and the introduction of reactants, both liquid and gaseous. Liquid reactants are introduced via a vacuum-compensated addition funnel. The glass system shown in Figure 2 was replaced with stainless steel system due to the continued mechanical freezing of the PTFE stopcocks. The stainless steel system uses polymer-free needle valves and allows the dried ester solutions to be degassed and purged at the same time as the chamber.

The gaseous atmospheres are introduced via a stainless steel manifold under the vacuum chamber base plate. Dry reagent gases are introduced directly, while H_2O-saturated gases are introduced through a heated bubbler containing distilled water. In all cases, the purge gases exit through an oil bubbler against a head of approximately 10 cm oil.

The temperature of the iron specimen was measured by means of a thermocouple pressed by spring pressure against the specimen surface ~1 cm away from the stylus contact point.

Reactants

Surface Preparation

The styli used in these experiments were made of hardened carbon steel. They 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.

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	Balance.

- Tensile strength: 42,000 psi
- Rockwell hardness: B40-50
- Modulus of elasticity: 30×10^6 psi.

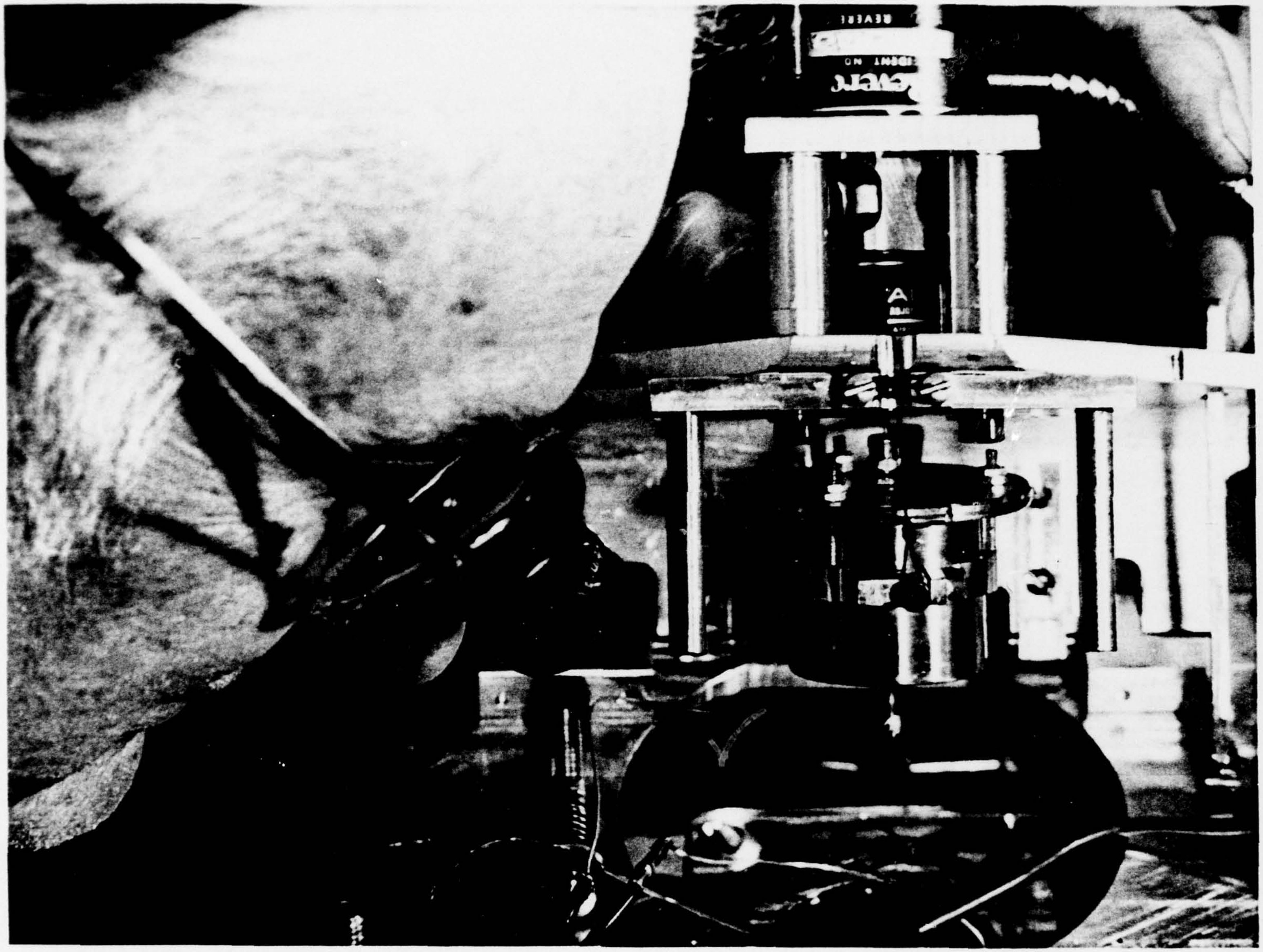

FIGURE 2. CLOSE-UP VIEW OF SPECIMEN PLATE AND STYLUS
(The stylus and associated hardware has
been rotated up out of position.)

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) Prior to experiment, polish to a high mirror finish with a deionized water slurry of Linde-B on solvent-extracted cotton (Xerox 825R)
(6) Rinse: tap H_2O
deionized H_2O
absolute CH_3CH_2OH.
Air Dry: filtered laboratory air at low flaw rate.

E-105/TCP

The liquid reactants used in these experiments were a diester of relatively high purity — 99 percent 2-ethylhexyl sebacate (E-105, 1 percent probab y monoester) and technical grade tricresyl phosphate (TCP). The TCP contained essentially 25 percent each of the four isomers with two other components at the 2 percent level. For dry experiments, the E-105/TCP solutions were dried for at least 24 hours over a Linde type 5A molecular sieve. The dry solution was poured directly into the addition funnel which was immediately sealed and evacuated. For "wet" experiments, the dry solution was shaken with distilled water in a separatory funnel and the water-saturated organic phase drawn off for immediate use.

The gaseous environments, air and argon, were introduced into the system directly from the bottle via Tygon and stainless steel tubing. The air used was Matheson dry grade with a dew point of -75 F, maximum. The argon was Matheson UHP grade with a dew point of -90 F maximum and containing 1 — 2 ppm O_2 maximum.

Experimental Techniques

Each experiment in controlled atmosphere was carried out according to the following sequence:

(1) The iron substrate was installed and the electrical connections made. The surface-contact thermocouple was put in place and checked out.

(2) A new stylus was installed.

(3) The bell jar was put in place.

(4) The E-105 solution, wet or dry, was placed in the addition funnel.

(5) The system was evacuated to a pressure of approximately 200 μ. The space above the liquid in the addition funnel was evacuated simultaneously.

(6) The system was back-filled with the appropriate atmosphere.

(7) Steps 5 and 6 were repeated five times.

(8) After the final purge, the controlled atmosphere was allowed to flow through the system for approximately 1 hour.

(9) Twenty load-to-rupture measurements were made on the bare iron plate. If the average exceeded 5 grams, of if any high values (> 20 grams) appeared, the experiment was aborted and the plate refinished.

The technique for making these measurements was the standard applied to all determinations: the readings were taken in rapid succession at surface sites ~10 mils apart. These and subsequent measurements were generally taken in a straight line across the center portion of the plate. A standard series consisting of 20 to 22 measurements took less than 5 minutes.

(10) The liquid reactant was introduced and allowed to flow over the specimen plate in a thick film.

(11) Approximately twenty 22-measurements were taken with the plate at room temperature.

(12) The specimen plate was heated to the experimental temperature level...the heating rate being ~2.3 C/minute. Input voltage was controlled to maintain the desired temperature.

(13) Once at temperature, an elapsed timer was started and a series of 20 to 22 load-to-rupture readings were taken. Subsequent readings were taken at ~30 minute intervals, each set of ~20 beginning at the specified elapsed time and taking ~3 minutes to complete.

The gas was allowed to flow at a low (1 bubble/second) rate throughout the experiment.

The data thus obtained consisted of a series of 20 to 22 loads to rupture. (See Appendix A for an example.) For most analyses, a simple average of these loads was taken and treated as an expression of average film strength at a given point in time. Points beyond the capacity of the apparatus, >130 grams, were averaged at 130 grams. In addition, the fraction of individual measurements in a given series over 20 grams was calculated.

Ellipsometry Measurements

Experiments performed with the film penetration apparatus provide a consistent set of useful data on the rupture strength of boundary films and can provide the basis for a partial understanding of the physicochemical nature of such films. For a more complete insight into the fundamentals of these films, data other than film penetration strengths are needed. As one supplement to the rupture pressure measurements, the optical properties of the films were studied by ellipsometry, an optical technique in which changes in the polarization state of polarized light upon reflection from a specimen are used to gain information about the optical properties of clean, solid surfaces or films in contact with solid surfaces.

Ellipsometry 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

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 absorbed films.

In the report covering the results of the first year of this program, ellipsometric experiments on rubbed films were described. Fair correlation between the ellipsometric results obstained on these films and the results obtained in the film penetration apparatus was achieved. However, to facilitate interpretation of the data and ensure that the same type of films was being formed in both types of experiments, a cell was constructed in which ellipsometric measurements could be made on a substrate and film immersed in bulk fluid. Such a cell was designed, constructed, and tested early in the second year of the program. This cell is constructed of stainless steel with 1 inch circular pyrex windows. Two heating elements installed at one end allow temperatures up to 175 C.

EXPERIMENTAL RESULTS

Air Environment

Several experiments were carried out using pure E-105 on a freshly prepared ARMCO iron surface in bone dry air (dew point < -65 C) and in air nearly saturated with water vapor (rh $\cong$ 85 percent). Figure 3 shows typical data from such experiments. In this figure, the data are average film strength (load needed for film rupture) as a function of time for four different specimens, each at a different temperature level. The environment was bone dry air and the E-105 had been thoroughly dried with molecular sieve. Duplicate data are shown for the 95 C level in order to given an indication of the reproducibility of the data from specimen to specimen. From the limited number of experiments carried out on the pure ester, there appears to be a relationship between both the rate of formation and the strength of the film and the presence or absence of water. Figure 4 shows the average equilibrium strength of films formed from pure E-105 as a function of substrate temperature. In the absence of water, the films seem to increase in strength with increasing temperature.

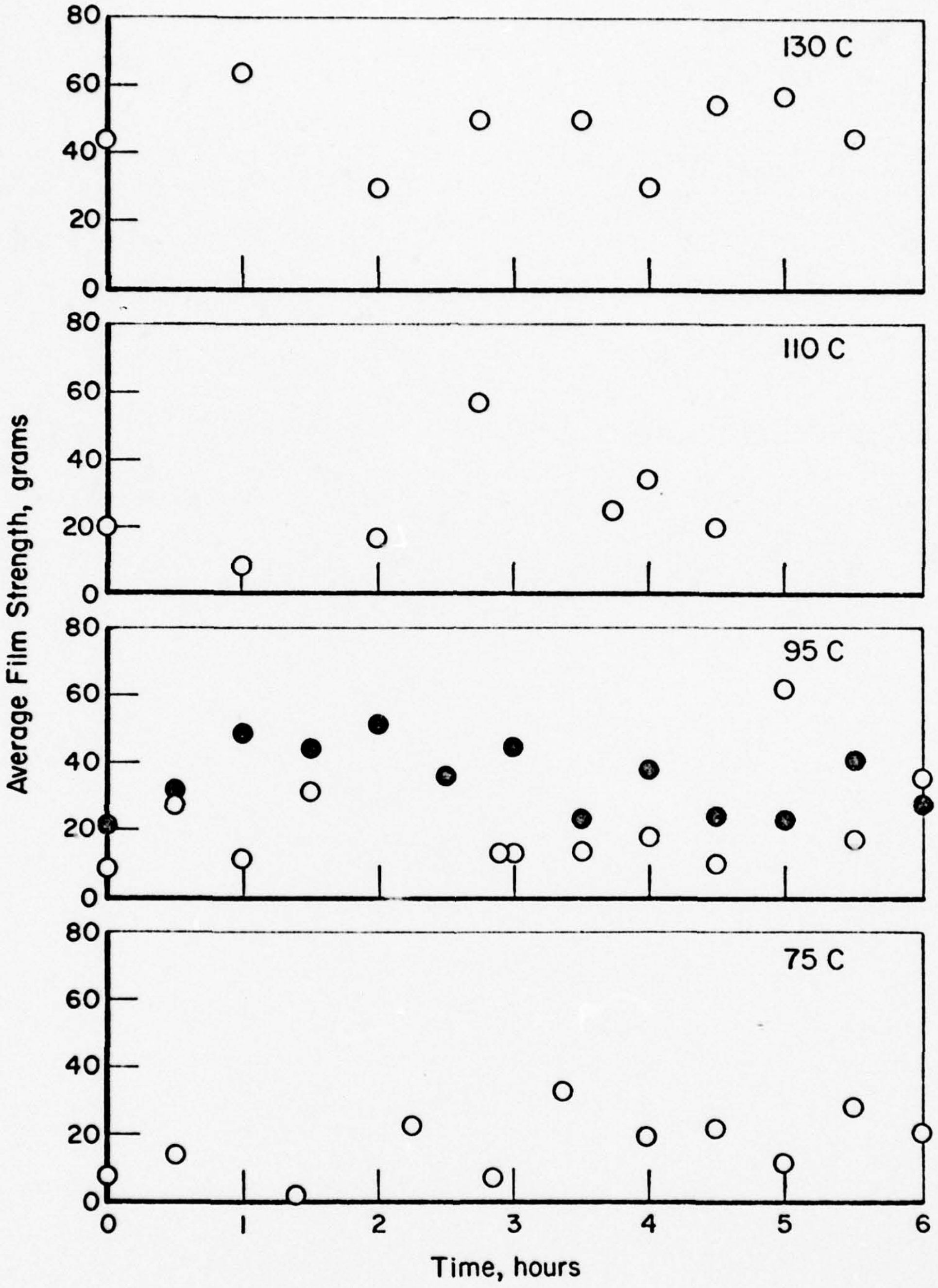

FIGURE 3. MEAN FILM RUPTURE STRENGTHS PROVIDED BY PURE E-105 FLUID ON ARMCO IRON IN "BONE DRY" AIR (Each Data Point Represents the Mean Value for 20 Determinations)

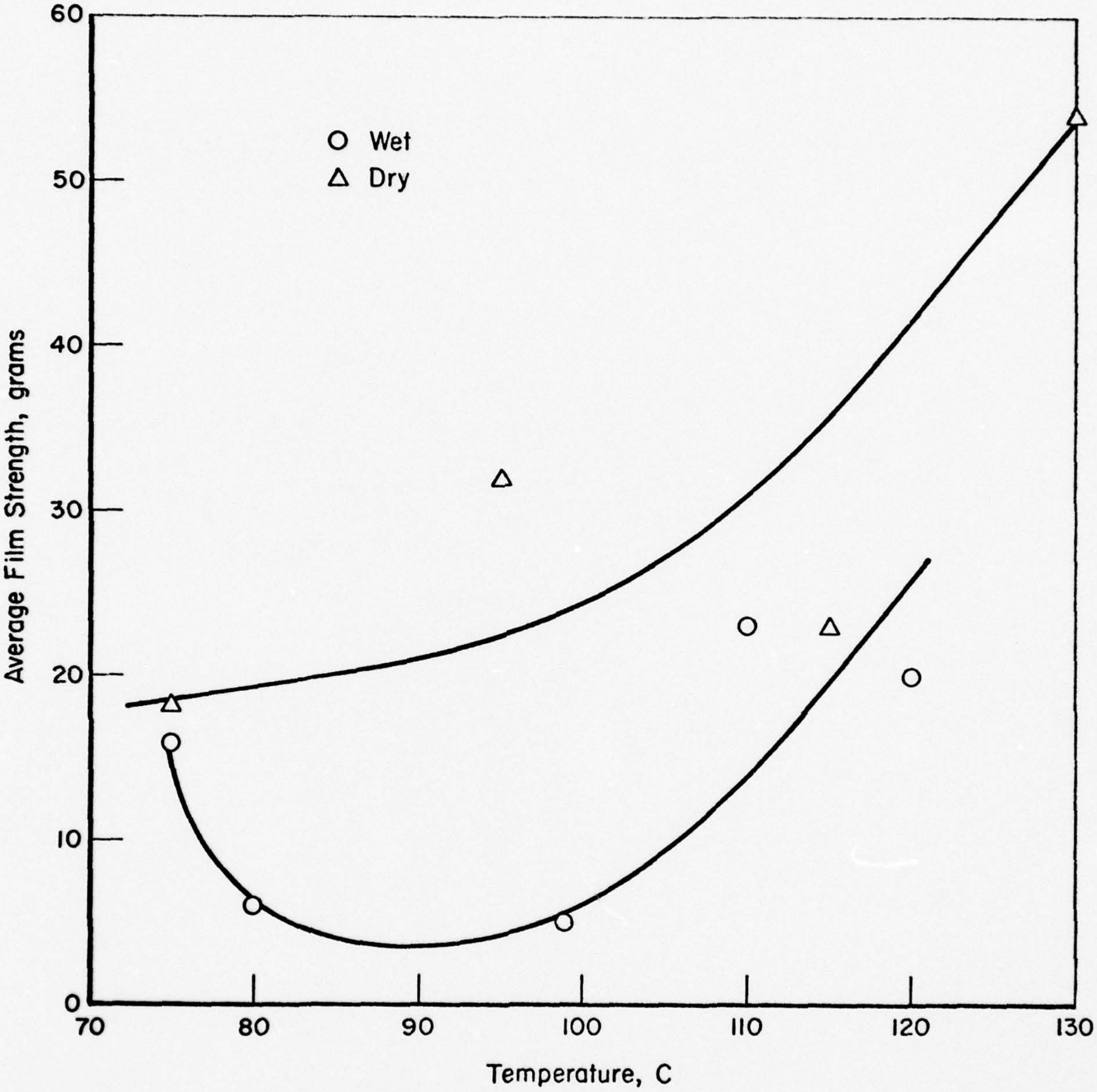

FIGURE 4. MEAN FILM RUPTURE STRENGTHS IN WET VERSUS DRY AIR ENVIRONMENTS FOR PURE E-105 FLUID ON ARMCO IRON (Each Data Point Represents the Mean Value for 20 Determinations.)

While in the presence of water, a minimum in strength is observed at approximately 80 to 100 C. It should be pointed out, however, that the experimental conditions — reactants in contact, with ample opportunity for continuing reaction as the isothermal measurements are taken — do not allow for the differentiation of kinetic effects and inherent film properties. Such differentiation would require the establishment of an equilibrium film, followed by removal of the reactants — E-105, air, and H_2O — prior to the mechanical characterization of the film at various temperature levels.

The major thrust of the second year of this research has been devoted to the study of solutions of commercial grad TCP in E-105. A standard 5 percent (volume) solution was used throughout these experiments. (Details of specimen preparation have been previously presented.) Figures 5 and 6 show the average film strength as a function of time for three temperature levels, in air, with and without water. (Each temperature and environment is represented by a separate experiment and iron substrate.) A slope, representing a rate of increase of film compressive strength was estimated from each of the curves. In the case of the 130 C wet data, the compressive strength increased rapidly at temperature levels above 110 C and the slope was estimated from the heat-up curve (not shown). The solid line shown on that graph is from that heat-up curve. If the various slops (rates) are plotted as a function of substrate temperature, two curves reflecting the relative rates of formation under dry and "wet" conditions are obtained as shown in Figure 7. Below temperatures of the order of 100 C, water appears to have a definite retarding effect on the rate of formation of compressively strong boundary films. Above this temperature range, the rpesence of water is either beneficial or of little consequence. Additional experiments, in both air and argon, do not eliminate this equivocacy.

Argon Environment

Experiments carried out in an atmosphere of pure argon — wet and dry — offer a dramatic contrast to those carried out in air. Figure 8 illustrates the behavior of E-105 + TCP films in dry argon in terms of the average film strength as a function of time at several temperature levels. Temperatures up to 300 C and reaction times of nearly 8 hours produced average strength films that were 2

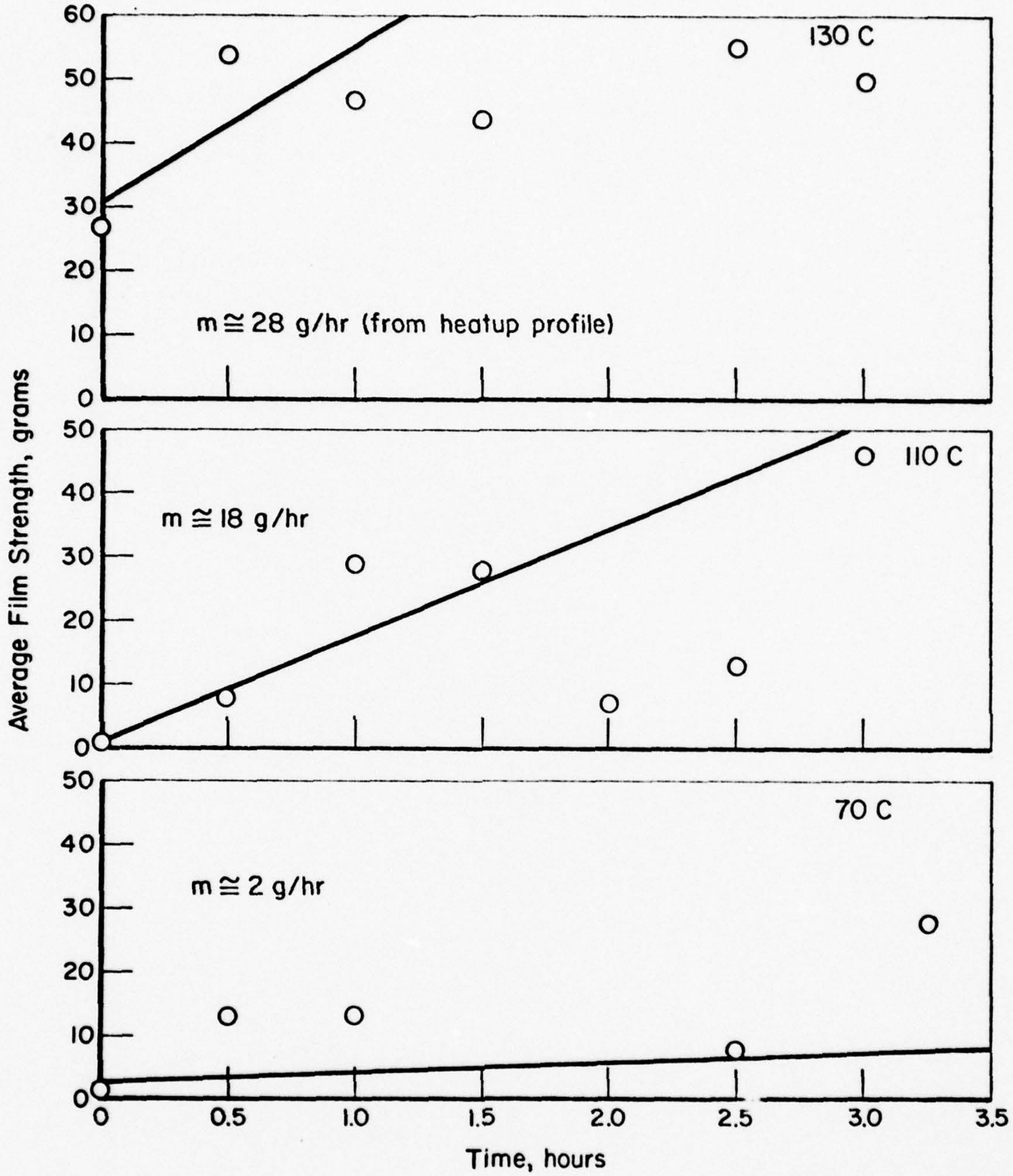

FIGURE 5. RATES OF INCREASE (m) IN FILM RUPTURE STRENGTHS FOR E-105 + 5 PERCENT TCP FLUID ON ARMCO IRON IN WET AIR ENVIRONMENTS

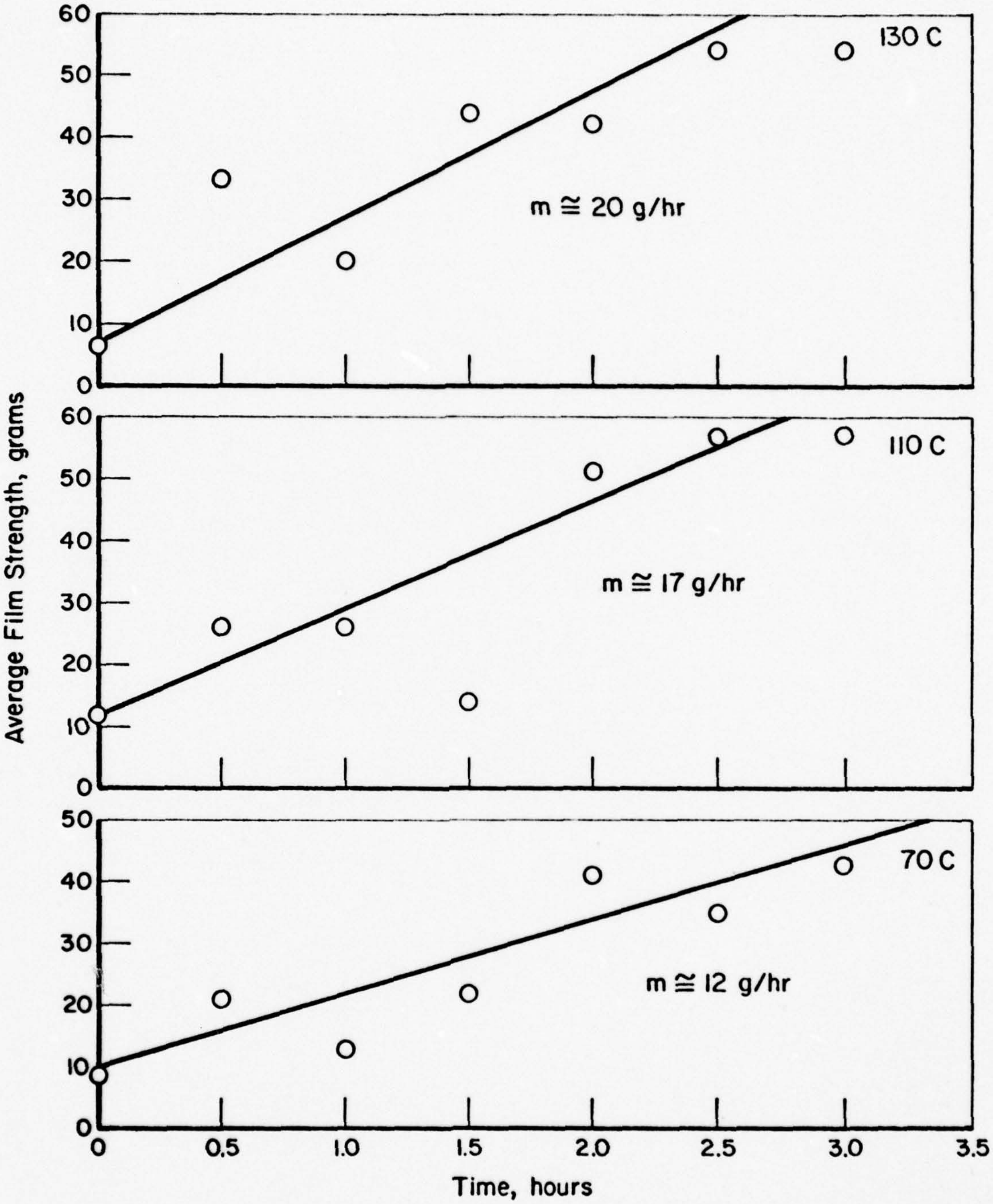

FIGURE 6. RATES OF INCREASED (m) IN FILM RUPTURE STRENGTHS FOR E-105 + 5 PERCENT TCP FLUID ON ARMCO (Run in Bone-Dry Air)

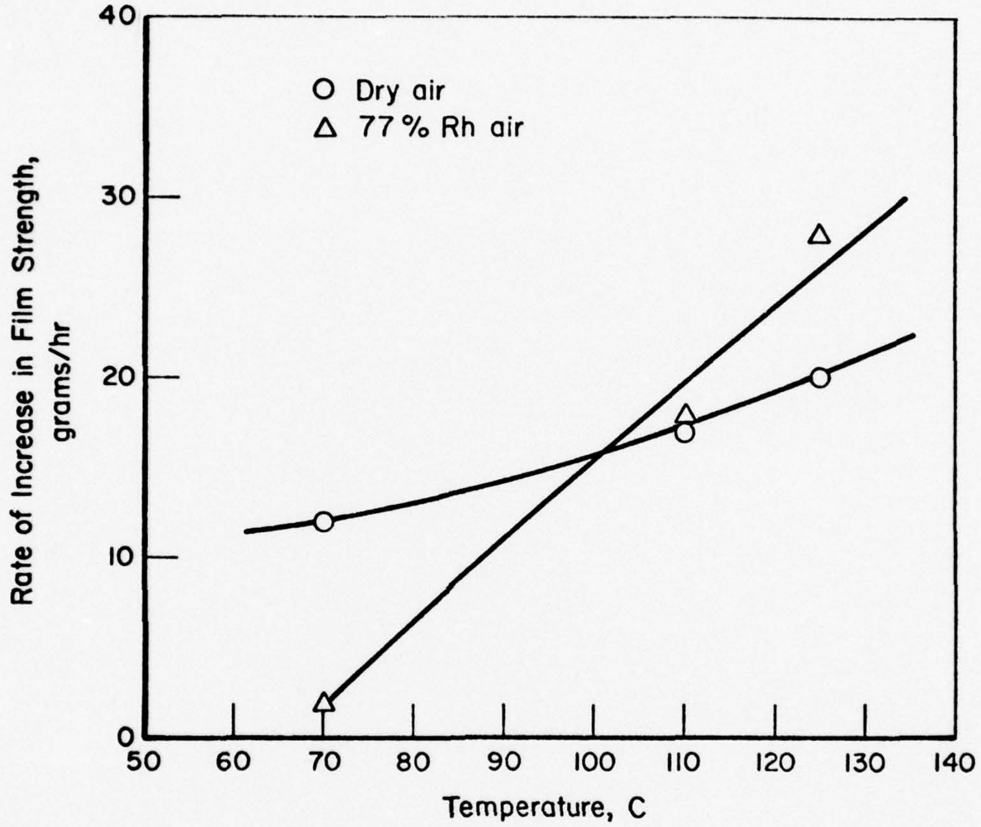

FIGURE 7. SURFACE FILM FORMATION RATES COMPARED FOR WET AND DRY AIR ENVIRONMENTS (E-105 + 5 PERCENT FLUID ON ARMCO IRON)

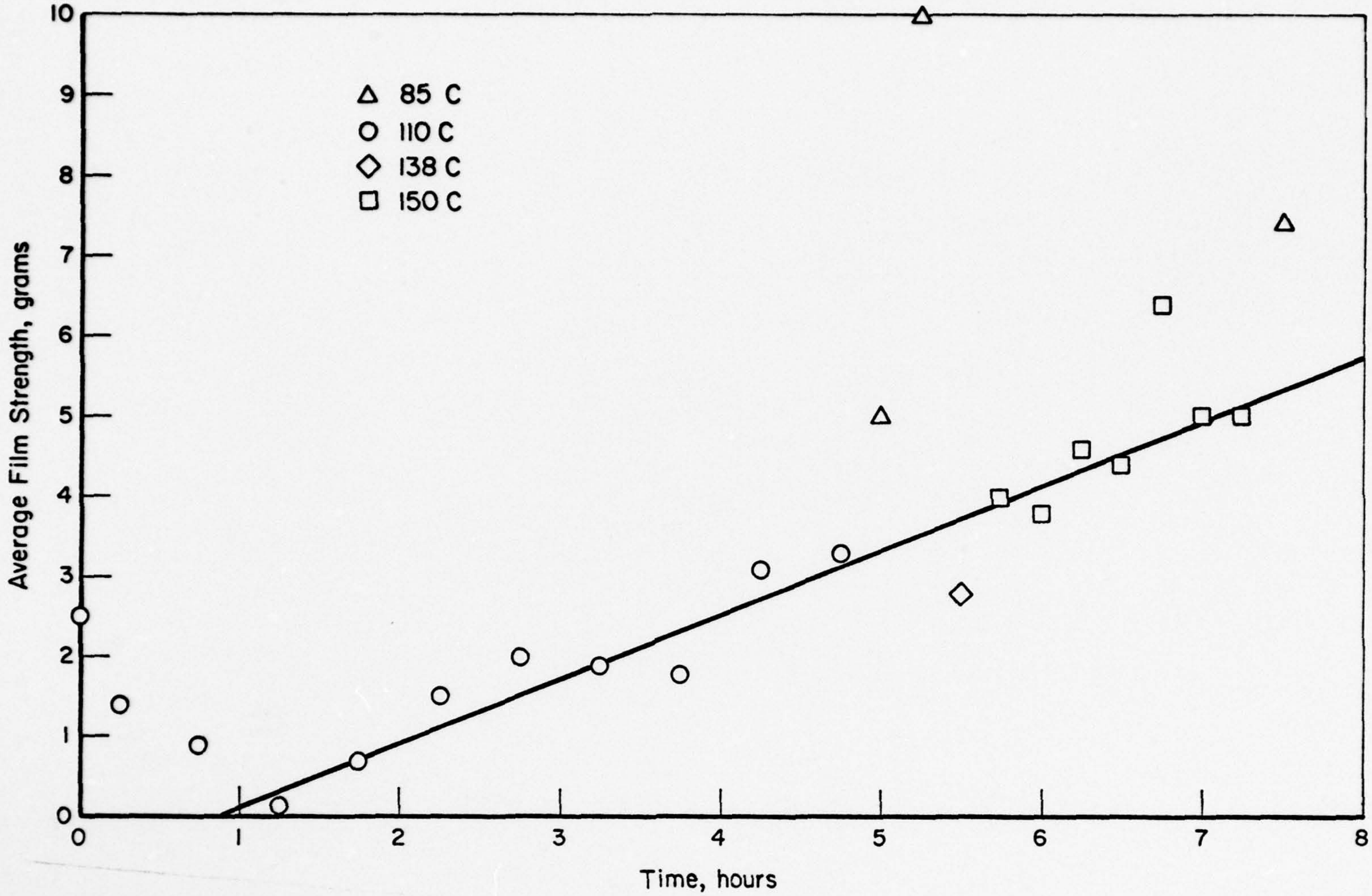

FIGURE 8. MEAN AVERAGE FILM RUPTURE STRENGTHS FOR E-105 + 5 PERCENT TCP FLUID ON ARMCO IRON IN DRY ARGON

to 10 times weaker than films formed in the presence of air. (The nearly linear time dependency of these data and the relative temperature independence suggest the possibility of air leaking into the system.) Figure 9 shows data comparing an experiment carried out in dry argon with one carried out in argon with a relative humidity of approximately 85 percent. Both experiments were carried out under isothermal conditions at 110 C. The presence of H_2O appears to influence the equilibrium film strength but not the rate at which the strength, such as it is, develops. The film formed in dry conditions is slightly stronger than that formed under wet conditions. Figures 10 and 11 show the data depicted in Figure 9 superimposed upon the average film strength as a function of time for two experiments carried out in air. The role of water, at temperatures above its boiling point, remains unclear. The differences between wet and dry in the various experiments, depicted in Figures 7, 9, 10, and 11 are probably within experimental error.

Several experiments were carried out on a film formed from E-105 + 5 percent TCP in dry argon. This film was formed at 110 C and was subjected to temperature exposures as high as 150 C in the dry argon environment. Throughout these experiments, the average strength remained relatively low — 3 to 8 grams. After several hours of thermal cycling — which indicated no temperature — dependency of film strength within experimental error — argon saturated with water vapor and E-105 liquid saturated with H_2O were admitted in such a way as to preclude the introduction of O_2 and average film strength measurements made as a function of time and temperature. Figure 12 shows the average film strength as a function of time from the introduction of water. Each data point on the graph represents the average of 21 individual, successive measurements of the load required to rupture the film. [The high average at $t = 0$ is probably anomalous, the average being dominated by two readings of an unusually high level. This apparent drop in strength with the introduction of water should not be construed as a water effect. The data point (not shown) just prior to that at $t = 0$ was 2.5 grams — a value consistent with the post-H_2O strength levels.] After some 6 hours of exposure to humid argon and H_2O-saturated E-105, the average film strength had not increased more than 2 grams over a wide temperature range. At this point, laboratory air was admitted (45 percent relative humidity). After an induction period of approximately 15 minutes, possibly reflecting the diffusion of O_2 through the oil film, the average film strength began to increase dramatically (right-hand portion of the curve in Figure 12).

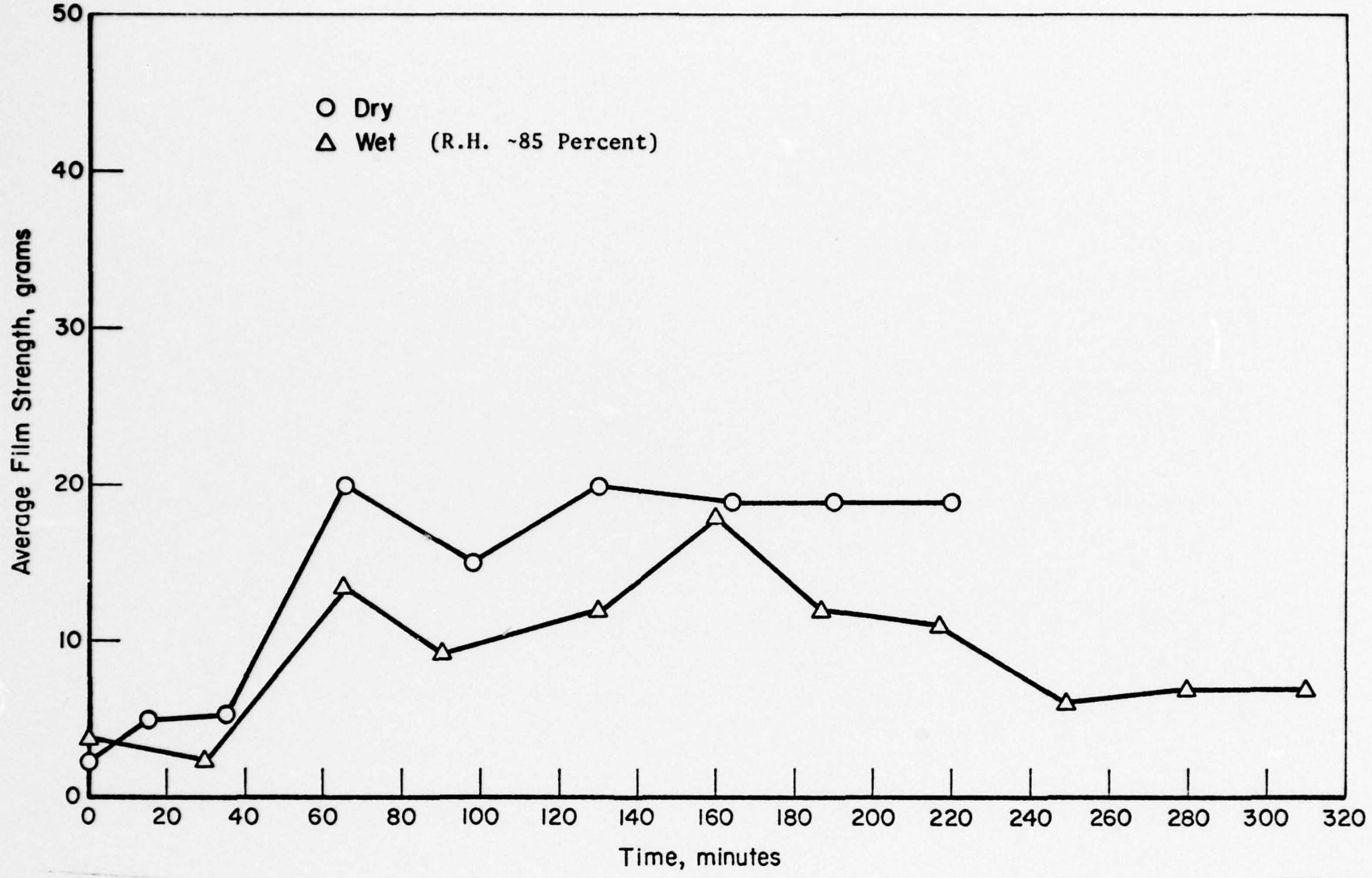

FIGURE 9. MEAN FILM RUPTURE STRENGTHS PROVIDED BY E-105 + 5 PERCENT TCP FLUID ON ARMCO IRON IN DRY AND IN WET ARGON AT A CONSTANT TEMPERATURE OF 110 C

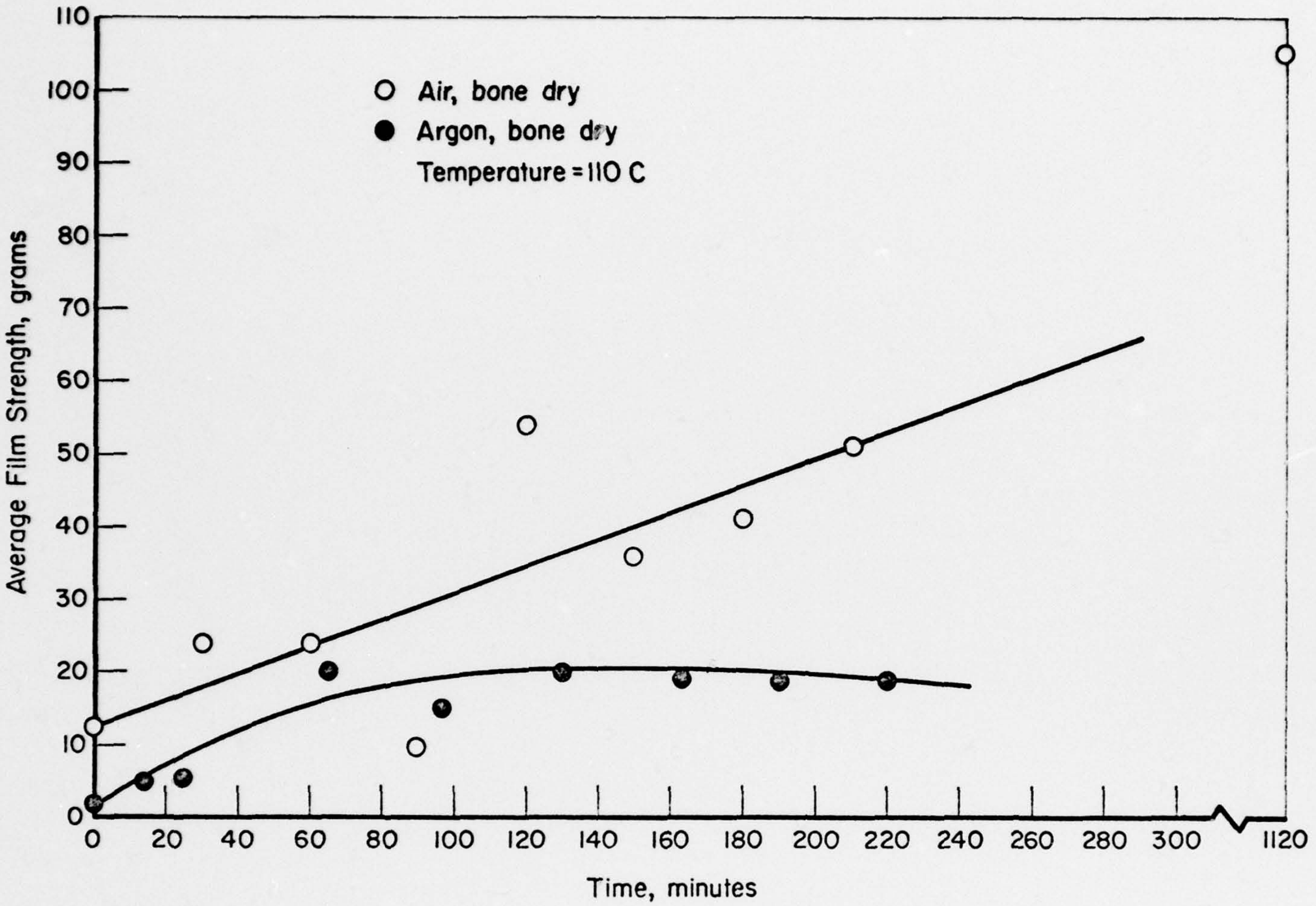

FIGURE 10. MEAN FILM RUPTURE STRENGTHS FOR DRY AIR AND DRY ARGON COMPARED (E-105 + 5 PERCENT TCP LIQUID PHASE) AT A CONSTANT TEMPERATURE OF 110 C

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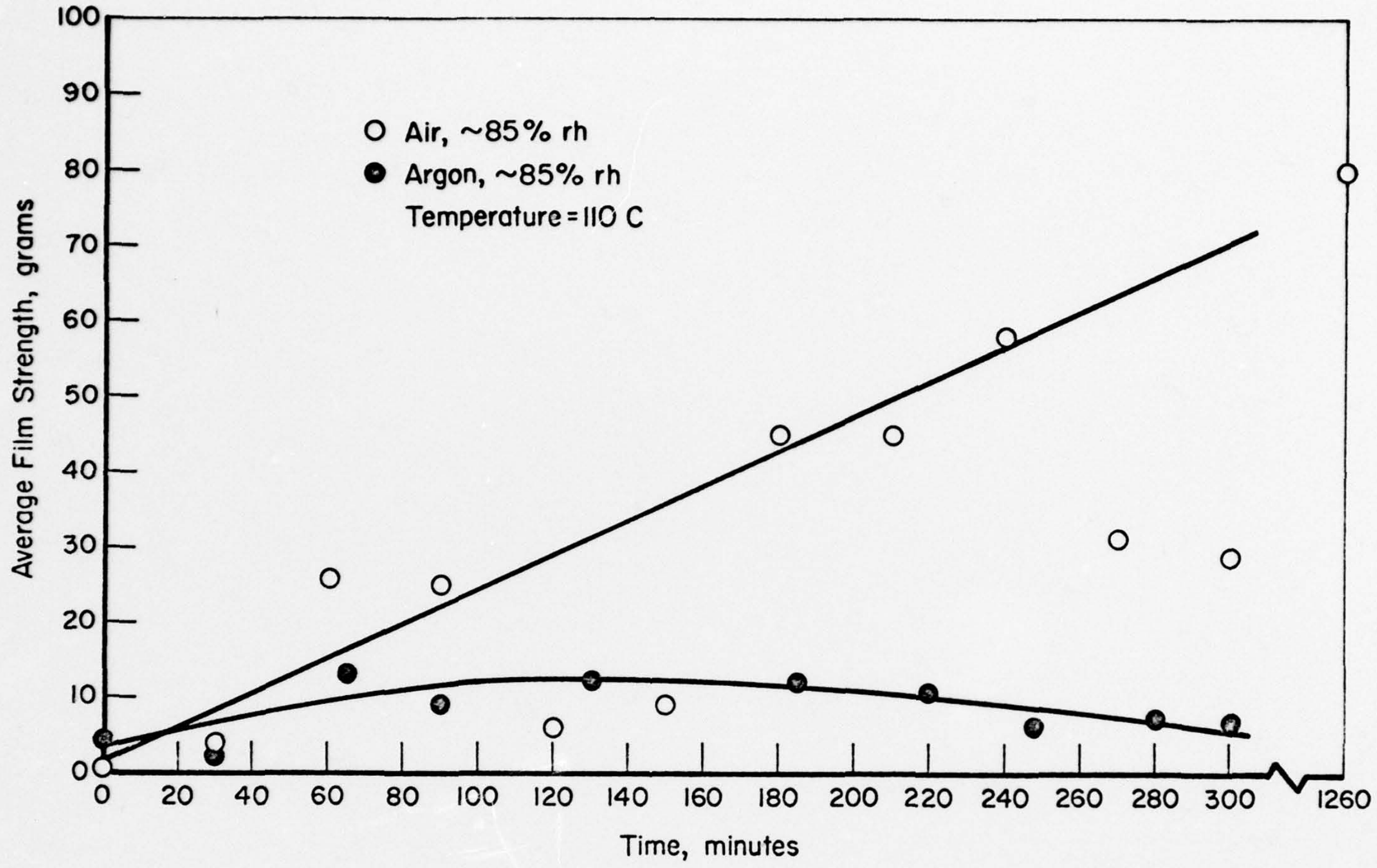

FIGURE 11. MEAN FILM RUPTURE STRENGTHS FOR WET AIR AND WET ARGON COMPARED (E-105 + 5 PERCENT TCP LIQUID PHASE) AT A CONSTANT TEMPERATURE OF 110 C

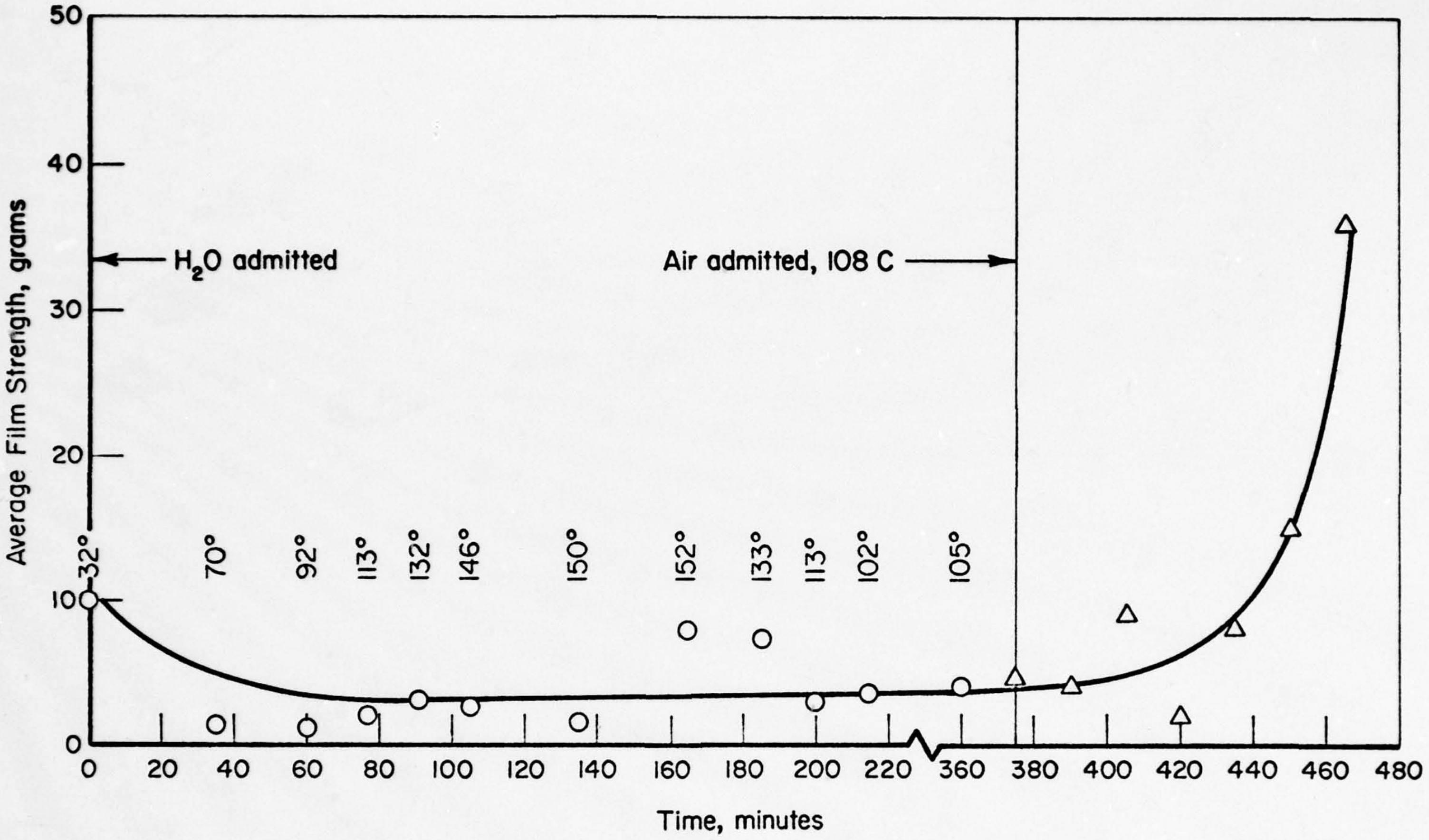

FIGURE 12. MEAN FILM RUPTURE STRENGTHS FOR E-105 WITH 5 PERCENT TCP ON ARMCO IRON BEGUN IN DRY ARGON

In contrast to films formed in air, those formed in argon tend to be more uniform with respect to strength with extreme values for individual readings absent. For example, none of the bimodality observed in air-formed films and reported in the first annual report is present. Readings of high- or low-compressive strength appear to occur in groups suggesting that the succession of measurements is traversing regions of high- and low-film strength and that the appearment scatter in the results is due to variation in the properties of the surface film and not necessarily to inherent experimental scatter. Figure 13 shows the rupture load values for a series of 36 readings, each approximately 10 mils apart, on a film formed in dry argon. Port A, B, and C suggest areas of high (B, C) and low strength on the surface.

As discussed in the first annual report, films formed in air show a wide variation in individual strength values at a given time and temperature. The distributions of values tend to fall into a bimodal distribution with low and high values and relatively few in between. Figure 14 shows the percent of values over 20 grams as a function of time for wet and dry air. The high-strength fraction tends to increase with time at approximately the same rate for both wet and dry conditions. Figure 15 shows the same treatment of the data for films formed in argon. There is virtually no high-strength component and no significant difference between wet and dry. Thus, it appears that the development of high-strength films depends upon a high-strength component that requires O_2 for its formation.

Ellipsometry Results

In the first experiment a freshly polished ARMCO iron disk was placed in the cell, which was then filled with E-105. The heaters were then turned on and the temperature raised from 20 C to 101 C over a period of 1 hour. No sudden changes in the ellipsometric parameter, Δ, were observed as the temperature was increased. In the second experiment, 5 percent TCP in E-105 was poured into the cell and the experiment repeated. This time, a sharp change in Δ was observed at a temperature of about 93 C indicating a sharp change in the optical constants of the substrate, brought about probably by a chemical reaction and the formation of a chemisorbed film. Another sharp change in Δ was observed at a temperature somewhere between 102 C and 135 C. More careful experimentation is needed to determine these temperatures more precisely.

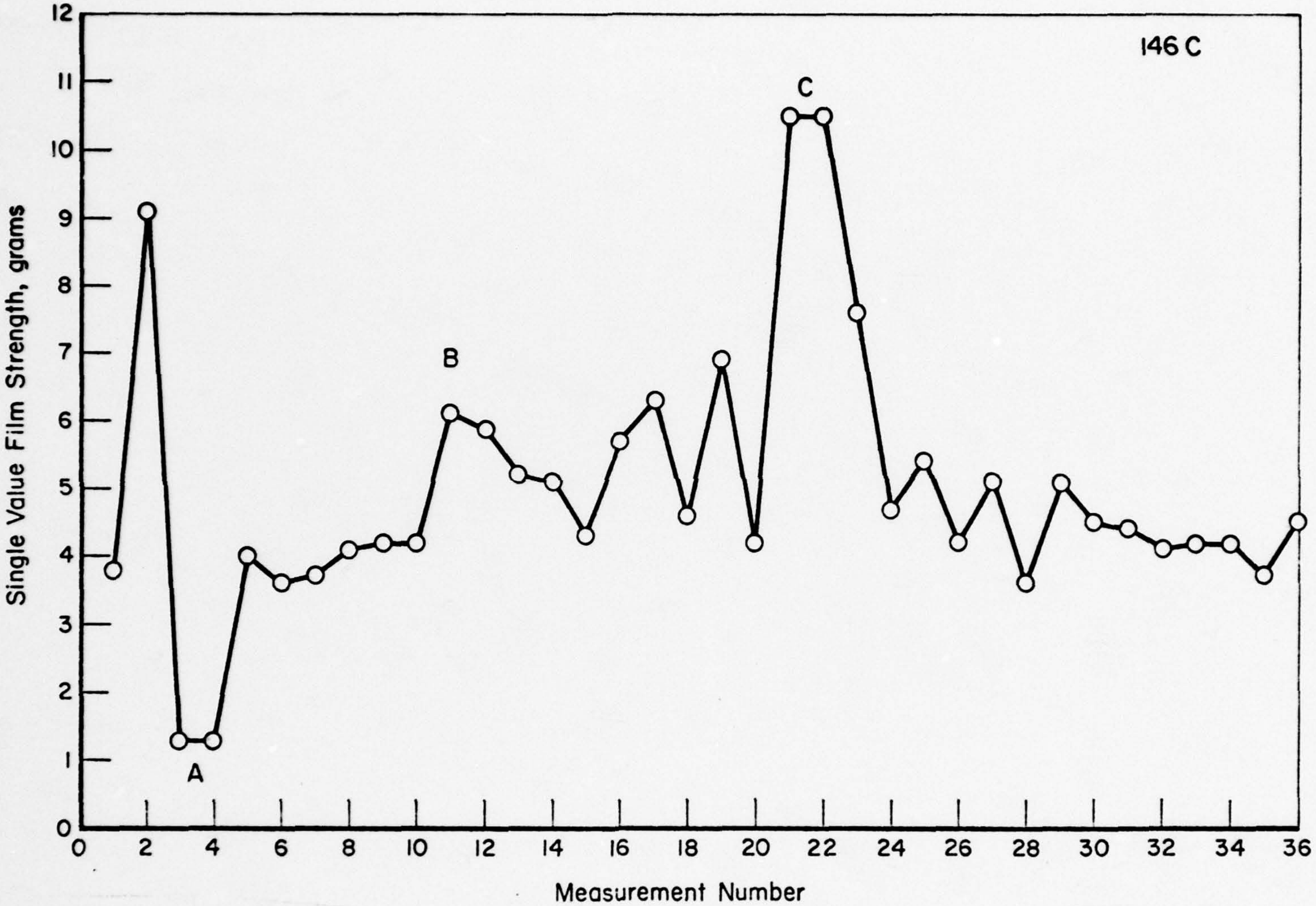

FIGURE 13. TYPICAL FILM RUPTURE STRENGTH VARIATION ACROSS SPECIMEN SURFACE FOR AN EXPERIMENT IN AN ARGON ENVIRONMENT

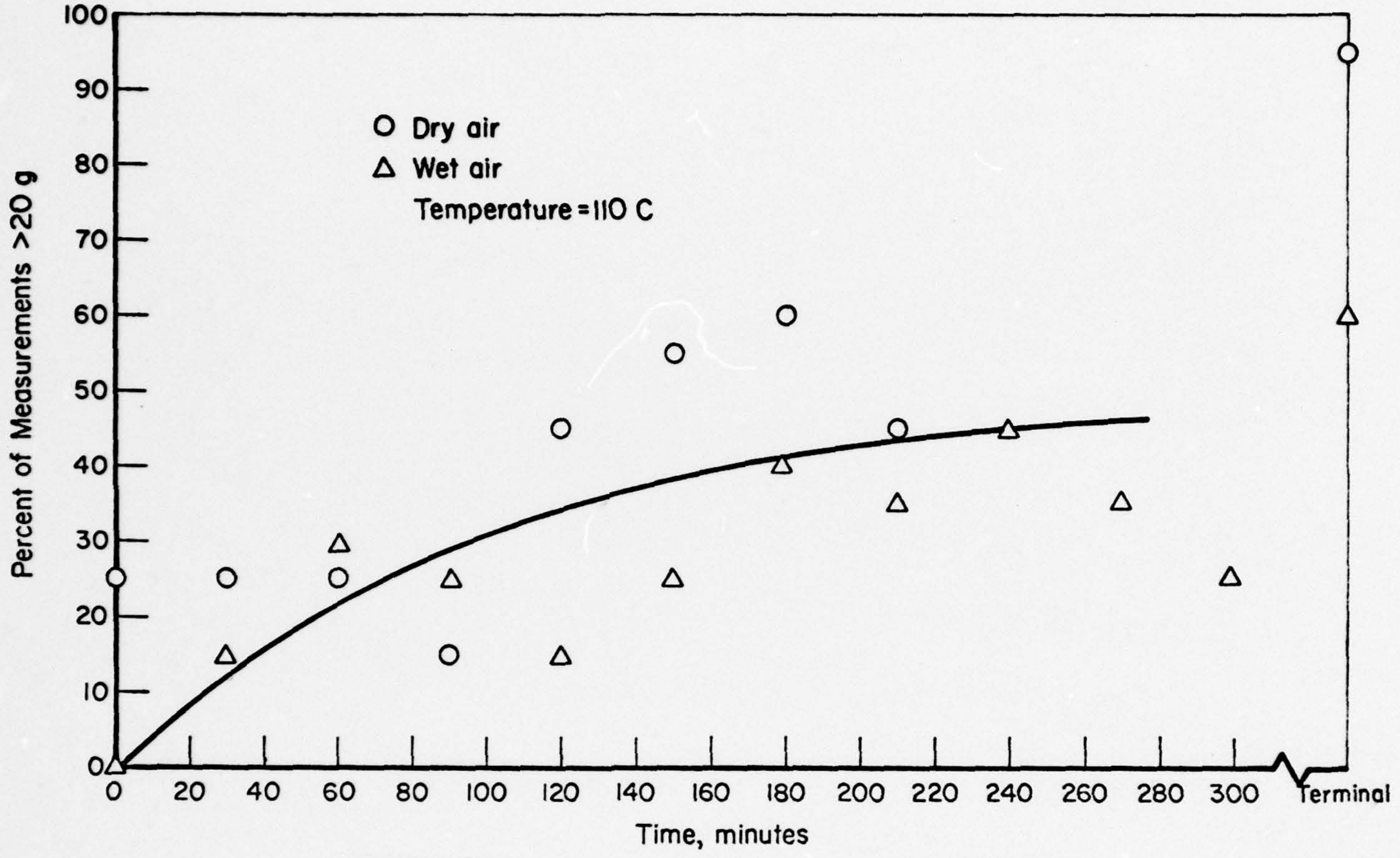

FIGURE 14. RATE OF INCREASE IN PERCENTAGE OF HIGH-STRENGTH POINTS FOR E-105 + 5 PERCENT TCP FILMS IN AIR ENVIRONMENTS (Compare with Figure 15.)

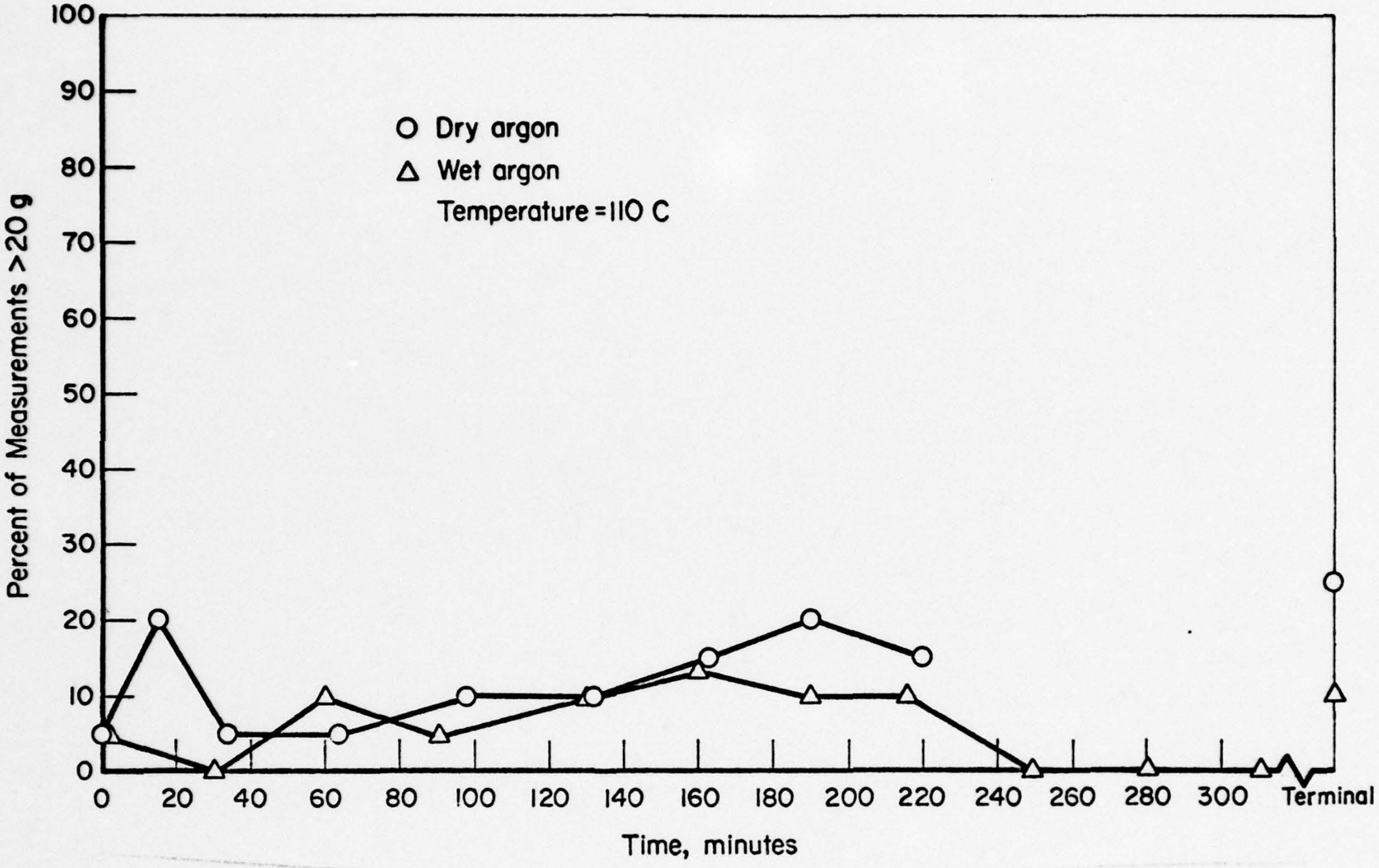

FIGURE 15. UNIFORMITY IN THE PROPORTION OF HIGH-STRENGTH POINTS FOR E-105 + 5 PERCENT TCP FILMS IN ARGON ENVIRONMENTS (Compare with Figure 14.)

DISCUSSION

In the past year, we have made considerable progress in the experimental investigation of the effects of waterand oxygen on the penetration strength of boundary films. The apparatus and methodology have been developed to the point where measurements can be made almost routinely under well-controlled conditions of temperature, moisture content, and oxygen content. The new apparatus has been used to perform experiments which demonstrate conclusively that, in the case of E-105 and TCP solutions of E-105, oxygen is essential for the formation of strong boundary films and that water inhibits the formation of such films.

In a previous report, we attempted to explain the temperature effects on strength of films formed in laboratory air (circa 50 percent relative humidity) by invoking the hydrolysis of the diester into ethylhexyl alcohol, the monoester, and sebacic acid. However, the new data, which show a retarding effect of water on film strength, seem to invalidate this reaction mechanism on the basis that the presence of water should enhance rather than retard the hydrolysis process. An alternative explanation of both the temperature behavior and the effects of water as a retardant is that all strong interactions needed to form mechanically strong boundary films occur (or are at least nucleated) at reactive surface sites and the ester, TCP, and water compete for such sites. Water must win this competition until the temperature reaches about 100 C at which point either the TCP or the ester competes more favorably.

Without better knowledge of the surface chemistry, it is difficult to determine the role of oxygen in promoting the growth of strong boundary films. However, for the purpose of defining further experimental investigations, it is desirable to adopt working hypotheses with respect to mechanism.

Two possible mechanisms forthe role of O_2 in the formation of these films come to mind.

(1) A two-step process wherein the TCP molecule either reacts with or is absorbed on the $Fe\text{-}Fe(O)_x$ surface to form an essentially "organic" film. This film is then attacked by O_2 and converted to an "inorganic" phosphate with the splitting out of the cresyl substituants.

(2) A one-step process involving the direct and parallel reactions of TCP and O_2 at various sites on the $Fe\text{-}Fe(O)_x$ surface. This mechanism would lead to a heterogeneous composite film.

At present, the only evidence supporting the one-step process is the observation that films formed in the absence of O_2 tend to be weak and uniform as compared to these formed in air.

The two-step hypothesis has several attractive features that, in general, explain more of the data than is possible with the one-step process. Perhaps the strongest evidence for the two-step mechanism is seen in Figure 12, where the introduction of air brought about a fairly rapid increase in the strength of a film formed in argon. Further, the rate of conversion of the weak film formed in argon is comparable to the rate of formation of an air-formed film at the same temperature.

The relative weakness of the film formed in the absence of air, the so-called organic film, may be due to a low film density resulting from steric effects. The bulky cresyl groups on the TCP will prevent any close packing at the TCP molecules on the substrate surface and can block potentially active surface sites. The subsequent reaction with oxygen, splitting out the cresyl groups and probably producing a phosphate molecule will expose more surface to TCP attack with the result that a dense, strong film gradually forms (see Figure 12).

In the next year of the program, we plan to further investigate the mechanisms of the formation of boundary films by combining a series of film penetration strength experiments with attempts to determine more about the surface chemistry of the E-105/TCP/iron oxide/iron system. First, attempts will be made to study the bonding of TCP to the iron/iron oxide substrate by means of ESCA. Measurements of the chemical shift of the energies of the electrons emitted from the phosphorus may tell us if the phosphorus is present in an adsorbed organic compound or an adsorbed inorganic compound. Fourier Transform Infrared Spectroscopy will also be used to study the bonding between ester and substrate and TCP and substrate. Both attenuated total internal reflection or external reflection spectroscopy can be utilized.

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APPENDIX A

DATA FROM A TYPICAL EXPERIMENT RUN IN WET AIR WITH E-105 + 5 PERCENT TCP

TABLE A-1. DATA FROM A TYPICAL EXPERIMENT RUN IN WET AIR WITH E-105 + 5 PERCENT TCP

Time of Day	0945	1000	1030	1045	1100	1130	1200	1230	1330	1400	1430	1500	1530
Elapsed Time					0 min	30 min	60 min	90 min	150 min	180 min	210 min	240 min	
Plate Temperature	87 F	87 F	200 F	230 F	262 F	265 F	266 F	267 F	266 F	265 F	264 F	265 F	130 F
	0	.7	1.2	1.5	0	32.4	.6	>130	.6	.9			
	-.3	.9	.6	15.2	0	15.8	>130	10.6	0	>130	>130	>130	>130
	+.5	.7	0	1.2	>130	-.7	-.4	>130	.1	-.3	>130	-.5	>130
	0	1.0	0	>130	1.3	>130	0	0	-.6	>130	.4	-.4	>130
	.1	.9	117	0	.2	>130	0	0	>130	10.4	>130	>130	>130
	24.5	5.7	0	0	.3	>130	0	>130	0	-.4	-.8	11.7	>130
	0	1.0	.2	0	.3	42.7	2.5	20.5	>130	-.7	>130	-.4	>130
	.1	.9	.4	67.0	121	0	-.8	20.3	>130	-.9	-1.1	>130	>130
	23.4	.8	.3	27.1	>130	70.6	0	0	>130	>130	1.6	>130	>130
	.1	.8	.3	0	.2	>130	-.8	-.3	>130	>130	17.2	>130	>130
	30.8	.9	.3	>130	.2	>130	>130	51.4	0	8.4	-1.1	-.6	>130
	87.2	.8	.4	0	0	>130	>130	>130	5.1	>130	.2	-.5	>130
	14.2	.8	.4	0	.5	-.6	-.4	0	0	-.8	>130	>130	>130
	115.2	.9	.3	0	.4	-.4	>130	-.4	0	>130	>130	-.5	>130
	55.2	.8	.3	>130	.4	-.9	-.3	0	27.7	>130	>130	-.4	41.1
	77.0	.8	.3	0	>130	-.8	20.2	-.4	0	1.1	>130	-.3	>130
	.1	.8	.2	.1	.3	0	>130	>130	>130	4.8	0	29.7	>130
	0	107	.3	>130	19.7	0	0	-.5	0	72	.1	>130	>130
	.1	67	>130	7.7	.4	>130	>130	0	>130	.8	17.0	-.4	>130
	.2	.6	.2	0	.3	.3	>130	>130	>130	>130	.3	0	>130
Average		10	13	32	27	54	47	44	55	50	54	54	
	(Dry)	(Oil Introduced)											