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TECHNICAL NOTE 2940

EFFECT OF HIGH BULK TEMPERATURES ON BOUNDARY LUBRICATION

OF STEEL SURFACES BY SYNTHETIC FLUIDS

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SUMMARY

High operating temperatures of new and projected turbine engines require that synthetic fluids be used as lubricants, because these fluids have better thermal stability and viscosity-temperature characteristics than petroleum oils have. An experimental study was conducted to learn the effect of high lubricant bulk temperatures on the boundary lubricating effectiveness of various types of synthetic fluid.

In general, under the conditions of the experiments described herein, the upper limit of temperature for effective lubrication was greater for synthetic lubricants (other than the silicone types studied) than for a petroleum lubricant of similar viscosity at 100° F. The experimental results tend to substantiate the hypothesis that lubrication with esters (and possibly other fluids) results from formation of a chemisorbed metal soap film by free acids in the lubricant. Since oxide films are important to both soap formation and to lubrication, the lubrication-failure mechanisms may be (1) failure of the soap film (by melting or decomposition), or (2) failure of the lubricant to maintain the metal soap or oxide films, or both, on the surface. It appears that bulk-fluid failure temperature is limited by either of these lubrication-failure mechanisms through the effect of temperature on thermal stability of the bulk fluid. Thermal stability can be associated with viscosity grade within a given class; however, no correlation could be made between temperature at which lubrication failure occurred and the viscosity at the failure temperature for the various fluids. At temperatures up to its decomposition point, a silicate ester showed more promise than the other lubricants studied. The phosphonate esters decompose at high temperatures to form products that are corrosive to steel but which prevent complete lubrication failure.

INTRODUCTION

As discussed in detail in references 1 to 6, future demands in gas-turbine engines for aircraft will require higher operating temperatures

than those encountered at present, and synthetic lubricants seem to show the most promise for operation at those temperatures. The transition from petroleum to synthetic lubricants is being accomplished gradually, but a great deal of information is required before satisfactory predictions can be made as to the maximum operating temperatures and conditions under which these synthetics can be used.

While some data on the friction properties under boundary lubricating conditions of synthetic lubricants are available (refs. 1, 7, 8, and 9), an important factor, which has not received much attention, is the effect of higher temperatures on the boundary lubricating characteristics of these fluids. Some data showing the effect of temperature on boundary lubrication with films of polar organic compounds (nonsynthetic lubricants) are reported in reference 10. A fundamental evaluation of the effect of temperature and the mechanisms by which the synthetic fluids lubricate would therefore be worthwhile. In order to obtain a partial answer to these problems, a study was made at the NACA Lewis laboratory to determine the boundary friction characteristics of steel specimens lubricated at temperatures up to about 600° F by several classes of lubricants. Attempts were made to relate the results to the possibility of a chemical reaction between the lubricant and the steel surface which results in the formation of low shear strength films.

This investigation was performed with a kinetic-friction apparatus having a hemispherical, hardened steel specimen sliding on a rotating mild-steel disk with both specimens submerged in the fluid under investigation. Experiments were conducted with various petroleum and synthetic fluids at a sliding velocity of 120 feet per minute with an initial Hertz surface stress of 149,000 pounds per square inch. The petroleum oils used included grade 1010 turbine oil, a pure hydrocarbon (cetane), and cetane with stearic acid as an additive. The synthetic fluids included the following classes of compounds: diesters, polyalkylene glycols, phosphonates, silicates, a dimethyl polysiloxane polymer, and a silicone-diester blend.

APPARATUS AND PROCEDURE

Friction apparatus. - The apparatus used is described in reference 9 and is shown schematically in figure 1. The basic elements are the rotating mild-steel disk specimen (hardness, Rockwell A-50; $2\frac{1}{2}$-in. diam.) and the cylindrical, hardened (hardness, Rockwell C-60), SAE 1095 steel rider specimen with a hemispherical (3/16-in. rad.) contact tip. The rotating specimen is driven through a belt system by an electric motor coupled with a variable-speed power-transmission unit. Loading is obtained by the use of dead weights to apply a force through the pulley system shown in figure 1. The load used in this investigation was 1000 grams (initial Hertz surface stress, 149,000 psi). The friction

force was measured by means of four strain gages mounted on a copper-beryllium dynamometer ring, and the readings were obtained from an indicating-type calibrated potentiometer. The friction coefficient μ is the ratio of friction force to applied load and was generally reproducible to within ± 0.02.

The general method of finishing both specimens included rotation in a drill press while the surface was rubbed with successive grades of abrasive cloth. The disks were finished with grade 1/2 polishing cloth, which left uniform circumferential finishing marks. The disks had a surface roughness of approximately 30 rms as measured with a profilometer. The rider specimens were finished with grade 3/0 emery paper. Prior to use, the specimens were cleaned by the following sequence of operations: soaking and wiping in naphtha, wiping with clean cloths saturated with an acetone-benzene solution, scrubbing with moist levigated alumina powder, rinsing under tap water to remove the alumina, testing for cleanliness by the ability of water to wet the surface, and removing the water by successive immersion and rinsing with redistilled acetone. In most cases, the specimens were used immediately after cleaning; in some cases, however, they were stored in a laboratory desiccator for several hours before use.

The experimental fluids and some of their properties are listed in table I. In the experiments, the fluids were contained in a pyrex beaker which was heated directly on a hot plate as shown in figure 1. Temperatures were measured by means of an iron-constantan thermocouple (contained in a stainless-steel sheath) immersed in the fluid and the readings obtained by a recording potentiometer. The accuracy of the temperature values is $\pm 5^\circ$ F. The temperature-failure points were reproducible to within $\pm 15^\circ$ F.

Experimental procedure. - For each test, 440 cubic centimeters of fluid and a new set of specimens were used. The apparatus was started simultaneously with the application of heat, and friction readings were taken at 25° C (45° F) intervals or more often if necessary. The average time required to raise the temperature of the fluid from 100° to 500° F was 55 minutes and did not vary by more than 5 minutes for any fluid tested. Lubrication failure was easily determined during the experiment as an increase in, or very unstable, friction force and audible chatter of the sliding specimens; these points are indicated on the friction plots to be discussed. After the runs in which failure occurred, visible surface damage was observed. In experiments that were run to determine thermal instability, the polyglycols ignited and the phosphonate and silicate esters thermally decomposed to white fumes and left a gel residue.

RESULTS AND DISCUSSION

During the course of each experiment, the following observations were considered most important:

(1) Onset of instability or a marked increase in the friction force

(2) Surface failure (incipient or mass) of the sliding specimen

(3) Thermal instability of the bulk lubricant

In figure 2 are shown photomicrographs of surfaces which are considered typical of those obtained with (a) effective lubrication, (b) incipient failure, and (c) mass failure. The specimens show, respectively, (a) no evidence of surface distress, (b) slight evidence of surface welding and metal transfer, and (c) violent welding and metal transfer. Interpretation of these results is prefaced on the knowledge that because of violent agitation there is a large supply of oxygen available in the lubricants, both in these experiments and in actual turbine engines.

Preliminary wear tests, conducted with some of these lubricants, showed that either unstable friction values or an increase in the coefficient of friction was accompanied by a sharp increase in the rate of wear. Figure 3 presents data from one of a series of experiments designed to correlate wear (qualitative) with friction instability as it was encountered in most of the experiments with increasing bulk lubricant temperatures. A dial indicator was attached to the loading system in such a manner that it would measure displacement in the rider holder assembly that resulted from wear of the rider. On the basis of incremental displacement values obtained during an experiment, cumulative values of wear volume were calculated. These wear volumes are indicated in the wear curve of figure 3. No significance should be attached to absolute wear values; the trend of the curve was, however, reproducible and indicates that there is a definite relation between instability or a marked increase in friction and a marked change in the rate of wear. The preliminary data of figure 3 were obtained with a heating rate approximately one-half that utilized in the rest of the experiments reported herein in order to accentuate the wear data.

The results of the experiments described herein are presented in figures 4 to 12 and also in table II, in which are summarized the pertinent observations on each fluid with respect to failure temperature, initial and final friction coefficients, thermal instability of lubricants, and surface appearance.

Petroleum Oils

The first oil considered was a typical petroleum base stock, MIL-O-6081a (grade 1010), which is currently in use as a gas-turbine-engine lubricant. The frictional values, shown in figure 4(a), indicate sudden lubrication failure just below 300° F.

One of the generally accepted hypotheses explaining effective lubrication with petroleum involves the presence of polar contaminants (ref. 11, p. 2) and the subsequent chemisorption of these contaminants on the surface. The data of figure 4(b) and 4(c) present results of a hydrocarbon lubricant (cetane) without and with a polar material (stearic acid), respectively. These fluids were included for purposes of comparison with the grade 1010 petroleum oil of figure 4(a).

The cetane was purified by percolation through an adsorption column as described in reference 12. The occurrence of immediate, incipient surface failure and the high friction values were characteristic of pure cetane containing no polar materials. At 257° F, the surface damage became so severe that complete seizure of the specimens took place and there was no further relative sliding. Similar friction and damage trends for steel surfaces lubricated with cetane were observed in reference 12 as sliding velocity was increased (thereby increasing heat generation at the sliding surfaces).

The data for a purified sample of cetane, containing 1 percent by weight of stearic acid, are shown in figure 4(c). Failure of this fluid occurred at approximately 315° F, a value in accord with the results obtained using grade 1010 oil which suggests a similar mechanism of lubrication. The point of failure of the bulk solution of stearic acid in cetane agrees quite well with the value obtained by Bowden (ref. 10, p. 203) of about 295° F for mild-steel surfaces lubricated with thin films of stearic acid. As reference 10 points out, this temperature coincides with the softening point of the iron soap which is formed by the reaction of stearic acid with the steel surfaces. Comparison of the results obtained with petroleum oils tends to substantiate the hypothesis that lubrication, with hydrocarbons, is the result of chemical attack of the metal surfaces by fatty acids.

Diesters

The next class of compounds to be considered were the diesters. The results obtained are shown in figure 5. Di(2-ethylhexyl) sebacate (fig. 5(a)) and di(2-ethylhexyl) adipate (fig. 5(b)) gave similar results, both showing mass failure at about 500° F. The higher point of mass failure (560° F) for diisooctyl adipate (fig. 5(c)) is somewhat surprising. It is also interesting to note that previous runs made with this compound at high sliding velocities (ref. 1) have shown that it also possesses slightly better properties than the other diesters in this respect. The higher failure temperature might be attributed to the better oxidation resistance of the diisooctyl adipate as compared with di(2-ethylhexyl) adipate, since the structure of the alcohol group exerts a considerable influence on the relative rates of oxidation of the diesters (ref. 13).

One lubricant that was compounded on the basis of the requirements stated in military specification MIL-L-7808 is included in this study. This lubricant is a blend of di(2-ethylhexyl) sebacate with 0.5 percent phenothiazine as an oxidation inhibitor, 5 percent tricresyl phosphate as an antiwear additive, approximately 4 percent methacrylate polymer viscosity-index improver, and 0.05 percent antifoam silicone oil. The results on the compounded diester lubricant (fig. 5(d)) were better than the base stock, di(2-ethylhexyl) sebacate, but were not significantly different from the diisooctyl adipate in final point of failure; however, the onset of incipient failure, as shown by a gradual rise in friction and instability of friction values, was appreciably delayed.

Separate solutions of 5 percent tricresyl phosphate in di(2-ethyl-hexyl) sebacate, 0.5 percent phenothiazine in di(2-ethylhexyl) sebacate, and 3.8 percent methacrylate polymer viscosity-index improver in di(2-ethylhexyl) sebacate were prepared, and the results are shown in figure 6. These results indicate that the increased lubricating effective-ness of the compounded diester over that of the di(2-ethylhexyl) sebacate (fig. 6(a)) at higher temperatures represents a partial lubrication con-tribution by the tricresyl phosphate (fig. 6(c)) and is not dependent on the presence of the oxidation inhibitor (fig. 6(b)) or the viscosity-index improver (fig. 6(d)). The curves show that instability starts at the same temperature for all except the solution of tricresyl phosphate in di(2-ethylhexyl) sebacate.

There are two possible explanations for the lubricating effective-ness of diesters at high temperatures: (1) physical adsorption and (2) chemisorption. Physical adsorption is considered an inadequate explanation for two reasons: First, the diesters do not have as strong a dipole moment as do many other compounds such as stearic acid; and second, at these temperatures it would be impossible to maintain a closely packed oriented film because of thermal agitation of the molecules. The chemisorption hypothesis suggested for petroleum is considered to be applicable also for diesters. Minute amounts of free fatty acid and alcohol are formed from decomposition of diesters by hydrolysis (ref. 10, p. 215) and probably also by high temperatures. This formation could be followed, as in the case of stearic acid, by a reaction between the free acid and the metallic surface to form a metallic soap film, which would provide effective lubrication. This hypothesis was supported by experi-ments reported in reference 1 showing that a diester would not lubricate nonreactive surfaces. The data of reference 14 further support this viewpoint in showing definite chemical attack of steel surfaces by esters; these studies were made by means of radioactive tracer methods. To further establish the validity of this hypothesis and to resolve its application to lubrication at high temperatures, the iron soap of sebacic acid was studied.

Since Bowden and Tabor (ref. 10) have previously shown that the tem-perature failure point of iron stearate films corresponds to the softening

point of this soap, an attempt was made to apply this criterion to the
iron sebacate soap. When a small amount of the soap powder was heated
on a melting-point apparatus under microscopic observation, decomposition
was detected at temperatures above 446° F; however, no apparent soften-
ing or melting point was detected. There was no visible change in
appearance of the samples up to 446° F. At 446° F the powder began to
turn slightly darker, and at 500° F complete decomposition by charring
had taken place. This powder was in bulk form, and oxidation of a thin
film could be expected to occur at somewhat lower temperatures. There-
fore, the trend of the friction curve for di(2-ethylhexyl) sebacate
above 400° F, shown in figure 5(a), could be related to the decomposition
of iron sebacate.

References 10 (p. 211) and 15 (pp. 98-99) show that oxides are neces-
sary for the formation of metallic soap films. In these experiments, if
the iron oxide film is present the corresponding soap film would be formed
and would be effective (for lubrication) to its melting point (ref. 10,
p. 210). On breakdown of the soap film, the oxide film might become
increasingly responsible for lubrication. The type of oxide (Fe_2O_3 or
Fe_3O_4) would determine the effectiveness of lubrication under these con-
ditions. Since experiments at this laboratory have shown that heating a
mixture of stearic acid and Fe_2O_3 reduces the Fe_2O_3 to Fe_3O_4, a
similar result might be expected with the chemisorbed iron sebacate
reducing the iron oxides which are always present on steel surfaces to
Fe_3O_4. The data of reference 16 show that, at room temperature and the
sliding velocity of 120 feet per minute used in these experiments, the
friction coefficient with the Fe_3O_4 film (approx. 0.47) is appreciably
higher than the friction coefficient with an effective boundary lubricant
(approx. 0.1). This mechanism may explain the rather slow increase in
friction for the sebacate diester at temperatures above the temperature
at which the first sign of decomposition of the metallic soap appears.
At a temperature corresponding to the failure point of the oil, oxidation
of the lubricant itself probably becomes so rapid that it takes up the
available oxygen and makes it impossible for an oxide film to be main-
tained at the sliding surfaces (ref. 17), and failure would therefore
result.

Polyalkylene Glycols

Next, a series of fluids designated chemically as polyalkylene
glycols and their derivatives was run; the results are shown in figure 7.
The first fluid is water-soluble and has a viscosity of 55 SUS (8.9 cen-
tistokes) at 100° F. It showed (fig. 7(a)) unstable friction-coefficient
values above 290° F, continually failing and recovering. A final point
of failure without further recovery was not obtained for this lubricant.
The next oil was a water-insoluble polyalkylene glycol with a viscosity

of 50 SUS (7.4 centistokes) at 100° F. The results (fig. 7(b)) indicate
that it possesses better lubricating properties, at intermediate temper-
atures, than the water-soluble fluid of figure 7(a). No attempt was
made to determine whether further running at higher temperatures would
also result in partial recovery, since at these points of incipient fail-
ure, surface damage increases rapidly and nullifies any advantages which
might be obtained by partial recovery.

The next lubricant, tripropylene glycol n-butyl ether, although not
commercially represented as a lubricant, is structurally similar to the
water-soluble polyalkylene glycol of figure 7(a) and is itself water-
soluble. The results are shown in figure 7(c). These two fluids, which
have viscosities in the same range, are not markedly different in their
lubricating properties. A final point of failure was obtained (at 490° F),
however, for the fluid of figure 7(c) that probably corresponds to the
temperature of thermal decomposition; since a dense white vapor was observed
immediately before failure, and the vapor ignited spontaneously just after
the test was concluded (at 501° F). The water-soluble polyalkylene glycol
of figure 7(a), which had a slightly higher molecular weight distribu-
tion (as shown by its higher viscosity), was on the verge of decomposi-
tion when the test was stopped. The best results were obtained with a
more viscous (300 SUS) water-insoluble polymer (fig. 7(d)) that contained
an oxidation inhibitor. This lubricant is included only for the purpose
of comparison, since its high viscosity (about 18,500 centistokes at
-20° F) precludes its use in aircraft engines. The results show that
this fluid was an effective boundary lubricant to 541° F, at which tem-
perature incipient surface failure took place. This result is to be com-
pared with that for the less viscous, water-insoluble fluid of fig-
ure 7(b), which showed failure at approximately 424° F.

In figure 8 are shown the frictional values for a series of water-
soluble polyalkylene glycol fluids that vary in viscosity from 55 to
3520 SUS (8.9 to 762 centistokes) at 100° F. Although the coefficient
of friction obtained below 212° F does not differ significantly for any
member of the series, the results obtained at higher temperatures show
a definite relation to some property commonly associated with viscosity
grade. At about 290° F, the 55-SUS fluid, (fig. 8(a)) shows instability
in friction values. At 360° F, the 190-SUS fluid, (fig. 8(b)) also
shows instability. The 660-SUS fluid (fig. 8(c)) gave stable values to
437° F; and the 3520-SUS fluid (fig. 8(d)), to 501° F.

It was impossible to obtain a significant correlation of failure
temperatures with any of the commonly measured physical properties (vis-
cosity, density, and flash point) of lubricants. This point will be
discussed further in the Evaluation of Results. The increased failure
temperatures are, therefore, considered to result not from the increase
in viscosity, but rather from the increase in the average chain length
of the polymer molecule. As would be expected under conditions of extreme

boundary lubrication, the low-temperature friction values are independent of viscosity. The average chain length is therefore an important factor in lubrication by these fluids.

The polyalkylene glycols decompose thermally by cracking and oxidation of the polymer chain into a series of shorter, more volatile aldehydes and acids (ref. 18, pp. 361-366) and leave relatively slight decomposition products on the surface as compared with the "coking" of petroleum oils. These polymer molecules are made up of a chain of ether groups with the chain generally terminated by a group that is more readily oxidized than the rest of the chain. Therefore, it is speculated that the formation of mono- and di-basic acids in small amounts should occur readily under oxidizing conditions before appreciable thermal cracking of the polymer chain takes place. These acids will then react with the ferrous surfaces to form soap films that would increase the lubricating effectiveness of the bulk fluid at high temperatures. This reaction explains why the long-chain (high-viscosity) polymers are more effective at higher temperatures, since the melting point or decomposition temperature of the soap formed by a long-chain acid is much higher than that of a short-chain acid.

It was suggested in reference 1 that absorbed water might have an important effect on the lubrication mechanism of polyethers (polyalkylene glycols) and of water-soluble polyethers in particular. In the experiments discussed herein, it is probable that the role of the water in the failure mechanism has been minimized, because bulk lubricant temperatures were sufficiently high to cause evaporation of the moisture before lubrication failure occurred. Prior to lubrication failure, however, the presence of moisture could influence the formation of organic acids.

Esters of Inorganic Acids

The next class of compounds studied were esters of inorganic acids, the phosphonates and the silicates. The first fluid, dioctyl isooctene phosphonate (fig. 9(a)), showed no lubrication distress throughout the entire temperature range (to 572° F). At this temperature, the fluid refluxed violently, decomposed, and left a reddish-brown gel as a residue. The wear track showed no damage and very slight wear, but the surface of the steel specimen appeared to be etched as if by acid wherever contact with the fluid had taken place.

The next compound, dioctyl benzene phosphonate (fig. 9(b)), showed a similar thermal instability above 535° F when heated in a beaker; therefore, the friction run was terminated at 510° F. No sign of lubrication failure could be detected up to this point. The fluid was opaque when cooled to room temperature, and the steel specimens also showed the same type of etching that was observed in the previous run. Chemical

attack of the surfaces at high temperatures is apparently a logical explanation for the lubricating effectiveness of these fluids, since visual inspection of the specimens showed that considerable etching had occurred.

The two silicate esters, shown in figure 10, were the same compound without (fig. 10(a)) and with (fig. 10(b)) an oxidation inhibitor. In both cases, these fluids were reported by the manufacturer to be thermally unstable above 500° F and were therefore tested only to about 510° F. No signs of lubrication failure could be detected, and the wear track showed no surface damage and extremely slight wear, as was the case with the phosphonate esters. The presence of the oxidation inhibitor, phenyl-α-naphthylamine, showed no discernible effect on the friction results. When heated in a beaker, these fluids were found experimentally to be thermally unstable above 540° F, a result which was also independent of the presence of an oxidation inhibitor. There was no visible evidence of etching of the steel specimens used in the experiments with the silicate esters. At this time there is no explanation for the lubricating effectiveness of the silicate esters at high temperatures.

Silicones and Silicone-Diester Blends

In figure 11 is shown the friction curve for a dimethyl polysiloxane which had a viscosity of 50 centistokes at 25° C (77° F). Friction was high throughout the test, and mass surface failure and appreciable wear occurred at all temperatures.

The hypothesis has been advanced (ref. 9) that the addition of a solvent to the silicone fluid will result in improved lubricating effectiveness. In figure 12 are shown the results of adding 33 percent by volume of di(2-ethylhexyl) sebacate to a silicone fluid. A degree of incipient failure was encountered at 307° F, although no point of mass failure was observed in the experiment. Observation of the specimens indicated that, even after lubrication failure occurred, surface damage and wear were not as severe as would be the case with silicone oil alone. The results of these tests are in good agreement with the results reported in reference 9.

Evaluation of Results

In spite of the fact that the results reported herein, which are summarized in table II, are relative and apply only to the conditions of load, speed, and so forth, defined previously, the method of experimentation used herein, which limits the number of possible variables, is believed to give valid trends.

The superior lubricating properties, at high temperatures, of synthetic oils over petroleum oils are clearly demonstrated for these conditions. Distinguishing between the various synthetic fluids is not as simple. In the case of the phosphonate and silicate fluids, no lubrication failure is observed in a region approaching the point at which the lubricant itself actually decomposes. It is speculated that esters, and possibly other synthetics, lubricate because minute amounts of contaminating free acids become chemisorbed on the lubricated metals. Lubrication failure may occur by (1) failure of the chemisorbed metal soap film (by melting or decomposition), or (2) failure of the lubricant to maintain the metal soap or oxide films, or both, on the surface as the lubricant becomes thermally unstable. Thermal stability, in turn, is influenced by structural changes in the molecule (such as different alcohol groups in the diesters). For diesters (as shown by a comparison of di(2-ethylhexyl) adipate with the more stable diisooctyl adipate), introduction of more stable alcohol groups increases thermal stability as well as the temperature at which lubrication failure occurs, in spite of the fact that both esters could react with the surface to form the same metal soap. The diesters also undergo rapid pyrolysis at temperatures in the same range as the general failure points. The polyalkylene glycol fluids show no permanent failure (without recovery) up to the point at which they crack and volatilize rapidly.

In each of these cases, physical adsorption of the lubricant on the steel surface must be followed by chemical attack, since the temperatures encountered are considerably higher than the temperatures at which disorientation and desorption of physically adsorbed films would take place. These tests also show that in the region of boundary lubrication, viscosity per se is an unimportant factor. Viscosity may be merely an indication of effectiveness, since an increase in viscosity is usually accompanied by an increase in other properties such as thermal stability.

For the diesters and polyalkylene glycols, it was found that the viscosities, at the failure temperature of each individual fluid, were appreciably different. The values of viscosity at the elevated temperatures were estimated by extrapolating the measured viscosity temperature data of table I, using as a basis the data of reference 19, which cover the temperature range from -40° to 700° F. Values of density at the failure point of each individual fluid were also appreciably different, as were the failure temperatures of those fluids that had approximately the same flash points. Therefore, it is believed that the lubrication failure of these synthetic fluids cannot be related specifically either to viscosity, to density of the fluid (at the temperature of failure), or to flash point.

SUMMARY OF RESULTS

Under the conditions of the experiments described herein, the following results were observed from boundary-lubrication studies of petroleum and synthetic lubricants conducted at elevated bulk lubricant temperatures:

1. In general, synthetic lubricants (other than the silicone types studied) provide effective boundary lubrication for steel surfaces at bulk temperatures that are significantly higher than those of a petroleum lubricant of similar viscosity (at 100° F). At temperatures up to its decomposition point, a silicate ester showed the most promise in these experiments.

2. The experimental results tend to substantiate the hypothesis that effective lubrication with esters (and possibly with other synthetic fluids) results from formation of a chemisorbed metal soap by free acids in the lubricants. The iron oxide film usually present on steel surfaces also makes some contribution to lubrication. Thus, at elevated temperature, the lubrication-failure mechanisms may be (1) failure of the soap film (by melting or decomposition), or (2) failure of the lubricant to maintain the metal soap or oxide films, or both, on the surface. It appears that the bulk-fluid failure temperature is limited by either of these lubrication-failure mechanisms through the effect of temperature on thermal stability of the bulk fluid.

3. Failure of the polyalkylene glycols appeared to be associated with some characteristics (such as thermal stability) that can be related to viscosity grade. No correlation could be made, however, between the temperature at which lubrication failure occurred and the viscosity at the failure temperature for the various fluids.

4. The phosphonate esters caused excessive corrosive etching of steel specimens, but no lubrication failure was obtained at temperatures approaching those at which the fluids became thermally unstable. Silicate esters behaved in the same manner, but did not cause any visible etching of specimens.

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TABLE I. - PROPERTIES OF EXPERIMENTAL FLUIDS

Fluid	Viscosity, centistokes, at -				A.S.T.M. pour point, °F	C.O.C. flash point, °F	C.O.C. fire point, °F
	-65° F	-40° F	100° F	210° F			
Petroleum:							
MIL-0-6081a (grade 1010)[a]	40,000	-------	9.95	2.47	< -70	300	---
Cetane[b]			[c]4.64				
Diesters:							
Di(2-ethylhexyl) adipate[a]	6,000	877	8.12	2.34	-94	395	418
Di(2-ethylhexyl) sebacate[a]	8,297	-------	12.78	3.32	< -70	440	472
Diisooctyl adipate[a]	6,962	-------	10.13	2.83	-103	408	418
Di(2-ethylhexyl) sebacate + additives[d,e,f,g]	16,000	2,700	20.8	5.3	< -75	450	475
Polyalkylene glycols (designated by viscosity at 100° F):							
Water-soluble							
42 SUS (4.9 centistokes)[g]	4,657	-------	5.07	1.42	-105	288	395
55 SUS (8.9 centistokes)[g]	------	1,800	8.9	2.4	-85	260	285
190 SUS (41 centistokes)[g]	------	30,000	41	8.2	-45	410	480
660 SUS (143 centistokes)[g]	------	[h]26,000	143	26.2	-30	430	545
3520 SUS (762 centistokes)[g]	------	-------	762	120	-20	440	545
Water-insoluble							
50 SUS (7.4 centistokes)[h,i]	4,587	905	8	2.52	< -70	270	335
300 SUS (65 centistokes)[h,i]	------	[h]18,500	65	11	-40	490	585
Phosphonates:							
Dioctyl benzene phosphonate[a]	------	[j]8,359	11.39	2.64	-87	---	---
Dioctyl isooctene phosphonate[a]	------	[j]9,003	12.22	2.77	-90	---	---
Silicates:							
Tetrakis (2-ethylhexyl) silicate[g]	1,400	260	6.8	2.4	< -100	395	450
Tetrakis (2-ethylhexyl) silicate + oxidation inhibitor[g,k]	1,400	260	6.8	2.4	< -100	395	450
Silicone:							
Dimethyl polysiloxane[a]	668	-------	39.75	15.3	< -103	520	585
Silicone-diester blend: $\frac{1}{3}$ di(2-ethylhexyl) sebacate[a,m] + $\frac{1}{3}$ dimethyl polysiloxane (50 centistokes at 77°) + $\frac{1}{3}$ dimethyl polysiloxane (10 centistokes at 77°)	------	205	15.5	5.75	< -80	---	---

[a]Measured values.

[b]Handbook data.

[c]At 70° F.

[d]4 percent methacrylate polymer.

[e]5 percent tricresyl phosphate.

[f]0.5 percent phenothiazine.

[g]Manufacturer's data.

[h]At -20° F.

[i]Contains oxidation inhibitor.

[j]At -50° F.

[k]Phenyl-α-naphthylamine (1 percent).
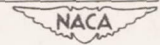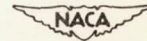
[m]Parts by volume.

TABLE II. - EFFECT OF TEMPERATURE ON LUBRICATION

	Petroleum			Uncompounded diesters			Compounded diesters			
	MIL-O-6081a (grade 1010)	Cetane	Cetane + 1 percent stearic acid	Di(2-ethylhexyl) adipate	Di(2-ethylhexyl) sebacate	Diisooctyl adipate	Di(2-ethylhexyl) sebacate + additives a,b,c[1]	Di(2-ethylhexyl) sebacate + additive a[1]	Di(2-ethylhexyl) sebacate + additive b[1]	Di(2-ethylhexyl) sebacate + additive c[1]
Temperature for:										
Incipient failure (based on instability of friction), °F	293	At all temperature below 260	316	392	410	392	505	414	None below 500	415
Mass failure (based on friction data and subsequent observation of surface welding), °F	297	260	317	496	511	559	560	490	Not run to mass failure	Not run to mass failure
Thermal instability of lubricant, °F	---	---	---	---	---	---	---	---	----------------	----------------
Friction coefficient:										
Initial	0.12	0.55	0.08	0.12	0.11	0.11	0.10	0.11	0.12	0.10
Final	>0.7	>0.8	>0.5	>0.8	>0.7	>0.8	>0.7	>0.5	0.12	0.13 - 0.16
Surface appearance of specimens after friction runs	Mass failure	Mass failure	Mass failure	Mass failure	Mass failure	Mass failure	Mass failure	Mass failure	Effective lubrication	Incipient failure
Friction data shown in figure	4(a)	4(b)	4(c)	5(b)	5(a)	5(c)	5(d)	6(d)	6(c)	6(b)

[1]Additives:
(a) Approximately 4 percent methacrylate polymer
(b) 5 percent tricresyl phosphate.
(c) 0.5 percent phenothiazine.
(d) 1 percent phenyl-α-naphthylamine.

TABLE II. - Concluded. EFFECT OF TEMPERATURE ON LUBRICATION
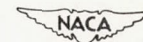
	Water-soluble polyalkylene glycols (designated by viscosity at 100° F)					Water-insoluble polyalkylene glycols (designated by viscosity at 100° F)		Phosphonates		Silicates		Silicone	Silicone-diester blend
	42 SUS (4.9 centistokes)	55 SUS (8.9 centistokes)	190 SUS (41 centistokes)	660 SUS (143 centistokes)	3520 SUS (762 centistokes)	50 SUS (7.4 centistokes)	300 SUS (65 centistokes)	Dioctyl isooctene phosphonate	Dioctyl benzene phosphonate	Tetrakis (2-ethylhexyl) silicate	Tetrakis (2-ethylhexyl) silicate + oxidation inhibitor d[1]	Dimethyl polysiloxane (50 centistokes at 25° C)	$\frac{1}{3}$ di(2-ethylhexyl) sebacate + $\frac{1}{3}$ 50-centistoke + $\frac{1}{3}$ 10-centistoke dimethyl polysiloxane
Temperature for:													
Incipient failure (based on instability of friction), °F	378	288	349	437	501	423	540	None	None	None	None	-----	307
Mass failure (based on friction data and subsequent observation of surface welding), °F	490	None	None	None	None	Complete mass failure never obtained	None	None	None	None	None	Mass failure at all temperatures	Complete mass failure never obtained
Thermal instability of lubricant, °F	490	----	----	----	----	--------	----	572	535	540	540	----	----
Friction coefficient:													
Initial	0.12	0.11	0.11	0.09	0.12	0.12	0.13	0.13	0.13	0.13	0.13	0.3	0.13
Final	>0.6	0.14	0.1 - 0.15	0.19- 0.23	0.09 - 0.12	0.34	0.34	0.11	0.13	0.14	0.14	0.44	0.21 - 0.24
Surface appearance of specimens after friction runs	Mass failure	Incipient failure	Incipient failure	Incipient failure	Incipient failure	Incipient to mass failure	Incipient failure	Effective lubrication	Effective lubrication	Effective lubrication	Effective lubrication	Mass failure	Incipient to mass failure
Friction data shown in figure	7(c)	7(a)	8(b)	8(c)	8(d)	7(b)	7(d)	9(a)	9(b)	10(a)	10(b)	11	12

[1]Additives:
(a) Approximately 4 percent methacrylate polymer.
(b) 5 percent tricresyl phosphate.
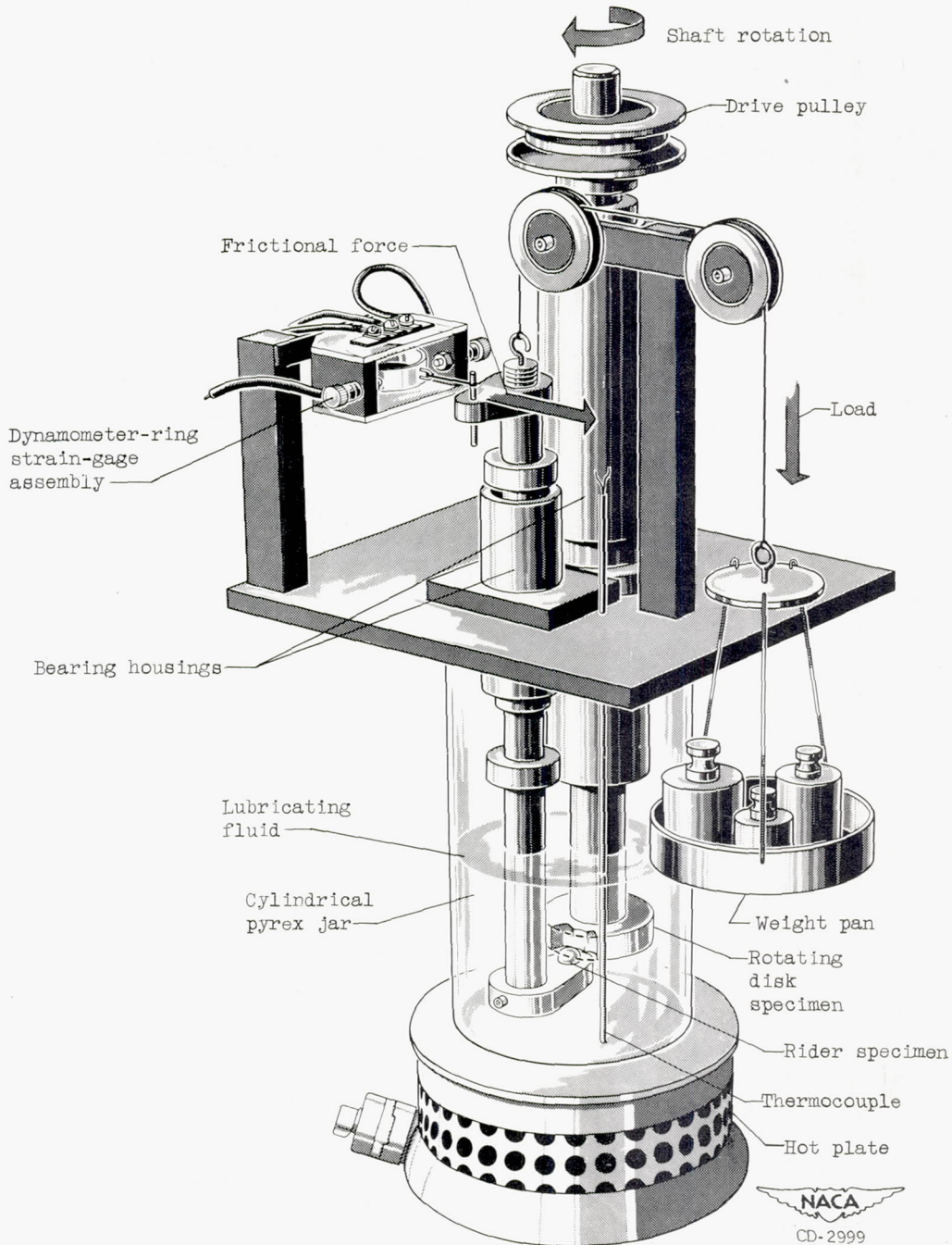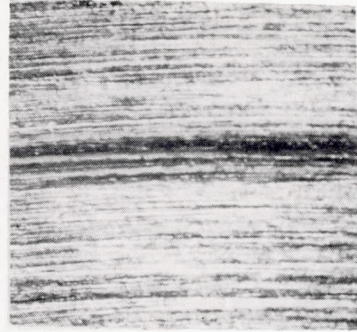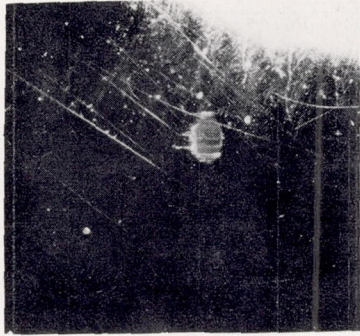(c) 0.5 percent phenothiazine.
(d) 1 percent phenyl-α-naphthylamine.
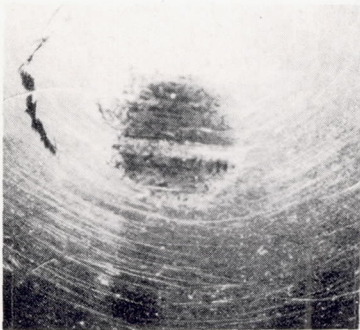
Figure 1. - Schematic diagram of friction apparatus for studying boundary lubrication by bulk lubricants.

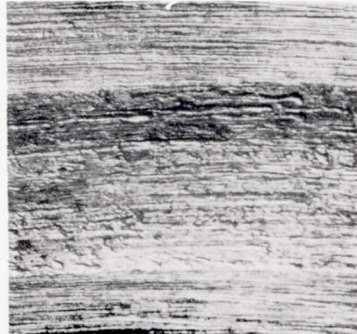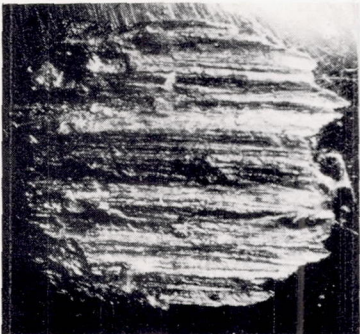Rider specimen   Disk specimen

(a) Effective lubrication.

(b) Incipient failure.

C-31912

(c) Mass failure.

Figure 2. - Photomicrographs showing typical wear areas on rider and disk specimens.
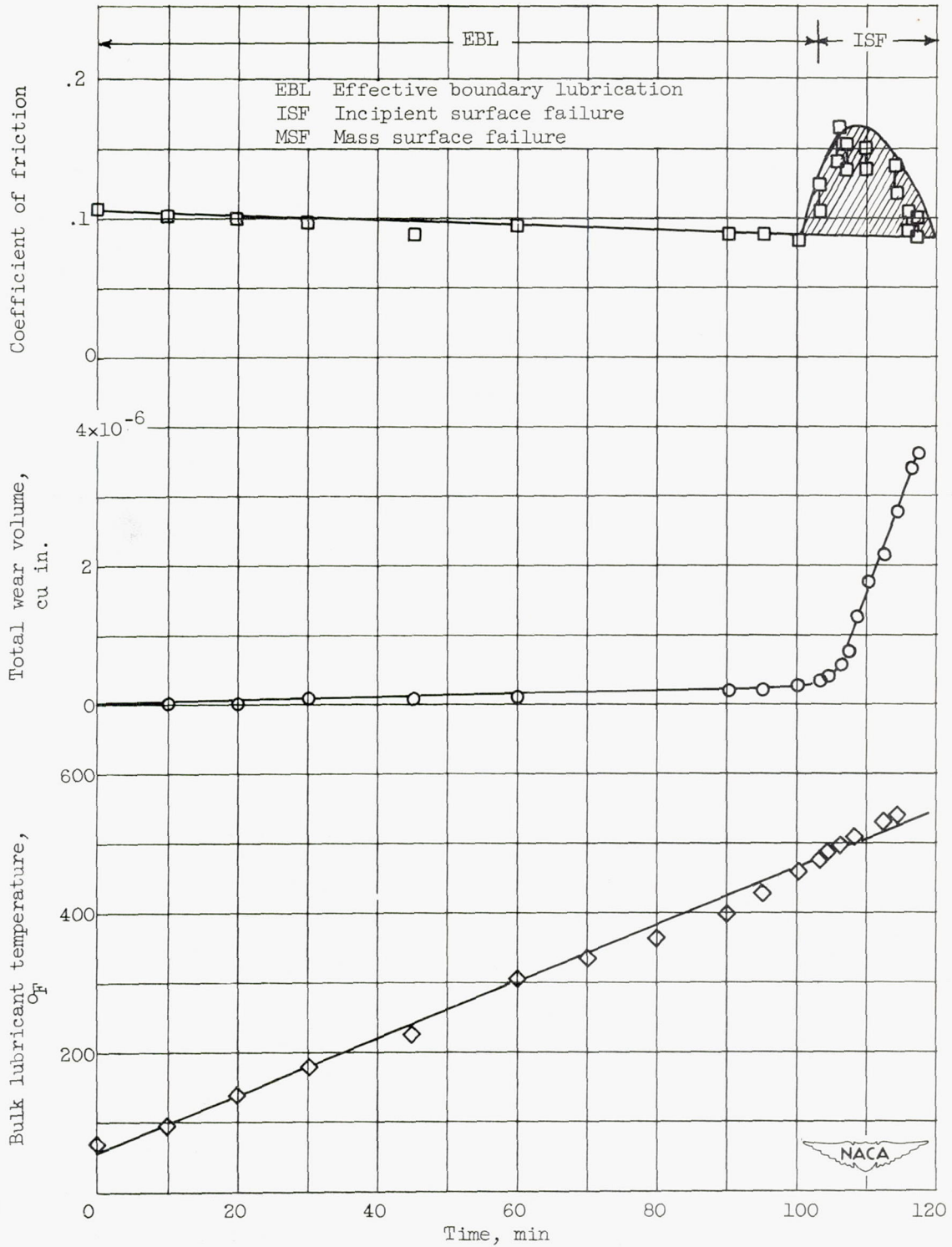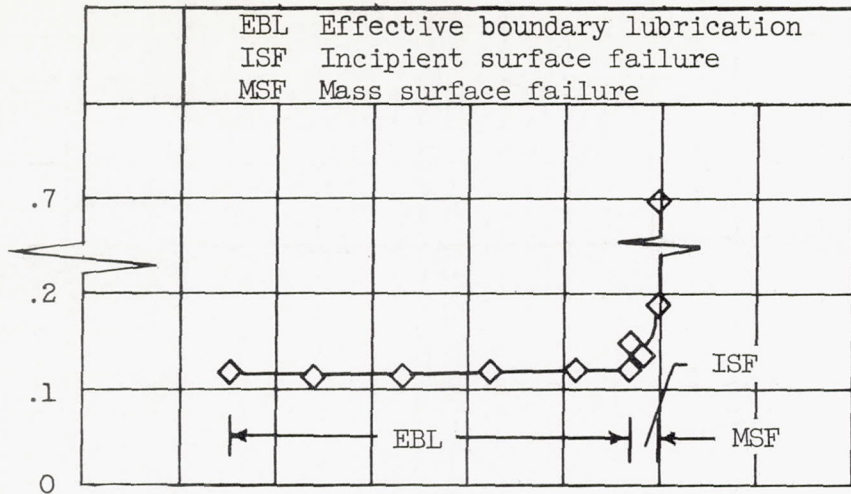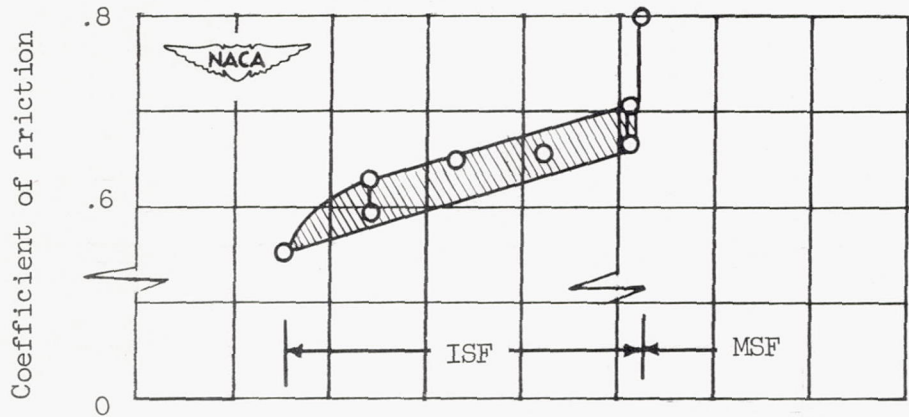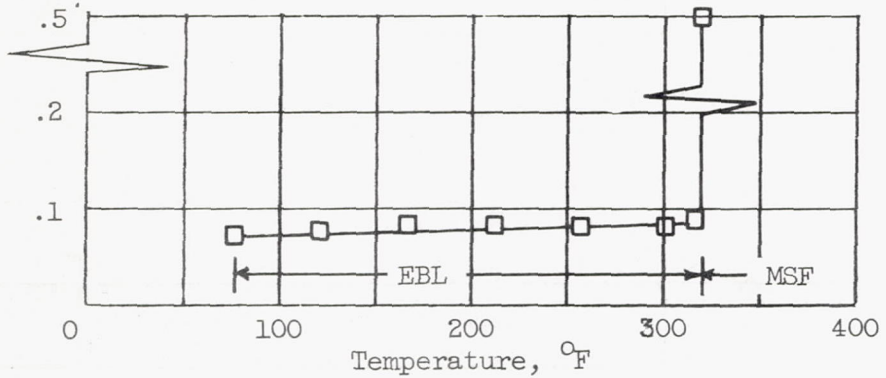X15.

Figure 3. - Relation between unstable friction (cross-hatched area) and wear for typical diester lubricant at increasing bulk temperatures. Load, 1000 grams; sliding velocity, 120 feet per minute.

(a) Grade 1010 turbine oil.

(b) Cetane.

(c) Cetane plus 1 percent stearic acid.

Figure 4. - Effect of temperature on friction of steel
specimens boundary-lubricated with hydrocarbons. Load,
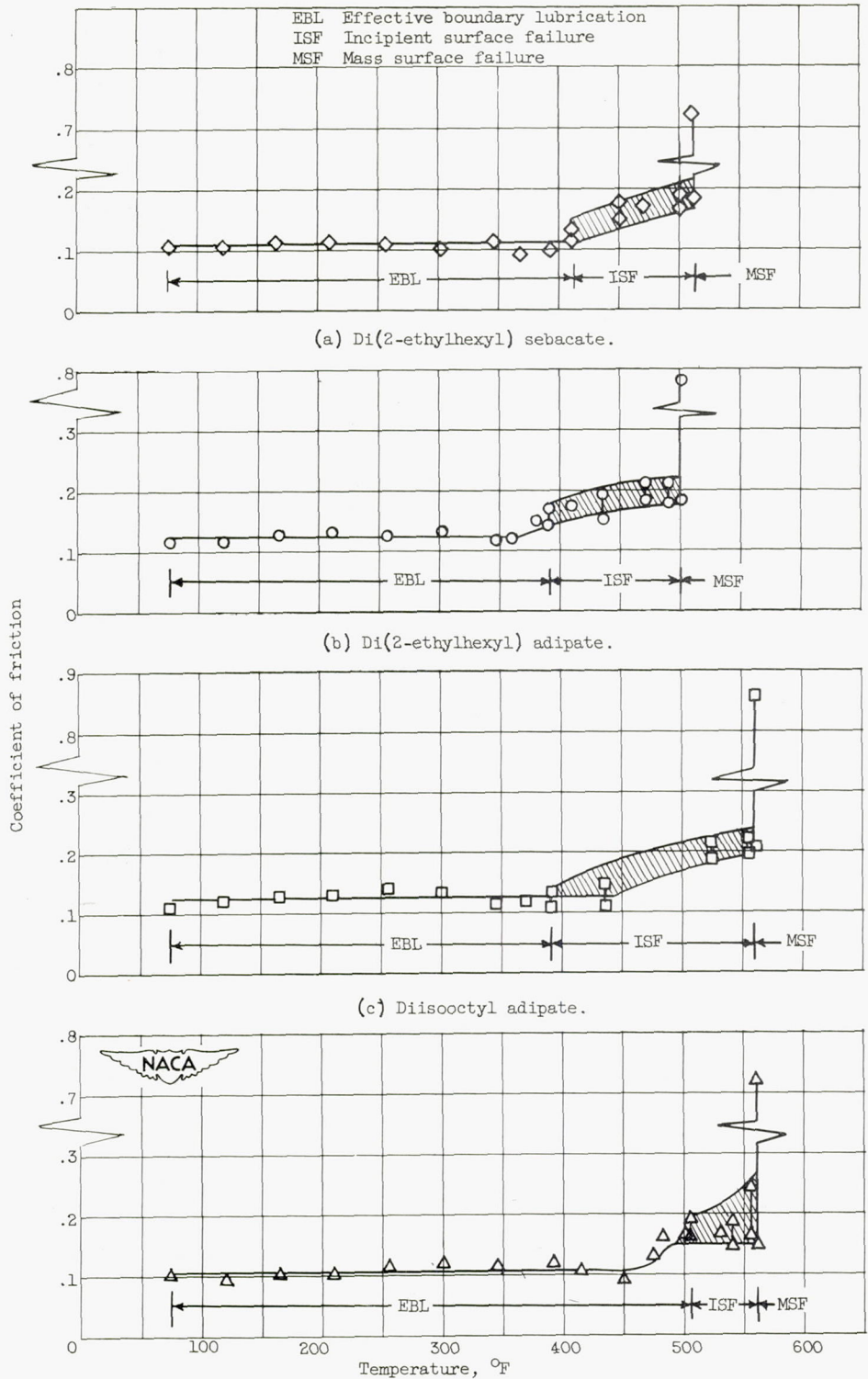1000 grams; sliding velocity, 120 feet per minute.

(a) Di(2-ethylhexyl) sebacate.

(b) Di(2-ethylhexyl) adipate.

(c) Diisooctyl adipate.

(d) Compounded diester: di(2-ethylhexyl) sebacate plus 5 percent tricresyl
    phosphate, 0.5 percent phenothiazine, and 3.8 percent methacrylate polymer.

Figure 5. - Effect of temperature on friction of steel specimens boundary-lubricated
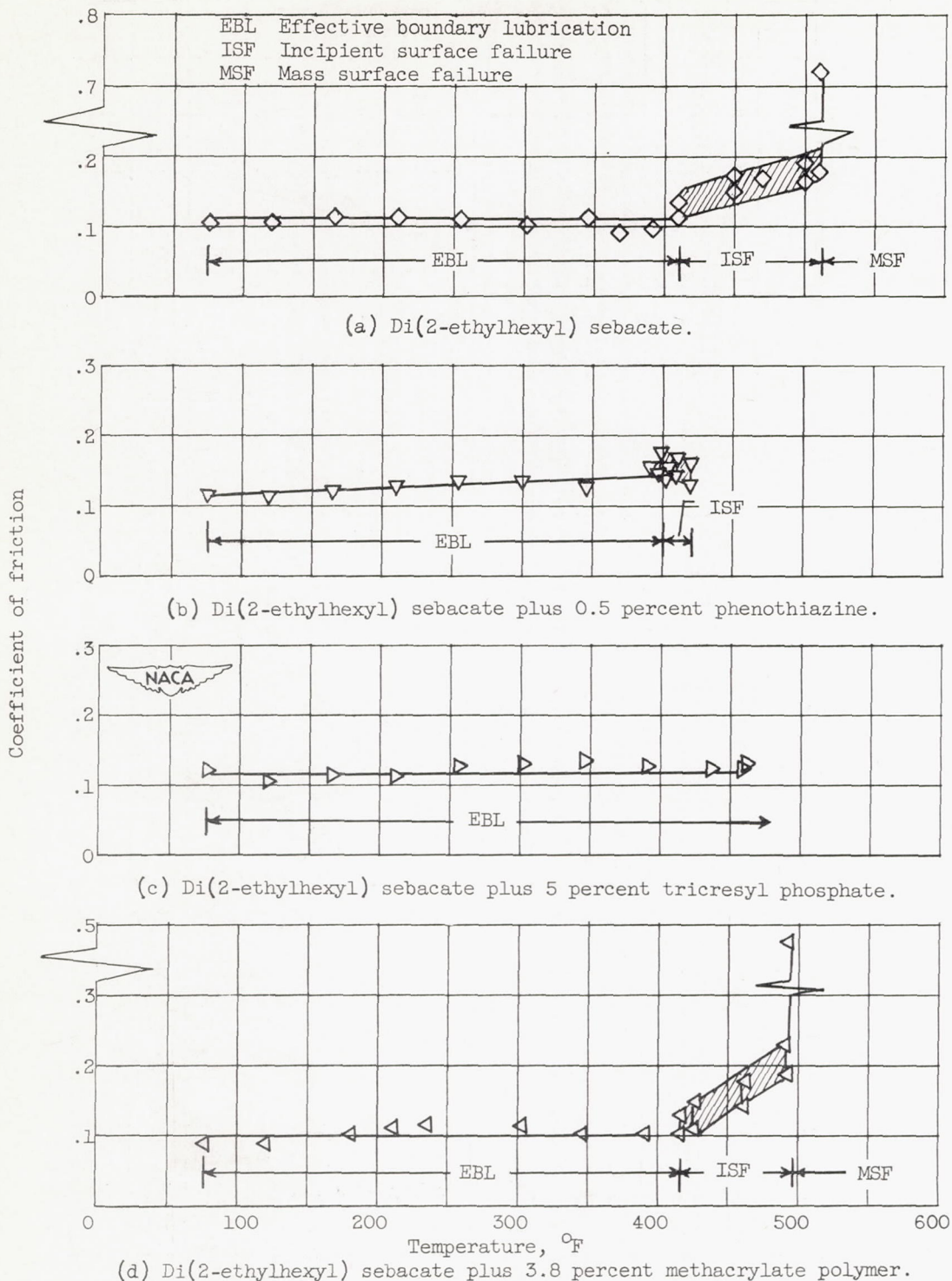   with diesters. Load, 1000 grams; sliding velocity, 120 feet per minute.

(a) Di(2-ethylhexyl) sebacate.

(b) Di(2-ethylhexyl) sebacate plus 0.5 percent phenothiazine.

(c) Di(2-ethylhexyl) sebacate plus 5 percent tricresyl phosphate.

(d) Di(2-ethylhexyl) sebacate plus 3.8 percent methacrylate polymer.

Figure 6. - Effect of temperature on friction of steel specimens boundary-
lubricated with di(2-ethylhexyl) sebacate containing various additives. Load,
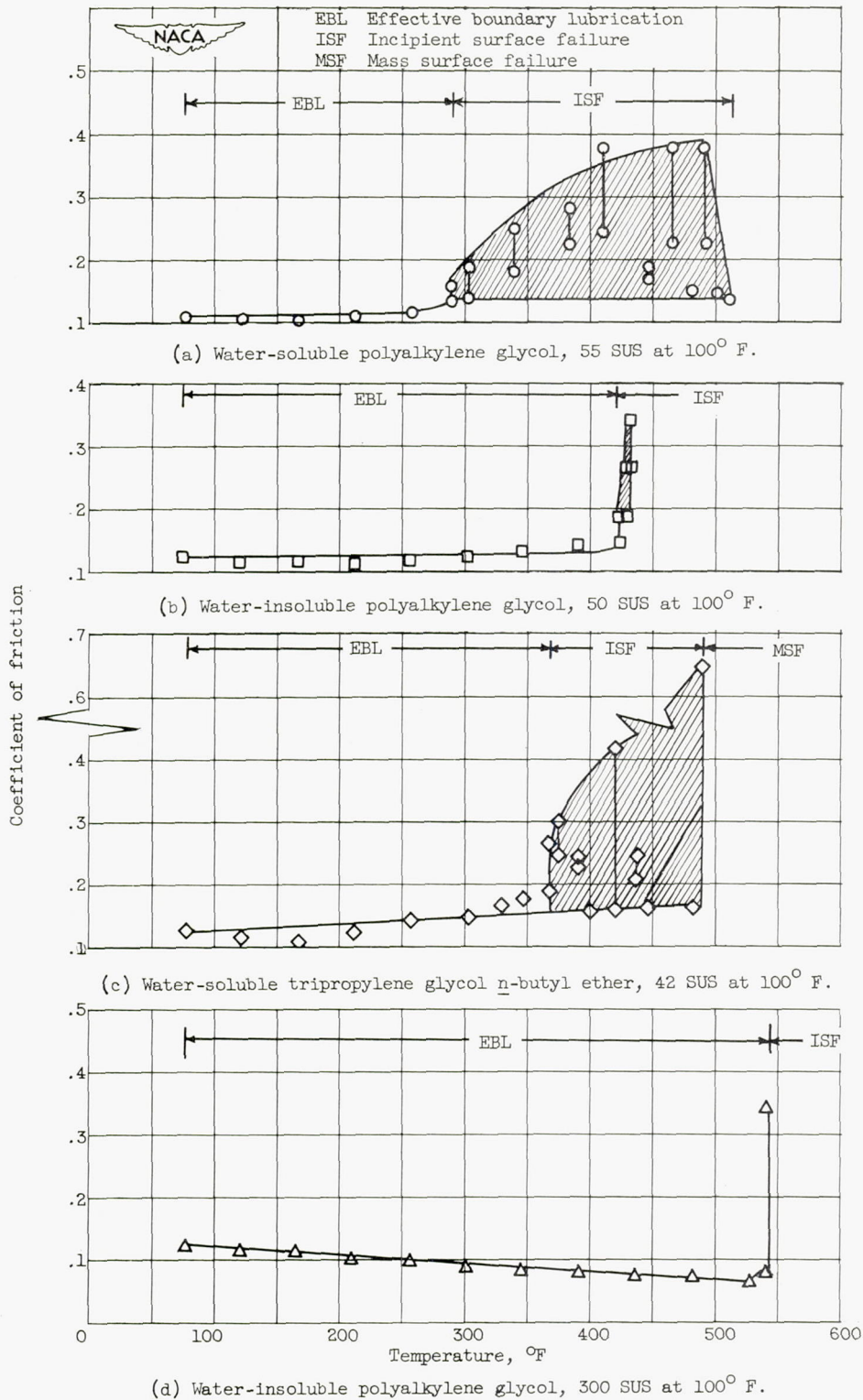1000 grams; sliding velocity, 120 feet per minute.

(a) Water-soluble polyalkylene glycol, 55 SUS at 100° F.

(b) Water-insoluble polyalkylene glycol, 50 SUS at 100° F.

(c) Water-soluble tripropylene glycol n-butyl ether, 42 SUS at 100° F.

(d) Water-insoluble polyalkylene glycol, 300 SUS at 100° F.

Figure 7. - Effect of temperature on friction of steel specimens boundary-lubricated with polyalkylene glycols. Load, 1000 grams; sliding velocity, 120 feet per minute.
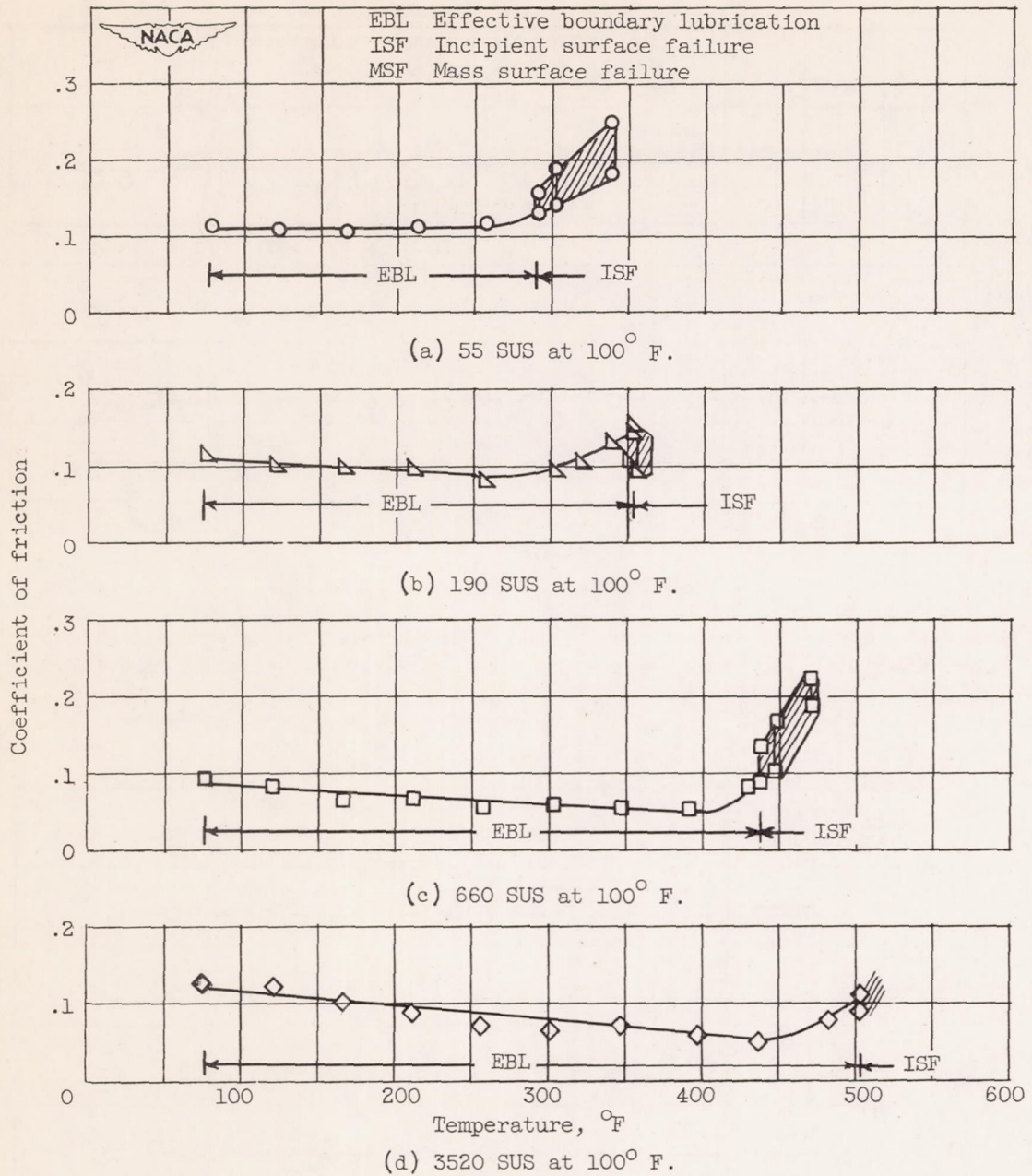
Figure 8. - Effect of temperature on friction of steel specimens boundary-lubricated with series of water-soluble polyalkylene glycol polymers having similar structures and differing only in viscosity. Load, 1000 grams; sliding velocity, 120 feet per minute.
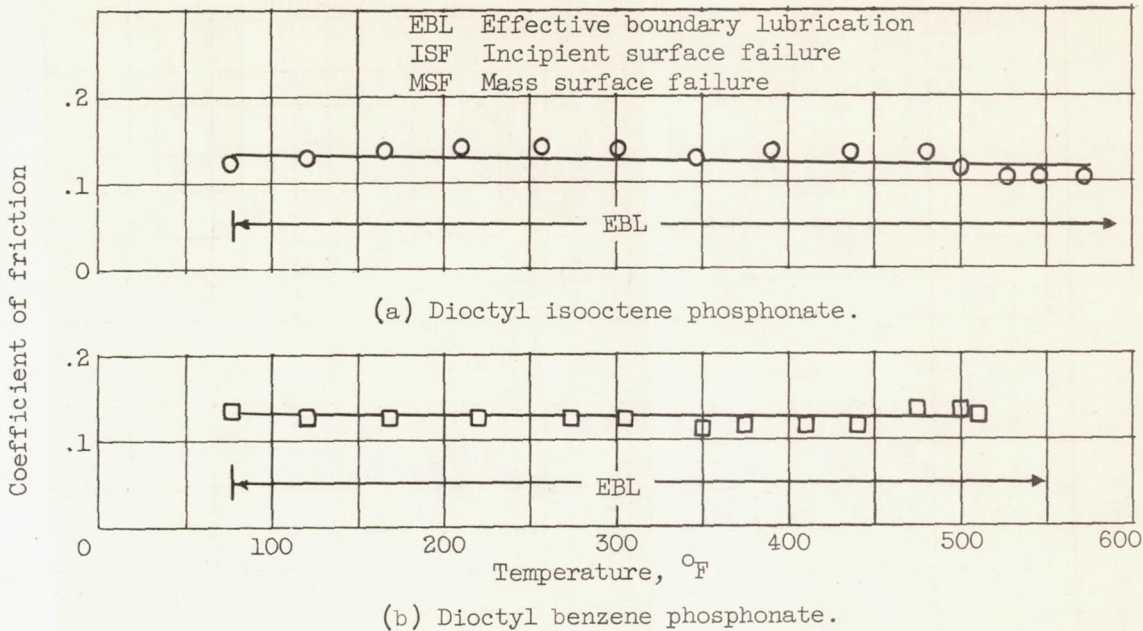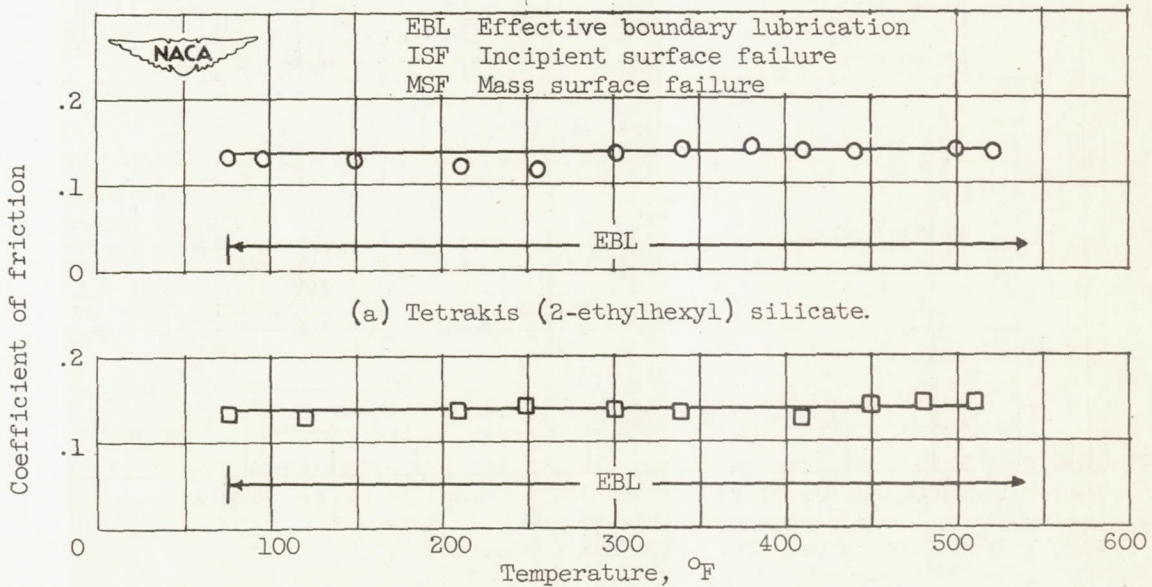
(a) Dioctyl isooctene phosphonate.

(b) Dioctyl benzene phosphonate.

Figure 9. - Effect of temperature on friction of steel specimens boundary-lubricated with phosphonate esters. Load, 1000 grams; sliding velocity, 120 feet per minute.

(a) Tetrakis (2-ethylhexyl) silicate.

(b) Tetrakis (2-ethylhexyl) silicate plus 1 percent phenyl-α-naphthylamine.

Figure 10. - Effect of temperature on friction of steel specimens boundary-lubricated with silicate ester. Load, 1000 grams; sliding velocity, 120 feet per minute.
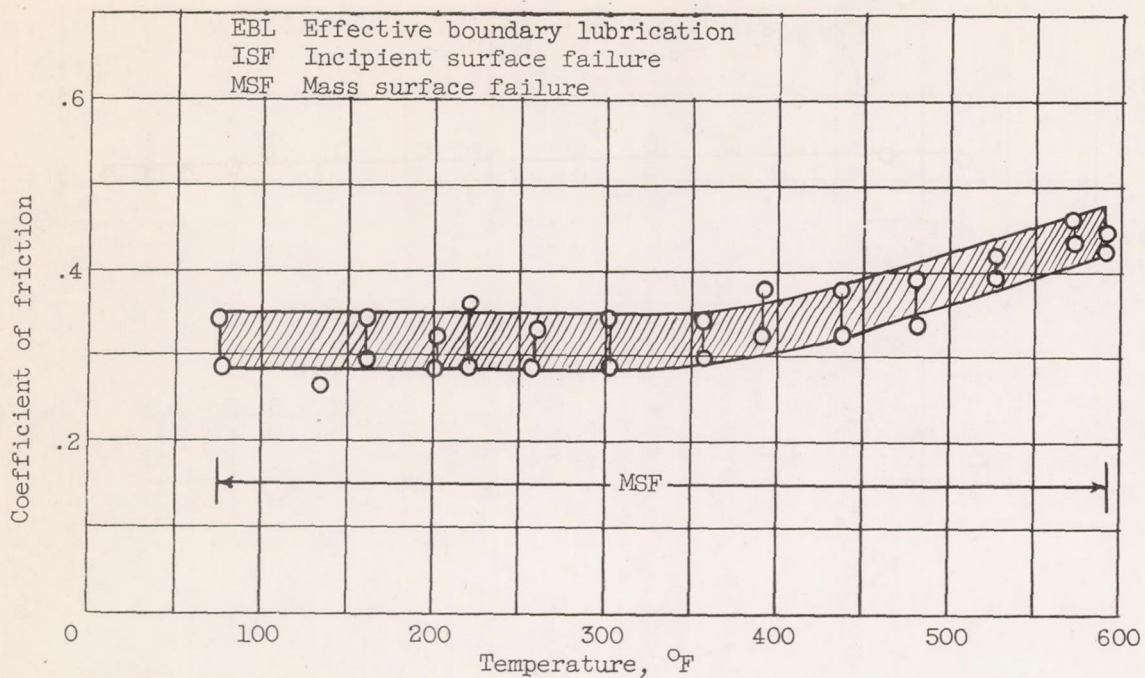
Figure 11. - Effect of temperature on friction of steel specimens boundary-
lubricated with 50-centistoke (at 25° C) silicone fluid. Load, 1000 grams;
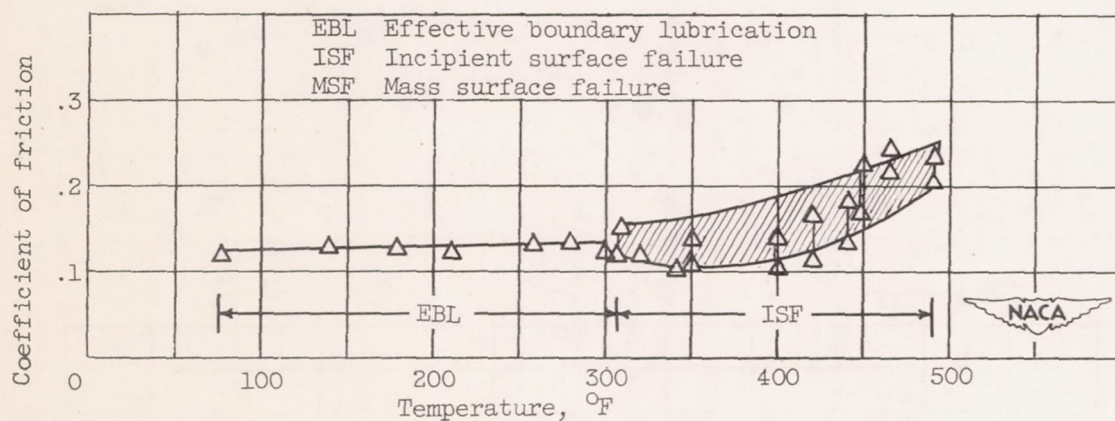sliding velocity, 120 feet per minute.

Figure 12. - Effect of temperature on friction of steel specimens
boundary-lubricated with silicone-diester blend (one-third
di(2-ethylhexyl) sebacate plus one-third silicone (50-centistoke)
plus one-third silicone (10-centistoke)).