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## TECHNICAL NOTE 2144

## EFFECT OF CHEMICAL REACTIVITY OF LUBRICANT ADDITIVES ON FRICTION AND SURFACE WELDING AT HIGH SLIDING VELOCITIES

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# EFFECT OF CHEMICAL REACTIVITY OF LUBRICANT ADDITIVES ON FRICTION AND SURFACE WELDING AT HIGH SLIDING VELOCITIES

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## SUMMARY

The effect of chemical reactivity of lubricant additives on friction at high sliding velocities was investigated. The investigation was conducted with a kinetic-friction apparatus consisting essentially of an elastically restrained spherical rider specimen sliding on a rotating steel disk lubricated with cetane (normal hexadecane) containing lubricant additives of different chemical reactivities. The lubricant additives investigated were benzyl chloride $C_6H_5CH_2Cl$, p-dichlorobenzene $C_6H_4Cl_2$, free sulfur S, benzyl disulfide $(C_6H_5CH_2)_2S_2$, and phenyl monosulfide $(C_6H_5)_2S$. The experiments were conducted over a range of sliding velocities from 75 to 7000 feet per minute and with loads from 269 to 1017 grams (initial Hertz surface stresses, 126,000 to 194,000 lb/sq in.). Supplemental surface studies were made using standard physical, chemical, and metallurgical equipment and techniques.

The data indicated that higher critical sliding velocities were obtained with additives the active atoms of which had the greatest chemical reactivity; that is, greater reactivity allowed operation at higher sliding velocities before lubrication failure occurred. The effect on critical sliding velocity of concentrations of active atoms between 1 and 10 percent was small indicating that, within the limits of the experiments, the factor of activity of the individual active atoms was of more importance than the number of such atoms available for reaction. For all additives, at velocities greater than the critical, the friction coefficient increased and surface welding occurred. Increase in load, for one concentration of sulfur atoms, decreased the critical sliding velocity. For both free sulfur and phenyl monosulfide additives, increase in initial Hertz surface stress decreased critical sliding velocity as a linear function. Such a change is to be expected because of the increased tendency toward surface welding at higher surface-contact stresses.

Rate of reaction between extreme-pressure lubricant additives and sliding surfaces was a factor of appreciable importance in establishing quality of lubrication obtained by use of additives at high sliding velocities.

## INTRODUCTION

The current trend in the selection of aircraft power-plant lubricants is to materials of low viscosity. The primary reason for this trend, as discussed in detail in reference 1, is to satisfy low-temperature operating and starting requirements. It may be expected that such usage will lead to difficulties because of low load capacities obtained with the light oils. One means of compensating for the reduced load capacity of the lighter oils is by the use of extreme-pressure lubricant additives. Among others, the authors of references 2 and 3 have summarized the work in the field of extreme-pressure lubrication. In these summaries, the generally accepted hypothesis explaining the mechanism of action of additive agents in lubrication is restated. This hypothesis involves chemical combination of the active atoms of the additive agent with the metal on the sliding surfaces to produce a protective coating. Under certain conditions, however, lubricant-additive failures have been known to occur (references 4 and 5); in these cases the additive did not perform its intended function. For example, Blok (reference 4) indicates that, under the condition of impact load on gears, viscosity is of prime importance among the oil properties that affect wear and that, in such cases,"... the viscosity of oils cannot satisfactorily be replaced by such factors as antiwelding activity... This finding has to be taken into account in the development of low viscosity oils for highly loaded gears." Another example of lubricant-additive failure is described in reference 5; in explanation, an hypothesis (which may also be applicable to the results of reference 4) is advanced that the rate of chemical reaction between surfaces and additives is a limiting factor in lubrication by extreme-pressure additives of surfaces operating at high sliding velocities. In support of this limiting-rate hypothesis, experimental evidence is presented in reference 5 for solutions of sulfur in cetane (normal hexadecane) indicating that increase in sliding velocities produced lubrication failures. The lubrication failures resulted in increased friction and in surface welding.

The velocity at which lubrication failures occur may be called a critical sliding velocity. Critical sliding velocity is defined therefore as that velocity corresponding to the conditions at which surface welding begins and at which the trend of decreasing friction

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with increasing velocity is reversed. Critical sliding velocities, such as obtained in reference 5, may possibly be obtained in practical applications, particularly in aircraft propulsion systems because of the emphasis on high speeds.

Because the available data that show the effect of sliding velocity on lubrication failure are limited (comprising principally that of reference 5), additional experimental evidence is required to substantiate the hypothesis. Inasmuch as differences in the chemical reactivity of additives should markedly affect the critical sliding velocity, investigation of additives of different reactivity should provide this additional information.

The primary object of the research reported herein, which was conducted at the NACA Lewis laboratory, is to determine, for surfaces lubricated with additives of the extreme-pressure type, whether change in chemical reactivity could appreciably change the rate of production of a protective film and thus appreciably change critical sliding velocity. A secondary object is to determine the effects on critical sliding velocity of concentration of the reactive compound and of load.

The kinetic-friction characteristics of steel specimens lubricated with cetane and with cetane containing additives of the extreme-pressure (antiweld) type were experimentally determined. The additives investigated were benzyl chloride, p-dichlorobenzene, free sulfur, benzyl disulfide, and phenyl monosulfide. Investigation was made with loads from 269 to 1017 grams (126,000 to 194,000 lb/sq in. initial Hertz surface stress) at sliding velocities up to approximately 7000 feet per minute. Friction measurements were made by an apparatus that consists basically of an elastically restrained spherical rider sliding in a spiral path on a rotating disk. The rider was made to follow a spiral path to insure that it was at all times contacting a virgin portion of the disk. The research is an extension of that reported in references 5 to 7.

## APPARATUS AND PROCEDURE

The experimental friction and wear studies were conducted with essentially the equipment described in reference 6. A diagrammatic sketch of the basic parts of the apparatus is presented in figure 1. The principal elements of the apparatus are the specimens, which are an elastically restrained spherical rider and a rotating disk. The rider is so clamped that only sliding results. The rider is loaded by weights applied along the vertical axis of the rider holder.

Friction force between the rider and the disk is measured by four strain gages mounted on a copper-beryllium dynamometer ring. The force is indicated by either a recording- or an indicating-type calibrated potentiometer; a permanent record of the force variation is obtained on movie film for subsequent analysis. The coefficient of friction $\mu_k$ is computed from the equation

$$\mu_k = \frac{F}{P}$$

where $F$ is the measured friction force and $P$ is the applied normal load.

A motor-driven radial-feed mechanism, calibrated to indicate radial position of the rider, causes the rider to traverse a spiral path on the rotating disk so that overlapping of the wear tracks is abnormal. (Overlapping occurs only when a wide track is produced as a result of surface failure.) This spiral-type motion produces a most extreme condition for lubrication by reactive compounds because there can be no cumulative effect of film formation by successive contacts of the same surface areas. The disk is mounted on a flywheel, which is supported and located by thrust and radial load bearings. The rotating disk is driven through a flexible coupling by a hydraulic motor operating under essentially constant pressure with speed adjusted by varying the flow of hydraulic fluid; this arrangement allows good speed control ($\pm 2$ percent) over a range of sliding velocities between 50 and 18,000 feet per minute. The disk and the rider are covered, permitting the preoperation atmosphere of dried air to be slightly pressurized. In these experiments, the dry air flows over the disk specimens to dry the disk surface before the liquid lubricants are applied. In order to decrease lubricant evaporation, air flow is not maintained during the experiment.

The system for drying the air for the preoperation atmosphere consists of a filter tube 48 inches long containing surgical cotton, six silica-gel drying tubes, and an 8-inch tube containing activated alumina in series. Air is supplied by the laboratory compressed-air system.

In conducting the experiments, the disk is rotated at a predetermined speed and, by means of a cam arrangement, the loaded rider is lowered onto the disk as the radial feed is started. As the rider traverses the disk, friction force is observed and recorded; disk rotative speed is determined with an electric revolution counter and a synchronized timer. The run is terminated

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by lifting the rider from the disk surface. The friction runs are obtained in a time interval of 3 seconds. The mean sliding velocity for the experiment was computed from the recorded disk rotative speed and the mean diameter of the rider path. Change in diameter of the rider path on the disk resulting from the radial travel of the rider caused a maximum deviation in sliding velocity of approximately 3 percent from the mean value. An unworn area of a rider was used in each run.

As reported in reference 6, uncontrolled variables, such as wear of the rider, natural frequency of the restraining assembly, and vibrations induced by the driving mechanism, had no appreciable effect on the accuracy of the data.

The physical and physicochemical conditions of the surfaces of the research specimens were studied before and after the sliding-friction experiments by means of surface-roughness and surface-hardness measurements as well as metallographic techniques. During the experiments, no measurable change in surface hardness occurred. Because of the mass surface welding that occurred and consequent extreme surface roughness, surface-finish measurements were insignificant.

The friction data presented are complete data from representative experiments for each lubricant-additive combination. In all but isolated cases, the limit of reproducibility in friction coefficient was $\pm 0.03$ and, in general, was considerably less.

The experiments were conducted over an approximate range of sliding velocities from 75 to 7000 feet per minute. The experiments were conducted in this range because of the general lack of information in this field at sliding velocities greater than approximately 1200 feet per minute and because the sliding velocities attained in aircraft propulsion systems are in this range or higher.

For comparison purposes, a load of 269 grams is used for most of the curves presented because the initial Hertz surface stress produced (126,000 lb/sq in.) is in the range of stresses commonly attained in aircraft-engine components that require lubrication. For example, this stress is representative of those obtained in reduction gearing and in rolling contact bearings as well as ordinary surfaces in contact under nominal loads. As discussed in more detail in reference 8, surfaces under nominal load and large apparent areas of contact can have stresses at the localized contact areas that are equal to the yield strengths (flow pressures) of the materials.

## ADDITIVES AND FRICTION SPECIMENS

The additives used in this investigation were benzyl chloride $C_6H_5CH_2Cl$, p-dichlorobenzene $C_6H_4Cl_2$, free sulfur S, and benzyl disulfide $(C_6H_5CH_2)_2S_2$, phenyl monosulfide $(C_6H_5)_2S$. These additives represent some generally employed (references 2, 9, and 10) and some that are relatively nonreactive, for comparison purposes. These compounds were of the highest chemical purity obtainable from commercial sources.

In the friction experiments reported herein, the additive compounds were mixed with cetane, purified according to the procedure given in reference 5. The desired concentration (1, 5, or 10 percent by weight) was obtained by adding to the cetane the quantity of the additive compound indicated by consideration of the proportion of sulfur (or chlorine) theoretically present in the additive. This concentration will hereinafter be called the weight concentration of sulfur (or chlorine).

The relative reactivities of the chlorine compounds, p-dichlorobenzene and benzyl chloride, are qualitatively indicated in reference 10, which indicates that "... In the case of the p-dichlorobenzene the chlorine is not labile, being attached to nuclear carbon, and this compound shows little or no E.P. [extreme pressure] properties." In comparison with the relatively low reactivity of p-dichlorobenzene, reference 10 states that "The very marked superior E.P. properties of ... benzyl chloride are due to the extreme lability of the chlorine atoms..."

The comparative reactivites of the chlorine additives, p-dichlorobenzene and benzyl chloride, are quantitatively shown in table I. In this case, the activity was determined by reacting a 10-percent-by-weight solution of each compound in white oil with an excess of iron wire in a closed ampule for 16 hours. At the end of the 16-hour period of time, a determination was made of the amount of chlorine that had reacted with the iron wire. The results of table I show that benzyl chloride was appreciably more reactive than the p-dichlorobenzene; no reaction with the iron wire of the p-dichlorobenzene could be detected even at the maximum temperature investigated (300° C).

The comparative reactivities of the sulfur additives, free sulfur, benzyl disulfide, and phenyl monosulfide were determined by reacting, with iron wire, solutions of each additive in cetane for 20 minutes at 225° C. In each case, the sulfur weight concentration was 0.5 percent. The activity of pure cetane toward iron

wire was also determined for comparison purposes. The results are presented in table II. The data, obtained as weight increases of the iron wire, indicate that free sulfur is more reactive than benzyl disulfide, which is in turn more reactive than phenyl monosulfide. The pure cetane showed no activity toward the iron wire under these conditions. Data of reference 2 relating to the reactivity of the sulfur additives, benzyl disulfide and phenyl monosulfide, when mixed in solution with SAE 90 oil and exposed to iron powder for 15 minutes at 250° C, support the results of table II. These data show that benzyl disulfide is appreciably more reactive than phenyl monosulfide.

Although table II shows an appreciable difference in reactivity between free sulfur and benzyl disulfide for a 20-minute period, unpublished data obtained at this laboratory for shorter periods of time indicated that free sulfur is only slightly more reactive than benzyl disulfide at temperatures of 204° to 225° C; the sulfur weight concentrations of these additives were 0.5 and 1.0 percent.

For the friction experiments, the lubricants were handled at all times in glassware cleaned in chromic acid - sulfuric acid cleaning solution and were deposited on the disk specimen by drops from a clean platinum dipper. After the lubricant had spread over the whole surface, the disk was rotated at the maximum speed of the experiment (approximately 2500 rpm) for 5 minutes to throw off excess lubricant and leave only a very thin film. All experiments for one disk were completed within 1 hour of deposition of the film in order to eliminate evaporation of the film as a variable. Preliminary experiments indicated that evaporation of the film was not a factor affecting reproducibility if the runs were obtained within the 1-hour period.

Preliminary experiments also indicated the effect of time on the lubricating ability of lubricants formed by adding chlorine compounds to cetane. The usual practice was to perform duplicate experiments with a given lubricant, using the same batch of lubricant solution. The elapsed time between the duplicate experiment was in the range of 2 to 4 hours, with the first experiment being completed within 1 hour after the lubricants were mixed. The data from several sets of runs showed poor reproducibility between duplicates, and the second set of data in all cases indicated lower friction values than were observed during the initial run. When time delay in the use of the lubricants was reduced by use of a new batch of lubricant solution for each run, reproducibility of the data became satisfactory. A possible explanation of this time effect may be found in the fact that chlorine atoms in hydrocarbons

in time produce polar compounds (reference 11) that improve the lubricants; apparently from these results, the formation of polar compounds in periods of time greater than 1 hour is enough to affect reproducibility adversely.

As pointed out in references 6 and 7, careful preparation of specimens was found to be the most important single requisite for success in the experiments. The disk specimens were finished and cleaned according to the detailed procedure given in reference 6. The disk surfaces were so finished as to minimize surface working and to give a uniform nondirectional surface finish with a roughness of 3 to 6 microinches rms as measured with a Profilometer. The 13-inch outside-diameter disk specimens were of normalized SAE 1020 steel, Rockwell A-50. The rider specimens used were commercial balls, 1/4-inch in diameter of SAE 1095 steel hardened to Rockwell C-60. They were not subjected to laboratory finishing operations before use but were cleaned and rinsed in 190-proof ethyl alcohol.

## RESULTS AND DISCUSSION

Data from the experiments made with various chlorine and sulfur additives for a number of concentrations, along with comparative data, are presented in figures 2 to 9. The effect of sliding velocity on the friction coefficient of specimens lubricated by pure cetane is shown in figure 2 (fig. 2 of reference 5). This curve is included for purposes of subsequent comparison with all the additive data to be presented because all the additives were mixed with cetane. Surface damage by welding occurred at all velocities for the runs with pure cetane as the lubricant.

Chlorine compounds. - The effect of sliding velocity on the friction coefficient of benzyl chloride and p-dichlorobenzene with concentration as a parameter is shown in figure 3. Figure 3(a) shows the results with benzyl chloride, figure 3(b) with p-dichlorobenzene, and figure 3(c) is a comparison of the two compounds at the three concentrations investigated.

From the data of figure 3(a), for chlorine weight concentrations of 1, 5, and 10 percent from benzyl chloride, the curves of friction coefficient show similar trends, which include characteristic break points. These break points, correspond to the critical sliding velocities as previously defined. The critical sliding velocities (based on both friction data and surface welding) are indicated on these and all subsequent

curves for which a critical sliding velocity exists. The particular shapes of these curves as well as those of figure 3(b) are based on the actual data plus additional evidence, which will be discussed in more detail later in this report.

It can be observed (fig. 3(a)) that increased concentration results in decreased friction coefficient although the effect of change of concentration from 5 to 10 percent is relatively small. The critical sliding velocities appear to be affected little by concentration change from 5 to 10 percent, although the data scatter makes it difficult to make such an observation with certainty; the curve for 1-percent weight concentration, however, has a break point at a lower sliding velocity than the higher concentrations.

The curves of the friction coefficient for chlorine weight concentrations of 1, 5, and 10 percent from p-dichlorobenzene, in figure 3(b) are of the same general form and exhibit trends similar to the curves of figure 3(a). For p-dichlorobenzene, however, the upward trend of the friction coefficient is marked. Increased concentration again results in decreased friction coefficient and, in these cases, results in slight increases in the critical sliding velocities.

A comparison of results from the two chlorine compounds, benzyl chloride and p-dichlorobenzene, at various chlorine weight concentrations is shown in figure 3(c); also included is the curve for pure cetane from figure 2. A simplified comparison of the critical sliding velocities for both these chlorine compounds is made in table III. These data show that the critical sliding velocities are lower for p-dichlorobenzene than for benzyl chloride for all concentrations. This result agrees with the premise that a compound of greater reactivity should have higher critical velocity and with the known reactivities of the two compounds, that is, the compound of greater reactivity, benzyl chloride, showed the higher critical velocity for each concentration. For example, at a chlorine weight concentration of 1 percent, the critical sliding velocity is approximately 900 to 1000 feet per minute with p-dichlorobenzene and the critical sliding velocity is approximately 1500 to 1600 feet per minute with the more reactive benzyl chloride. This agreement of the critical sliding velocities with the known reactivities of the two additive compounds substantiates the limiting-rate hypothesis relative to extreme-pressure lubrication at high sliding velocities.

The data of figure 3(c) show that, for all concentrations except 1-percent benzyl chloride, the friction coefficients are

in the same general range at velocities greater than approximately 3500 feet per minute. The friction coefficients are also in the same general range at velocities less than the critical.

The data of figure 3 and table III for various concentrations also indicate that, within the limits of the experiments at the concentrations used, the factor of reactivity of the chlorine atoms available for reaction is of greater importance than the number of such atoms available for reaction. With one exception, increase in the concentration (from 1 to 10 percent) of chlorine atoms of equal activity had, in general, relatively little effect on the critical sliding velocity; whereas increase in reactivity for equal concentration had appreciable effect on this critical velocity. The one exception is for 1-percent chlorine from benzyl chloride; difference between 1-and 5-percent chlorine weight concentrations caused an appreciable change in critical sliding velocity. As an example of the relative effects of concentration and reactivity, the data of figure 3 and of table III show that, for the maximum concentration (10 percent) of the less reactive compound p-dichlorobenzene, the critical sliding velocity was still lower than for the minimum concentration (1 percent) of the more reactive compound benzyl chloride. The critical sliding velocities for 10 percent p-dichlorobenzene and 1 percent benzyl chloride in cetane are 1100 to 1200 and 1500 to 1600 feet per minute, respectively. Consideration of these data on the basis of molecular concentration rather than weight concentration does not change this general observation.

As previously mentioned, the shapes of the curves of figure 3 were based on the actual data plus additional evidence. Because the generally accepted hypothesis suggests that the protective film formed through the use of an extreme-pressure additive of the chlorine type is a chloride, a search was made for information on prepared chloride films. Reference 12 presents curves for prepared films of chloride on steel; these curves are plots of static friction coefficient against temperature. Plots of friction coefficient against velocity for a film of ferrous chloride $FeCl_2$ on steel are included in reference 7. Figure 4 shows plots of these data from references 7 and 12. Whereas the friction data of figure 4(a) (fig. 1 of reference 12) are plotted against temperature instead of sliding velocity, these curves are, in general, quite similar to the curve of figure 4(b) (from fig. 7(c) of reference 7) in that each of these curves shows two minimum points and a maximum point. In general, because heat generation at the contacting surfaces is directly dependent on sliding velocity, the temperature at the sliding surfaces will increase with velocity of the sliding surfaces; conse-

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quently, it is permissible to make a general comparison of trends on this basis. The abrupt changes in trend of the curves of figure 4 comforming to zones 1-2 or 3-4 may indicate changes in structure or actual phase changes of the film.

The shapes of the curves in figure 3 are generally similar to the shapes of the curves of figure 4; similar changes in trend and maximum and minimum points appear in most cases. In all probability therefore the trends indicated by the curves of figure 3 are reasonable. It is possible that the films formed by the additives in these experiments at velocities greater than the critical were ineffective with respect to preventing surface welding although they may have been effective in influencing friction.

A series of photomicrographs of wear areas on rider specimens after friction runs at various sliding velocities with cetane containing chlorine from benzyl chloride is shown in figure 5. The appearance of these wear areas is generally representative of all wear areas obtained in runs with additive lubricants reported herein. The general extent of the damage that results from welding at sliding velocities equal to or greater than the critical velocity and also the smooth sliding and lack of damage at sliding velocities less than the critical are shown in figure 5. These results are in agreement with the results reported in reference 5, which shows that lubrication failures consisting of increased friction, abnormal surface disturbance, or both, occurred in a similar manner when the additive was free sulfur. As previously mentioned, the velocity at which the lubrication failure of reference 5 takes place is defined in the same manner as the critical sliding velocity of this report.

The photomicrographs of figure 6 show the track worn on a disk at a sliding velocity less than critical and a track worn on the disk during operation at a velocity greater than critical. The appearance of these wear tracks is generally representative of all wear tracks obtained in runs with additive lubricants reported herein. This figure again indicates the general extent of the damage by welding that takes place at velocities greater than critical and the lack of damage at velocities less than critical.

From these data, it is apparent that rate of reaction between chlorine additives and sliding surfaces is an important factor in lubrication by these additives and that increased reactivity can serve to maintain adequate lubrication (including protection from welding) to higher sliding velocities. Whenever sliding velocities are in a range such that lubrication by certain additives is impossible because reaction cannot progress sufficiently to produce an

effective low-shear-strength film, the critical sliding velocity can be increased by utilization of an additive of greater reactivity.

Sulfur compounds. - The data of table II show that the difference in reactivity of free sulfur (or benzyl disulfide) and phenyl monosulfide is appreciable. As previously stated, free sulfur is only slightly more reactive than benzyl disulfide under conditions of shorter time increments than those of table II. 1325

Data from reference 5 on the effect of sliding velocity on friction for steel surfaces lubricated with cetane containing sulfur from either benzyl disulfide or free sulfur are shown in figure 7. In each case, the sulfur weight concentration was 0.5 percent. The approximate critical sliding velocities are indicated in figure 7 and are also tabulated in table IV under the 269-gram load. These data show that the slight difference in reactivities of the sulfur atoms from these two sources is such that the critical sliding velocity is slightly different. The more reactive sulfur atoms (from free sulfur) show slightly higher critical sliding velocity as well as slightly lower values of friction coefficient in a range of sliding velocities where the upward trend of the curves is most pronounced.

The data of figure 8 show a comparison of results obtained with cetane containing sulfur from the two sources, free sulfur and phenyl monosulfide. The sulfur weight concentration was 0.5 percent. Loads of 519 (fig. 8(a)) and 1017 (fig. 8(b)) grams were used in order to make the lubrication failure or critical sliding velocity more apparent. These loads result in initial Hertz stresses of 155,000 and 194,000 pounds per square inch, respectively. A simplified comparison of the critical sliding velocities for both these sulfur additives is made in table IV. These data show that the critical sliding velocity is appreciably lower for phenyl monosulfide than it is for free sulfur at loads of both 519 and of 1017 grams. With the 519-gram load (fig. 8(a)) in the region at velocities slightly greater than the critical, in which the upward trend of the curves is most marked, the more reactive sulfur atoms (from free sulfur) also show values of friction coefficient lower than those for phenyl monosulfide. Very little difference in friction coefficient is shown, however, (fig. 8(b)) in this same region with the 1017-gram load.

The difference in critical sliding velocities, which is quite marked at both loads, corresponds to the known chemical reactivities of these compounds; that is, sulfur atoms of greater reactivity

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(from free sulfur) show the higher critical sliding velocity. This agreement of critical sliding velocities with the known reactivities of the two additive compounds further substantiates the limiting-rate hypothesis relative to extreme-pressure lubrication at high sliding velocities.

A comparison is made in figure 8(c) of free sulfur and phenyl monosulfide at the two loads of 519 and 1017 grams. These data and that of table IV show that increase in load decreases the critical sliding velocity; the change in critical sliding velocity is not, however, a linear function of load. In any consideration of the severity of conditions at the contact area, magnitude of the applied load is less important than the resulting surface stress (pressure). The Hertz equations (which assume elastic deformation) for calculation of the initial surface stress at the point of contact show that the stress is proportional to the cube root of load. Critical sliding velocity is shown in figure 9 as a function of the initial Hertz surface stress for both free sulfur and phenyl monosulfide. Figure 9 shows that the function is linear under these conditions and that critical sliding velocity decreases linearly with increase of initial Hertz surface stress. This trend is to be expected because of the increased tendency toward surface welding at higher surface contact stresses.

During any run of 3-seconds duration, the initial rapid wear of the sperical rider specimen can change the apparent area of contact and consequently can change the localized contact surface stress (pressure) from the value calculated by use of the Hertz equations to a value approaching the yield strength of the softer of the two contacting materials. The softer of the materials used in this investigation has a yield strength of 65,000 pounds per square inch. Whereas the initial Hertz surface stresses of figure 9 vary from 126,000 to 225,000 pounds per square inch, localized contact surface stress at the conclusion of all runs would tend to approach the value of 65,000 pounds per square inch. In spite of this constancy of final surface stress, initial surface stress probably plays an important role in determining whether welding is to take place. Thus, if the initial Hertz surface stress is high enough to cause welding, subsequent reduction in severity of surface conditions may not prevent further damage because the initial welding may contribute to progressive surface failure.

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## SUMMARY OF RESULTS

The effect of additive reactivity on extreme-pressure lubrication was studied with a kinetic-friction apparatus consisting of a spherical rider sliding on a rotating disk, which was lubricated with common chlorine and sulfur compounds in cetane. Experiments were made over a range of sliding velocities from 75 to 7000 feet per minute with loads from 269 to 1017 grams (initial Hertz surface stress 126,000 to 194,000 lb/sq in.). Supplemental studies were made using standard physical, chemical, and metallurgical equipment and techniques. The following results were observed:

1. Greater chemical reactivity of the active atoms from various additives resulted in a higher critical sliding velocity, that is, a higher velocity was attained before lubrication failures (comprising increase in friction and surface welding) occurred. This result further substantiated the limiting-rate hypothesis relative to extreme-pressure lubrication at high sliding velocities. Analysis of the data indicated that rate of reaction between extreme-pressure lubricant additives and sliding surfaces is a factor of importance in establishing the effectiveness of lubrication by additives at high sliding velocities.

2. Data obtained with various concentrations of a number of additivies indicated that, within the limits of the experiments, a factor of more importance than the number of active atoms available for reaction was that of activity of these active atoms. Difference in concentration (from 1 to 10 percent) of active atoms of equal activity had less effect on the value of critical sliding velocity than an increase in activity of the atoms for equal concentration.

3. For all additives, the existence of a critical sliding velocity where the friction coefficient increased and surface welding occurred was verified.

4. Increase in load, for one concentration of sulfur atoms, decreased the critical sliding velocity. For both free sulfur and phenyl monosulfide additives, increase in initial Hertz surface stress decreased critical sliding velocity as a linear function. Such a change is to be expected because of the increased tendency toward surface welding at higher surface contact stresses.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, January 25, 1950.

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## REFERENCES

1. Bisson, E. E., and Johnson, R. L.: NACA Friction Studies of Lubrication at High Sliding Velocities. Lubrication Eng., vol. 6, no. 1, Feb. 1950, pp. 16-20.

2. Prutton, C. F., Turnbull, David, and Dlouhy, George: Mechanism of Action of Organic Chlorine and Sulfur Compounds in Extreme-Pressure Lubrication. Jour. Inst. Petroleum, vol. 32, no. 266, Feb. 1946, pp. 90-118.

3. Evans, E. A.: Extreme Pressure Lubrication. Jour. Inst. Auto. Eng. (London), vol. XI, no. 1, Oct. 1942, pp. 1-16.

4. Blok, H.: Gear Wear as Related to Viscosity of Oil. Mechanical Wear, Am. Soc. Metals, 1950, pp. 199-227.

5. Johnson, Robert L., Swikert, Max A., and Bisson, Edmond E.: Friction at High Sliding Velocities of Surfaces Lubricated with Sulfur as an Additive. NACA TN 1720, 1948.

6. Johnson, Robert L., Swikert, Max A., and Bisson, Edmond E.: Friction at High Sliding Velocities. NACA TN 1442, 1947.

7. Johnson, Robert L., Godfrey, Douglas, and Bisson, Edward E.: Friction of Solid Films on Steel at High Sliding Velocities. NACA TN 1578, 1948.

8. Johnson, Robert L., Godfrey, Douglas, and Bisson, Edmond E.: Friction of Surface Films Formed by Decomposition of Common Lubricants of Several Types. NACA TN 2076, 1950.

9. Simard, G. L., Russell, H. W., and Nelson, H. R.: Extreme Pressure Lubricants. Film-Forming Action of Lead Napthenate and Free Sulfur. Ind. and Eng. Chem. (Ind. ed.), vol. 33, no. 11, Nov. 1941, pp. 1352-1359.

10. Davey W.: The Extreme Pressure Lubricating Properties of Some Chlorinated Compounds as Affected by the Four-Ball Machine. Jour. Inst. Petroleum, vol. 31, no. 255, March 1945, pp. 73-88.

11. Donath, and Schiffman: Lubricating Oils. Trans. Fl-167, Consultants Bur. (New York), pp. 11-15.

12. Gregory, J. N.: The Lubrication of Metals by Compounds Containing Chlorine. Jour. Inst. Petroleum, vol. 34, no. 297, Sept. 1948, pp. 670-676.

TABLE I - COMPARATIVE REACTIVITIES OF CHLORINE ADDITIVES[a]

| Additive (10 percent by weight in white oil) | Theoretical total chlorine in blend (percent) | Percentage of available chlorine reacting with iron wire in 16 hours | | |
|---|---|---|---|---|
| | | Temperature, °C | | |
| | | 100 | 200 | 300 |
| p-Dichlorobenzene | 4.83 | --- | --- | 0 |
| Benzyl chloride | 2.80 | 89 | 72 | 97 |

[a]Data obtained through courtesy of Shell Development Company, Emeryville, California.

TABLE II - COMPARATIVE REACTIVITIES OF SULFUR ADDITIVES

[Activity determined by reacting, with iron wire, solutions of each additive in cetane for 20 minutes at 225° C.]

| Solutions | Original weight of iron (grams) | Weight of iron[a] after heating in solution (grams) | Increase in weight of iron (grams) | Increase (percent) | Appearance of iron wire |
|---|---|---|---|---|---|
| 0.5-percent free sulfur in cetane | 0.3284 | 0.3290 | 0.0006 | 0.18 | Uniform blue-black coating |
| 0.5-percent sulfur from benzyl disulfide in cetane | 0.3282 | 0.3286 | 0.0004 | 0.12 | Nonuniform brown-black coating |
| 0.5-percent sulfur from phenyl monosulfide in cetane | 0.3283 | 0.3283 | 0.0000 | 0 | Very slightly tarnished |
| Pure cetane | 0.3280 | 0.3280 | 0.0000 | 0 | Unchanged |

[a]Cleaned in alcohol and dried.

TABLE III - EFFECTS OF REACTIVITY AND CONCENTRATION ON

CRITICAL SLIDING VELOCITIES OF CHLORINE ADDITIVES[a]

| Additive | Approximate critical sliding velocity, ft/min | | |
|---|---|---|---|
| | Chlorine weight concentration, percent | | |
| | 1 | 5 | 10 |
| Benzyl chloride | 1500 - 1600 | 2000 - 2200 | 2000 - 2100 |
| p-Dichlorobenzene | 900 - 1000 | 1000 - 1100 | 1100 - 1200 |

[a]Values based on both friction data and surface welding.
Load, 269 grams.

TABLE IV - EFFECTS OF REACTIVITY AND LOAD ON CRITICAL

SLIDING VELOCITIES OF SULFUR ADDITIVES[a]

| Additive (0.5-percent sulfur weight concentration) | Approximate critical sliding velocity, ft/min | | |
|---|---|---|---|
| | Load, grams | | |
| | 269 | 519 | 1017 |
| Benzyl disulfide | 800 - 900 | --------- | --------- |
| Free sulfur | 1000 | 800 - 900 | 600 - 700 |
| Phenyl monosulfide | --------- | 400 - 500 | 300 - 400 |

[a]Values based on both friction data and surface welding.

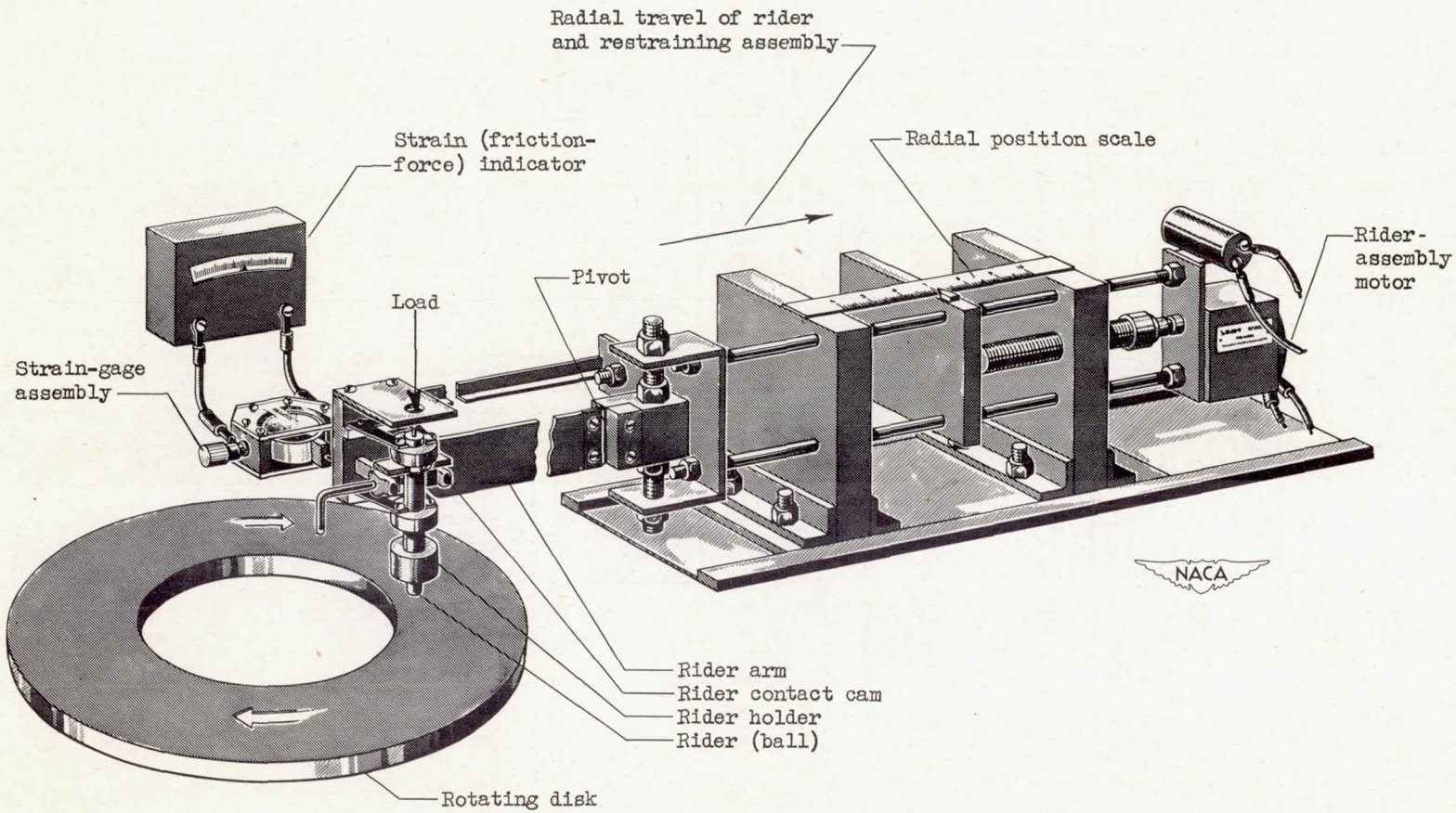



Figure 1. - Schematic diagram of sliding-friction apparatus.

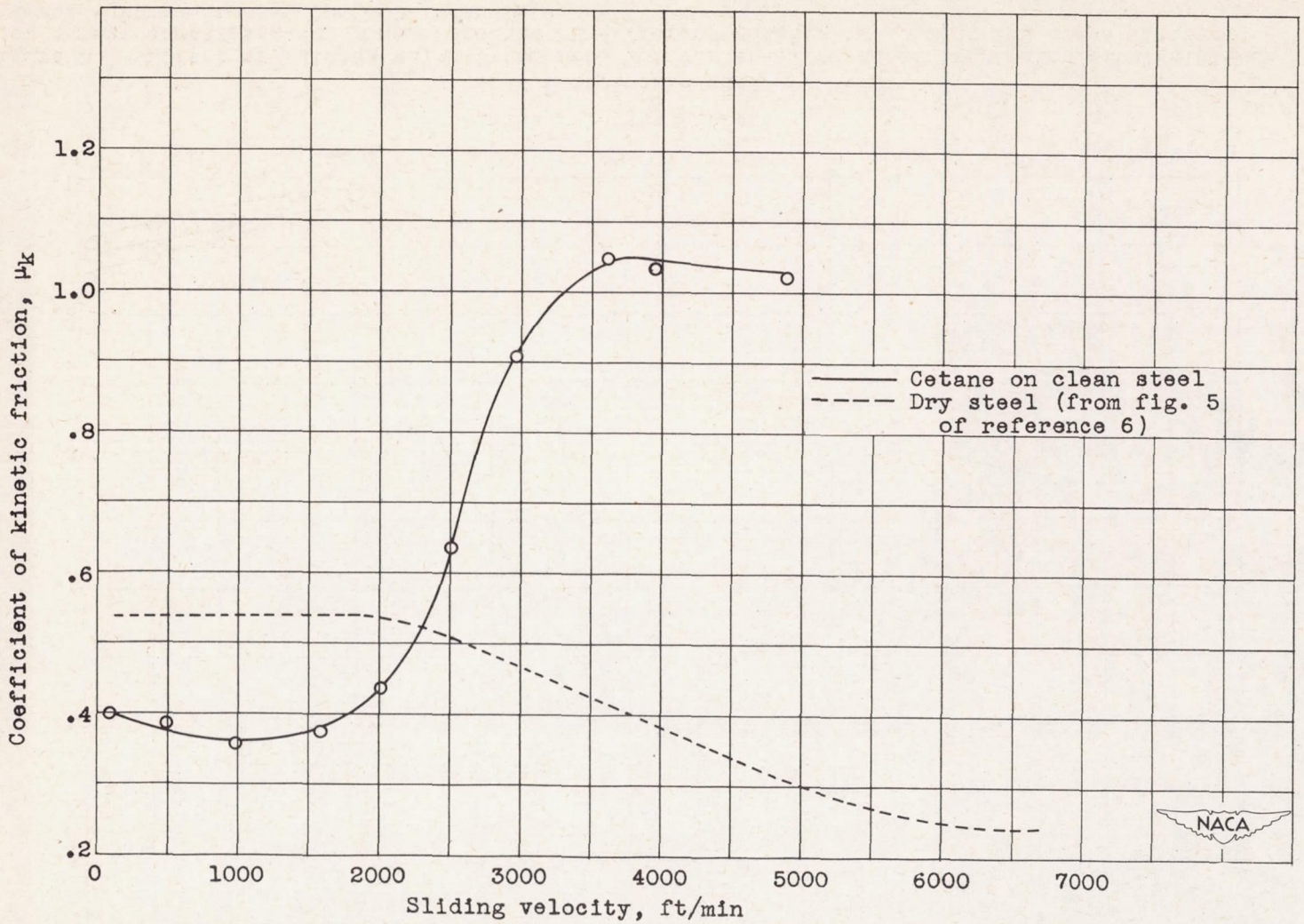
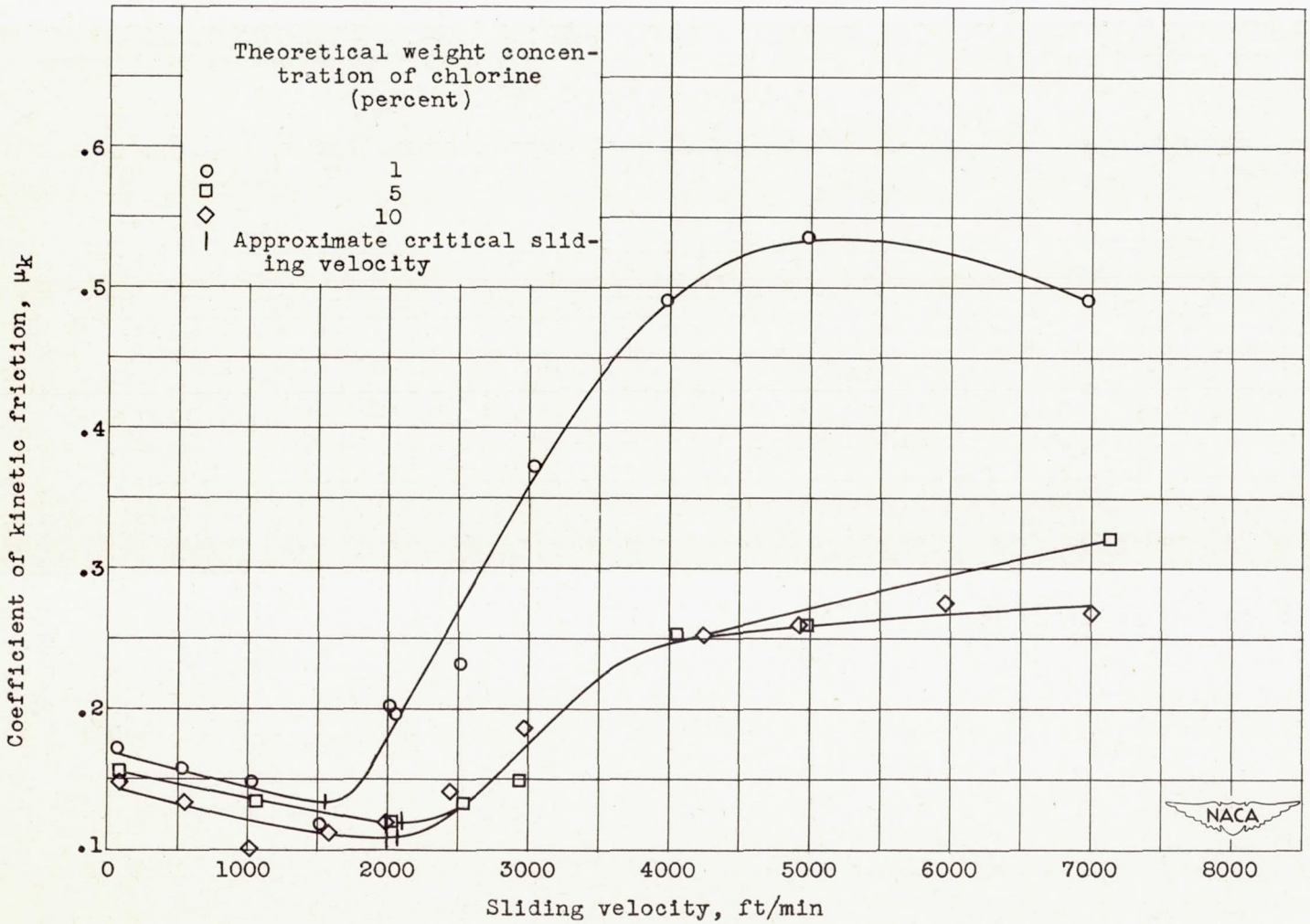
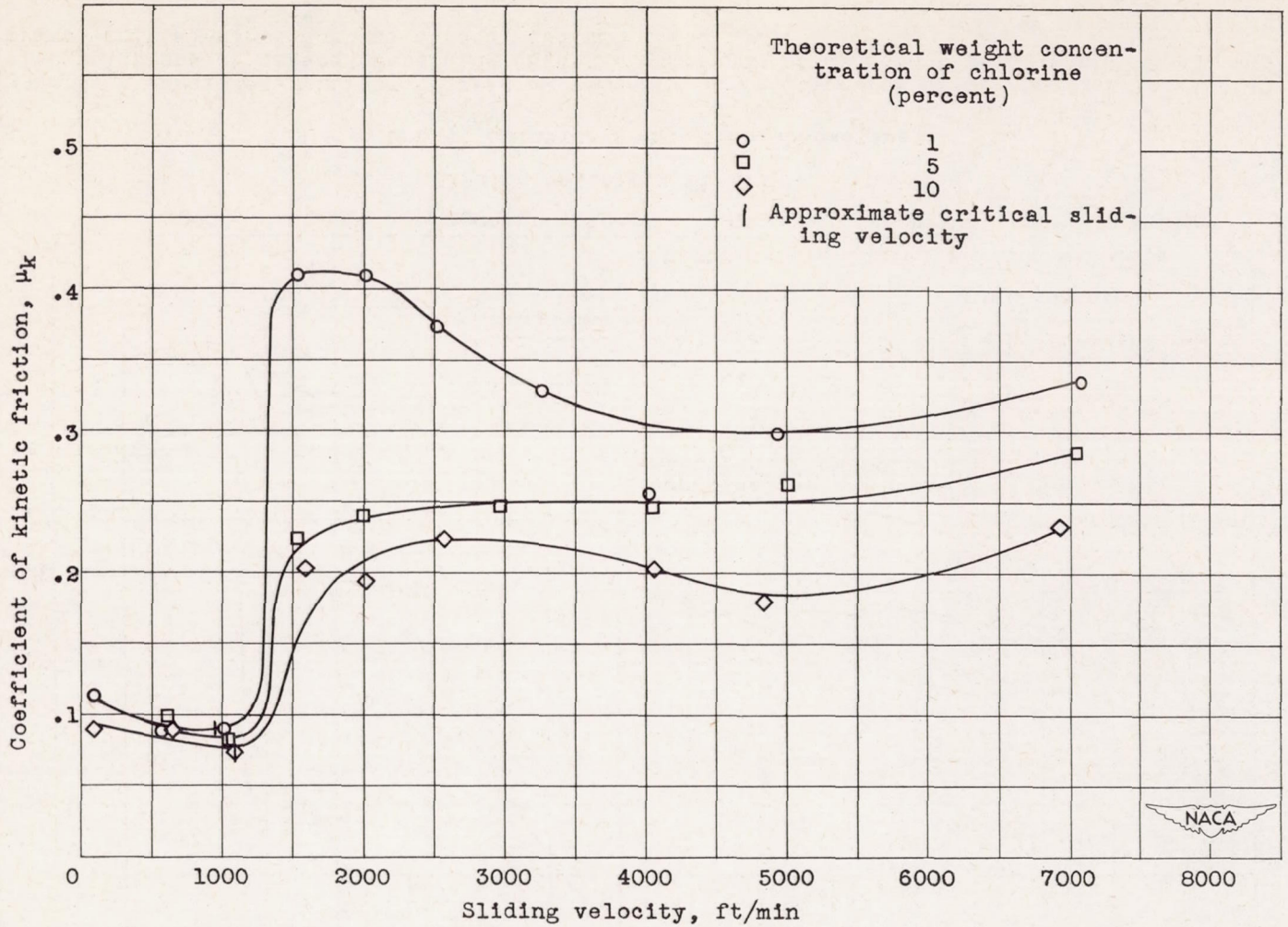



Figure 2. - Effect of sliding velocity on friction for steel surfaces lubricated with pure cetane. Load, 269 grams (initial Hertz stress, 126,000 lb/sq in.). (From reference 5.) Welding occurred at all sliding velocities.



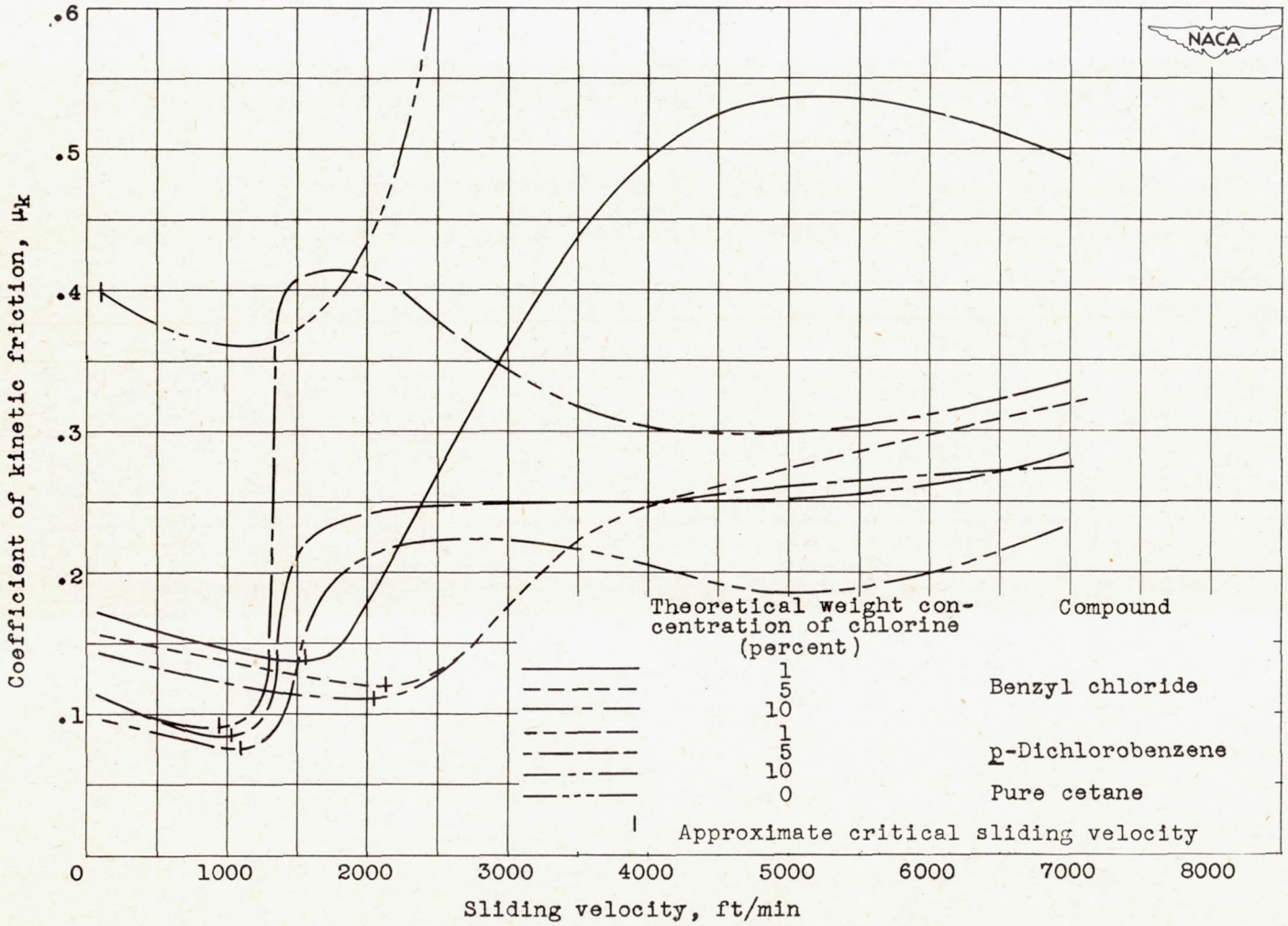

(a) Benzyl chloride.

Figure 3. - Effect of sliding velocity on friction for steel surfaces lubricated with solutions of cetane containing chlorine compounds of different reactivity. Load, 269 grams (initial Hertz surface stress, 126,000 lb/sq in.).



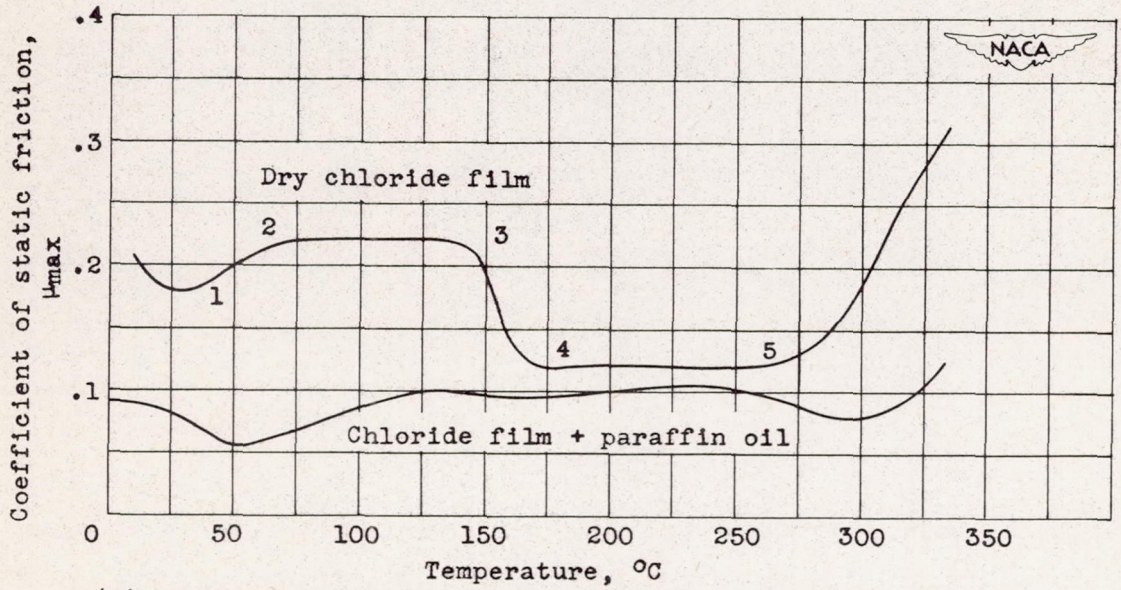

(b) p-Dichlorobenzene.

Figure 3. - Continued. Effect of sliding velocity on friction for steel surfaces lubricated with solutions of cetane containing chlorine compounds of different reactivity. Load, 269 grams (initial Hertz surface stress, 126,000 lb/sq in.).

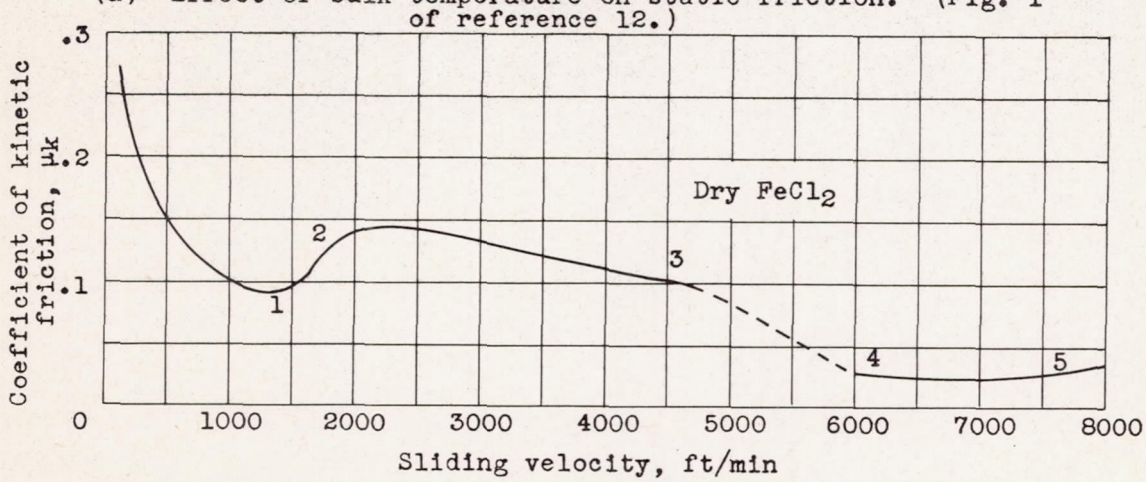



(c) Benzyl chloride and p-dichlorobenzene.

Figure 3. - Concluded. Effect of sliding velocity on friction for steel surfaces lubricated with solutions of cetane containing chlorine compounds of different reactivity. Load, 269 grams (initial Hertz surface stress, 126,000 lb/sq in.).

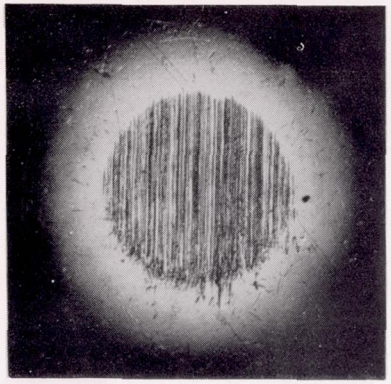



(a) Effect of bulk temperature on static friction. (Fig. 1 of reference 12.)

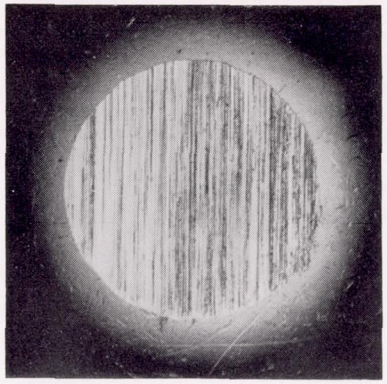



(b) Effect of velocity on kinetic friction. Load 269 grams. (From fig. 7(c) of reference 7.)

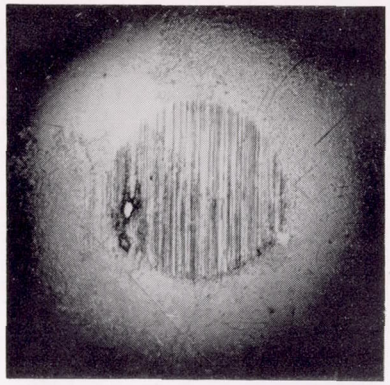
Figure 4. - Correlation between effects on friction of temperature and velocity for chloride films on steel surfaces. Zones 1-2 and 3-4 may indicate changes in structure or actual phase changes of film.



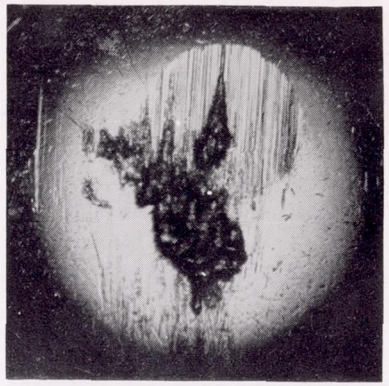
(a) 5-15 percent.



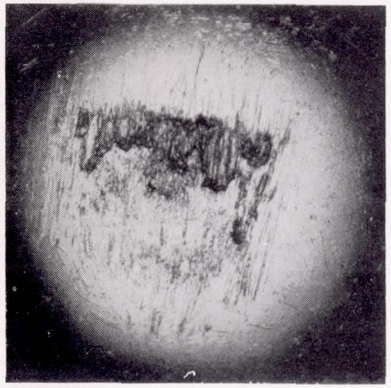
(b) 50 percent.



(c) 100 percent.

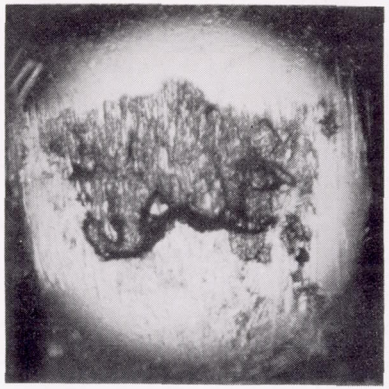


(d) 150 percent.

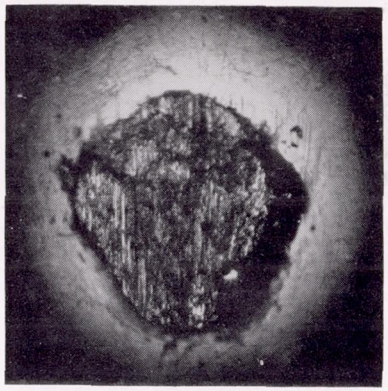


(e) 250 percent.

(f) 300 percent.



(g) 400 percent.



(h) 500 percent.

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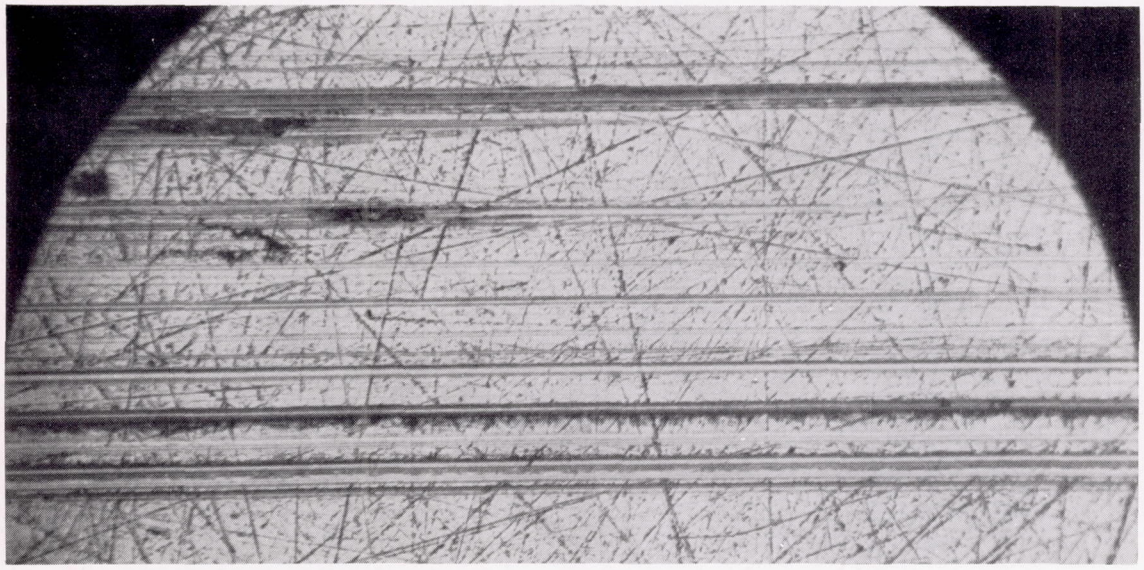
Figure 5. - Representative photomicrographs of wear areas on rider specimens after friction runs at various sliding velocities, expressed as percentages of critical sliding velocity. Load, 269 grams (initial Hertz stress 126,000 lb/sq in.); SAE 1020 steel lubricated with cetane containing chlorine from benzyl chloride; X50.



(a) Velocity, 50 percent of critical.

(b) Velocity, 200 percent of critical.

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Figure 6. - Representative photomicrographs of wear track on disk specimens after friction runs at two sliding velocities. Load, 269 grams (initial Hertz surface stress, 126,000 lb/sq in.); specimen, SAE 1020 steel lubricated with cetane containing chlorine from benzyl chloride; X50.

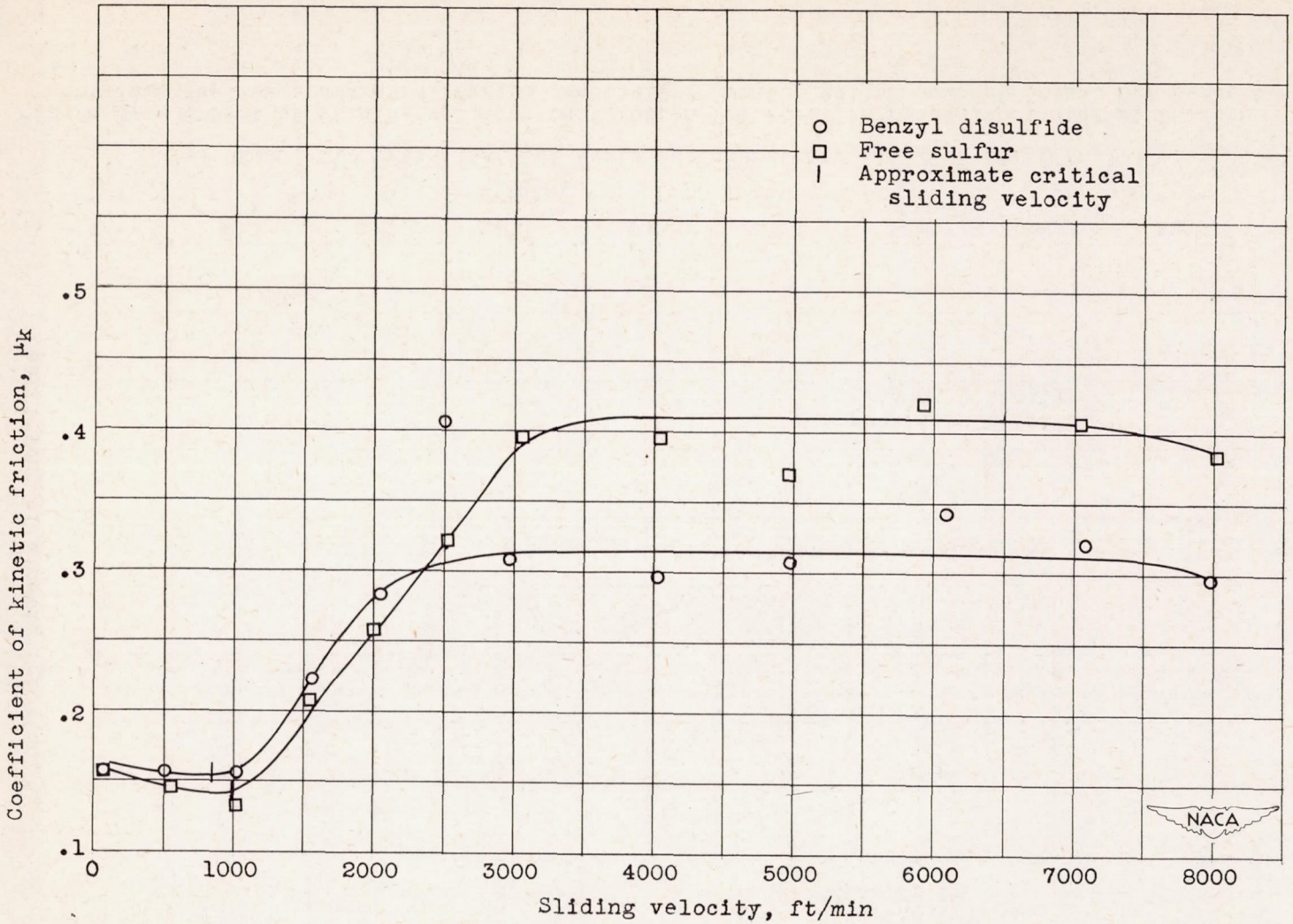
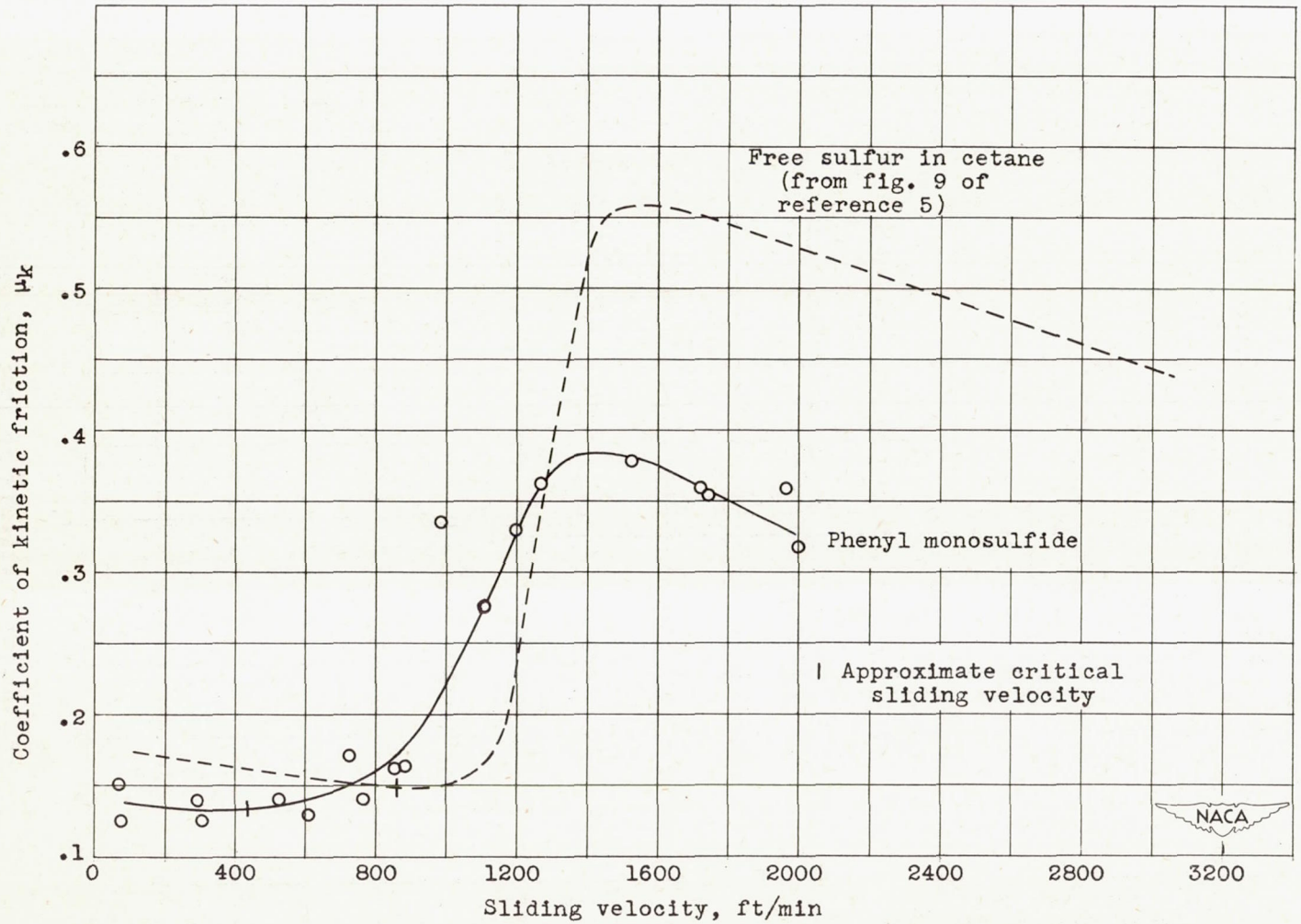
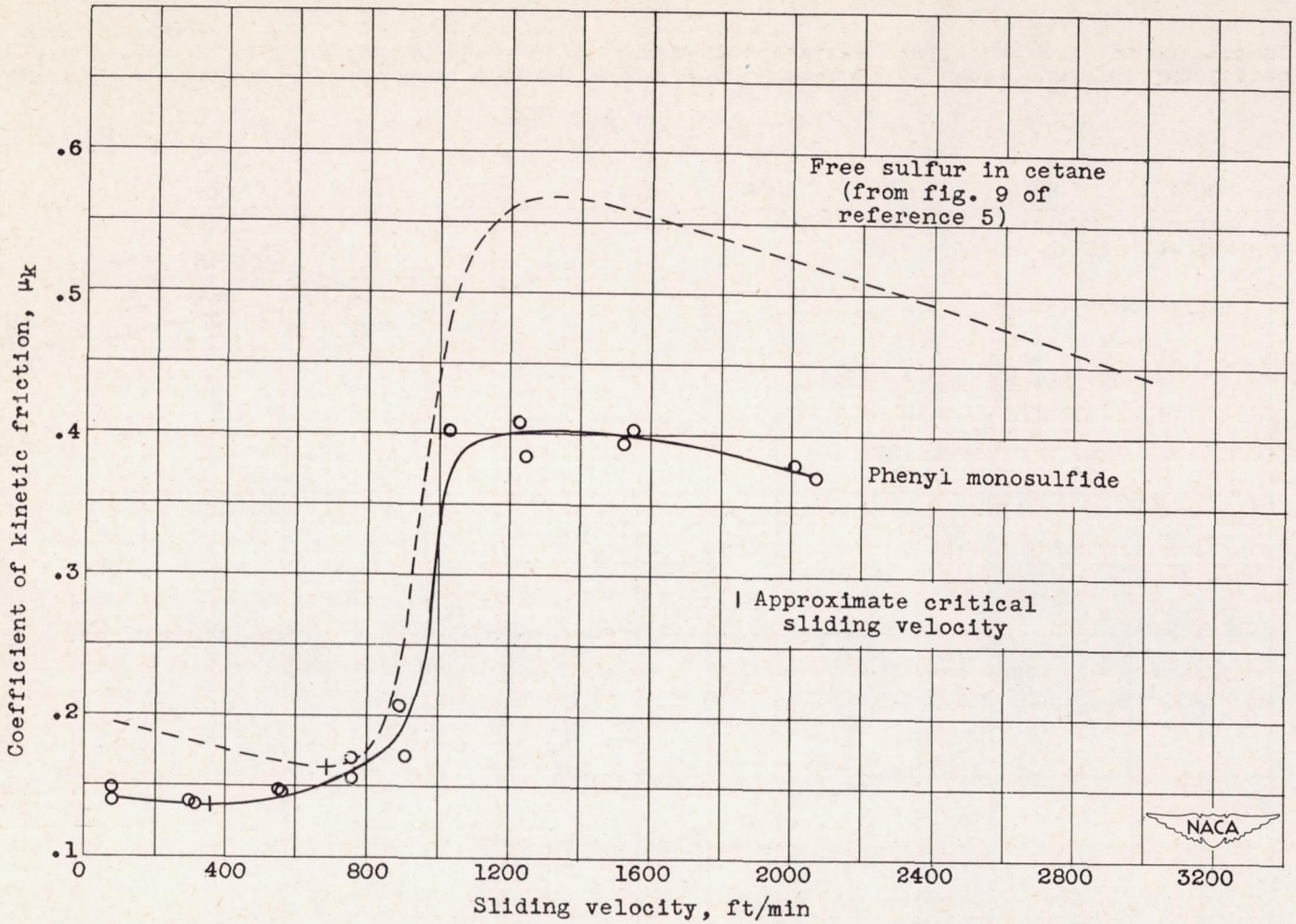



Figure 7. - Effect of sliding velocity on friction for steel surfaces lubricated with cetane containing sulfur from different additives. Load, 269 grams (initial Hertz stress, 126,000 lb/sq in.); theoretical sulfur weight concentration, 0.5 percent. (Data from fig. 8 of reference 5.)



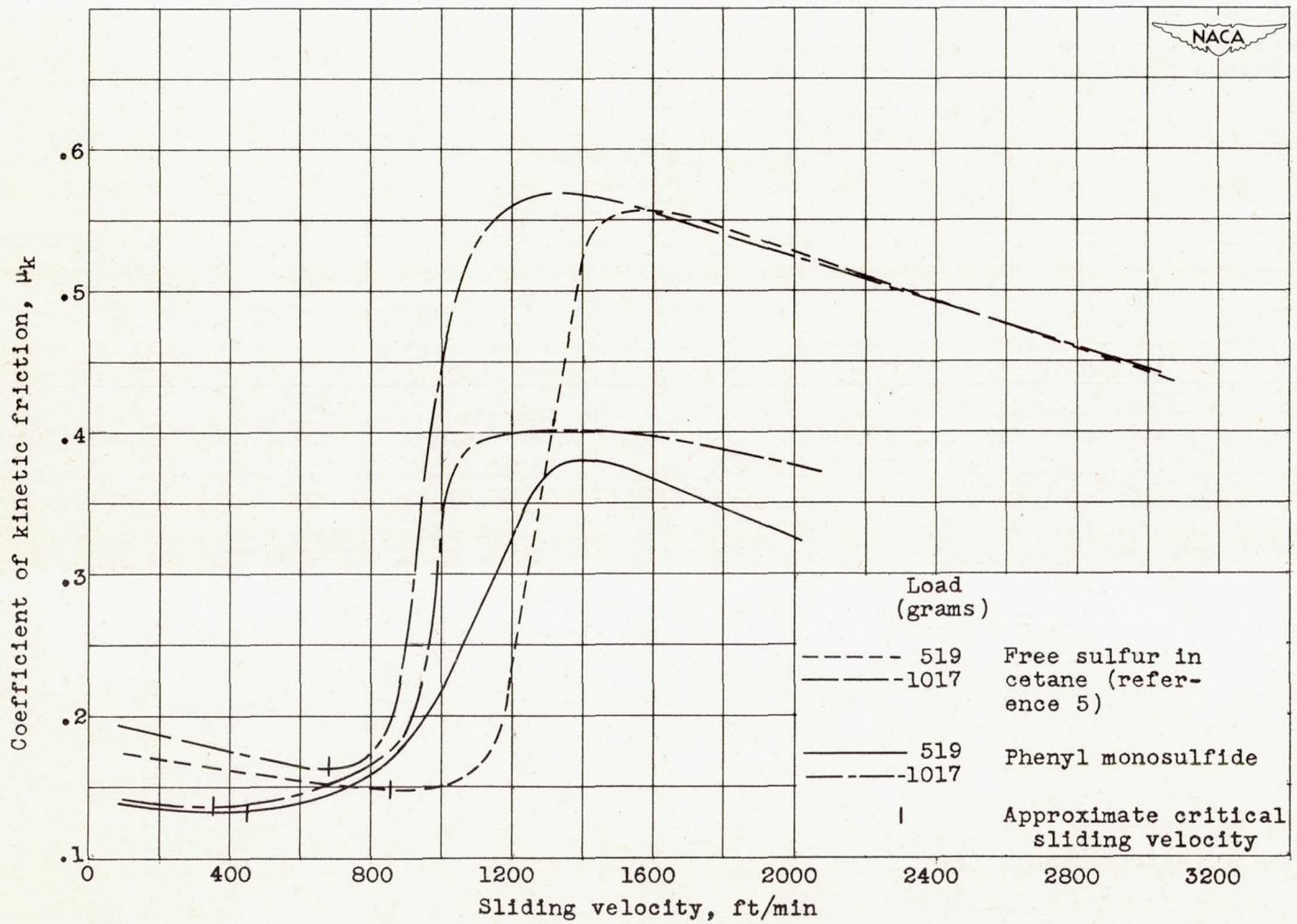

(a) Load, 519 grams (initial Hertz surface stress, 155,000 lb/sq in.).

Figure 8. - Effect of sliding velocity on friction for steel surfaces lubricated with cetane containing sulfur atoms of different reactivity. Sulfur weight concentration, 0.5 percent.




(b) Load, 1017 grams (initial Hertz surface stress, 194,000 lb/sq in.).

Figure 8. - Continued. Effect of sliding velocity on friction for steel surfaces lubricated with cetane containing sulfur atoms of different reactivity. Sulfur weight concentration, 0.5 percent.




(c) Loads, 519 and 1017 grams.

Figure 8. - Concluded. Effect of sliding velocity on friction for steel surfaces lubricated with cetane containing sulfur atoms of different reactivity. Sulfur weight concentration, 0.5 percent.

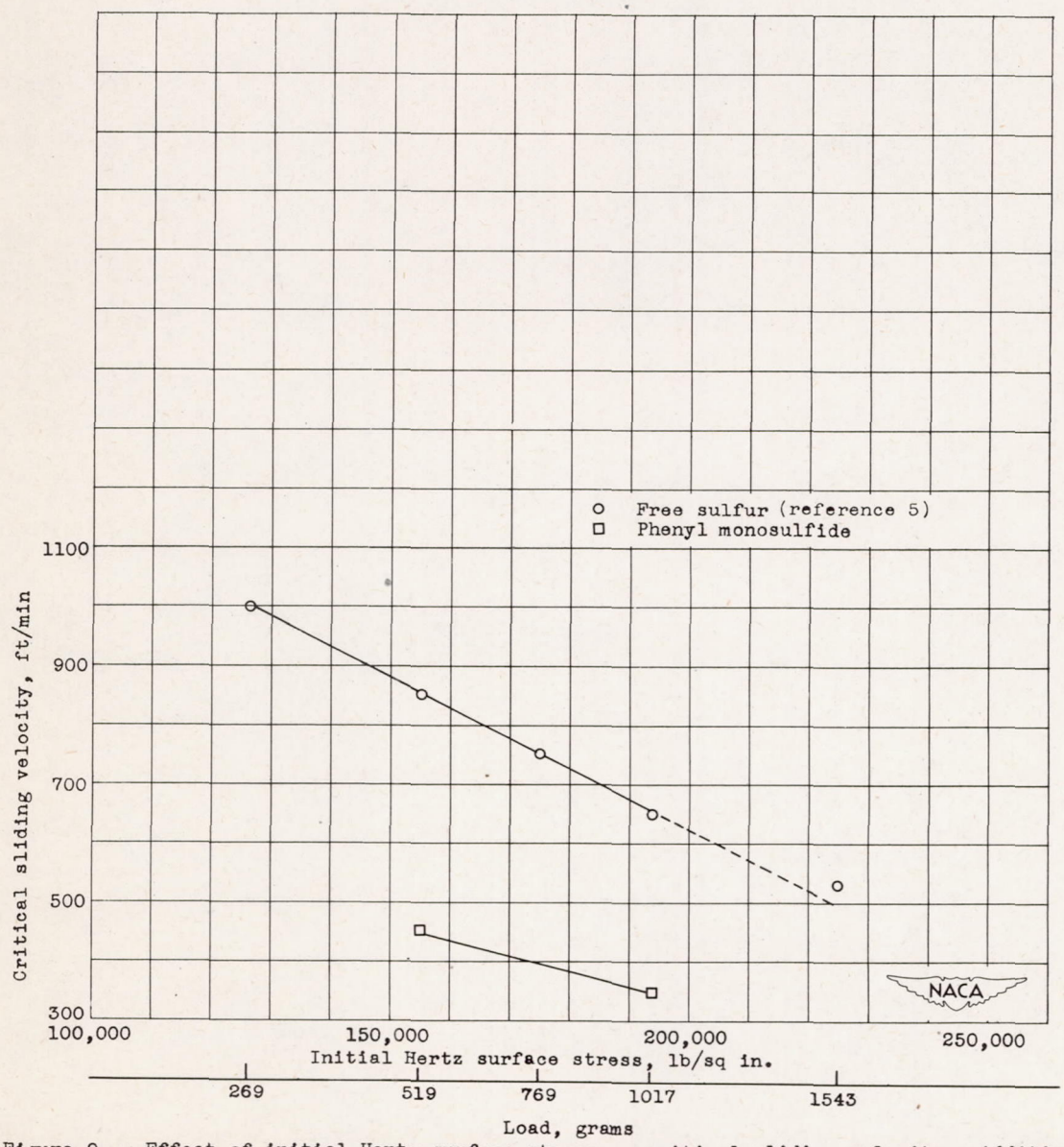



Figure 9. - Effect of initial Hertz surface stress on critical sliding velocity. Additives free sulfur and phenyl monosulfide in cetane; sulfur weight concentration, 0.5 percent.