Effect of Lubricant Composition on Friction as Measured with Thrust Ball Bearings

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COMPOUNDING of lubricants to satisfy the specific friction requirements of many mechanical devices has been hampered by the difficulty of extrapolating friction data from simple bench tests to service problems. To obtain directly applicable friction data, a bench test which simulates the conditions occurring at rubbing surfaces in many types of machines was used to measure the friction of lubricated steel on steel. Data from a wide range of straight mineral oils, synthetic oils, and mineral oil–additive blends have facilitated the development of lubricants for use in devices such as lubricated plate clutches and friction drive units.

TEST EQUIPMENT AND PROCEDURE

In the lubricant test machine shown in Figure 1, the test elements are two thrust ball bearings. When such bearings are rotated under load, the individual balls tend to spin on an axis through the center of the ball as well as roll around the race. This spinning motion causes sliding of the balls relative to the race. As a result, both rolling and sliding contribute to the friction, with sliding friction the most important. Because of this combination of sliding and rolling, the observed coefficients of friction should not be expected to be the same as those that have been reported for pure sliding. Of even greater importance is the fact that the friction values are comparable to those measured in actual mechanical devices. Test bearings are described in Table I.

Operation of the lubricant test machine can be understood by referring to Figure 1. Torque is transmitted from the drive shaft to the torque arm through the test bearings which are submerged in the test lubricant. The transmitted torque is measured on the end of the damped torque arm with a dial-indicator weighing device. Loads are applied to the thrust ball bearings by compressing calibrated Belleville springs. A tachometer geared to the drive shaft measures the rotational speed. Two iron-Constantan thermocouples located within 1/8 inch of the balls of the test bearings measure the test lubricant temperature, which is held constant by heating or cooling the jacket oil as required.

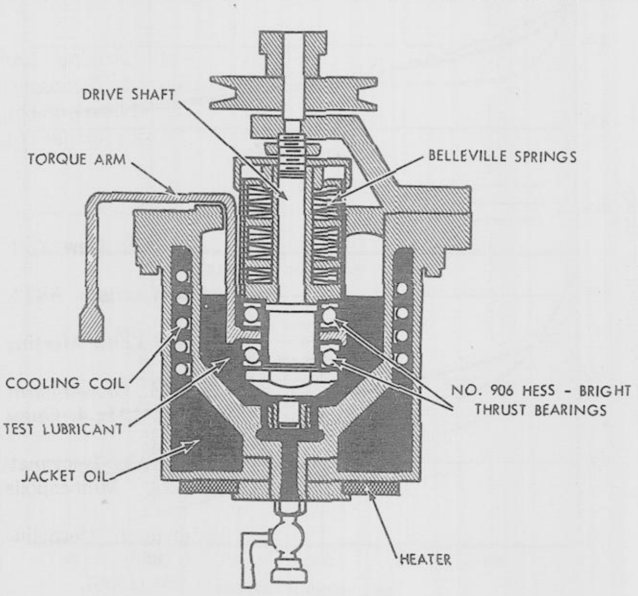

Figure 1. Friction drive lubricant test machine

Table I. Description of Test Bearings

Test bearing Hess Bright No. 906 thrust ball bearings, ABEC Class I

Bearing Size, Inches	
Bore	1.811
Outside diameter	2.087
Height	0.610
Ball complement and size (*15*)	0.3125-inch balls
Materials of Construction	
Races[a]	52100 steel, R_c 58–60 hard
Balls[a]	52100 steel, R_c 60–62 hard
Retainer	Pressed low carbon steel

[a] Heat stabilized for operation at temperatures up to 300° F.

The procedure for evaluating the friction properties of a lubricant consists of breaking in a set of thrust bearings in the test lubricant and then measuring the torque transmitted through the bearings as a function of load, speed, and oil temperature. To eliminate the possibility of carryover from one lubricant to the next, a new set of bearings is used for each test lubricant. Prior to installation, the bearings are cleaned by washing in a mixture of acetone, toluene, and chloroform. After installation, 200 cc. of the test lubricant are added and the break-in procedure is started. This consists of operating the unit at 2000 r.p.m. and 200° F. oil temperature for 10 minutes at no load, followed by at least 10 minutes at each of the three test loads.

After the test bearings are broken in, the transmitted torque is measured at no load and at test loads of 300,000, 400,000, and 500,000 p.s.i. Hertz. Point by point measurements at all loads are made at oil temperatures of 100, 200, and 300° F. and speeds of 0 to 5000 r.p.m. Several starting torque measurements are averaged to obtain a static friction value. To check the reliability of each test, the initial 300,000 p.s.i., 100° F. condition is repeated at the conclusion of the test. If the results differ by more than 10%, a new test is run or friction change, if excessive, is reported. From the torque measurements, the average coefficient of friction can be calculated using the following formula:

$$\mu_{av.} = \frac{T_1 - T_0}{P\,B\,K} = \frac{T_s}{P\,B\,K}$$

where

$\mu_{av.}$ = average coefficient of friction
T_1 = torque under load, pound-inches
T_0 = no load torque (torque required to churn test oil), pound-inches

T_s = spinning torque, pound-inches
P = total normal load, pounds
B = semiminor axis of the contact ellipse, inches
K = proportionality constant depending on geometry of the bodies in contact
$\mu_{av.}$ = 0.0315 T_s at 400,000 p.s.i. load

All lubricants were evaluated in the condition in which they were received. Repeatability data obtained over a 9-month period, using bearings from several lots, have shown that differences in the measured coefficient of friction of less than 10% should not be considered significant.

Effect of Test Variables. The effects of load, temperature, and velocity on the coefficient of friction for a naphthenic base straight mineral oil are illustrated in Figure 2. In general the coefficient of friction decreases as oil temperature, ball velocity, or load increases.

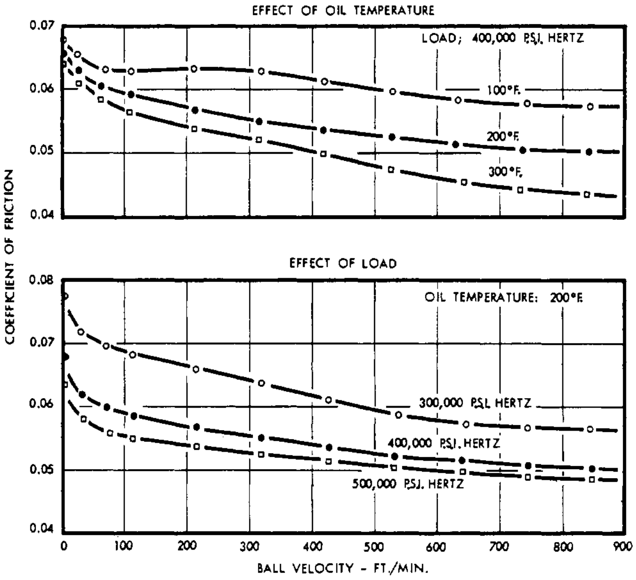

Figure 2. Effects of load, oil temperature, and velocity

For all loads and oil temperatures the curves appear to have two distinct regions, the dividing line being about 100 feet per minute. In the high velocity region, the coefficient of friction tends to increase slightly with decreasing velocity; in the low velocity region it tends to increase rapidly as the velocity approaches zero. The speed control characteristics of the bench test rig were such that the data are less reliable in the low velocity region, especially below 50 feet per minute, than in the high velocity region. This was unfortunate because the low velocity region is of greatest interest for some practical applications.

For most lubricants studied, the load and temperature effects on the coefficient of friction were comparable to or less than those shown in Figure 2. Certain additives lowered the friction values appreciably more with an increase in oil temperature or load than did a straight mineral oil. Because the results at 200° F., 400,000 p.s.i. Hertz load were usually representative of the data at the other loads and temperatures, only the results at this condition are presented in the remainder of this article.

LUBRICANT FACTORS AFFECTING FRICTION

Lubrication Conditions. The lubrication conditions in the ball contact areas determine the lubricant factors affecting friction. Under hydrodynamic conditions, the coefficient of friction is proportional to the lubricant viscosity and speed but inversely proportional to load (*4*). As a result, viscosity is the only lubricant factor which controls friction. Under boundary lubrication conditions, on the other hand, fluid viscosity ceases to be important, and the presence or absence of surface coatings formed by the lubricant controls friction.

Test results for the more than one hundred lubricants evaluated have indicated that friction and oil viscosity were independent in these tests. As an illustration, the data in Figure 3 for straight mineral oils show the effects of varying the viscosity at 200° F. from 1.3 centistokes (a Diesel fuel) to 39 centistokes (a bright stock). Practically no effect of viscosity on friction was observed for the naphthenic base oils which were different distillation cuts from the same crude and thus similar in composition. Possible exceptions were the paraffinic base oils which did show a small effect of viscosity on friction. However, the paraffinic base oils came from different crudes and hence composition as well as viscosity varied.

Several other observations have contributed to an understanding of the lubrication conditions present. In contrast to hydrodynamic theory, the measured friction in all cases decreased with speed. Furthermore, for many lubricants, coefficient of friction was essentially independent of load. In those cases where load did have an effect, an increase in temperature due to increasing the load may have been the contributing factor. Oil additives reduced friction at all test conditions by as much as 40% without significantly changing the lubricant viscosity. Although one interpretation of the speed effect might be that partial hydrodynamic lubrication conditions were present at the higher velocities, the other observations and, especially, the pronounced effects of additives indicate that boundary lubrication conditions were present at all times in these tests.

Straight Mineral Oil Composition. Comparison of the data for the naphthenic and paraffinic base oils shown in Figure 3 reveals that the naphthenic base oils caused substantially higher friction than did the paraffinic base oils. This effect of base oil has type also been observed by Lane (*10*) and others. Cetane (oil H) gave low friction in these tests, whereas Murray, Johnson, and Bisson (*13*) have reported relatively high friction values for cetane by using a hemispherical rider on a flat plate. The cetane used by Murray, Johnson, and Bisson was purified prior to testing; cetane used in these tests was purified 9 months prior to testing. Thus, the low friction in the present tests may have been due to the presence of traces of partially oxidized materials formed in the cetane during storage.

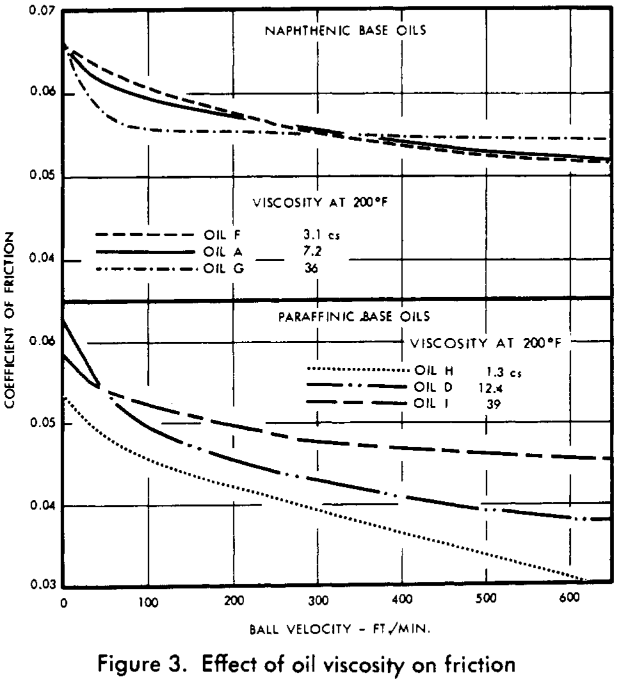

Figure 3. Effect of oil viscosity on friction

To investigate further the effect of base oil type, tests were run on several additional oils from widely different crudes. The friction data are compared in Figure 4. Oil A, a distilled naphthenic oil, and oil B, a highly refined, water-white naphthenic base oil, gave the highest friction values. Oils D and E, both conventionally refined paraffinic base oils, gave the lowest friction values. Intermediate friction values were obtained with oil C, a conventionally refined mixed base oil.

The five oils shown in Figure 4 were analyzed by the method of van Nes and van Westen (*16*) to determine their hydrocarbon composition. The results are given in Table II. Little or no relationship was found between the composition of the oils as measured by the hydrocarbon type analyses and the friction data.

Friction values were also obtained on naphthenic base oils that had been fractionated by thermal diffusion, fractionated by chromatography, or hydrogenated. The friction data, hydrocarbon type analyses, and the viscosity data for the various products are given in Table III. The two methods of separation as well as hydrogenation yielded products differing appreciably from each other and from the original oils in composition. However, the friction data show that neither method of separation yielded fractions giving friction values significantly different from that for the whole oil except for the top thermal diffusion fraction which reduced static friction. Hydrogenation appears to have increased friction slightly at low velocities.

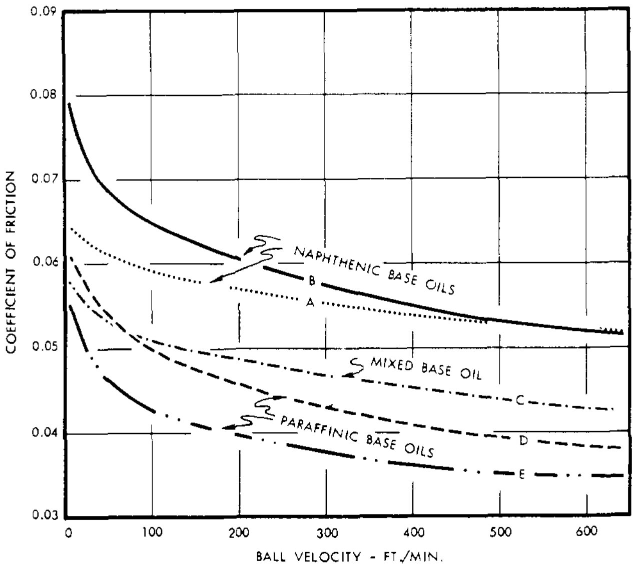

Figure 4. Effect of base oil composition on friction

Table II. Analysis of Mineral Oils Tested

Oil	Viscosity, C.S. 100° F.	Viscosity, C.S. 210° F.	Viscosity Index	Hydrocarbon Type, Analysis,ᵃ C, % Paraffinic	Naphthenic	Aromatic
A	66.7	6.3	5	44	38	18
B	10.03	2.45	65	49	49	2
C	134.8	11.3	71	57	37	6
D	101.6	11.0	102	71	15	13
E	39.6	6.0	107	65	31	4

[a] Method of van Nes and van Westen (*16*).

Summarizing, the straight mineral oil studies indicate that naphthenic base oils give significantly higher friction values than paraffinic base oils. However, these differences in friction do not appear to be related to the composition of the oil as measured by hydrocarbon type analyses (*16*). Further, fractionation and hydrogenation of a selected oil had, at most, only a minor effect on friction. The lack of correlation between the friction data and the hydrocarbon type analyses indicates that specific hydrocarbons or limited groups of hydrocarbons, such as partially oxygenated compounds, may control the observed friction. Zisman (*17*) suggested that the friction of mineral oils depends on small amounts of fatty acids either present naturally or formed by oxidation.

Synthetic Oil Composition. Representative results from a study of a wide range of different synthetic fluids are illustrated in Figure 5. The kinetic friction values obtained with the synthetic fluids varied from high values with the fluoroalkyl camphorate to very low values with ethylene glycol. Other synthetic fluids such as silicone and diester gave values falling inside the mineral oil range, as indicated by the shaded area.

A summary of the friction data for all the synthetic fluids evaluated is given in Table IV. The results in the table for three fatty acids varying in chain length from C_9 to an estimated C_{24} show that two longer chain acids reduced both static friction and kinetic below the range for straight mineral oils. In contrast, the C_9 acid gave higher friction values than the other two acids, especially at low velocities. The reduced effectiveness of the C_9 acid as compared to the C_{18} and C_{24} acids is consistent with the data obtained by other investigators studying the effect of carbon chain length on friction (*3*, *12*).

Data for alcohols having varying numbers of OH groups

Table III. Analysis of Specially Prepared Mineral Oils

Oils or Oil Fractions	Viscosity, C.S. 100° F.	Viscosity, C.S. 210° F.	Viscosity Index	Hydrocarbon Type, Analysis,ᵃC,% Naphthenic	Aromatic	Paraffinic	Coefficient of Friction 0 ft./min.	50 ft./min.	100 ft./min.	200 ft./min.	400 ft./min.	600 ft./min.
				Chromatographic Separation								
Whole oil	173.1	10.1	−12	44	38	18	...	...	...	...	...	...
Aromatic fraction	9747	33	−806	[b]	[b]	[b]	0.060	0.048	0.047	0.047	0.048	0.048
Paraffinic fraction	104.1	8.6	36	46	46	8	0.068	0.053	0.051	0.048	0.046	0.043
				Thermal Diffusion Separation								
Whole oil	46.4	5.3	11	45	38	17	0.060	0.054	0.051	0.048	0.044	0.042
Top fraction	20.2	3.67	55	59	30	11	0.050	0.051	0.050	0.048	0.046	0.044
Bottom fraction	199.0	9.1	−99	29	49	22	0.063	0.052	0.049	0.047	0.046	0.044
				Hydrogenation								
Original oil	34.9	4.46	−20	40	42	18	0.064	0.059	0.057	0.055	0.052	0.049
Hydrogenated oil	31.1	4.36	8	39	58	3	0.077	0.066	0.063	0.060	0.055	0.051

[a] Method of van Nes and van Westen (*16*).
[b] Could not determine hydrocarbon type, aromatic carbon content was greater than 1.5 times naphthenic carbon content.

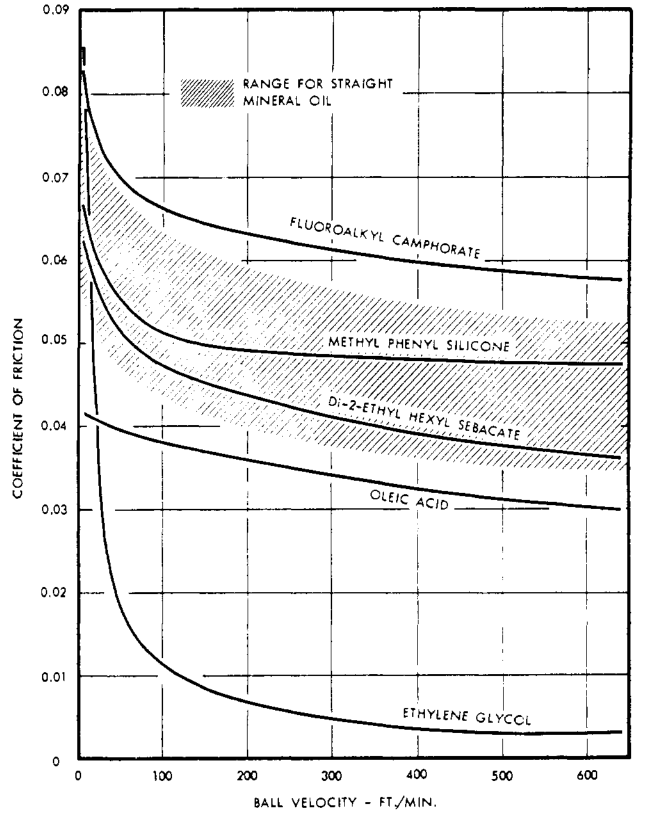

Figure 5. Effect of representative synthetic fluids on friction

per molecule are illustrated in Figure 6. Increasing the number of OH groups in the alcohol molecule from one to two or three not only reduced kinetic friction radically but also raised static friction. The kinetic friction values obtained with glycerol and ethylene glycol were by far the lowest in these tests. Similar effects of glycerol have been observed by Neeley (*14*).

To explain the large effects of ethylene glycol and glycerol, several modifications of the ethylene glycol molecule were evaluated. If methyl groups are attched to each carbon atom of ethylene glycol to form 2,3-butanediol, kinetic friction is increased almost to the mineral oil range. If, on the other hand, the chain length between the OH groups is increased (as was done for the data in Figure 7) kinetic friction increases and static friction diminishes as the glycol chain length increases. These results suggest that for glycols the presence of OH groups on adjacent carbon atoms is required to obtain low friction. The effectiveness of these adjacent OH groups can be greatly reduced by the presence of other groups attached to the molecule. Thus, the low kinetic friction which appears specific for ethylene glycol and glycerol may be associated with cleavage of the carbon-carbon bond followed by polmerization to form a methylene oxide type polymer or reaction of acidic oxidation products with the surface to form a low friction coating.

The fatty acids and alcohols produced some interesting effects on the surfaces of the balls and races. With most oils, the balls and races were frequently discolored but the races still retained the original grind marks at the end of a test. Fatigue failure was never observed with mineral oils. In the tests with the C_9 and C_{24} acids, however, the races failed at the highest test load before the test was completed. The use of either glycerol or ethylene glycol, on the other hand, resulted in highly polished balls and races. Even though the grind marks disappeared from the loaded areas of the races, the total combined wear for both bearings was less than 0.0001 inch. The other glycols studied had less pronounced effects on the surface condition of the bearings. Infrared and x-ray diffraction analyses of a precipitate found in the used ethylene glycol indicated the presence of organic compounds containing about 10 weight % combined iron but no free iron. These results suggest that ethylene glycol and glycerol as well as the fatty acids (*4*) react chemically with the metal surface to form a friction-reducing coating.

To determine whether bearings conditioned by running in ethylene glycol would retain the low coefficient of friction when the lubricant was changed, a test was run with a naphthenic base oil using bearings that had been used previously for an ethylene glycol test. The bearings were cleaned with solvents in the usual manner prior to the second test. The results of this study are illustrated in

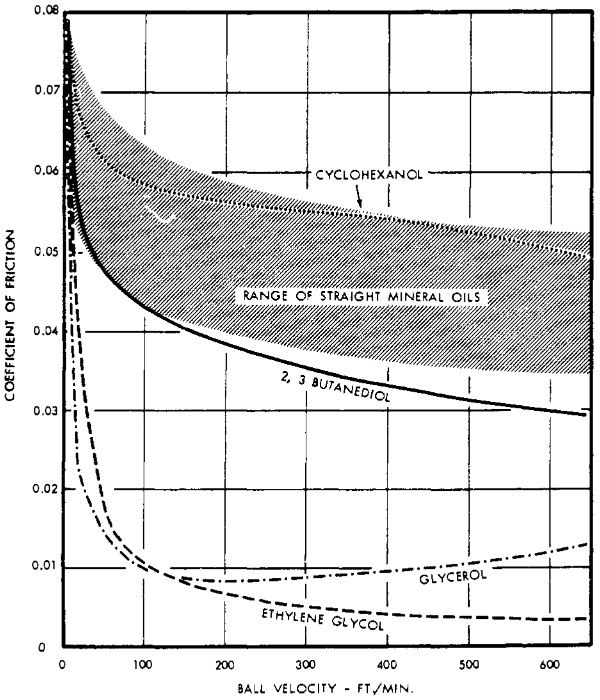

Figure 6. Effect of alcohols on friction

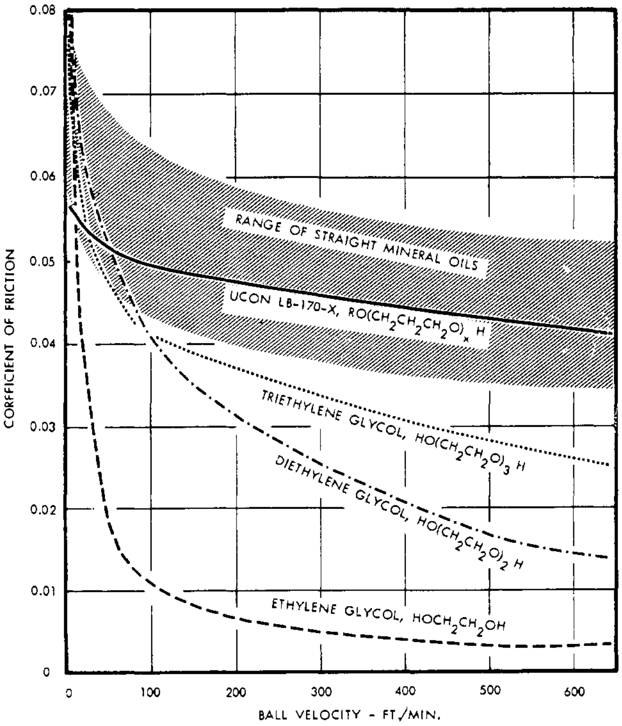

Figure 7. Effect of glycol chain length on friction

Figure 8. As can be seen, the friction obtained with the mineral oil after the ethylene glycol test was intermediate between that for ethylene glycol alone and the mineral oil alone. These results illustrate the importance of carry-over effects. Radioactive tracer studies are being made to determine whether a surface film formed during the ethylene glycol test or an improvement in surface finish is responsible for the reduction in friction with oil B.

Included in Table IV are friction results for the most common types of ester lubricants. The diester made from a dicarboxylic acid and a monohydroxy alcohol (di-2-ethylhexyl sebacate) gave friction values falling at the bottom of the mineral oil range, whereas the diester made from a dihydroxy alcohol and a monocarboxylic acid (dipropylene glycol dipelargonate) gave values near the top of the mineral oil range. The pentaerythritol and phosphate esters gave values comparable to that for the sebacate. Although the friction values for the silicate ester were substantially higher than those for the sebacate initially, the silicate darkened appreciably during the test and the observed friction decreased to a value similar to that for the sebacate. A possible explanation for the friction values obtained with most esters suggested by Murray, Johnson, and Bisson (*13*) is that the presence of free fatty acids in the esters determines their friction characteristics. These acids may be present as impurities or as oxidation or hydrolysis products.

The data for the silicone fluids in Table IV show that, except for high static friction with the methyl phenyl silicone, little difference was detected among a methyl

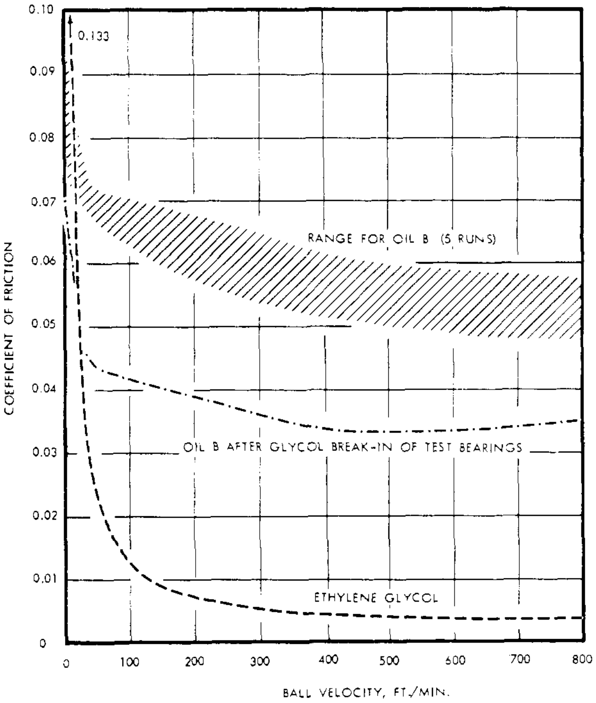

Figure 8. Carry-over of ethylene glycol

Table IV. Friction Characteristics of Synthetic Lubricants

Chemical Composition	Source, Trade Name	Coefficient of Friction at, Ft./Min. 0	50	100	200	400	600
Mineral oil range							
Max.	. . .	0.080	0.067	0.064	0.059	0.055	0.052
Min.	. . .	0.059	0.047	0.043	0.040	0.036	0.035
Fatty acids							
Pelargonic acid (C_9)	Emery	0.106	0.073	0.064	0.054	0.043	0.032
Oleic acid (C_{18})	Emery	0.042	0.040	0.038	0.036	0.033	0.030
Saturated fatty acid (est. C_{24}, based on mol. wt.)	Emery, X-998-R	0.047	0.043	0.040	0.037	0.034	0.032
Alcohols		0.077	0.062	0.058	0.056	0.054	0.051
Cyclohexanol	Eastman	0.135	0.021	0.012	0.007	0.004	0.004
Ethylene glycol		0.084	0.048	0.043	0.038	0.033	0.030
2,3-Butanediol	Eastman	0.126	0.052	0.040	0.031	0.022	0.015
Diethylene glycol	Union Carbide	0.079	0.049	0.043	0.037	0.031	0.026
Triethylene glycol	Union Carbide	0.145	0.020	0.014	0.010	0.010	0.011
Glycerol							
Polyalkylene glycol	Union Carbide, UconLB-170-X	0.057	0.052	0.049	0.047	0.045	0.042
Esters							
Di-2-ethylhexyl sebacate	Rohm & Haas, Plexol 201	0.067	0.052	0.048	0.044	0.039	0.036
Dipropylene glycol dipelargonate	Emery	0.073	0.062	0.059	0.055	0.051	0.047
Ethyl ricinoleate	Eastman	0.071	0.057	0.049	0.041	0.034	0.030
Pentaerythritol ester	Hercules Powder Herco Flex 610	0.068	0.057	0.052	0.047	0.042	0.038
Tetra-2-ethylhexyl silicate	Union Carbide	0.077	0.067	0.063	0.059	0.054	0.047
Tritolyl phosphate	Monsanto	0.071	0.051	0.047	0.044	0.041	0.039
Silicones							
Hexa (2-ethylbutoxy) disiloxane	Union Carbide	0.066	0.060	0.056	0.052	0.049	0.044
Methyl phenyl silicone	Dow Corning, DC-510	0.095	0.056	0.051	0.049	0.048	0.047
Chlorinated methyl phenyl silicone	General Electric, Versilube F-50	0.079	0.065	0.058	0.054	0.053	0.052
Methyl phenyl silicone with polyglycol side chains	Linde X-522	0.076	0.057	0.054	0.050	0.047	0.045
Halogenated Compounds							
Chlorinated biphenyl	Monsanto, Arochlor 1248	0.173	0.046	0.038	0.035	0.034	0.032
Fluoroalkyl camphorate	Du Pont	0.091	0.072	0.066	0.064	0.061	0.058
Trifluorochloroethylene poylmer	M.W. Kellogg, Kel-F No. 3	0.097	0.069	0.066	0.064	0.063	0.061
Other							
Diamyl naphthalene	Sharples	0.068	0.059	0.056	0.053	0.051	0.048
Polybutene	Indiol Indopol L-50	0.073	0.062	0.058	0.056	0.054	0.051

phenyl silicone, a disiloxane, a chlorinated methyl phenyl silicone, and a silicone with polglycol type side chains. In contrast, Bowers, Cottington, Thomas, and Zisman (*5*), using a hemispherical rider on a flat plate, reported relatively high friction values for the methyl phenyl silicone and a significant reduction in friction due to the addition of chlorine to the silicone molecule.

Both the Kel-F polymer and the fluoroalkyl camphorate gave friction values higher than those observed with mineral oil; the chlorinated biphenyl gave lower friction values. Although all three of these halogenated fluids have been reported to have outstanding stability, marked discoloration and a precipitate were noted in the used chlorinated biphenyl after the complete friction test. Furthermore, the bearings run in the chlorinated biphenyl had a yellow brown coating resembling that found on bearings run in oils containing reactive chlorine additives, whereas the bearings run in the other halogenated fluids had no such coating. The low friction with the chlorinated biphenyl may have resulted from the formation of ferrous chloride on the bearing surfaces, which is known to reduce friction (*9*), and the higher friction values for the fluorinated fluids may have been due to lack of reaction with the bearing surfaces.

Both the polybutene fluid which is paraffinic and diamylnaphthalene gave slightly lower friction values than those for most naphthenic mineral oils. In contrast, Lane (*10*), who used a different test device to simulate conditions in friction drive units, reported that alkylated naphthalenes give higher friction values than naphthenic mineral oils at velocities above 100 feet per minute.

Most of the commonly used synthetic oils investigated had friction characteristics similar to mineral oils. The synthetic fluids which gave kinetic friction values higher than those for mineral oils were the very stable fluorinated compounds. Fluids which gave kinetic friction values lower than those for mineral oils were the fatty acids, some polyhydroxy alcohols, and the chlorinated biphenyl, all believed to react with the steel surface to form a low friction coating. Thus, kinetic friction appears to be associated with the reactivity of the fluid with the rubbing

Table V. Effects of Additives on Friction

Reported Chemical Composition	Source, Trade Name	Conc. Used, Wt. %	General Effect on Friction	Friction Ratio At, Ft./Min.					
				0	50	100	200	400	600
Base Oil									
Max.				1.17	1.05	1.07	1.10	1.10	1.10
Min.				0.89	0.97	0.94	0.93	0.92	0.91
Acids and Alcohol									
Oleic acid^a	Emery	1.0	Type II a	0.44	0.60	0.63	0.67	0.74	0.79
Stearic acid^a	Emery	1.0	Type II	0.45	0.75	0.80	0.85	0.91	0.95
Saturated fatty acid (C_{24} est.)^a	Emery, X-998-R	1.0	Type II	0.57	0.79	0.82	0.86	0.91	0.93
Oleyl alcohol	Monsanto	1.0	Type I	0.83	0.92	0.90	0.91	0.92	1.02
Perfluorohexanoic acid^b	Minn. Mining & Mfg.	0.05	Type I	0.90	0.85	0.83	0.81	0.80	0.79
Sulfur and Chlorine Compounds									
Dibenzyl disulfide^b	Fine Organics	2.5	Type I	1.00	0.89	0.86	0.87	0.87	0.86
Sulfurized terpene oil^{b,c}	Std. of Ind., Stan Add 48	2.5	Type IV a	0.76	0.73	0.66	0.57	0.54	0.56
Sulfurized sperm oil^a	Socony Mobil, Floyd's Base 28	2.5	Type II a	0.62	0.77	0.77	0.77	0.73	0.75
Chlorinated wax^b	Lubrizol, Anglamol 40	2.5	Type III	0.63	0.67	0.68	0.69	0.67	0.67
Hexadecyl chloride^b	Monsanto	2.5	Type IV	1.09	0.96	0.85	0.70	0.69	0.69
Nitrogen Compounds									
tert. C_{18}-C_{24} amine^d	Monsanto	2.0	Type III	0.78	0.77	0.75	0.74	0.74	0.74
Phenyl-1-naphthylanime^c	DuPont	1.0	Type I	0.95	1.07	1.06	1.07	1.08	1.06
Tallow fat diamine^{a,d}	Armour, Duomeen T	1.0	Type II	0.53	0.78	0.81	0.86	0.92	0.96
Dimethyl soya amine^d	Armour, Armeen DMS	1.0	Type II	0.71	0.88	0.91	0.92	0.95	0.96
Octadecyl nitrile	Monsanto	2.0	Type I	0.83	0.92	0.93	0.95	0.98	1.00
Phosphorus Compounds									
Tritolyl phosphate^b	Monsanto	2.0	Type I	0.85	0.97	0.96	0.97	0.99	0.99
Dilauryl phosphate^{a,b}	DuPont, Otholeum 162	2.0	Type II a	0.42	0.61	0.63	0.66	0.66	0.72
Triphenyl phosphite	Eastman	2.0	Type I	0.79	0.91	0.90	0.88	0.88	0.88
Dibutyl phosphite^b	Oldbury	2.0	Type IV a	0.74	0.70	0.66	0.63	0.59	0.58
Dibutyl butyl phosphonate	Oldbury	2.5	Type I	0.84	0.84	0.83	0.86	0.89	0.90
Dimethyl methoxymethyl phosphonate^b	Oldbury	0.5	Type IV	1.13	0.83	0.80	0.79	0.78	0.77
Bis(β-chloroethyl)vinyl phosphonate^b	Monsanto, N-30	1.0	Type IV	1.03	0.68	0.62	0.55	0.52	0.54
Metal Organic Compounds									
Barium dithiophosphate^b	American Cyanamid, Aerolube 68	2.0	Type I	0.78	0.95	0.95	0.96	1.01	1.03
Barium phenate + Sulfur^f	Enjay, Paranox 56	2.0	Type V a	1.61	0.93	0.81	0.76	0.78	0.82
Barium sulfonate, basic salt^f	Vanderbilt, Na-Sul BSB	2.0	Type V a	1.85	1.12	0.90	0.76	0.80	0.85
Cadmium diamyl dithiocarbamate^c	Vanderbilt, Vanlube 61	2.0	Type V a	2.55	1.35	0.90	0.73	0.71	0.75
Sulfurized calcium alkyl phenate^f	Oronite, OLOA 216	2.0	Type I	0.84	0.96	0.96	0.96	0.99	1.03
Calcium petroleum sulfonate^f	Oronite, OLOA 246B	2.0	Type V	1.26	0.95	0.93	0.91	0.92	0.96
Lead diamyl dithiocarbamate^{b,c}	Vanderbilt, Vanlube 71	2.0	Type II	0.74	0.90	0.91	0.91	0.85	0.86
Lead naphthenate^b		2.0	Type II	0.71	0.82	0.82	0.93	0.87	1.08
Lead alkyl phenate^f	Oronite, OLOA 310	2.0	Type II	0.75	0.85	0.85	0.85	0.87	0.90
Dibutyl tin dilaurate^b	Metal & Thermit	2.0	Type I	1.06	0.90	0.85	0.84	0.84	0.87
Zinc diamyl dithiocarbamate^c	Vanderbilt, Vanlube AZ	2.0	Type V	2.89	1.43	0.90	1.01	0.90	0.92
Zinc dithiophosphate^{b,c}	Lubrizol, LZ 1060	2.0	Type I	0.83	0.87	0.86	0.88	0.92	0.95
Others									
2,6-Di-*tert*-butyl-4-methyl phenol^c	Enjay, Paranox 441	1.0	Type I	0.88	0.93	0.92	0.92	0.93	0.95
Dilauryl selenide^c	Oronite, OLOA 250	1.0	Type I	0.96	1.03	1.01	1.01	1.00	1.00
Methacrylate polymer^e	Rohm & Haas, Acryloid 710	3.0	Type I	0.86	0.95	0.93	0.92	0.92	0.94
Methacrylate-nitrogen copolymer^{e,f}	Rohm & Hass, Acryloid 917	3.0	Type II	0.74	0.89	0.91	0.92	0.93	0.96
Polybutene polymer^e	Enjay, Paratone N	3.0	Type I	0.81	0.93	0.91	0.88	0.88	0.89

^{a} Friction modifier. ^{b} Antiwear. ^{c} Antioxidant. ^{d} Antirust. ^{e} V.I. Improver. ^{f} Detergent.

surfaces, the more reactive fluids generally causing the lower observed friction.

Oil Additive Composition. If friction under boundary lubrication conditions is controlled by coatings on the rubbing surfaces, many lubricant additives such as antiwear additives, rust inhibitors, and detergents, which are surface active or react with the surface to perform their function, might be expected to have a pronounced effect on friction. Representative additives of the various types normally used in finished lubricants were evaluated with the results in Table V. For these studies, the additives were evaluated by blending them individually into a highly refined naphthenic base oil (oil B). No attempt was made to study the effects of additive mixtures on friction.

To emphasize the effect of a particular additive, the data are presented in terms of the friction ratio. This is defined as the ratio of the friction with base oil plus additive to that observed for the base oil alone. A friction ratio greater than unity indicates that the additive increased friction and a ratio less than unity indicates that the additives decreased friction. Repeatability tests on the base oil alone gave friction ratio values falling approximately between 1.10 and 0.90. Consequently, for an additive to be considered to have a significant effect on friction, the observed friction ratio should fall well outside the base oil range.

To simplify the discussion, the additives have been classified according to their effect on friction. Examples of the various types of additive effects are illustrated in Figure 9, *a* and *b*. In general, the additive effects can be described by saying the Type I additives have no effect on friction, Type II additives lower the friction ratio at low velocities (below 100 feet per minute), Type III additives lower the friction ratio at all velocities, Type IV additives lower the friction ratio at high velocities (above 100 feet per minute), and Type V additives raise the friction ratio at low velocities.

It has been shown by Bowden and others (*3, 4, 6, 12*) that long-chain hydrocarbons containing a polar group on one end, such as a carboxyl, amine, or hydroxyl group, reduced friction at low velocities. For steel surfaces, fatty acids are generally believed to react with the metal to form an adherent soap film; the amines and monohydroxy alcohols are believed to be physically adsorbed. All three fatty acids listed in Table V had a Type II friction effect. Changing the polar group in the molecule from the carboxylic acid group such as that in oleic acid to the phosphoric acid group in dilauryl phosphate did not change the type of friction effect. Oleic acid and the acid phosphate were also effective in reducing friction at high velocities; the other two fatty acids were not. The two tertiary fatty amines containing only one long hydrocarbon chain were also effective Type II additives, whereas the tertiary amine with three long hydrocarbon chains was effective at all velocities (Type III effect). Octadecyl nitrile, oleyl alcohol, and the perfluoroacid are examples of polar molecules that did not affect friction. These results confirm the observations of previous investigators that fatty acids and amines having one long hydrocarbon chain are effective additives for reducing friction at low velocities. The ineffectiveness of alcohol and the nitrile demonstrates that not all long-chain polar molecules are adsorbed strongly enough to form a protective coating in the contact area.

The sulfur and chlorine additives used in extreme pressure lubricants are also known to form coatings on metal surfaces. It has been shown that chlorine-containing additives such as a chlorinated wax and sulfur-containing additives such as dibenzyl disulfide react with steel to form iron chloride and sulfides, respectively (*7, 8, 15*). Of the two coatings, ferrous chloride is reported to be the more effective in reducing friction (*9*).

In Table V, the three sulfur and two chlorine additives show quite different friction characteristics even though one might expect similar coatings to be formed in each class. For example, sulfurized sperm oil reduced static friction (Type II effect) whereas the sulfurized terpene oil had a greater effect on the kinetic friction (Type IV effect). Hexadecyl chloride also had a Type IV effect, but the chlorinated wax reduced friction over the entire velocity range (Type III effect). These differences show that the coatings formed with these additives are not the same but include something in addition to iron sulfides or iron chloride.

Phosphorus additives such as tritolyl phosphate are reported to reduce friction by the formation of a phosphide which acts as a polishing agent for improving surface finish (*1*). The friction data in Table V show that the phosphorus additives differ widely in their effect on friction. The dialkyl phosphate and phosphite as well as the substituted phosphonates all reduced kinetic friction (Type II a or IV effects) whereas the unsubstituted trialkyl compounds had no effect. Further, the long-chain dilauryl phosphate was effective in reducing static friction, whereas the short-chain dibutyl phosphite was not. If it is assumed that tritolyl phosphate is typical of the compounds that

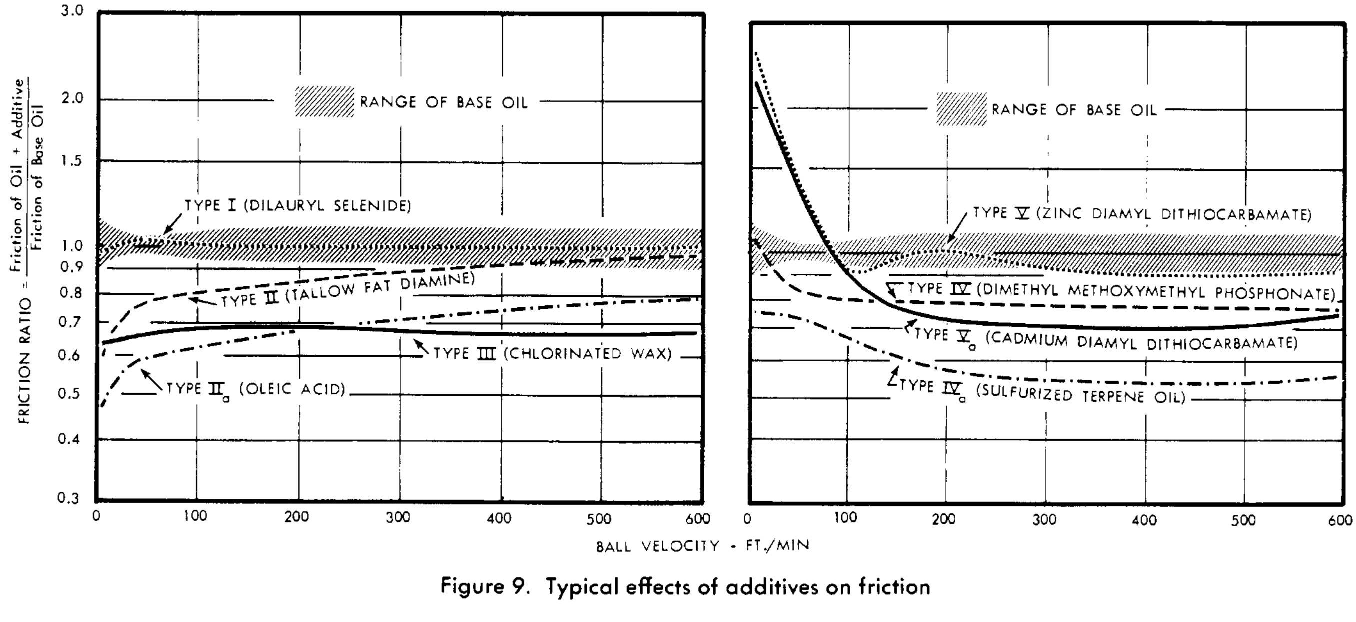

Figure 9. Typical effects of additives on friction

form polishing agents, the results suggest that dialkyl phosphates and phosphites reduce friction through the formation of a protective coating rather than by changing the surface finish. The effectiveness of the chlorinated phosphonate may be due to the chlorine atoms in the molecule which can react to form ferrous chloride on the metal surface.

The metal-organic additives evaluated had one of three effects on friction. The barium phenate and sulfonate, the cadmium and zinc dithiocarbamates, and the calcium sulfonate were Type V additives, the three lead compounds were Type II additives, and the remainder were Type I additives. The importance of the metal portion of the molecule is demonstrated by the three phenates or the three dithiocarbamates. Similarly, a comparison of the three barium compounds, the two calcium compounds, or the two zinc compounds shows that the organic portion of the molecule is also important in controlling friction. In contrast, changing the metal in two dithiophosphates or two sulfonates or changing the organic group attached to lead did not alter the observed friction significantly.

Differences in test results for the various metal-organic compounds suggest that the coatings formed differ widely. For example, recent radioactive tracer wear studies have shown that zinc dithiophosphate type additives form coatings on iron surfaces containing zinc, phosphorus, and sulfur (*11*). The proportions of these three elements are not the same in the coating as in the original molecule, indicating that chemical reaction with the surface occurs. In contrast, metallic detergents (phenates and sulfonates) are believed to perform their function through physical adsorption on surfaces (*2*). The differences in barium and calcium detergents on static friction may be due to selective displacement of polar molecules from the surface by the barium detergents but not by the calcium detergent. Although most of these metal-organic compounds contain appreciable amounts of sulfur, the kinetic friction results suggest that the sulfur available to form an iron sulfide coating varies.

The naphthylamine, the substituted phenol, and the selenide oxidation inhibitors as well as the three polymeric viscosity index improver additives had little or no effect on friction in these tests. This behavior was not surprising, as these additives primarily affect the bulk oil properties rather than the surface activity of the lubricant.

RELATIONSHIP BETWEEN OIL COMPOSITION AND FRICTION

The studies described above have shown that oil composition has a pronounced effect on the friction of lubricated steel on steel. Although a change in the base oil generally tends to raise or lower the entire coefficient of friction-velocity curve, a few base oils increased static friction preferentially. Additives, on the other hand, may lower the high velocity portion of the friction-velocity curve, raise or lower the low velocity portion of the curve, or affect both the low velocity and the high velocity portions of the curve. No additives raised kinetic friction. A summary of the more effective base oils and oil additives for changing friction is given in Tables VI and VII, respectively.

Only two synthetic oils gave kinetic coefficient of friction values higher than those for the straight mineral oils. Both of these oils are low viscosity index materials—i.e., they show much change in viscosity with change in temperature. Further , low viscosity index naphthenic base mineral oils gave higher friction values than the higher viscosity index paraffinic base mineral oils or diesters. Therefore, one might postulate with Lane (*10*) that kinetic friction is associated with the viscosity-temperature properties of the fluid. However, the chlorinated biphenyl, also a very low viscosity index material, gave low kinetic friction. This plus the fact that measured friction with mineral oils is essentially independent of viscosity tends to refute Lane's suggestion. A more reasonable explanation is that the high kinetic coefficient of friction obtained with the fluorinated materials is related to the reduced reactivity of these fluids with steel surfaces.

Low kinetic coefficients of friction were obtained with base oils and additives. In comparing Tables VI and VII, it will be noted that the most effective materials for lowering kinetic friction are materials that readily react with steel, with the possible exception of the polyhydroxy alcohols. Many of the less effective additives are also capable of reacting with the surface. Wear studies show that the chemical activity of the additives must be adjusted to form the wear-preventing coating rapidly enough to replace the coating as it is worn away but not to corrode the metal parts excessively (*15*). The rate at which the various additives react with the surface may determine their effectiveness in reducing friction. This implies that additives effective under one set of conditions may not be under another set of conditions.

To reduce static friction, additions of fatty acids and related long hydrocarbon chain polar materials were most effective. The fatty acid type additives most effective for reducing static friction were not as effective for reducing kinetic friction as chlorine, sulfur, and phosphorus additives.

For an additive to be effective in reducing friction, the additive must form a suitable coating on the metal surface. As the relative velocity of the two rubbing surfaces increases from zero, the temperature in the contact area tending to decompose these coatings increases. At the higher velocities, only the more stable coatings would be expected to maintain an effective coating between the metal surfaces. The reduced effectiveness of fatty acid type materials at the

Table VI. Effective Base Fluids for Changing the Friction of Steel on Steel

(Basis of comparison, oil B)

Higher Coefficient of Friction	Lower Kinetic Coefficient of Friction
Kinetic	Ethylene glycol
Trifluorochloroethylene polymer	Glycerol
Fluoroalkyl camphorate ester	Diethylene glycol
Naphthenic mineral oils	Triethylene glycol
Static	Chlroinated biphenyl
Chlorinated biphenyl	Oleic acid
Glycerol	Saturated fatty acid (C_{24} estd.)
Ethylene glycol	2,3-Butanediol
Diethylene glycol	Paraffinic mineral oil
Pelargonic acid	
Trifluorochloroethylene polymer	
Methyl phenyl silicone	

Table VII. Effective Additives for Changing the Friction of Steel on Steel

(Basis of comparison, oil B)

Increase Coefficient of Friction,[a] 0 to 100 Ft./Min.
Zinc diamyl dithiocarbamate
Cadmium diamyl dithiocarbamate
Barium sulfonate
Barium phenate
Calcium sulfonate

Decrease Coefficient of Friction	
0 to 100 Ft./Min.	100 to 600 Ft./Min.
Dilauryl phosphate	Bis(β-chloroethyl)vinyl phosphonate
Oleic acid	Sulfurized terpene oil
Stearic acid	Dibutyl phosphite
Tallow fat diamine	Dilauryl phosphate
Saturated fatty acid (C_{24} estd.)	Chlorinated wax
Sulfurized sperm oil	Hexadecyl chloride
Chlorinated wax	Oleic acid

[a] 100 to 600 ft./min., no effective additive.

higher velocities compared to some chlorine, sulfur, and phosphorus additives may be due to the poorer stability of the films formed by fatty acid type materials.

High static friction was obtained with both selected base oils and certain metal-organic additives. The base oils that gave high static friction are generally considered rather poor in their antiwear performance. Other studies have shown that the addition of metal-organic detergents to a base oil increases wear compared to that for the base oil alone. Because both wear and friction are believed to depend on surface films, these observations suggest that high static friction results from failure by certain lubricant compositions to maintain a low friction coating under low velocity, low surface temperature conditions.

During limited friction studies conducted in the bench test rig and in full scale equipment, it has been observed that the effects of one additive, such as a fatty acid to reduce static friction, can be canceled by the addition of a more reactive additive. Thus, in a finished lubricant containing several additives, the friction characteristics of the lubricant are the net result of competition by the additives for the surface.

Lubricants for Mechanical Devices. The magnitude of the coefficient of friction between lubricated moving parts and its variation with changes in velocity are two important factors governing the operating characteristics of mechanical devices such as lubricated plate clutches and friction drive units. Both factors can be controlled by lubricant composition. Moreover, the use of different construction materials in the rubbing surfaces may significantly alter lubricant effectiveness. What friction characteristics are desired in mechanical devices? Figure 10 shows some representative curves of coefficient of friction *vs.* velocity that will aid in explaining this.

The use of a lubricant giving a curve similar to *A* or *B* in lubricated plate clutches may lead to noisy or harsh clutch engagements. The noise is believed to be the result of stick-slip type motion caused by the rapid increase in friction as the velocity approaches zero. If the lubricant gives a curve similar to *C* or *D*, the clutch engagement is silent and smooth. In some clutches a lubricant giving a curve similar to *D* allows excessive plate slippage causing damage to the clutch plates. Consequently, a fluid giving a curve similar to *C* is generally preferred for lubricated plate clutches.

For lubricated friction drive units, the power transmitted by a given unit is proportional to the product of the coefficient of friction and the applied load. Because the fatigue life of drive members varies inversely with the cube of the applied load, the lubricant should provide the maximum kinetic coefficient of friction between mating parts. Thus for a friction drive unit, curve *B* would be preferred to curve *A*.

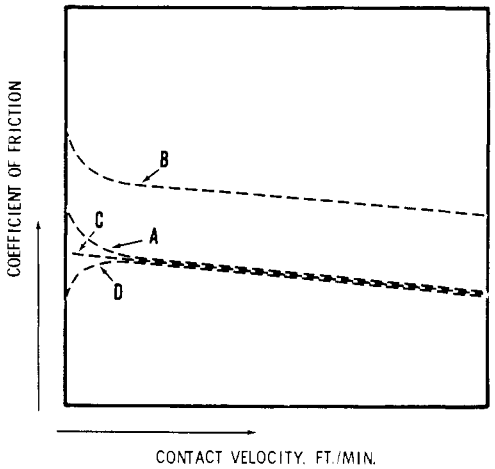

Figure 10. Typical effects of lubricants on friction

SUMMARY

A device employing two thrust ball bearings as the test elements was used to determine the effects of lubricant composition on the friction of lubricated steel on steel. Tests on straight mineral oils, synthetic oils, and oil additives, showed that both the base oil and the additive treatment have a pronounced effect on friction.

Naphthenic base oils gave higher friction values than paraffinic base oils, but no correlation with hydrocarbon type analyses was found. Limited attempts to change the friction properties of a naphthenic base oil by fractionation and hydrogenation were unsuccessful.

Most of the commonly used synthetic fluids had friction characteristics similar to straight mineral oils. Kel-F fluid and a fluoroalkyl camphorate ester gave higher kinetic friction values than those for naphthenic based oils. Several synthetic fluids have lower kinetic friction values than paraffinic based oils; ethylene glycol and glycerol were the most effective.

Additives were found that would lower kinetic friction and/or raise or lower static friction. For preferentially lowering static friction, fatty acids and related compounds were most effective. To lower kinetic friction at velocities above 100 feet per minute, reactive chlorine and sulfur compounds were required. Some metal-organic compounds raised static friction.

The data presented support the theory that films formed by lubricants rubbing surfaces control the friction of steel on steel under boundary lubrication conditions.

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LITERATURE CITED

(1) Beeck, O., Givens, J.W., Williams, E.C., *Proc. Roy. Soc. (London)* **A177**, 103–18 (1941).
(2) Bondi, A., "Physical Chemistry of Lubricating Oils," Reinhold, New York, 1951.
(3) Bowden, F.P., Leben, L., *Trans. Roy. Soc. (London)* **A239**, 1–27 (1940).
(4) Bowden, F.P., Tabor, D., "The Friction and Lubrication of Solids," Oxford Univ. Press, London, 1954.
(5) Bowers, R.C., Cottington, R.L., Thomas, T.M., Zisman, W.A., *Ind. Eng. Chem.* **48**, 943–50 (1956).
(6) Bristow, J.R., *Inst. Mech. Engrs. (London)* **160**, 384–99 (1949).
(7) Davey, W., *J. Inst. Petrol.* **31**, 73–88 (1945).
(8) *Ibid., pp. 154–8.*
(9) Johnson, R.L., Godfrey, D., Bisson, E.E., "Friction of Solid Films on steel at High Sliding Velocities," Natl. Advisory Comm. Aeronaut. Tech. Note **1578** (1943).
(10) Lane, T.B., *Lubrication Eng.* **13**, 85–8 (1957).
(11) Larson, R., *Sci. Lubrication (London)* **10**, No. 8, 12–16, 18–19 (1958).
(12) Murray, S.F., Burwell, J.T., *Ann. N. Y. Acad. Sci.* **53**, 906–18 (1951).
(13) Murray, S.F., Johnson, R.L., Bisson, E.E., Natl. Advisory Comm. Aeronaut. Tech. Note **2940** (1953).
(14) Neeley, G.L., Proc. Am. Petrol. Inst. (Div. of Refining) Meeting, June 1932, vol. **13M-3**, pp. 60–73.
(15) Prutton, C.F., Turnbull, D., Dlouhy, G., *J. Inst. Petrol.* **32**, 90–118 (1946).
(16) van Nes, K., Westen, H.A., "Aspects of the Constitution of Mineral Oils," Elsevier Publ. Co., Amsterdam, 1951.
(17) Zisman, W.A., Chem. Div., Naval Research Lab. Rept. **4080** (Nov. 26, 1952).

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