

Lubrication & Chemical Constitution

by

Stewart Robertson McDougall



LUBRICATION AND CHEMICAL CONSTITUTION

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LUBRICATION AND CHEMICAL CONSTITUTION.

INTRODUCTION -

In the last four or five years a great deal of interest has been aroused in the subject of lubrication. It has been a well known fact ever since mineral lubricating oils came into general use, that they were on the whole inferior to animal and vegetable oils. The reason for this difference was never looked into until just recently. So far, however, there has been no satisfactory theory developed in explanation of this dissimilarity. Nor have we had until now any method of determining the lubricating properties of an oil without trying it out in practice. An attempt has been made by several investigators to find a relation between the chemical constitution and the lubricating quality of an oil, but no final results have yet been obtained.

PURPOSE OF RESEARCH -

In this research an attempt has been made to determine the effect of varying amounts of alcohols, esters, unsaturated hydrocarbons and fatty acids in mineral lubricating oils, on the coefficient of static friction of the latter when applied to different metal surfaces. It was also hoped to develop a simple means for ascertaining the lubricating quality of an oil without trying it in practice.

EARLY INVESTIGATIONS -

(a) The Coefficient of Friction of Dry Surfaces.

The first recorded investigation of friction was in 1699, when Amontons (Mem.d. l'Acad. Roy. des Sciences, (1699), p. 206) found that resistance to relative motion varied with the normal pressure, but was independent of the area of the applied surfaces. He expressed this relation as follows:

$F = \mu \cdot P$
where F = force necessary to cause motion
 P = total pressure
 μ = coefficient of friction

In general he found that F was equal to one-third P . His theory was that friction is due to asperities in the surfaces. This view was later upheld by Euler (Berlin Acad. Memoirs, (1748), p.122).

The next experiment along this line was conducted by Coulomb (Mem.d.l'Acad.Roy. des Sciences,(1785), vol.10,p.161), who in 1785 showed that there was a difference between static and kinetic friction, but that the above law held for both. Then in 1830, Morin (Mem. d.Scavanes Etrangers IV.,(1833), pp.1, 591; VI. p.641) proved with a more refined apparatus, that the kinetic was usually less than the static friction. Finally Jenkin and Ewing (Phil.Frans.A. 167, 509, (1877) discovered that there was continuity from the state of static to that of kinetic friction.

(b) The Coefficient of Friction of Journal Bearings.

A different line of experiments was commenced by B. Tower (Proc. Inst. Mech. Eng. (1883), p. 632; (1884), p. 29), who determined the coefficient of friction of a standard bearing and the effect of variations in pressure, speed, temperature, methods of lubrication and the kind of oil used. This marked the advent of the modern journal friction testing machine. Tower used a 4 in. journal in a half bearing with loads from 100 lbs. to 500 lbs., and speeds ranging from 100 r.p.m. to 450 r.p.m. He found that the friction was independent of the load, but proportional to the velocity. It was also affected by a change in temperature, and by different methods of lubrication.

By using a similar method to Tower, O. Reynolds (Phil. Trans. Vol. 177, (1886), p. 157) showed that the friction depended on the viscosity of the lubricant. He improved the mathematical theory of lubricated bearings by the introduction of hydrodynamics. The mathematical end of the subject has also been highly developed by Sommerfeld (Zeitschr. f. Math. t. 50, (1904), p. 97) and Harrison (Camb. Trans. vol. XXII, (1913), p. 39).

RECENT DEVELOPMENTS -

(a) Boundary Lubrication and Galling.

The more important recent investigations have

been carried out in a different field, namely "Boundary Lubrication". Boundary Lubrication occurs when the solid faces are close enough together to influence directly the properties of the lubricant, and is found in ordinary dry surfaces. This is quite different from the ordinary condition in bearings which is known as "Flooded Lubrication". Here the metal surfaces are separated by an oil film of appreciable thickness which prevents metal to metal contact. In such cases the friction depends entirely upon the viscosity of the lubricant; while in the case of Boundary Lubrication, it depends on ^{the} oiliness of the lubricant and the chemical nature of the metal surfaces. That in Flooded Lubrication, the value of the lubricant depends on viscosity is shown by the use of molasses as a lubricant on sugar-making machinery, of air on spinning machinery and of water on the propeller shafts of boats.

The vital importance of Boundary Lubrication is because of its continual occurrence in the actual operation of all machinery. It is encountered under the following conditions:

- (1) The starting and stopping of bearings, which causes the perfect oil film to be squeezed out, thus allowing abrasion if an oil with a high degree of oiliness is not used.
- (2) When the oil supply, due to negligence or a break in the lubricating system, has been allowed to get low.
- (3) Between the piston rings and cylinder walls, and also in the cross head of an engine.

- (4) In cases where high pressures and slow speeds are used, such as in gears and in cutting and threading. In the latter case, lard and fish oils are used in preference to mineral oils.

Oiliness is a new hypothetical property of an oil which makes it a better lubricant than another oil of the same viscosity. It is the only difference between good, poor and non-lubricants.

(b) First Experiments on Boundary Lubrication.

Lord Rayleigh in 1918 (Phil. Mag. 3.6. Vol.35, (1918), p. 157) studied the action of a glass bottle sliding on an inclined glass plane. He noticed that for a dry, clean plate the bottle slid quite easily; but when he breathed on the plate or flooded it with water, the angle causing slip was much greater. On evaporation of the moisture he obtained his original values. Then he tried the same experiment using paraffin oil and a brass plate in which he obtained similar results to those with water. The conclusions drawn from these determinations was that the friction was greater, the larger the amount of lubricant present, and that in the dry state the plate had a thin film of about 10^{-4} mm. in thickness adsorbed onto its surface. This film lowered the friction a large amount.

Just before he performed the above work Lord Rayleigh went into an involved mathematical discussion of

the subject which is given in detail in the Philosophical Magazine, 3.6. Vol.35, (1918), p.1. For two plates the conclusion drawn was that

where $F/P = 4.091 \ h/c$
 F = friction
 P = pressure
 h = distance between plates
 c = length of upper and shorter plate.

(c) The Viscosity Theory.

Prof. O. Faust at Göttingen (Z. physik.chem.86, (1914), pp. 479-94) found that the viscosity of ether, carbon disulphide and ethyl alcohol increased enormously for pressures of 3,000 atmospheres. As shown by H.M. Martin (Proc. Phys.Soc.Vol.32, (1919-20) p. 11s), it was believed, that in a case of imperfect lubrication, wear was due to a concentration of the load in a few spots of limited area, thus giving a very high pressure on the oil film. This caused a rise in the viscosity of the oil, which would then prevent metal to metal contact.

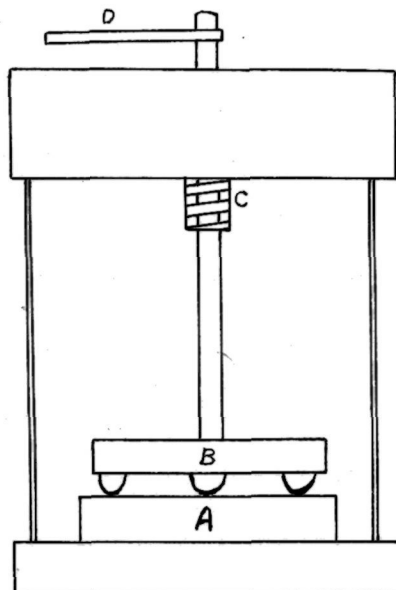
This led to the theory that animal and vegetable oils were better lubricants than mineral oils in cases of imperfect lubrication, because it was believed that the viscosity of the latter did not increase as much as the former under pressure. This view was overthrown in 1919, by T. E. Stanton, L. Archbutt and J. C. Southcombe (Engineering 108, (1919) pp. 759-60) in measurements of the transmission of power through a worm gear. They found

that, contrary to the above theory, an increase in pressure to 900 atmospheres raised the viscosity of animal and vegetable oils four fold, and that of mineral oils sixteen fold. This showed that viscosity could not be the only factor in lubrication.

They noticed that there was very little change in the efficiencies of animal and vegetable oils with a rise in temperature, but that it was accompanied by a rapid fall for mineral oils. It was found that this fall in the latter could be prevented by the addition of small amounts of fatty acids. From these results oiliness was believed to be due to chemical affinity between the metal surfaces and the lubricant.

(d) The Deeley Machine.

R. M. Deeley (Proc. Phys. Soc. Vol. 32, (1919-20), p. 1 S.) concluded from the above investigation, that the property of oiliness would show up best, by measuring the static coefficient of friction for oils between different metal surfaces. For this purpose he constructed what is now known as the Deeley Machine.



This machine consisted of a smooth, flat, circular plate, A, of any desired metal, which could be rotated at various speeds. On it rests another plate, B, of adjustable weight. This plate is supported by three small hemispherical pegs of any metal. When A is rotated, B is dragged along at the same speed by the friction between the two metal surfaces, until the torque set up in the calibrated spring, C, overcomes the resistance to slip. To C is attached a pointer, D, which indicates on a special scale the coefficient of friction. Just at the point where slip occurs the indicator gives the coefficient of static friction, and from then on the coefficient of kinetic friction. To get any consistent results with this machine, it has been found necessary to remove the last

traces of water.

Deeley noticed, that with this machine for clean surfaces without any lubricant, the coefficient of static friction gets greater and greater as the surfaces are rubbed on each other. For mild steel on cast iron, his coefficient at first was 0.154, while after running for ten minutes he got a value 0.417. He found very little difference between static and kinetic friction, but observed a marked difference in the friction of the same oil when used on different metals. This dissimilarity is shown in the following table.

Kind of Oil	SOURCE	Coefficient of Friction.	
		Mild Steel on Cast Iron	Mild Steel on Lead Bronze
H.B. Clock oil	M	0.271	0.275
Bayonne oil	M	0.213	0.234
Typewriter oil	M	0.211	0.294
Victory Red oil	M	0.196	0.246
F.F.F. cylinder oil	M	0.193	0.236
Manchester spindle oil	M	0.183	0.262
Castor oil	V	0.163	0.129
Valvoline cylinder oil	B	0.143	
Sperm oil	A	0.127	0.180
Trotter oil	A	0.123	0.152
Olive oil	V	0.119	0.196
Rape oil	V	0.119	0.136

M = mineral oil; V = vegetable oil; A = animal oil
B = blended oil

This table brings out the fact that Rape and Olive oils are the best lubricants, with mineral oils the worst, and castor oil about half way in between. Rape

and Olive oils seem to reduce the friction the same amount for mild steel on cast iron, but the former is better with mild steel on lead bronze.

From these results, Deeley concluded that the coefficient of static friction varies not only with the lubricant, but also with the metals in contact. Therefore, oiliness would appear to be an effect of the oil upon the metal surfaces, rather than any physical property of the lubricant itself. This, he believed, was due to the unsaturated molecules of the lubricant entering into a firm physico-chemical union with the metal surfaces, thus forming a friction reducing medium composed of oil and metal, which would appear to be more than a molecule in thickness.

(c) Hardy's Method and Results.

Hardy determined the static friction by measuring the force necessary to start a hemisphere sliding over a smooth plate. In his article, "A Problem in Lubrication", (Journ. of Soc. Chem. Ind. Vol. 38, (1919), p. 77) he states that, "with a true lubricant the facility for slipping is maximal when a layer of such excessive tenuity separates the solid faces that nothing is gained by increasing the thickness of the layer". This film he found to be about 1×10^{-7} cm. in thickness. He verified

this statement by showing that some liquids were better lubricants in thin than in thick layers, as shown by the following results for glass on glass.

Liquid	Pull in grams	
	Film	Flooded
Acetic Acid	40	47
Sulphuric Acid	37	47
Oleic Acid	10	13

He believed this indicated that lubrication depends wholly on the chemical constitution of the liquid, and that films being better lubricants, pointed to the fact that lubrication is accomplished by a fluid adsorbed onto the solid face.

In a paper published by the same investigator in 1919, (Phil. Mag. Vol. 38, (1919), p. 32) it was pointed out that there is a variation in the surface energy at an interface between two liquids and a composite surface, which is closely related to the chemical constitution of these substances. If this interface is formed by chemical forces, we would expect that they could be saturated or neutralized. This seems to be the action of a lubricant in reducing the cohesion and resistance to slip between two surfaces.

Hardy also found evidence of orientation of the molecules of a lubricant, because at an interface the compounds, such as, acids, bases and esters, which produce the greatest surface energy changes are readily polarisable. This orientation of molecules at surfaces was also pointed out by Langmuir. (Journ. Am. Chem. Soc. Vol. 38, (1916), p. 2221; vol.39, (1917), p.1648)

According to Hardy, the theory of static friction which best suits these facts is that friction is due to cohesion between the metal surfaces.

W. B. Hardy and Ida Doubleday (Proc. Royal Soc. Vol. 100 A, March 1922, p. 550) carried out numerous experiments in the field of Boundary Lubrication, from which they came to the following conclusions:

- (1) that variation in the weight of the sliding hemisphere did not affect their results.
- (2) that variation in the radius of curvature of the hemisphere had no effect
- (3) that for steel, bismuth and rubbed quartz a change in temperature had no appreciable effect. (Proc. Royal Soc. Vol. 101a, Sept. 1922, p. 467) However, it was noticed that for glass and clean quartz, a rise in temperature lowers the coefficient of friction. The low value obtained was retained on cooling to the original temperature. They also found that for a lubricant, which is solid over part of the range of temperature, there is a rapid drop to a very low value just below and at the melting point, while just above the melting point there is a sudden rise to a constant value.

(4) that the thickness of the film did not effect the friction providing there was enough of the lubricant present to cover the whole surface. The friction, however, gradually diminished as the concentration of the lubricant increased, until a minimum was reached, when further concentration produced no change.

(5) that an equation, such as,
$$u = b - aM$$
fitted each chemical series investigated.

u = coefficient of static friction

M = molecular weight of lubricant

a = a constant dependent on the chemical type of the series.

b = a constant dependent on the chemical nature of the solid surfaces.

It was noticed that the friction for the same lubricant varied when applied to different solid substances, for steel gave a higher coefficient than bismuth, but lower than glass. In the case of metals, the friction was found to vary directly as the hardness, while two different metals on each other gave values intermediate to those for each metal on itself.

In the Journal of the Chemical Society for December 1922 (p. 2875), Miss Ida Doubleday gives an account of some measurements which she made of the coefficient of static friction for a series of optically active carbinols ($C_2H_5CHOH C_nH_{2n+1}$). She found their lubricating power to be independent of the sign of rotation, or of any spiral arrangement of the carbon atoms.

The Fourth Report on Colloid Chemistry (British Association for Advancement of Science (1922), p. 185) contains an article by W. B. Hardy, in which he indicates the affect of chemical constitution on the value of the coefficient of friction for pure liquids, when measured with Bismuth on Bismuth. In some chemical series, such as, the paraffins and benzenes, the static friction was shown to be a linear function of the molecular weight. In other series the effect of molecular weight was overshadowed by that of chemical constitution. However, if he went high enough in any simple series of chain compounds, e.g. alcohols and fatty acids, he found a good lubricant, except in the case of the aliphatic esters. It also became evident, that similar changes in the molecular structure of ring and chain compounds produced opposite effects on the two series. No ring compound was encountered which proved to be a really good lubricant. Hardy found that atoms placed symmetrically about a central carbon atom produced very bad lubricants, an example being carbon tetra chloride.

The only generalisation which he could draw in the case of bismuth on bismuth, was that the addition of a single OH group to a molecule increases its lubricating power. However, a second or third group diminishes the effect of the first. Single -OH groups on a ring or

closed chain compound appeared to be more effective than on an open chain. Also when he replaced Cl by H, or H by CH₃ a better lubricant was obtained.

(f) Regions of Lubrication in a Bearing

Robert E. Wilson and Daniel P. Barnard (Journ. Ind. and Eng. Chem. Vol. 14, No. 8 Aug. 1922, p. 682) showed from experiments on a friction journal testing machine, that for any bearing there are three regions of lubrication, namely:

- (a) A region of fluid film lubrication where the metal surfaces are held apart by a perfect film of liquid. Here viscosity is of prime importance, the oiliness of the lubricant and the nature of the metal having no effect.
- (b) A region of partial lubrication where the metal surfaces are in close contact with each other. Here, we are not concerned with the viscosity of the lubricant, but with its oiliness and the nature of the bearing metal.
- (c) A critical point just between these two regions which is lowered by an increase in the oiliness of a lubricant, and is affected by the nature of the bearing metal.

From these results it appears that the ordinary journal friction testing machine operates in region A thus being nothing more than a rough viscometer. This was definitely proven by Winslow H. Herschel (Chem. & Met. Eng. Vol. 28, No. 13, March 1923, p. 594).

(g) Attempts to Measure Oiliness by Various Methods

Wilson and Barnard (Journ. Ind. and Eng. Chem. Vol. 14, No. 8, Aug. 1922, p. 683) give an account of several different methods which they used in an attempt to measure oiliness.

Deeley's method was employed first, because with it both the static and kinetic frictions could be measured. Their conclusions were that:

- (1) the kinetic friction is lower than the static friction
- (2) for metals there is a continuous change from static to kinetic friction
- (3) pressure on the bearing had very little effect
- (4) Animal and vegetable oils have a lower coefficient of friction than refined mineral oils
- (5) the addition of a small amount of fatty acid, or a considerably larger amount of a neutral vegetable oil to a mineral oil, produces a marked lowering of the coefficient of friction.
- (6) the maximum difference on metal surfaces between the friction of different oils is at zero velocity. This would suggest the coefficient of static friction to be the best single measurement of oiliness.

They considered oiliness to be due to a tenaciously adsorbed film of the lubricant to the metal surfaces, the presence of which diminishes or prevents metal to metal contact. The ability of this film to

withstand the high and prolonged pressures to which it is exposed without being squeezed out would indicate that it was more than monomolecular and more of the nature of a plastic solid than of a liquid.

They next used Langmuir's Inclined Plane Method with similar results to those obtained above. However, p-cresol, which is known to lower the surface tension of water, did not give a low coefficient of friction. This shows that an adsorbed film can not be the only necessity of a lubricant and that its chemical structure must have some effect. This is brought out in the following table.

Static Friction Measurements			
Inclined Plane Method		Spherical Segment Slider	
Load = 100 grms.			
OIL	Coefficient of Friction		
	Speculum on Steel	Speculum on Spec- ulum	Alloy 5 on Steel
Glycerol	0.20	0.20
Velocite "B" oil	0.182	0.173	0.152
Velocite "B" + 2% Stearic acid	0.125	0.121	0.123
Velocite "B" + 1% Iron Stearate	0.120	0.120
Neutral lard oil	0.125	0.126	0.093
Velocite "B" + 2% p - cresol	0.186	0.178
Velocite "B" treated twice with Fe by H	0.190	0.180

Measurements of the lowering of the surface tension between lubricants and mercury were also made. Mercury was used because it is the only pure metal in the liquid state under ordinary conditions. From this they only found that the lowering of the surface tension indicated a tendency for some substance to concentrate on a metal surface, and that the film formed was a solid rather than a fluid, and of colloidal rather than molecular dimensions.

A method was then devised to measure the electrical resistance of an adsorbed film. They took two hardened, polished steel surfaces and held them firmly together by a definite pressure, while their resistance was measured by means of a wheatstone bridge. Then the surfaces were exposed to some oil and their resistance again measured. It was noticed, that the longer the faces were kept in contact with the oil, up to a period of about twenty-four hours, the higher was the resistance obtained. This indicates that it takes some time for an adsorbed film to build up. It took longer for the film of mineral oil to form than for an animal or vegetable oil, due, it was believed, to the small amount of film forming constituents present in the former and the time it takes for them to diffuse to the metal surfaces.

The rate of clogging of metal and glass capillaries was also studied, yielding the fact, that on steel and glass mineral oils gave a thicker film than lard-oil. Therefore the thickness of an adsorbed film is no indication of the oiliness of a lubricant. The films in the capillary tubes proved to be of the order of 0.1 mm. in thickness. The film forming tendency of oils which had been filtered through Fuller's Earth was the same as before the treatment.

Finally an attempt was made to separate the "oiliness" of a lubricant by treating it with very finely divided iron formed by the reduction with hydrogen of a ferric hydroxide gel at 450° C. This iron seemed to adsorb to itself all the film forming constituents of the oil leaving behind an inferior lubricant as shown by the table on page 17 and by the following.

Original concentration of stearic acid in oil, percent	0.60
Stearic acid left after treating 50 gms. of soln. with 10 gms. of reduced iron	0.28
Stearic acid removed per gm. of iron, gms.	0.016

In the bibliography are listed quite a number of other recent articles on the subject which come to about the same conclusions as the above.

REVIEW OF THE COMPOSITION AND CHEMICAL NATURE
OF LUBRICANTS.

Animal and vegetable oils are known to consist of esters of the glyceril group $-C_3H_5$. This gives compounds of the form $C_3H_5R_3$, where R is the fatty acid radicle. In solid fats, Stearin and Palmitin predominate, while in liquids, we usually find a large amount of Olein. The composition of these common esters is:

Triglyceryl Stearate - $C_3H_5(O_{18}H_{35}O)_3$

Triglyceryl Palmitate - $C_3H_5(O_{16}H_{31}O)_3$

Triglyceryl Oleate - $C_3H_5(O_{18}H_{33}O)_3$

Sperm oil contains esters of mono- and tri-valent alcohols instead of glyceril.

Mineral oils, on the other hand, are hydrocarbons, the ultimate structure of which very little is known. Dunstan and Thole (Journal of the Institution of Petroleum Technologists, Vol. IV, (1918), pp. 191-228) say that all mineral oils which are good lubricants contain unsaturated molecules. They also state that: "In no case has the chemical constitution of a compound of a lubricating oil been established, but the chemical behaviour of these oils indicate that among the components are unsaturated hydrocarbons (possibly open chain, but more probably naphthenic and polynuclear, or perhaps both types), saturated hydrocarbons (naphthenic and

probably to some extent polynuclear, but not to any appreciable extent paraffinoid), and aromatic hydrocarbons (to an unknown and possibly a limited extent). The unsaturated compounds constitute between 20 and 40 per cent. of most lubricating oils. It appears then, that the true lubricant is an unsaturated compound, possessing all the attributes of such a compound, i. e.: -

- (1) Capacity to absorb iodine, bromine, oxygen and so on.
- (2) Solubility in strong Sulphuric Acid.
- (3) Higher C/H ratio than the saturated derivative.

"Apparently the same facts hold good in regard to fatty lubricants. Rape oil, castor oil and olive oil contain in their molecules double bonds, and are superior to such a saturated product as, for example, tallow.

"In recent years the progress of organic chemistry has largely been due to the realisation that unsaturation, or the possession of residual affinity, plays an all important part in the reactivity and the very personality of a compound. Colour, odour, taste, physiological activity, and, in a word, all the characteristic properties of bodies are influenced by this condition. It appears now that we may add lubricating ability to the already long list of effects proceeding from this one prime cause.

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Another view held by some as to the cause of oiliness of lubricants is their colloidal nature. W. Ostwald (Introduction to Theoretical and Applied Colloid Chemistry, 1917) says that a colloid tends to concentrate on the surfaces, the phenomena being called adsorption. In their article mentioned above Dunstan and Thole say that: "Recent work on colloid chemistry points to the fact that heavy oils must be included in the category of iso-colloids, i.e., polyphase systems in which the disperse component is of the same chemical nature as the dispersion medium. Just as water must be regarded as a system in which molecules, such as, $(H_2O)_3$ co-exists with simple H_2O molecules, so in a lubricating oil the disperse phase is a molecular aggregate suspended in a dispersion medium of simpler and similar structure."

DESCRIPTION OF APPARATUS.

From consideration of the previous work done on this subject it was decided in this research to use the method employed by S. B. Hardy. The apparatus used is shown in Plate I.

It consists of a glass case set on a three legged levelling stand, which in turn rests on a solid table. The glass case is covered by a tightly fitting, ground glass, top. The metal plate used in measuring

the coefficient of static friction is placed inside the case by means of a pair of tongs, after which, the apparatus is carefully levelled. On the plate is set a spherical segment of any desired metal. This is connected, by means of a fine thread over a well balanced pulley running on ball bearings, to a beaker into which mercury is run in a very fine stream from a burette. When the weight of the beaker becomes great enough the hemisphere is pulled along the plate. At the instant movement is first noticed the stream of mercury is immediately shut off. Then the beaker is detached and weighed, to the second decimal place, with that part of the string which is below the pulley.

During all the experiments a stream of carefully dried and filtered air was passed through the apparatus by means of a water pressure pump. This precaution was taken to prevent the cleaned plate from adsorbing a film of grease from the atmosphere. The drying and filtering of the air was accomplished by passing it through six wash bottles of concentrated sulphuric acid, an absorption tower containing solid sodium hydroxide, two tubes of phosphorous pentoxide and finally a tube of glass wool. The sulphuric acid, as well as acting as a drying agent, took up a considerable amount of dust from the air and was renewed

whenever it became dark in color. The purpose of the Sodium Hydroxide was to prevent any sulphuric acid spray from being carried through.

Difficulties Encountered

A scale pan on which weights were placed was first used to determine the force necessary to cause movement, but proved unsatisfactory. This was due to the inevitable jar caused by adding and removing the weights, which started the hemisphere moving too soon. This difficulty was overcome by replacing the scale pan with a beaker into which a fine stream of mercury was run until the necessary weight was obtained. The weight of the beaker and mercury was then found by weighing on a balance.

The steel plates and hemispheres, first used, and were mild steel, caused a great deal of trouble by not giving any consistent results as shown by the following figures in table I.

Pull in Grams. (Dry Surfaces)	
Mild Steel	Hard Tool Steel
54.23	75.69
50.14	76.32
45.12	77.20
52.72	77.00
57.78	76.47

In this case a steel hemisphere of 214 gms. in weight was used on a dry steel plate. The trouble was eliminated by getting a plate of hard tool steel which was of the same composition as the hemisphere. This new plate gave very little trouble from rusting after it was cleaned where as the others rusted very readily. The results for the new plate are also given in table I.

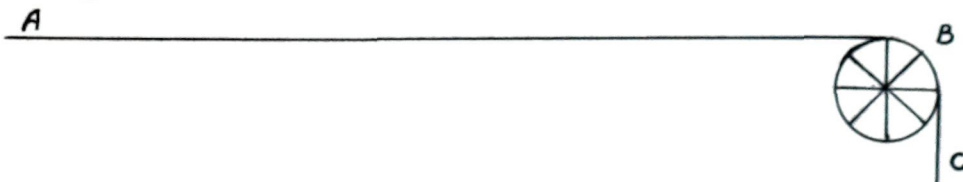
Cleaning the plates and hemispheres turned out to be a difficult task. The plates were ground by rubbing two of them together with very fine emery and water. The emery was then removed and the plate polished by rubbing with a fresh cork in clean flowing water, after which the plate was rubbed vigorously by the fingers with a little pure soap in the running water until a clinging feeling was produced. When the plate was clean water would cover its entire surface. The real test for a clean surface is a constant value for the coefficient of friction which can be reproduced. After cleaning the plate was placed in the glass case and dried by a rapid stream of dry air. The hemisphere was cleaned and dried in a similar manner.

When solutions of Stearic Acid in Liquid Petrolatum were used the former solidified out and could not be kept in solution. This difficulty was

surmounted by placing an electric radiation heater next the glass case, so the temperature could be kept high enough to melt the Stearic acid. However, for solutions over thirty per cent. stearic acid the temperature was not high enough so recourse was had to dilute ether solutions. The stearic acid and liquid petrolatum were heated in a flame and thoroughly mixed. A small portion of this solution was dissolved in some ether which was poured onto the plate and allowed to evaporate. This left^a a very thin film on the plate on which measurements could be made.

Corrections -

The force necessary to cause the string to move over the pulley when it was loaded was found to be 0.5 gms. This amount has been subtracted from all the values given in this article.



A source of error arises in the angle $\angle ABC$ over the pulley not being a right angle thus causing a very slight lifting motion on the hemisphere. The angle $\angle BCA$ was measured by taking two points ten inches apart directly beneath the thread on the table and measuring

the difference in height of the string at points above the ends of the line. This difference was found to average 0.29 in. which gives for the tangent of the angle BAC a value 0.029. This the angle BAC is $1^{\circ} 43'$. So the value of the desired force AC equals $AB \cdot \cos BAC = AB \times 0.9996$, which gives a negligible correction and therefore has been omitted.

Experimental Data -

(a) Steel on Steel-

(1) Measurements were first made to determine the force necessary to cause steel to move on dry steel. The coefficient of friction was calculated by means of Amontons' equation. The results are given in Table II.

TABLE II.

For Steel on Steel (Dry)	
Pull in Grams	Coefficient of Static Friction
75.69	0.3537
76.32	0.3567
77.20	0.3608
77.00	0.3598
76.47	0.3573
	Av. 0.3576

The weight of the steel hemisphere used throughout all the determinations was 214 gms.

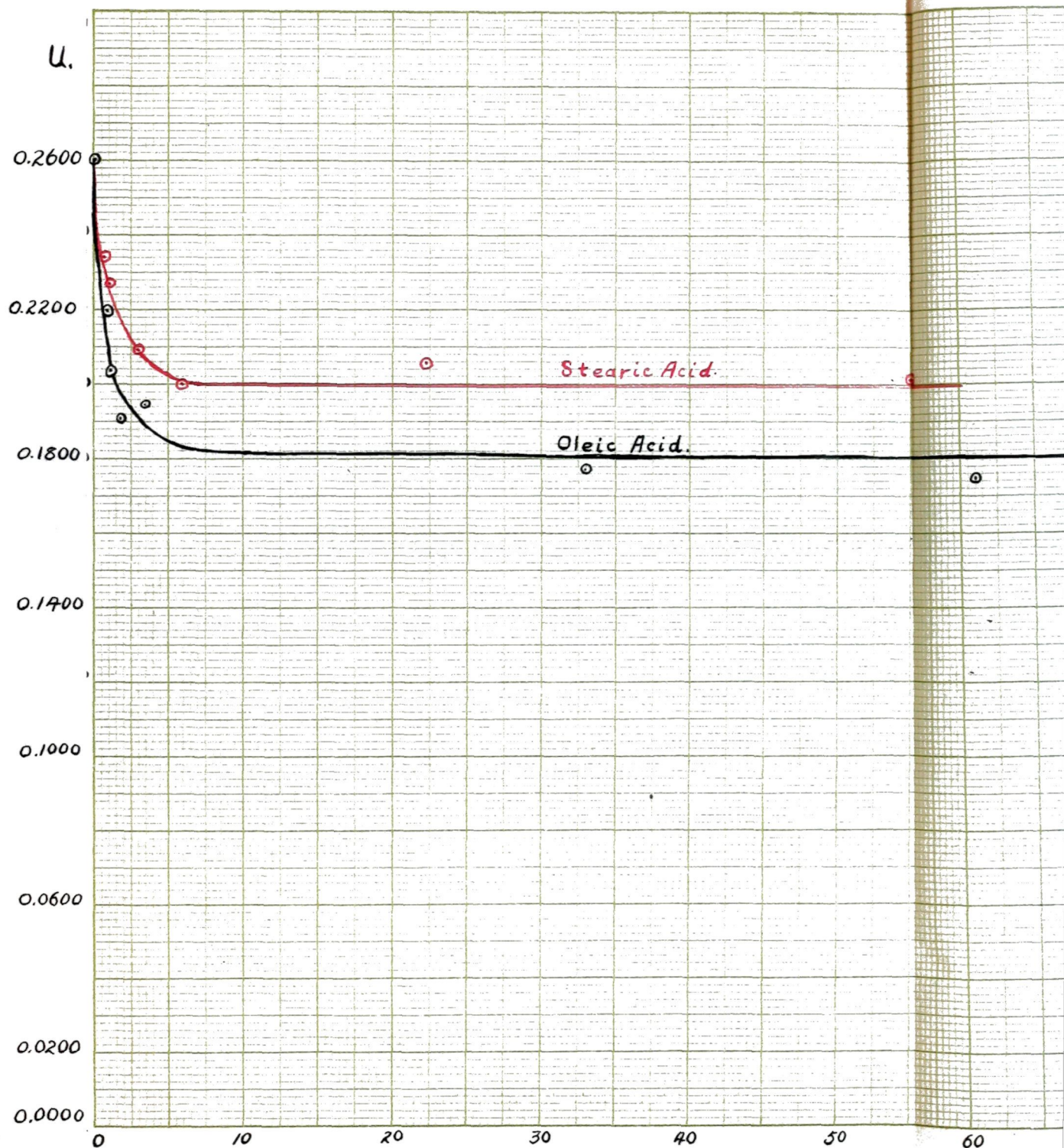
(a) Steel on Steel - (cont)

(ii) Oleic Acid -

The coefficient of static friction for steel on steel, using liquid petrolatum with various percentages of oleic acid as a lubricant, was next measured. The liquid was applied to the plate by means of a clean glass tube in such amounts that the hemisphere stood in a visible film. The results obtained are given in Table III and their averages plotted in Graph I.

TABLE III.

Steel on Steel.			
Oleic Acid 0% Liquid Petrolatum 100%		Oleic Acid 0.65% Liquid Petrolatum 99.35%	
W	u	W	u
55.36	0.2587	46.93	0.2193
55.80	0.2607	47.18	0.2205
55.67	0.2601	47.56	0.2223
55.48	0.2592	45.97	0.2148
55.76	0.2606	47.40	0.2215
Av. 0.2599		Av. 0.2197	
Oleic Acid 0.97% Liquid Petrolatum 99.03%		Oleic Acid 1.73% Liquid Petrolatum 98.27%	
W	u	W	u
43.14	0.2016	41.69	0.1948
42.84	0.2002	40.51	0.1893
43.58	0.2036	41.56	0.1942
44.15	0.2063	40.14	0.1875
43.86	0.2049	40.29	0.1882
Av. 0.2033		Av. 0.1908	



GRAPH I.

TABLE III. (cont.)

Steel on Steel.			
Oleic Acid 3.33% Liquid Petrolatum 96.67%		Oleic Acid 32.79% Liquid Petrolatum 67.21%	
W	u	W	u
41.67	0.1947	38.23	0.1787
41.30	0.1931	37.26	0.1741
42.21	0.1968	38.22	0.1786
41.01	0.1916	36.80	0.1720
41.75	0.1951	38.49	0.1799
Av. 0.1943		Av. 0.1767	
Oleic Acid 60.99% Liquid Petrolatum 39.01%		Oleic Acid 100% Liquid Petrolatum 0%	
W	u	W	u
37.99	0.1775	36.77	0.1812
37.06	0.1732	39.72	0.1856
36.80	0.1720	38.66	0.1806
37.59	0.1756	37.21	0.1749
37.34	0.1745	39.04	0.1824
Av. 0.1746		Av. 0.1809	

W = pull in grams

u = coefficient of static friction

(c) Stearic Acid

A similar experiment was made, using varying amounts of stearic acid in liquid petrolatum, to determine the effect of the unsaturated bond. The results are given in Table IV and the averages plotted in Graph I.

TABLE IV.

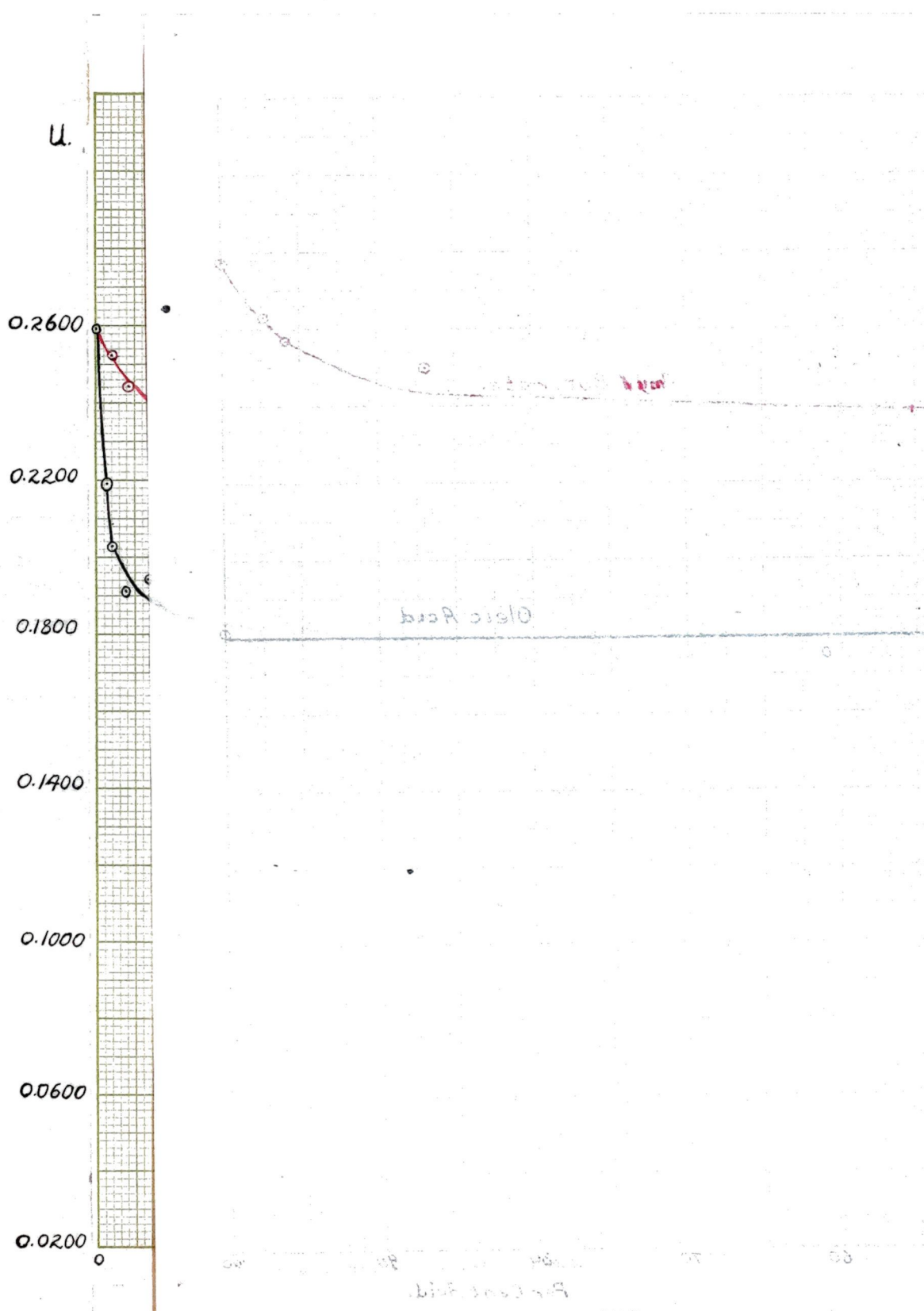
Steel on Steel			
Stearic Acid 0.42% Liquid Petrolatum 99.58%		Stearic Acid 0.97% Liquid Petrolatum 99.03%	
W	u	W	u
49.95	0.2334	48.86	0.2283
49.31	0.2304	48.88	0.2284
51.11	0.2388	48.03	0.2246
49.99	0.2336	48.61	0.2272
	Av. 0.2341		Av. 0.2271
Stearic Acid 2.73% Liquid Petrolatum 97.27%		Stearic Acid 5.76% Liquid Petrolatum 94.24%	
W	u	W	u
45.63	0.2133	42.58	0.1990
44.16	0.2064	43.00	0.2010
44.81	0.2095	42.32	0.1977
44.02	0.2057	43.87	0.2050
44.90	0.2098	42.15	0.1970
	Av. 0.2090		Av. 0.2000
Stearic Acid 24.3% Liquid Petrolatum 75.7%		Stearic Acid 54.99% Liquid Petrolatum 45.01%	
W	u	W	u
43.76	0.2045	43.57	0.2036
44.61	0.2084	42.78	0.1999
44.34	0.2072	43.46	0.2031
44.01	0.2056	42.36	0.1979
43.50	0.2033	43.18	0.2018
	Av. 0.2058	ether solution	Av. 0.2012

TABLE IV. (Cont.)

Stearic Acid 100 % Liquid Petrolatum 0%	
W	n
32.01	0.1495
32.77	0.1531
33.33	0.1558
33.32	0.1557
ether solution	Av. 0.1535

(d) Amyl Butyrate

The effect of the addition of an ester to a
^{oil}
 mineral [^] was studied by using various amounts of Amyl
 Butyrate in Liquid Petrolatum with the results given in
 Table V and plotted in Graph II.



GRAPH II.

TABLE V.

Steel on Steel.			
Amyl Butyrate 1.06%		Amyl Butyrate 2.19%	
Liquid Petrolatum 98.94%		Liquid Petrolatum 97.81%	
W	u	W	u
54.58	0.2550	52.23	0.2440
54.11	0.2529	52.53	0.2454
53.92	0.2520	51.61	0.2412
54.19	0.2532	52.66	0.2461
53.96	0.2533	51.12	0.2389
Av. 0.2533		Av. 0.2431	
Amyl Butyrate 8.8%		Amyl Butyrate 20.33%	
Liquid Petrolatum 91.2%		Liquid Petrolatum 79.67%	
W	u	W	u
50.01	0.2337	49.16	0.2292
49.29	0.2304	49.34	0.2306
49.08	0.2294	50.08	0.2340
49.76	0.2326	50.63	0.2366
49.99	0.2336	49.99	0.2336
Av. 0.2319		Av. 0.2328	
Amyl Butyrate 50.49%		Amyl Butyrate 86.99%	
Liquid Petrolatum 49.51%		Liquid Petrolatum 13.01%	
W	u	W	u
50.77	0.2373	53.57	0.2504
50.03	0.2338	53.61	0.2506
51.01	0.2384	52.89	0.2471
51.15	0.2390	53.11	0.2482
50.27	0.2349	53.72	0.2510
Av. 0.2367		Av. 0.2495	

TABLE V. (Cont.)

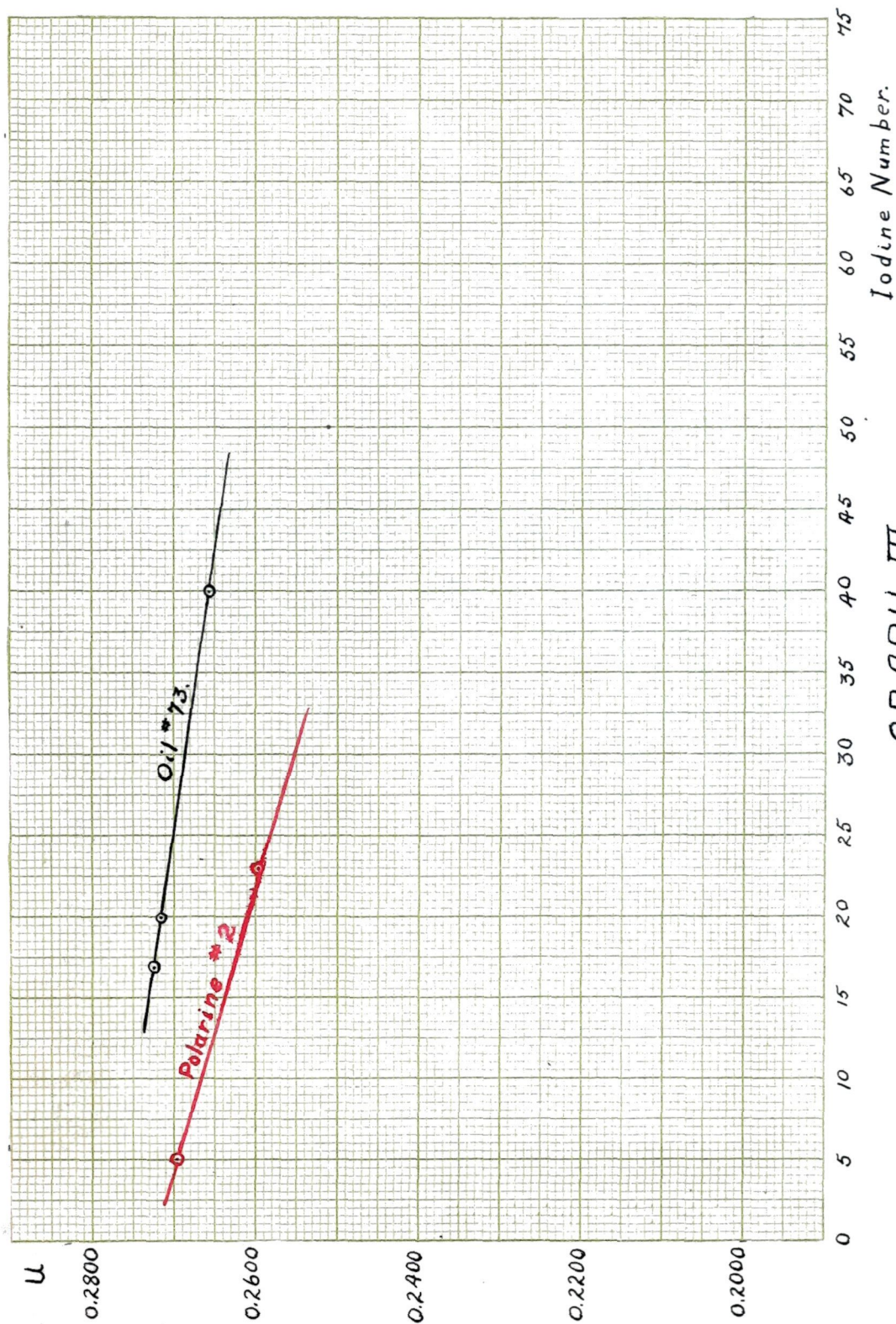
Amyl Butyrate 95.9% Liquid Petrolatum 4.1%		Amyl Butyrate 97.35% Liquid Petrolatum 2.65%	
W	u	W	u
54.77	0.2560	56.32	0.2632
55.26	0.2583	55.72	0.2604
55.11	0.2576	56.60	0.2643
54.36	0.2541	55.96	0.2615
54.91	0.2567	56.31	0.2631
Av. 0.2565		Av. 0.2625	
Amyl Butyrate 100% Liquid Petrolatum 0%			
W	u		
59.49	0.2780		
59.02	0.2758		
58.60	0.2738		
59.09	0.2762		
58.21	0.2720		
Av. 0.2752			

(c) The Effect of Unsaturation

The coefficient of static friction of mineral oil with different iodine numbers to find the effect of unsaturated hydrocarbons. The results are found in Table VI and Graph III.

TABLE VI.

Steel on Steel.			
Oil #73 Iodine No. 17		Oil #73 Iodine No. 20	
W	u	W	u
58.38	0.2728	58.24	0.2721
58.66	0.2740	58.20	0.2719
58.15	0.2718	58.30	0.2724
57.97	0.2709	58.06	0.2712
58.18	0.2719	58.19	0.2719
Av. 0.2723		Av. 0.2719	
Oil #73 Iodine No. 40		Polarine # 2. Iodine no. 5	
W	u	W	u
57.65	0.2693	57.32	0.2679
58.61	0.2646	58.46	0.2731
57.42	0.2683	57.64	0.2693
56.37	0.2634	57.96	0.2709
56.25	0.2629	57.24	0.2675
Av. 0.2657		Av. 0.2697	
Polarine #2 Iodine No. 23			
W	u		
56.22	0.2627		
55.31	0.2585		
55.00	0.2570		
55.17	0.2577		
56.13	0.2623		
Av. 0.2596			



GRAPH III.

A test was also attempted with Butyric acid but had to be abandoned as it attacked the steel even in very dilute solutions.

(b) Babbitt on Steel -

(i) Dry -

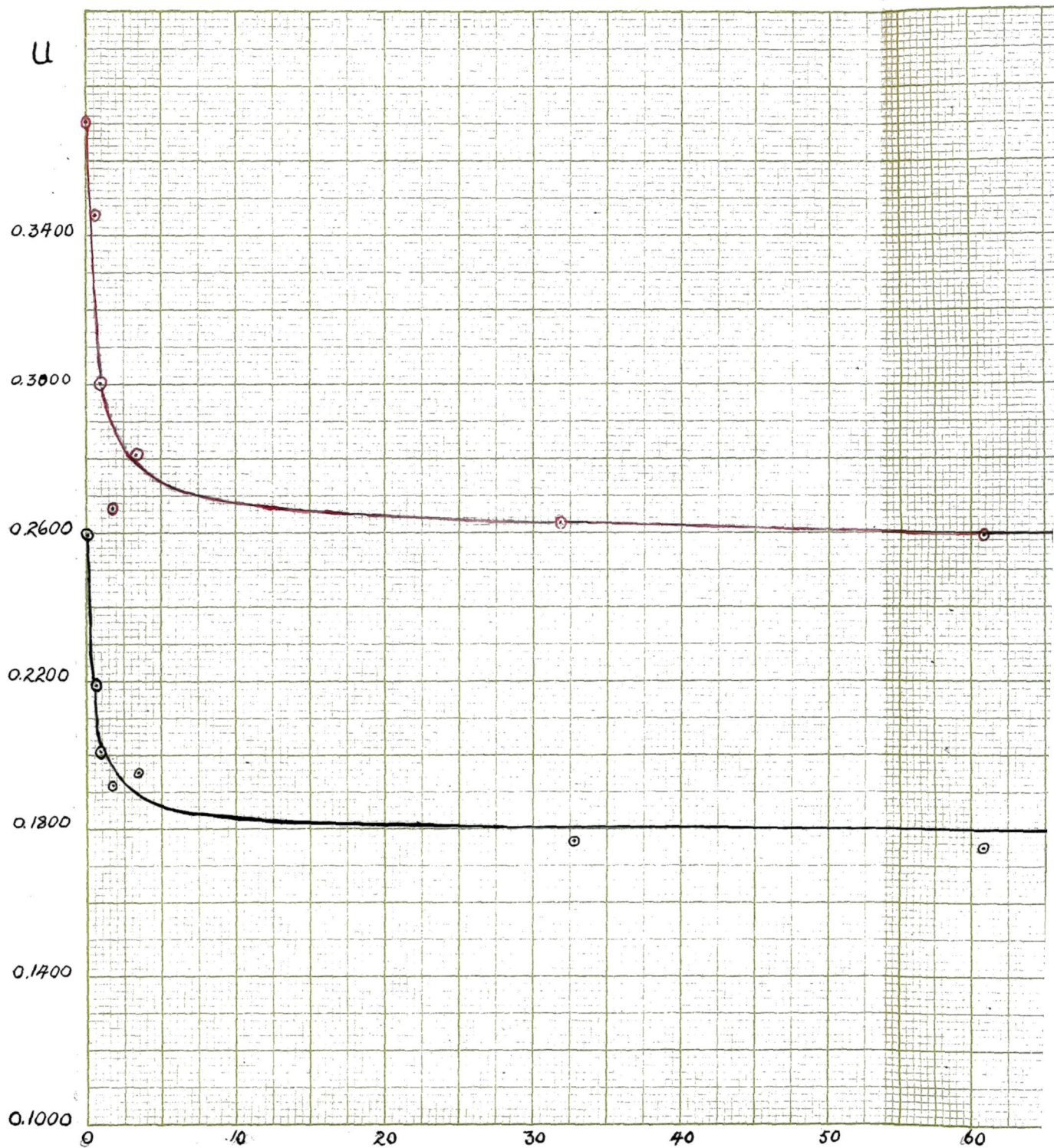
The coefficient of babbitt on steel with out any lubricant was measured with difficulty. The soft babbitt was abraded so badly by the hard steel that it was had to get consistent results with the dry surfaces. The weight of the babbitt hemisphere was 135.7 gms. The results for dry surfaces are given in Table VII.

TABLE VII.

Babbitt on Steel. (Dry)	
Pull in Grams	Coefficient of Static Friction
77.52	0.5043
78.80	0.5126
78.00	0.5075
Av.	0.5081

(ii) Oleic Acid -

In order to ascertain the affect of different metals on the coefficient of static friction of a lubricant the same solutions of oleic acid used on the steel were tired with the babbitt. The results obtained are given in Table VIII and plotted in Graph IV.



GRAPH IV

TABLE VIII.

Babbitt on Steel			
Oleic Acid 0% Liquid Petrolatum 100%		Oleic Acid 0.65% Liquid Petrolatum 99.35%	
V	u	V	u
57.72	0.3756	53.11	0.3455
55.25	0.3594	52.77	0.3433
56.86	0.3699	53.04	0.3451
57.97	0.3772	53.43	0.3475
56.95	0.3705	53.27	0.3465
	Av. 0.3705		Av. 0.3456
Oleic Acid 0.97% Liquid Petrolatum 99.03%		Oleic Acid 1.73% Liquid Petrolatum 98.27%	
V	u	V	u
47.10	0.3064	41.59	0.2705
46.38	0.3017	40.51	0.2636
46.33	0.3014	40.78	0.2753
46.84	0.3047	41.56	0.2703
46.58	0.3031		
	Av. 0.3035		Av. 0.2674
Oleic Acid 3.33% Liquid Petrolatum 96.67%		Oleic Acid 32.79% Liquid Petrolatum 67.21%	
V	u	V	u
42.73	0.2780	40.63	0.2643
43.28	0.2816	40.22	0.2617
43.49	0.2829	40.25	0.2619
43.37	0.2822		
	Av. 0.2812		Av. 0.2626

TABLE VIII. (Cont.)

Oleic Acid 60.99% Liquid Petrolatum 39.01%		Oleic Acid 100% Liquid Petrolatum 0%	
W	u	W	u
40.12	0.2610	40.41	0.2629
39.25	0.2554	39.76	0.2587
39.06	0.2542	39.28	0.2556
40.43	0.2630	40.42	0.2629
40.29	0.2621	38.89	0.2530
Av. 0.2591		Av. 0.2586	

Oleic Acid was observed to attack the babbitt when ever 3.33 per cent. was used in the liquid petrolatum.

DISCUSSION OF RESULTS.

The above results show that the coefficient of static friction of mineral lubricating oils is materially lowered by the addition of fatty acids. From the curves for oleic and stearic acid it appears that the chemical constitution materially affects the degree of lowering. Both these acids are of practically the same molecular weight the only difference being that stearic acid contains two more hydrogen atoms than oleic acid. However, the latter is unsaturated and contains one double bond which seems to be the cause of its greater effect. This would indicate that the double bond contains some residual

affinity, which is attracted by forces on the surfaces of the solid, thus forming a very tenacious film.

From the difference in the lowering of the friction due to the addition of the oleic and stearic acids and that of the amyl butyrate it is seen that the molecular weight of the compound added is of prime importance. Amyl butyrate has a molecular weight of 158, while ^{for} oleic and stearic acids it is 282.36 and 284.36, respectively, thus showing that the greater the molecular weight of the substance added to the mineral oil, the more the coefficient of friction is lowered.

Also, from the curves for the acids, it is seen that the coefficient of friction varies inversely as the amount of acid present, until a concentration of about five per cent of acid is obtained in the oil. For greater concentrations of acid there is no appreciable lowering of the coefficient of friction. The -COOH group of the acid is practically insoluble in the oil while the hydrocarbon end is very soluble. This causes the acid to concentrate at the surface of the oil so the -COOH group is free to be adsorbed onto the metal surface. When the concentration of acid is such that the surface of the oil contains all the molecules it can, the effect is the same as if pure acid were being used.

The curve for amyl butyrate is an exception to this theory and none has so far been suggested to account for it. However, when tested with different metals its behaviour may suggest an explanation.

Graph IV shows that the metal surfaces with which the lubricant is in contact have a very decided influence on the coefficient of friction, which must be due to the chemical nature of the metals themselves. It is seen quite distinctly that for the same lubricant steel on steel gives a much lower value than does babbitt on steel.

The latter part of the stearic acid curve is discontinuous due to the stearic acid becoming solid on the plate.

The experiments with mineral oils of different iodine numbers shown that there is a slight decrease in the friction for an increase in iodine number. This is undoubtedly due to an increase in unsaturation. It is thought that this increase in unsaturation has a similar effect to the addition of a fatty acid. If the oil to begin with had no iodine number and the unsaturation was gradually increased a curve similar to that for oleic acid would likely be obtained.

INDUSTRIAL APPLICATION.

The above information could be used in compounding of lubricating oils. If it is desired to obtain a cheap oil with the same lubricating properties of some expensive animal or vegetable oil, it is only necessary to take a mineral oil and add to it not more than five per cent. of an animal or vegetable acid^{to} produce a lubricant of the required quality. In some cases where a fatty acid in the pure state attacks the bearing, its full effect can be obtained without injury to the bearing, by using a dilute solution of the acid in a mineral oil, as shown above in the case of babbitt and oleic acid.

SUMMARY.

The above results may be summarized as follows:

- (1) The coefficient of static friction of a mineral lubricating oil is lowered by the addition of esters and fatty acids.
- (2) The addition of an unsaturated compound lowers the coefficient of friction more than does the corresponding saturated compound.
- (3) The coefficient of a lubricant is affected by the metal's surfaces with which it is in contact.
- (4) Five per cent of an acid added to a mineral oil gives as low a coefficient as the pure acid.

- (5) Increase in iodine number of an oil lowers its coefficient of friction.

In conclusion, the writer wishes to express his thanks and appreciation to Dr. W. F. Seyer for his assistance and advice in directing this work.

CHEMICAL LABORATORIES

The University of British Columbia.

BIBLIOGRAPHY.

- Amontons: Mem. d. l'Acad. Roy. des Sciences, (1699), p.206.
- Euler: Berlin Acad. Memoirs, (1748), p.122.
- Coulomb: Mem. d. l'Acad. Roy. des Sciences, (1785), vol. 10, p. 161.
- Morin: Mem. d. Scavans Etrangers IV., (1833), pp.1, 591; VI. p. 641.
- Jenkin and Ewing: Phil. Trans. 1.167, (1877), p.509
- B. Tower: Proc. Inst. Mech. Eng. (1883), p. 632;
(1884), p. 29.
- O. Reynolds: Phil. Trans. Vol. 177, (1886), p. 157.
- Sommerfield: Zeitscher.f. Math. t.50, (1904), p.97.
- Harrison: Camb. Trans. vol. XXII. (1913), p. 39.
- O. Faust: Z. physik. chem. 86, (1914) pp.479-94.
- Lord Rayleigh: Phil. Mag. s.6. Vol.35.(1918), pp.1, 157.
- T. E. Stanton, L. Archbutt and J. E. Southcombe: Engineering 108, (1919) pp. 759-60.
- H. E. Wells and
J. E. Southcombe: Petroleum Times 3, pp. 173-5, 201-3,
(1920). Journ. Soc. Chem. Ind. 39,
pp. 51 - 60 T (1920)
- Langmuir: Journ. Am. Chem. Soc. vol.38, (1916) p. 2221;
vol. 39, (1917), p. 1848.
Trans. Faraday Soc. 15, III (1920) p. 62.
- W. B. Hardy: Journ. Soc. Chem. Ind. Vol. 38, (1919), p.7T
Phil. Mag. Vol.38, (1919), p.32;
Vol.40, (1920), p.201
Fourth Report on Colloid Chemistry
British Association for Advancement of
Science, (1922), p. 185.
- W. B. Hardy and
Ida Doubleday: Proc. Roy.Soc.Vol.100A (1922)p.550;
Vol. 101A (1922), p. 487.

BIBLIOGRAPHY (Cont.)

- Ida Doubleday: Journ. Chem. Soc. (1922) p. 2875
- R. M. Deeley: Proc. Phys. Soc. Vol. 32, (1919-20) p.18
- Dunstane and Thole: Journ. Inst. Pet. Tech. Vol. IV.
(1918), pp. 191-228.
Chem. and Met. Eng. Vol. 28. No 7
(1923), P. 299
- A. Baucke: Seifensieder - Ztg. 47, (1920) p. 759
- G. F. Robertshaw: Petroleum Times, 3, (1920) pp. 441-2,
469-71, 511-2.
- S. S. Bhatnagar and
Wm. G. Garner: Journ. Soc. Chem. Ind. 39, (1920),
pp. 185-7 T.
- J. H. Hyde: Engineering III., (1921) pp. 708-9
- R. E. Wilson and
D. P. Barnard: J. Soc. Autom. Eng. 1922
Journ. Ind. Eng. Chem. Vol. 14, (1922)
pp. 682, 683.
- W. H. Herschel: Chem. and Met. Eng. Vol. 28, (1923),
pp. 302, 594.