

vance of agriculture—moles, for instance, and field voles, besides both insectivorous and grain-eating birds.

The author follows the late Dr. Günther in giving specific rank to what are now recognised as no more than local varieties of the brown trout

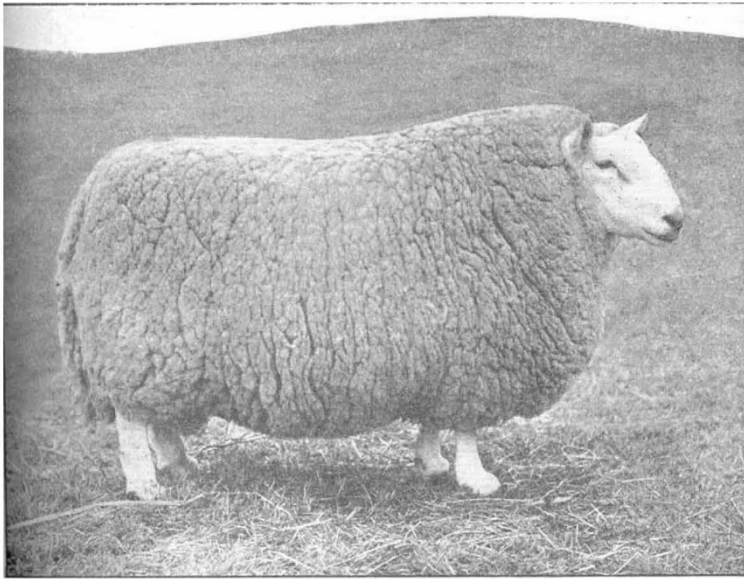


FIG. 2.—Cheviot sheep—a modern result of selective breeding (champion, Highland Show, 1914.)  
From "The Influence of Man on Animal Life in Scotland."

—*Salmo fario* (misnamed *S. trutta* on p. 278). The signal success which rewarded the acclimatisation of this fish in New Zealand was first achieved with trout, not from Lochleven, but from the Wooburn at High Wycombe. A

few slips and misprints await correction in a future edition. Loch Askaig (p. 134) should be Loch Arkaig; Loch-an-Eilein on the same page appears as Loch-an-Eilan on p. 192, the correct Gaelic being Loch-an-eilain. Dr. Ritchie would probably wince if we were to write about "North-umberlandshire," just as we did when we read "Sutherlandshire" on p. 126.

Few of the numerous illustrations are worthy of Dr. Ritchie's interesting treatise. The beaver (Fig. 37) and the bittern (Fig. 64) are mere caricatures, and poor at that. Some of the figures, however, serve well to illustrate the influence of domestication and selective breeding upon primitive types of mammal, as in the case of the sheep. Although it may not be possible to define with precision the various species which have contributed to produce the modern breeds, sheep, though a race almost exclusively Palæarctic and Ne-arctic, are peculiarly liable to modification by food and environment, and are more plastic in that respect than cattle, horses, or swine.

While indicating some hesitation in accepting all Dr. Ritchie's conclusions, we congratulate him on his useful contribution to zoological literature, and we are grateful for the excellent index to the book.

### Some Problems of Lubrication.<sup>1</sup>

By W. B. HARDY, F.R.S.

IN lubrication, a fluid or other body is used to decrease the friction between opposed solid faces. The lubricant may act in one of two ways. It may separate the faces by a layer thick enough to substitute its own internal friction, modified by the mechanical conditions in which it finds itself, for that of the solid faces; or it may be present as a film, too thin to develop its properties when in mass, which reacts with the substance of the solid faces to confer upon them new physical properties. In the latter case the solid faces continue to influence each other, not directly, but through the intermediation of the film of lubricant. There are indications that these two types of lubrication—one in which the solid faces intervene only owing to their form, rate of movement, etc., and not by their chemical constitution; the other in which the chemical constitution is directly involved—are discontinuous states in that one cannot be changed gradually into the other by

simply thinning the layer of lubricant. The change from the one to the other is probably abrupt.

It may by no means be asserted that resistance to relative motion is always least when the solid faces are floated completely apart; it would, indeed, probably be truer to say of the best lubricants that friction is least when the "boundary conditions," to use Osborne Reynolds's phrase, are fully operative.

This address is concerned wholly with "boundary conditions," and we get directly to the heart of the problem by certain simple experiments. If a glass vessel, such as a bottle, is placed upon an inclined pane of glass at a certain angle it slips smoothly down. The glass plate is an ordinary plate cleaned with a cloth. In the usual sense of the word, the plate is not lubricated; the surface is "dry." The lower half of the plate is then wetted with water, and the bottle is now found to slip on the unwetted part, and to be pulled up sharply by friction when

<sup>1</sup> A Friday evening discourse delivered at the Royal Institution on February 27, 1920.

it reaches the wetted part. It is not sufficient, therefore, to interpose a liquid film between solid faces to get lubrication; indeed, as the experiment proves, water increases the friction; it is an anti-lubricant for ordinary faces of glass.

Is, then, the quality of lubricant a property of a fluid? Does water fail to act merely because it does not possess that property to which the name "oiliness" is sometimes given? Another simple experiment supplies the answer. Instead of a glass plate, let us use a plate of ebonite. The glass plate does not readily slip on this. The angle at which slipping occurs is steeper than when a glass plate is used. Now, when the lower half of the ebonite plate is wetted, it is found that a glass bottle encounters relatively high friction on the unwetted part, but slips quite freely on the wetted part. Water, in short, is an admirable lubricant for glass on ebonite. Here is another plate, picked up at random in the laboratory of the Royal Institution. Its composition is unknown. Tested in the same way, water has no detectable influence on the friction between glass and the surface of this plate.

It will be well to confess at once that these simple experiments raise questions which are as yet without an answer, and that much of what follows concerning them is merely tentative. They seem to establish two things, the first being the curious paradox that a film of fluid introduced between two surfaces does not always decrease friction—it may, indeed, very much increase it. The second is that the quality of "oiliness"—the quality, that is, which enables a substance to act as a lubricant—seems to be not the property of a given fluid, but only of that fluid considered in reference to a particular surface.

It is necessary at this stage to clear away a possible explanation of the paradox. When two solid faces are separated by a thin film of fluid, capillary forces operate, and, in certain cases at any rate, these forces act so as to resist slipping. They will so act, for instance, when the movement of one face past the other increases the area of the free surface of the film. Water has a high surface-tension; the capillary forces to which it gives rise are usually large; therefore it is pertinent to ask whether, when a layer of water diminishes the facility for the slipping of glass on glass, it is owing to capillary action. A qualitative answer is to be found in the fact that water does in some cases, as when glass is applied to ebonite, increase the facility for slipping; and the late Lord Rayleigh furnished the quantitative answer. He calculated the magnitude of the capillary effect and found it negligible compared with the actual friction of glass on glass wetted with water. An appeal to capillary forces of this type will not solve the paradox.

Some light is thrown upon it when we inquire into the state of the surface of glass that has its friction increased by water. Surfaces of glass "cleaned" in the ordinary way by rubbing with a glass cloth, or glass faces which have been simply exposed to the air, are in point of fact not clean,

but highly lubricated with a film of matter derived from the cloth or condensed from the atmosphere. This "grease" film is of invisible thinness. It is probably of the order of  $1 \mu\mu$  in thickness—that is to say, one-millionth of a millimetre. It can be removed by soap and water, which in turn must be removed by a stream of water, and the plates dried in clean air out of contact with solids. The film reforms quickly—very quickly in London air, and less quickly in the country. A "grease" film also creeps over a cleaned glass face from ordinary solids with which it may be in contact. Still, when due precautions are taken—and they are many—it is possible to get a glass face which seems to be really clean.

The first property of clean faces is that their friction, one for the other, is very high; indeed, it is impossible to make them slip past one another. One glass plate may be forced past another, but true slipping does not take place; they tear at the point or points of contact. It is easier, in short, to disrupt the actual substance of the glass itself than to get the surfaces to slip over one another. Clean glass faces "seize" when they touch.

When chemical substances are tested as lubricants on clean glass faces, a remarkable fact emerges—namely, that some are quite neutral in that they do not alter the resistance to slip in the least; such are water, alcohol, benzene, and strong ammonia. Other substances have some lubricating action, great or small—that is to say, they decrease the force needed to produce slipping; such are the alkalis, trimethylamine and tripropylamine, the fatty acids—*e.g.* acetic acid—and the paraffins. Those fluids which act as lubricants are not necessarily fluids of any considerable viscosity; indeed, a high viscosity is compatible with the absence of any lubricating action other than flotation. Thus glycerine facilitates the slipping of clean glass on clean glass only when it is present in quantity sufficient to float the surfaces apart. On the other hand, acetic acid and tripropylamine—substances of low viscosity—are admirable lubricants of glass.

None of the fluids tested was found to raise the friction of clean glass faces. They were either neutral, or decreased friction to a greater or less extent. The power of increasing the friction of glass faces which neutral fluids, such as water, possess is due, not to their action on the glass itself, but to the fact that they interfere with the action of the invisible grease film. Water on an ordinary glass face acts as an anti-lubricant; on really clean glass it is "neutral."

All solid faces, however, do not distinguish chemical substances into those which are "neutral" and those which possess lubricating properties. Nearly one hundred substances have been tested on burnished faces of bismuth, and in every case some decrease of friction was observed.

A comparison of the lubricating action of simple chemical substances on clean faces of glass or of bismuth would seem to show that the quality

of oiliness is due to some reaction between the substance and the solid face. Much is still obscure, but certain facts seem to be capable of interpretation in no other way. Thus water and ethyl alcohol have no detectable lubricating action on clean glass, whilst both are moderate lubricants for clean bismuth.

The thickness of the layer needed to lubricate is astonishingly small. It is quite invisible, and probably only one or a very few molecules thick. To discuss this adequately would take too long, but the fact may be instanced by an experiment of great beauty. A tiny drop of, say, acetic acid or tripropylamine is placed near one corner of a plate of clean glass 6 cm. square; nothing detectable by the senses happens; the drop is there, and that seems to be all. But the whole surface of the plate has, in fact, been changed fundamentally. It is now fully lubricated by an invisible film which has spread rapidly over it from the drop. The presence of this film may be detected by measuring the friction or by following the migration of two drops of fluid over the face of the plate. It will be found that the drops attract one another under conditions which point to the cause being the contractility of the invisible film.

This brings me to the second part of my subject—namely, the relation of lubricating power to chemical constitution.

In particular experiments with bismuth, a slider having a curved surface was applied to a plain surface of metal, both surfaces being highly polished, and the force required to initiate movement was measured. This force measures what is usually called static friction as opposed to the kinetic friction when the surfaces are in relative motion. The static friction was found to be a function of the weight of the slider. Therefore, the ratio of the weight of the slider to the friction was used as a relative measure. The results appear in the following table:—

*Static friction 0.5 when the faces were clean.*

CHAIN COMPOUNDS.

Alcohols.

	Static Friction.		Static Friction.
Methyl ... ..	0.29	isoPropyl ... ..	0.32
Ethyl ... ..	0.32	isoButyl ... ..	0.30
Propyl ... ..	0.34	Allyl ... ..	0.29
Butyl ... ..	0.30	Glycol ... ..	0.30
Amyl ... ..	0.27	Glycerol ... ..	0.22
Octyl ... ..	0.25	Penterythritol ... ..	0.40
Cetyl ... ..	0.17		

Acids.

	Static Friction.		Static Friction.
Formic ... ..	0.45	n-Octane ... ..	0.32
Acetic ... ..	0.40	Stearic ... ..	0.15
Propionic ... ..	0.31	Oleic ... ..	0.10
Valeric ... ..	0.28	Ricinolic ... ..	0.02
Caprylic, fluid ... ..	0.19	α-Lactic ... ..	0.20
Caprylic, frozen on plate ... ..	0.05	Glyceric ... ..	0.22

	Static Friction.		Static Friction
Acetone ... ..	0.32	Ethyl ether ... ..	0.33
Methyl ethyl ketone ... ..	0.29	B.P. "Paraffin" ... ..	0.20
Ethyl acetate ... ..	0.36	Solid paraffin, m.p. 30.5° ... ..	0.09
Ethyl valerianate... ..	0.35	Solid paraffin, m.p. 46° ... ..	0.07
Tristearin ... ..	0.24	Carbon tetrachloride ... ..	0.43
Triolein ... ..	0.14	Chloroform ... ..	0.30
Acetone dicarboxylic diethyl ester ... ..	0.29	Amylene ... ..	0.26
n-Hexane ... ..	0.37	Octylene ... ..	0.28
n-Heptane ... ..	0.346	Butyl xylene ... ..	0.27

RING COMPOUNDS.

	Static Friction.		Static Friction.
Benzene ... ..	0.34	Ethyl cinnamate ... ..	0.32
Ethyl benzene ... ..	0.32	Thiophenol ... ..	0.22
Iodobenzene ... ..	0.30	Benzyl hydrosulphide ... ..	0.23
Toluene ... ..	0.28	Pyridine ... ..	0.33
Xylene ... ..	0.30	Piperidine ... ..	0.32
p-Cymene ... ..	0.31	Naphthalene ... ..	0.29
Phenol ... ..	0.25	Anthracene ... ..	0.26
Catechol ... ..	0.39	β-Naphthol ... ..	0.38
Quinol ... ..	0.40	Naphthoic acid ... ..	0.39
m-Cresol ... ..	0.26	Carvacrol ... ..	0.23
Benzyl alcohol ... ..	0.31	Thymol ... ..	0.24
Benzoic acid ... ..	0.38	Menthol ... ..	0.26
Phthalic acid ... ..	0.37	Dipentene ... ..	0.31
Cinnamic acid ... ..	0.27	Camphor ... ..	0.24
Benzilic acid ... ..	0.45	Active ethyl ester of camphor oxime ... ..	0.33
Salicylic acid ... ..	0.41	isoCholesterol ... ..	0.27
Ethyl benzoate ... ..	0.33		
o-Phthalic ester ... ..	0.27		
Ethyl hydrocinnamate ... ..	0.28		

CYCLIC COMPOUNDS.

	Static Friction.		Static Friction.
cycloHexane ... ..	0.31	cycloHexanone ... ..	0.35
Methyl cyclohexane ... ..	0.30	1:2-Methyl cyclohexanone ... ..	0.32
1:3-Dimethyl cyclohexane ... ..	0.29	1:3-Methyl cyclohexanone ... ..	0.35
cycloHexanol ... ..	0.20	1:4-Methyl cyclohexanone ... ..	0.33
1:2-Methyl cyclohexanol ... ..	0.28		
1:3-Methyl cyclohexanol ... ..	0.25		
Ammonia fortiss... ..	0.34	Castor oil ... ..	0.03
Triethylamine ... ..	0.30	Water ... ..	0.33
Tripropylamine ... ..	0.26		

It will be seen that static friction is a function of the molecular weight of the lubricant, and in a simple chemical series of chain compounds, such as fatty acids and alcohols or paraffins, a good lubricant will be found if one goes high enough in the series; but it is not a simple function. The friction, for instance, rises sharply in moving from CHCl<sub>3</sub> to CCl<sub>4</sub>, and from phenol to catechol and quinol. The influence of molecular weight is overshadowed by the influence of chemical constitution.

In some simple chemical series the relation appears to be a linear one. Examples are paraffins

and the series benzene, naphthalene, anthracene.

The relation of lubricating qualities to viscosity broadly resembles that to molecular weight. In a simple chemical series lubrication and viscosity change in much the same way with molecular weight, but that there is no fundamental relation between viscosity and lubrication is shown by the following figures:—

	Viscosity at 20°.	Static Friction.
Carbon tetrachloride ...	0.0096	0.43
Chloroform ...	0.0056	0.30
Acetic acid ...	0.0122	0.40
Octylic acid ...	0.0575	0.19
Benzene ...	0.0065	0.39
Toluene ...	0.0058	0.28
Benzyl alcohol ...	0.0558	0.31

Fluidity of the lubricant has no constant significance. The curves for acids, alcohols, and paraffins show no break where, with increasing molecular weight, the lubricant becomes a solid at the temperature of observation. Compare also benzene, naphthalene, and anthracene, menthone and menthol, thymol and carvacrol.

Perhaps the most unexpected result is the distinction between ring and chain compounds. The simple ring compounds, benzene, naphthalene, and anthracene, show the linear relation to molecular weight, and values are much the same as those for paraffins of the same molecular weight. The similarities, however, end here, for any change in the molecular structure produces opposite effects according as it takes place in a chain or a ring. Thus a double bond decreases the lubricating action of a ring compound, but increases that of a chain compound. As examples, compare naphthoic acid with double-bonded oxygen, with naphthalene, menthone with menthol, *cyclohexanone* with *cyclohexane*, benzoic acid with benzene. As examples of double-bonded carbon, compare cinnamic ester with hydrocinnamic ester, dipentene, having two unsaturated carbon atoms, with menthol and *cyclohexane*. Also the more saturated cyclic compounds are better lubricants than the less saturated ring compounds. When a ring and a chain are joined, as in butyl xylene, the result is a better lubricant than either.

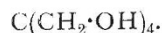
The esters occupy a quite unexpected position. The simple aliphatic esters are worse lubricants than their related acids and alcohols. The ring esters, on the contrary, are better lubricants than are their related acids (e.g. ethyl benzoate and benzoic acid).

Perhaps the most interesting substances are the hydroxy-acids with CH and COOH groups. This conjunction produces a remarkable increase in the lubricating power of a chain compound (lactic acid and ricinolic acid), and almost destroys lubricating action in the case of the ring compounds (salicylic and benzylic acids).

In the ring compounds the replacement of hydrogen decreases lubricating power in the case of N, :O, or .COOH, and increases it in the case of other groups in the order  $C_2H_5 < CH < OH$ .

The effect of a second group of the same or of a different kind is to decrease the effect of the first. Compare, for instance, toluene with xylene; catechol, quinol, and cresol with phenol; and methyl *cyclohexanol* with *cyclohexanol*. The simpler the group, the more effective it is. Compare cymene with toluene or xylene, and benzyl alcohol with phenol.

When the atoms are disposed with complete symmetry about a carbon atom, the result is a very bad lubricant, as we see in carbon tetrachloride and the alcohol penterthritol



It will be noticed that no ring compound is a good lubricant. Even cholesterol with the molecular weight 366 is no exception.

The group SH acts much as the group OH, thiophenol,  $C_6H_5 \cdot SH$ , and benzyl hydrosulphide,  $C_6H_5 \cdot CH_2 \cdot SH$ , resembling phenol and benzyl alcohol respectively.

Concerning one matter—and that the most fundamental—some conclusion must be reached, even though it be upset later. What is friction due to? The "Encyclopædia Britannica" is in no doubt as to this. Friction, it says, is due to inequalities of the surface. This conclusion cannot, I think, be accepted. Why, if it be true, should clean burnished faces of glass or bismuth refuse to slide over one another? It does not even accord with such simple facts as we now know. For instance, the friction of an optical face of glass was found to be the same as that of ordinary plate glass within the limits of accuracy aimed at; and both the optical face and the ordinary plate were found to give higher values than ground glass.

The subject cannot be fully discussed here, but I think we may conclude with some confidence that the friction both of lubricated and of clean faces is due to true cohesion to the force, that is, which binds together the molecules of a solid or of a fluid. If there were no seizing, there would be no friction. The function of the lubricant is to diminish the capacity for seizing by saturating more or less completely the surface forces of the solid. In some cases it seems to abolish it completely, so that static friction vanishes.

The subject of lubrication is of interest to the engineer, but it is perhaps of more interest to the physicist, for it offers a means of exploring the most difficult regions of the physics of boundary zones—namely, the surface energy of solids. It will, for instance, I believe, enable us to prove that the simplest chemical change at the surface of a metal takes place only when the surface energy is decreased thereby. The film of oxide of sulphide which forms on copper acts as a very effective lubricant, and it acts also like a grease film in preventing water from wetting the surface; and from both of these facts we may conclude that the presence of the film lowers the surface energy of the metal.