Studies on the Oiliness of the Liquids. IX. Measurements of the Static Friction Coefficients of Cyclic Compounds for Glass Surfaces.

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The measurements of the static friction coefficients of many organic liquids for glass or silver surfaces had been reported in the preceding communications.[1] The liquids which had been tested, were mostly normal chain compounds such as aliphatic hydrocarbons, alcohols, acids, ketones and esters. It was recognised that long chain compounds, especially long chain acids, are suitable as lubricant for the boundary lubrication. In practice, such compounds are often added to the lubricating oil in order to increase the oiliness of it. Concerning the oiliness of the cyclic compounds, few results are hitherto reported. In this connection, the present experiments were undertaken to study the oiliness of some cyclic compounds. The friction coefficients have been measured for fifteen compounds of both isocyclic and heterocyclic series, and as the results it has been noticed that in cyclic compounds is there not a good lubricant. However, two of them, namely *m*-cresol and hexahydrophenol, are moderately active as lubricant.

The experiments were conducted by the balance method for the measurement of the static friction coefficient. The friction surfaces consisted of an optical glass plate and a glass of spherical surfase whose radius of curvature is 6.5 cm. The method of measuring the friction and the conditions were the same as described in the preceding papers. The samplels of liquids were purified as described in the following lines. Decahydronaphthalene was first shaken with the mixture of concentrated

(1) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, **11** (1936), 659; H. Akamatu and J. Sameshima, *ibid.*, **11** (1936) 791; J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127; H. Akamatu, *ibid.*, **13** (1938), 127; T. Isemura, *ibid.*, **14** (1939), 270, 297.

surphuric acid and fuming sulphuric acid and with sodium carbonate solution and then with distilled water. After drying on metallic sodium, it was fractionated by distillation. Nitrobenzene was recrystallised and distilled several times in vacuum after drying with calcium chloride. Benzyl alcohol was purified by careful fractional distillation in reduced pressure with exclusion of air by passing nitrogen gas. Cyclohexanone was purified by the formation of the addition compound with sulphite which then decomposed with sodium carbonate and distilled in vacuum. All the other samples were purified by repeated distillation under atmospheric pressure or in vacuum after drying with appropriate drying agents ($CaCl_2$ or P_2O_5 for halogenated benzenes and methyl salicylate, KOH for aniline, its derivatives and quinoline, and anhydrous Na_2SO_4 for cyclohexanol) prior to each experiment.

The results obtained are summarized in the following table. In the table, W denotes the weight of slider in gram, F the tangential force acting on slider in gram and μ the static friction coefficient.

As it has been mentioned, all the substances investigated showed poor lubricating activity, namely the friction coefficients of them were larger than 0.66. Above all, decahydronaphthalene showed a very large friction coefficient as high as 0.87. This value is the highest friction coefficient of all liquids for glass surface excepting that of water. The aliphatic saturated hydrocarbons are poor lubricants, however, still they show somewhat lower friction coefficients than this.[2] For good lubrication, adsorption of the lubricants by the friction surfaces is a necessary condition although adsorption alone is not a sufficient one. The poor lubricating activities of both chain and cyclic hydrocarbons are ascribable to the lack of a polar group by which the lubricant molecule can be adsorbed on the sliding surfaces. *m*-Cresol and cyclohexanol have moderate activity as lubricant. They were the most active lubricants among the cyclic compounds. Hardy by using bismuth surfaces showed in his experiment that *m*-cresol and cyclohexanol have relatively low friction coefficients among the ring compounds.[3] In this point the results with bismuth surface and those with glass surface are consistent with each other. Although benzyl alcohol is inferior to these compounds with respect to their lubricating activities, it shows also relatively low friction coefficient among the cyclic compounds. At any rate, it will be noticed that the compounds which have a OH-group in the molecule, show comparatively low friction coefficient. By analogy with the results on the aliphatic compounds, the acids of cyclic series may also be good lubricants.[2] However, all the acids of cyclic series, such as benzoic acid and toluic acid are unfavorably solid, and they have not been tested. Chloro-, bromo- and iodobenzene show almost the same friction coefficient irrespective to the considerable differences among their molecular weights. Nitrobenzene has almost no lubricating activity. It has a very large dipole moment. If the adsorption of the lubricant by the friction surfaces was achieved by the dipole force, nitrobenzene may perhaps be strongly adsorbed by the friction surfaces, for the dipole moment of it is exceedingly large. Therefore, a little more lubricating activity may be expected for this substance. This is contrary

(2) This Bulletin, **11** (1936), 659; **13** (1938), 127.
(3) *Phil. Mag.*, **40** (1920), 201.

Table 1.

	W	F	μ
Decahydronaphtnalene	23.40	19.78	0 85
	23 50	21.25	0.91
	23.75	21.90	0.92
	24 10	20 90	0 87
	26.90	22 60	0.84
	27.75	23.20	0.84
			0.87
m-Cresol	23 00	15.25	0.66
	24.20	15 20	0 63
	26 40	16.97	0.64
	30.90	20.10	0.65
	31 00	20.00	0.65
	33.40	24.40	0.73
			0.66
Cyclohexanol	20 90	13 51	0.65
	24 65	15.79	0.64
	25.50	17 28	0.68
	26.85	16.87	0 63
	23.90	20.74	0.72
			0.66
Benzyl alcohol	22.20	15.90	0 72
	26.35	18 25	0.69
	26 35	20.60	0.78
	26 25	19 50	0 74
	27.80	20 60	0.74
	30 30	22.00	0.73
			0.73
Chlorobenzene	22.55	18 50	0.82
	23 25	19 30	0.83
	25 00	19 75	0 79
	25 50	20 90	0 82
	25.90	21.16	0 82
	27.60	22.23	0.81
	29.50	23.00	0.78
			0.81
Bromobenzene	21.35	16.10	0.75
	21 55	16.61	0.77
	22.40	18.40	0.82
	23 05	17.55	0.76
	24.30	19.00	0.78
	26.25	20.40	0.78
			0.78
Iodobenzene	23 90	18.75	0.78
	24.00	17.95	0.82
	21.90	17.95	0 82
	20.70	17.00	0 82
			0.81
Nitrobenzene	25.40	21.30	0.84
	26.00	22.00	0 85
	27 80	22.60	0 81
	28.75	24.00	0.84
			0.84

	W	F	μ
Methyl salicylate	15.70	11.15	0.71
	23 60	18.47	0.78
	23.70	18.22	0.77
	26.05	20 02	0.77
	27.90	21.02	0.75
	28.00	21.55	0 77
			0.76
Aniline	23.20	17.80	0.77
	26.05	18.27	0.70
	26.30	19 85	0.76
	26 80	20 00	0.75
	27 20	19.03	0.70
	27.90	19.30	0.69
			0.73
o-Toluidine	21 80	15.78	0.73
	26.25	18.80	0.72
	26 70	20.62	0 80
	23.80	21.10	0.74
	30.30	22.40	0.74
			0.75
Dimethyl aniline	21 55	15.83	0.74
	24 50	18.30	0.75
	25.15	18.86	0 75
	25 20	18.93	0.75
	28 50	21.30	0.75
	29.50	24.20	0.82
			0.76
o-Chloraniline	22 65	20.65	0.91
	24 40	21 78	0.89
	25 55	22.41	0.88
	25 65	22 00	0.83
	28.65	24.75	0.87
			0.86
Quinoline	19.80	15.40	0.78
	20 60	16 03	0.78
	21 55	18.48	0.86
	23 00	18.50	0.80
	26.30	20.80	0.79
	28.70	24.90	0.87
			0.82
Cyclohexanone	21.25	17.40	0.82
	22 00	16 58	0.76
	24.00	18.60	0.78
	25.65	20.28	0.79
	27.95	22.60	0.81
			0.79

to the experimental fact. Accordingly nitrobenzene may not be adsorbed by glass surface and the adsorption is not attained only by the dipole force.[4]

Aniline and its derivatives show somewhat smaller friction coefficients than the compounds just mentioned. However, *o*-chloroaniline has an exceptionally high friction coefficient among them. Quinoline shows also a high friction coefficient. It was already reported that aliphatic ketones are poor lubricants.[5] The cyclic ketones can not be exceptional, cyclohexanone shows also a high friction coefficient. Hardy states[3] that the most interesting substances which he had investigated are the hydroxy-acids with OH and COOH groups. This conjunction almost destroys the lubricating action in the case of the ring compounds such as salicylic acid. Owing to the existence of two polar groups, the present author had expected a high friction coefficient also in the case of methyl salicylate. Nevertheless, the friction coefficient is not so high as the author had expected. Although salicylic ester has two polar groups in the molecule, the ester group has probably no or little ability of anchoring on the friction surfaces. And the molecule behaves as if it were a phenol derivative.

It is considered that the adsorption by the friction surface by only one active group is a necessary condition for good lubrication, though not a sufficient one. Regular arrangement of the lubricant molecules or adequate orientation of the molecules is an important factor for good lubrication. Further discussion on the lubricating activity of liquids and friction will be given in a later paper.

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Summary.

(1) The measurements of the static friction coefficients of cyclic compounds for glass surfaces were reported.

(2) It is noticed that no cyclic compound is a good lubricant, however, among them *m*-cresol and cyclohexanol are moderately active as lubricant.

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(4) This fact has been recently verified by Mr. Akamatu in our laboratory by the direct measurement of adsorption of nitobenzene by glass powder from its toluene solution with a very sensitive method.

(5) This Bulletin, **14** (1939), 270.