

THE EXTREME PRESSURE LUBRICATING PROPERTIES OF SOME CHLORINATED COMPOUNDS AS ASSESSED BY THE FOUR-BALL MACHINE.

By W. DAVEY.

SUMMARY.

A study of the Extreme Pressure (E.P.) Lubricant properties of some chlorinated compounds has been made, using the Four-Ball machine. Anglamol 40, a proprietary chlorinated compound, was used as the standard reference material, and other materials were rated on their performance relative to this standard. On this rating, benzo-trichloride, benzyl chloride, hexachlorethane, and carbon tetrachloride are superior to Anglamol 40, whilst tetrachlorethane, chloroform, *p*-chloronitrobenzene, ethylene dichloride, trichlorethylene, and *p*-dichlorbenzene are inferior in E.P. properties. The mechanism of the development of E.P. properties due to chlorinated compounds is discussed. The results enable the E.P. properties of a chlorinated compound to be predicted from its formula.

THE Four-Ball Extreme-Pressure Lubricant Testing Apparatus was designed for the testing of E.P. Lubricants,¹ and offers a simple and reliable means of rating such lubricants. E.P. properties are shown by "active" chlorinated and "active" phosphorus compounds and by reactive or free sulphur in mineral oil, and such materials impart high load-bearing capacity and low wear when blended in mineral oil.

In the present work certain chlorinated compounds have been tested in the Four-Ball Apparatus, as neat compounds (where liquid), and blended in genuine Penna 150 Neutral Oil, since chlorinated compounds have found some use as lubricants for drawing and deep tapping operations. It is generally agreed that chlorinated compounds produce E.P. effects by the formation of additive chloride films which prevent metal-to-metal contact, by analogy with the similar films formed by phosphorus and sulphur compounds. This theory is confirmed by the present work, and the mechanism by which E.P. effects are produced by chlorinated compounds is explained.

The development of E.P. properties by chlorinated compounds is governed by two factors :—

- (1) the lability of the chlorine atoms in the compound,
- (2) the degree of "chlorine saturation" of the compound.

In the case of *p*-dichlorbenzene the chlorine is not labile, being attached to nuclear carbon, and this compound shows little or no E.P. properties. In the case of *p*-chloronitrobenzene the chlorine atom is rendered somewhat labile by the *p*-nitro-group, and this results in producing slight E.P. properties. This shows that in compounds having only chlorine atoms attached to an aromatic nucleus, no E.P. properties will be shown without the presence of activating groups in the molecule.

The decomposition of carbon tetrachloride under the extreme conditions of the test would produce carbon and atomic chlorine, whilst in the case

of ethylene dichloride, chloroform, etc., hydrogen chloride might be formed. The formation of hydrogen chloride under these conditions would lead to the formation of chloride ions with traces of moisture present, and this would produce corrosion of the metal surface and high wear. This mechanism is confirmed by the differences observed between compounds such as chloroform and ethylene dichloride containing available hydrogen and those such as carbon tetrachloride which are completely saturated with chlorine. This is particularly the case with ethylene dichloride, which has no chlorine atoms in excess of the hydrogen atoms, and thus exhibits only very slight E.P. properties. It would appear that "excess chlorine" is the important criterion in development of E.P. properties, and also the more hydrogen chloride which can be produced the lower the E.P. rating of the compound.

The very marked superior E.P. properties of benzotrichloride and benzyl chloride are due to the extreme lability of the chlorine atoms and the stability of the radical resulting from decomposition, the stability of such radicals to which a benzene nucleus is attached being well known. The possibility of hydrogen chloride formation from benzyl chloride would account for the superior E.P. properties of benzo-trichloride, where such a possibility does not exist. The difference in E.P. properties between benzyl chloride and benzo-trichloride is marked only under extreme conditions, and the above explanation would meet the facts rather than any difference in chlorine content of these compounds.

EXPERIMENTAL.

Apparatus and Method of Test.

The Four-Ball Machine consists essentially of a chuck holding a $\frac{1}{2}$ -inch hard steel ball, which is rotated at constant speed in the cavity formed by three identical balls clamped in a cup holding the lubricant under test. Load is applied to the balls by means of a pivoted lever, and this load produces a frictional torque when the apparatus is working, the displacement of an indicator bar attached to the cup being recorded on a chart placed on a constant-speed drum. The deflection produced is proportional to the frictional torque produced, and the chart is therefore a Friction/Time curve. Conditions during test approach those obtained in boundary lubrication, and when breakdown of the lubricant film (seizure) occurs, small metal particles are torn out of the surface of the balls, producing wear spots on the balls in the cup and a corresponding wear ring on the rotating ball. E.P. lubricants show either no seizure or rapid recovery after seizure, *i.e.*, a rapid reforming of the film between the metal surfaces. The wear spots, which are usually circular, are measured along the line of wear and at right angles to this line, and a mean value for the wear diameter obtained. Plotting of mean wear diameter against load yields curves which show a sharp break in the case of E.P. lubricants. In the present work the "short duration test," *i.e.* the performance during one complete revolution of the recording drum (60 secs.), was used throughout. A detailed description of the apparatus, etc., is given by Clayton.²

Results.

The results obtained are given in tabular form below and wear/load diagrams are included. Examples of Friction/Time curves are also given.

The neat liquid chlorinated compounds and 10 per cent. weight blends of these compounds in genuine Penna 150 Neutral Oil were tested. Further 5 per cent., 3 per cent., and 1 per cent. blends of Anglamol 40, carbon tetrachloride, hexachlorethane, benzyl chloride, and benzo-trichloride were tested, since these compounds showed good E.P. properties in 10 per cent. blends.

SECTION I.
Neat Compounds.

Load (kg.).	Mean Wear Diameter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
1 (a). Anglamol 40.							
50	0.50	No seizure : smooth wear throughout.	—	—	0.07	—	Smooth wear.
70	0.70	" "	" "	—	0.05	—	" "
85	0.73	" "	" "	—	0.07	—	Staining of balls.
119	0.80	" "	" "	—	0.07	—	" "
170	0.85	" "	" "	—	0.05	—	" "
210	0.83	Almost instant	7.5	0.03	0.03	0.05	" "
270	1.10	" "	7.5	0.03	0.05	0.06	" "
310	1.15	" "	8.5	0.03	0.06	0.09	" "
410	1.65	Instant	24	0.15	—	0.17	" "
1 (b). Chloroform.							
30	0.50	No seizure : smooth wear throughout.	—	—	0.05	—	—
56	0.60	Immediate seizure and recovery.	—	0.14	—	0.10	—
70	0.60	" "	" "	0.07	—	0.07	—
85	0.65	" "	" "	0.19	—	0.13	—
119	0.70	" "	" "	0.11	—	0.10	—
170	0.75	" "	" "	0.09	—	0.08	Slight staining of balls.
210	0.80	" "	" "	0.10	—	0.08	" "
270	1.30	" "	" "	0.16	—	0.07	" "
310	1.40	" "	" "	0.16	—	0.07	" "
410	2.10	" "	" "	0.15	—	0.05	Irregular wear of balls.
1 (c). Carbon Tetrachloride.							
56	0.50	Immediate seizure and recovery.	—	0.04	—	0.03	Slight staining of balls.
70	0.65	" "	" "	0.08	—	0.04	" "
85	0.65	" "	" "	0.11	—	0.04	" "
119	0.70	" "	" "	0.15	—	0.05	" "
170	0.80	" "	" "	0.15	—	0.05	" "
210	0.95	" "	" "	0.10	—	0.04	" "
270	0.90	" "	" "	0.07	—	0.05	" "
310	1.10	" "	" "	0.10	—	0.07	Blackening and heavy deposit on balls.
410	1.45	" "	" "	0.15	—	0.06	" "
1 (d). Ethylene Dichloride.							
50	0.40	No seizure : smooth wear throughout.	—	—	0.05	—	—
70	0.50	" "	" "	—	0.09	—	—
85	0.58	" "	" "	—	0.11	—	—
119	0.65	" "	" "	—	0.10	—	—
170	0.75	" "	" "	—	0.07	—	—
210	0.98	" "	" "	—	0.10	—	—
270	2.15	Instant.	0.7	> 0.25	—	0.11	Blackening of balls.
310	2.75	" "	1.0	> 0.25	—	0.10	" "
410	Welding.	" "	1.7	> 0.25	—	0.14	" "

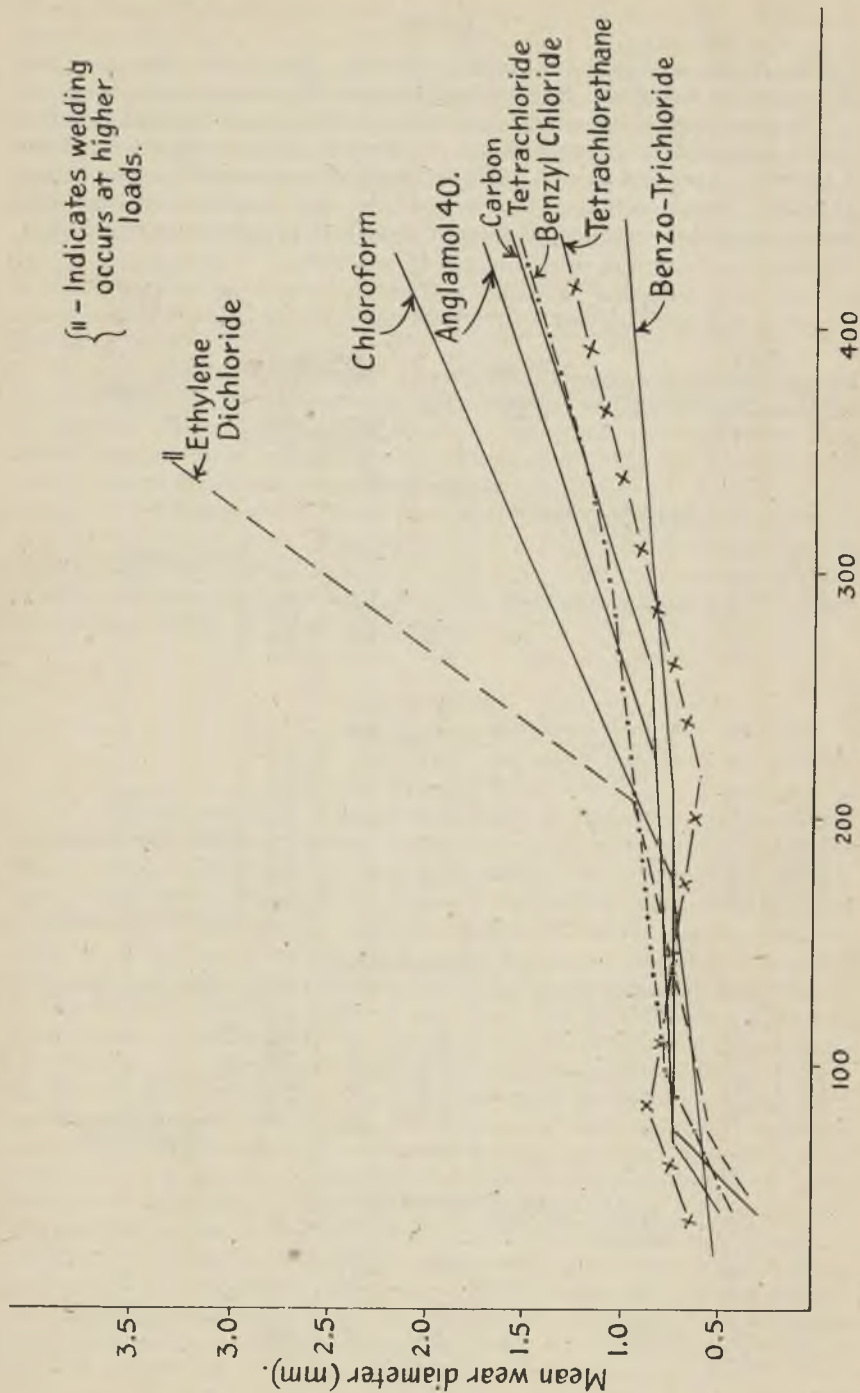


Fig. 1.

WEAR DIAGRAM—NEAT COMPOUNDS.

FRICION-TIME CURVES.

KEY. The following reference system is used throughout.

Load 56 70 85 119 170 210 270 310 410 (kg.)

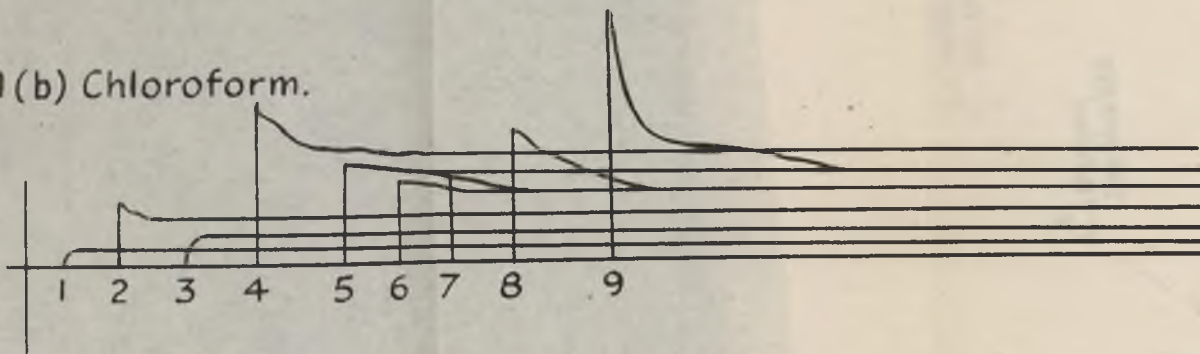
Ref. 1 2 3 4 5 6 7 8 9

Scale 1 cm. horizontal = 3.2 sec. 1 cm. vertical = 0.086 (coefficient of friction).

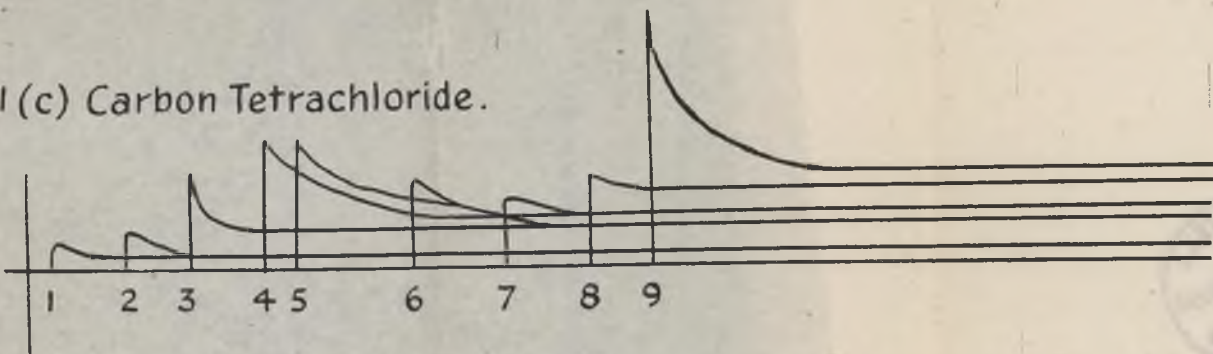
NOTE. 1 and 2 in each case are on half vertical scale i.e. 1 cm. = 0.17 (coefficient of friction).

SECTION 1. NEAT COMPOUNDS.

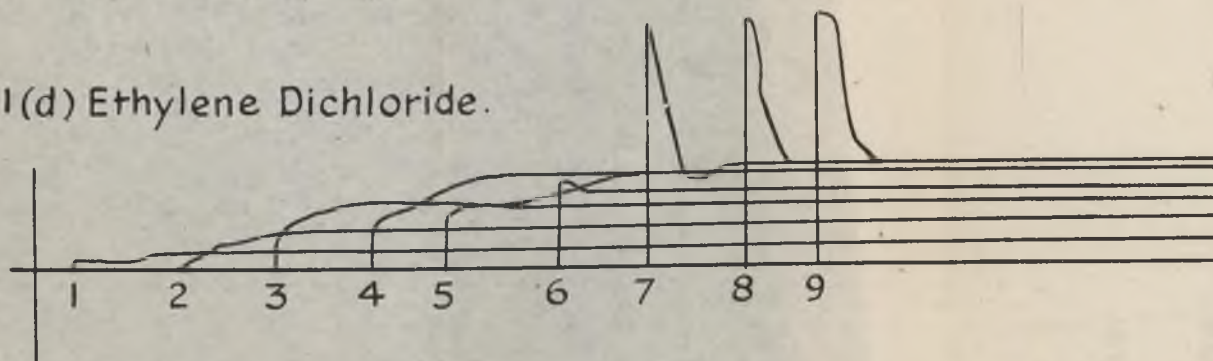
I(b) Chloroform.



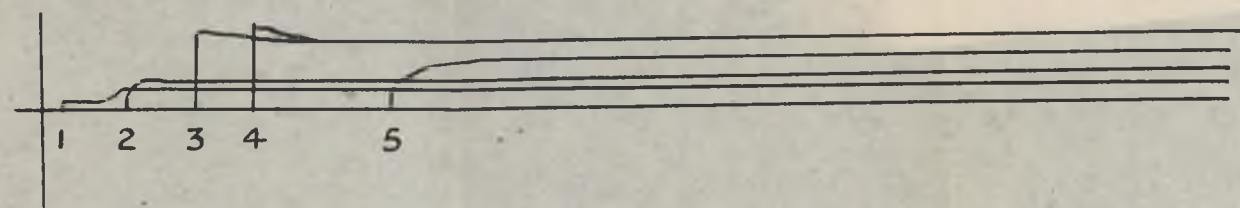
I(c) Carbon Tetrachloride.



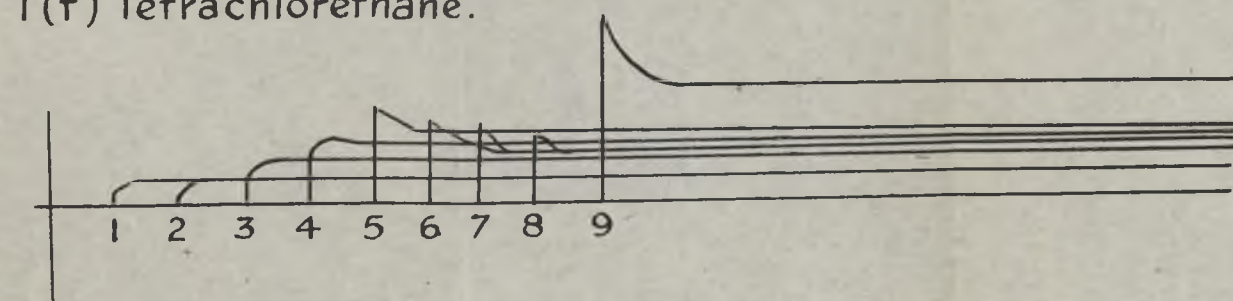
I(d) Ethylene Dichloride.



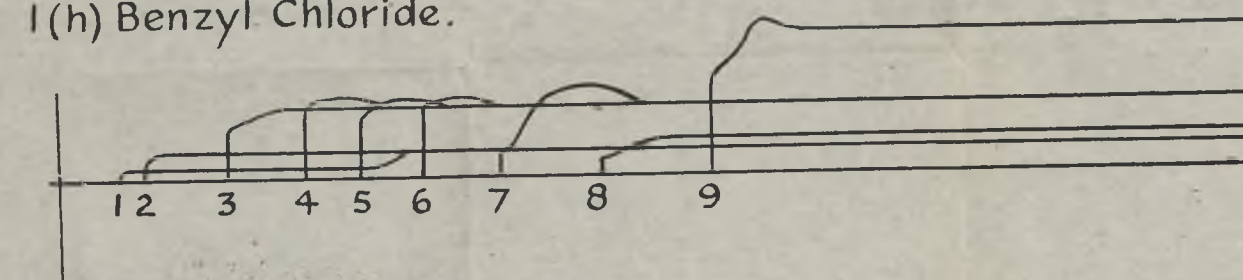
I(e) Trichlorethylene.



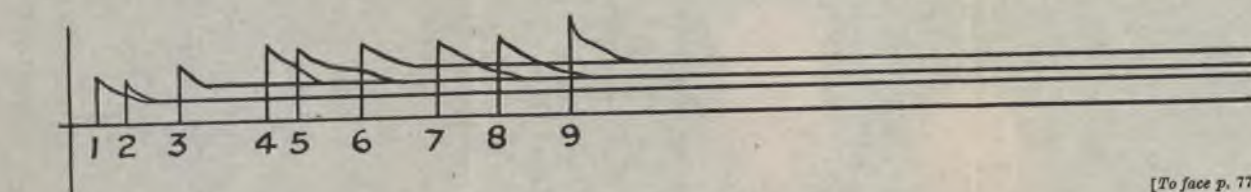
I(f) Tetrachlorethane.



I(h) Benzyl Chloride.



I(i) Benzo-Trichloride.



SECTION 1—(continued).

Load (kg.).	Mean Wear Diameter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
<i>1 (e). Trichlorethylene.</i>							
56	0.55	No seizure.	—	—	0.03	—	—
70	0.65	"	—	—	0.06	—	Deposit on balls.
85	0.80	"	—	—	0.09	—	" "
119	0.65	"	—	—	0.09	—	" "
170	0.55	"	—	—	0.06	—	" "
210	Welding after 4.6 seconds.		—	—	—	—	" "
<i>1 (f). Tetrachlorethane.</i>							
56	0.75	No seizure; smooth wear throughout.	—	—	0.04	—	Deposit round wear pattern.
70	0.82	" " "	—	—	0.04	—	" " "
85	0.85	" " "	—	—	0.05	—	" " "
119	0.80	" " "	—	—	0.07	—	" " "
170	0.70	Immediate seizure and recovery.	—	0.11	—	0.07	" " "
210	0.65	" " "	—	0.08	—	0.06	" " "
270	0.85	" " "	—	0.09	—	0.06	Slight staining. Trace of welding.
310	0.85	" " "	—	0.08	—	0.06	" " "
410	1.30	" " "	—	0.08	—	0.07	Staining and trace of welding.
<i>1 (g). Hexachlorethane.</i>							
This being a solid, no determinations could be made.							
<i>1 (h). Benzyl Chloride.</i>							
56	0.50	No seizure; smooth wear throughout.	—	—	0.05	—	Staining of balls.
70	0.60	" " "	—	—	0.07	—	" " "
85	0.70	" " "	—	—	0.06	—	" " "
119	0.83	" " "	—	—	0.07	—	" " "
170	0.85	" " "	—	—	0.08	—	" " "
210	1.19	" " "	—	—	0.08	—	" " "
270	1.19	" " "	—	—	0.09	—	" " "
310	1.10	" " "	—	—	0.05	—	" " "
410	1.43	1.0	4.6	0.03	0.05	0.07	" " "
<i>1 (i). Benzo-trichloride.</i>							
56	0.60	Instant seizure and recovery.	—	0.04	—	0.04	Smooth wear.
70	0.75	" " "	—	0.04	—	0.04	" " "
85	0.75	" " "	—	0.03	—	0.03	" " "
119	0.75	" " "	—	0.04	—	0.04	" " "
170	0.77	" " "	—	0.05	—	0.05	" " "
210	0.75	" " "	—	0.06	—	0.06	" " "
270	0.85	" " "	—	0.05	—	0.06	" " "
310	0.95	" " "	—	0.05	—	0.06	" " "
410	1.00	" " "	—	0.06	—	0.06	" " "

These results indicate that neat Anglamol 40, carbon tetrachloride, tetrachlorethane, benzyl chloride, and benzo-trichloride exhibit similar E.P. properties, whilst ethylene dichloride and chloroform exhibit somewhat higher wear for the same loads. It is of interest to note that the wear diagrams of benzyl chloride and benzotrachloride are almost straight lines showing unique E.P. properties. Volatile compounds such as chloroform are vaporized to some extent by the heat liberated by the frictional forces, and this might lead to somewhat erroneous rating of E.P. properties. Such a rating has therefore been made on the results obtained from performance of these compounds blended in mineral oil.

The Friction/Time curves were similar for the neat compounds, except that benzo-trichloride showed the immediate seizure and recovery characteristic of a good E.P. lubricant.

SECTION 2.

10 per cent. Weight Blends in Penna 150 Neutral.

Load (kg.).	Mean Wear Diameter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
<i>2 (a). Anglamol 40.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.05	—	—
70	0.40	" "	" "	—	0.05	—	—
85	0.55	" 5.0 "	2.0	0.09	0.06	0.09	—
119	0.67	" 1.0 "	5.3	0.09	0.04	0.08	—
170	0.86	<0.5	10.5	0.08	0.04	0.09	—
210	1.05	Instant.	10.5	0.13	—	0.10	Slightly irregular wear.
270	2.25	" "	" "	0.22	—	0.09	Irregular wear.
310	2.46	" "	" "	0.24	—	0.09	" "
410	Welding.	" "	" "	>0.25	—	0.16	" "
<i>2 (b). Chloroform.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.03	—	—
70	0.40	" "	" "	—	0.03	—	—
85	0.50	" 1.7 "	5.0	0.10	0.04	0.07	—
119	0.70	" 1.7 "	5.0	0.10	0.04	0.07	—
170	0.85	Almost instant.	10.5	0.11	0.04	0.09	—
210	2.25	Instant.	6.0	>0.25	—	0.10	Irregular wear.
270	2.45	" "	6.0	>0.25	—	0.10	" "
310	2.78	" "	7.0	>0.25	—	0.10	" " Slight staining of balls.
410	Instant welding.	" "	" "	" "	" "	" "	" "
<i>2 (c). Carbon Tetrachloride.</i>							
56	0.10	No seizure : smooth wear throughout.	—	—	0.03	—	—
70	0.30	" "	" "	—	0.03	—	—
85	0.45	" "	" "	—	0.04	—	—
119	0.65	" 1.7 "	3.0	0.03	0.05	0.07	—
170	0.76	Almost instant.	7.0	0.07	0.05	0.07	—
210	1.00	" "	8.5	0.08	0.05	0.07	—
270	1.20	Instant.	8.0	0.08	—	0.07	Channelling of balls.
310	1.73	" "	7.5	0.08	—	0.07	Irregular wear.
330	2.15	" "	8.0	0.22	—	0.07	" "
410	Welding after 12.5 secs. 2.50	" "	" "	" "	" "	" "	" "
<i>2 (d). Ethylene Dichloride.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.04	—	—
70	0.40	" "	" "	—	0.04	—	—
85	0.50	" "	" "	—	0.04	—	—
119	2.07	" 0.7 "	6.6	>0.25	0.06	0.09	Irregular wear.
170	2.80	Instant.	16.0	>0.25	—	0.10	" " Staining of balls.
<i>2 (e). Trichlorethylene.</i>							
56	0.30	No seizure : smooth wear throughout.	—	—	0.04	—	—
70	0.40	" "	" "	—	0.05	—	—
85	2.05	" 2.0 "	9.3	>0.25	0.06	0.14	Irregular wear.
119	2.30	" 0.7 "	7.5	>0.25	0.07	0.11	" "
170	Instant welding.	" "	" "	" "	" "	" "	" "

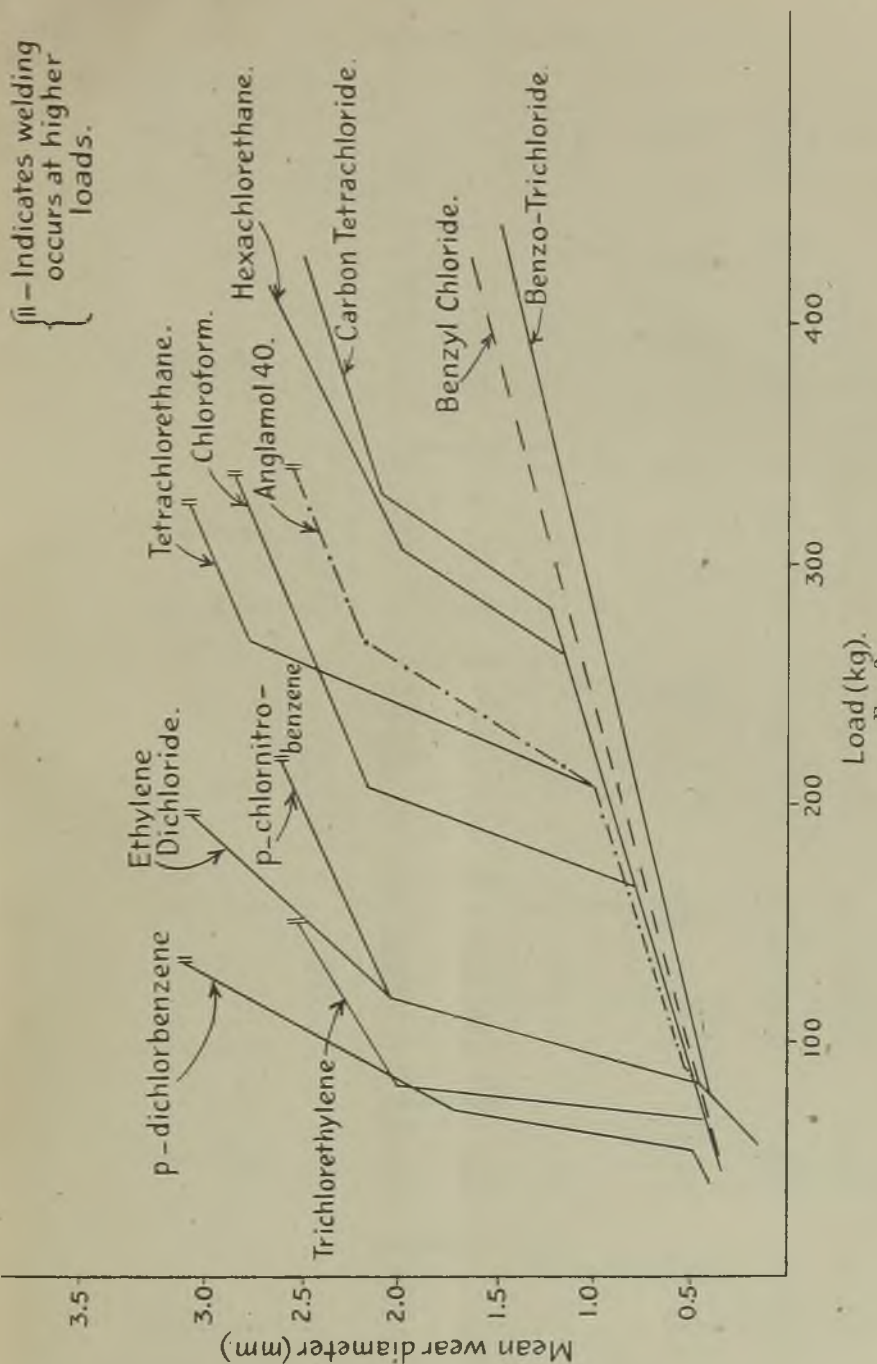


FIG. 2.

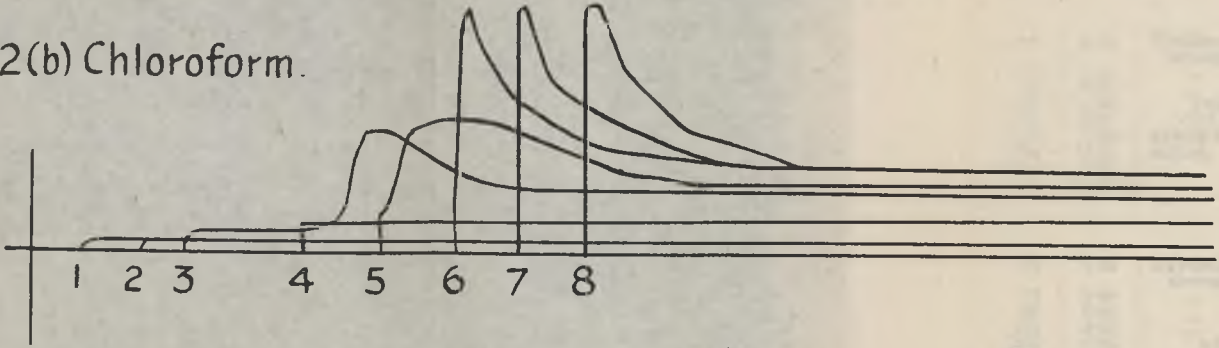
WEAR DIAGRAM—10% BLENDS IN PENNA NEUTRAL.

SECTION 2—(continued).

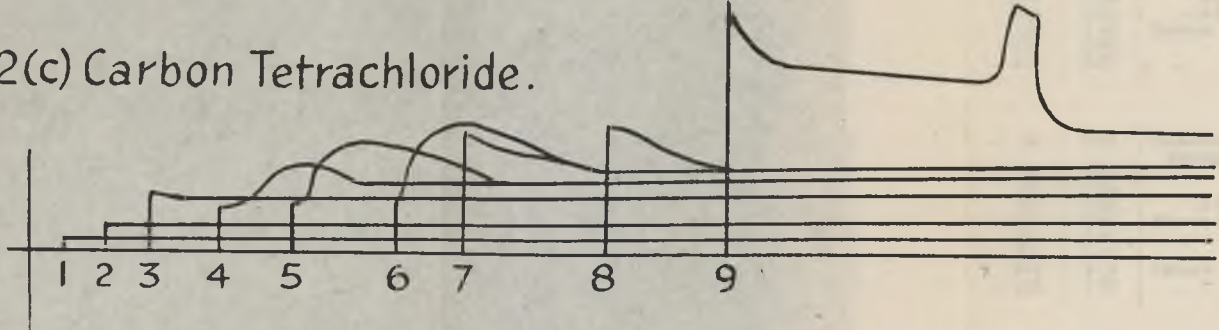
Load (kg.).	Mean Wear Diameter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
<i>2 (f). Tetrachlorethane.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.04	—	Smooth wear.
70	0.40	" " "	"	—	0.04	—	" "
85	0.45	" " "	"	—	0.05	—	" "
119	0.80	" 1.65 "	15.0	0.14	0.03	0.08	" "
170	0.87	" <0.5 "	18.0	0.13	0.04	0.08	" "
210	1.00	Almost instant.	14.5	0.10	0.04	0.11	" "
270	2.85	Instant.	11.5	> 0.25	—	—	Slight irregular wear.
310	3.08	" "	11.5	> 0.25	—	0.11	Irregular wear.
410	Welding.	" "	1.65	> 0.25	—	0.17	" "
<i>2 (g). Hexachlorethane.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.04	—	—
70	0.40	" " "	"	—	0.04	—	—
85	0.45	" " "	"	—	0.05	—	—
119	0.50	" " "	"	—	0.03	—	—
170	0.85	" 0.6 "	6.6	0.09	0.04	0.08	Channelling of balls.
210	1.00	" <0.5 "	7.0	0.09	0.04	0.08	" " "
270	1.32	Instant.	7.0	0.09	—	—	" " "
310	2.06	" "	8.0	0.17	—	0.08	" " "
410	2.68	" "	8.0	> 0.25	—	0.06	Irregular wear.
<i>2 (h). Benzyl Chloride.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.04	—	—
70	0.40	" " "	"	—	0.04	—	—
85	0.45	" " "	"	—	0.06	—	—
119	0.59	" 0.7 "	10.0	0.06	0.03	0.08	—
170	0.85	Almost instant.	9.0	0.06	0.06	0.09	—
210	1.00	" " "	6.5	0.11	—	0.10	Channelling of balls.
270	1.18	" " "	5.0	0.11	—	0.09	Irregular wear.
310	1.23	Instant.	—	0.09	—	0.09	" "
410	1.60	" "	7.5	0.16	—	0.09	" "
<i>2 (i). Benzo-trichloride.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.04	—	Smooth wear.
70	0.40	" " "	"	—	0.04	—	" "
85	0.45	" " "	"	—	0.06	—	" "
119	0.60	" 1.8 "	2.0	0.02	0.06	0.06	" "
170	0.75	" <0.5 "	6.5	0.06	0.04	0.07	" "
210	0.83	Almost instant.	6.0	0.03	0.07	0.07	" "
270	0.97	Instant.	6.0	0.03	—	0.07	" "
310	1.08	" "	8.0	0.09	—	0.07	" "
410	1.45	" "	13.0	0.13	—	0.06	Staining of balls.
<i>2 (j). p-Dichlorbenzene.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.03	—	—
70	1.42	12.5	7.0	0.24	0.04	0.10	Irregular wear.
85	1.95	1.3	15.2	> 0.25	0.03	0.09	" "
119	2.85	0.5	20.0	> 0.25	0.03	0.10	" "
<i>2 (k). D-Chlornitrobenzene.</i>							
56	0.45	No seizure : smooth wear throughout.	—	—	0.04	—	—
70	0.55	" " "	"	—	0.04	—	—
85	0.65	" " "	"	—	0.06	—	—
119	2.05	Instant.	4.5	> 0.25	—	0.10	Irregular wear.
170	2.38	" "	3.5	> 0.25	—	0.11	" "

SECTION 2. 10% WT. BLENDS IN PENNA 150 NEUTRAL.

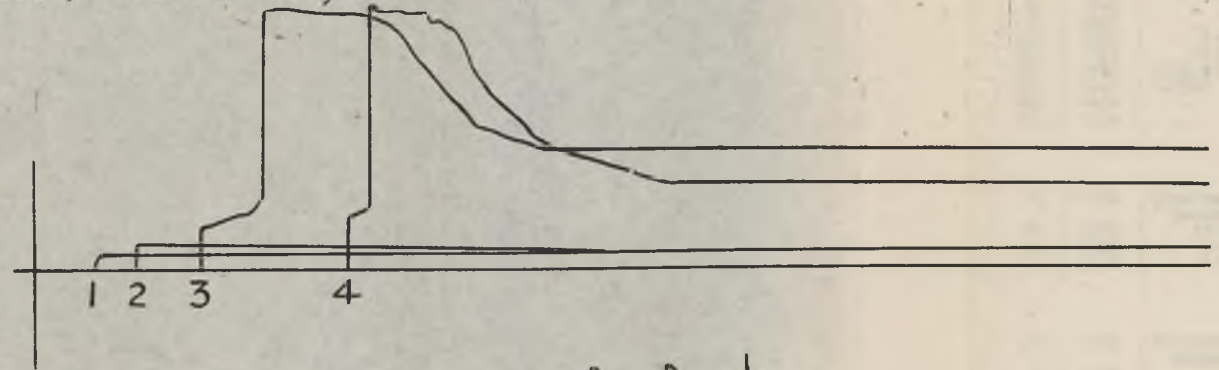
2(b) Chloroform.



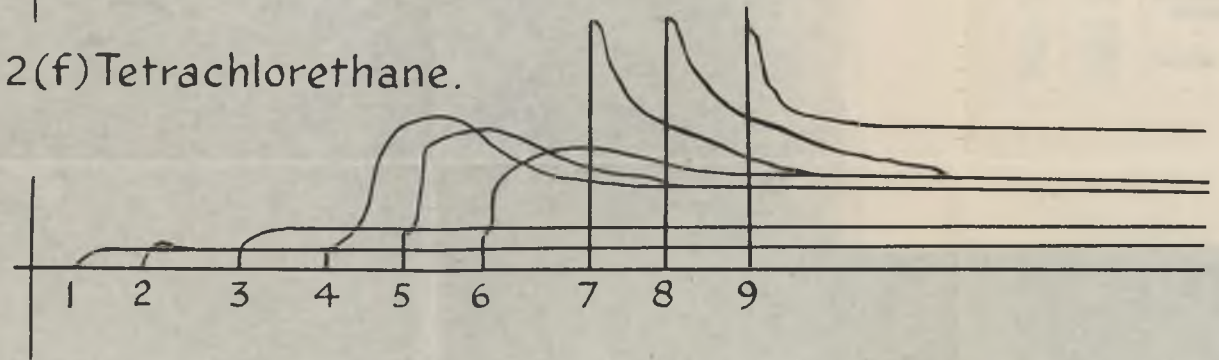
2(c) Carbon Tetrachloride.



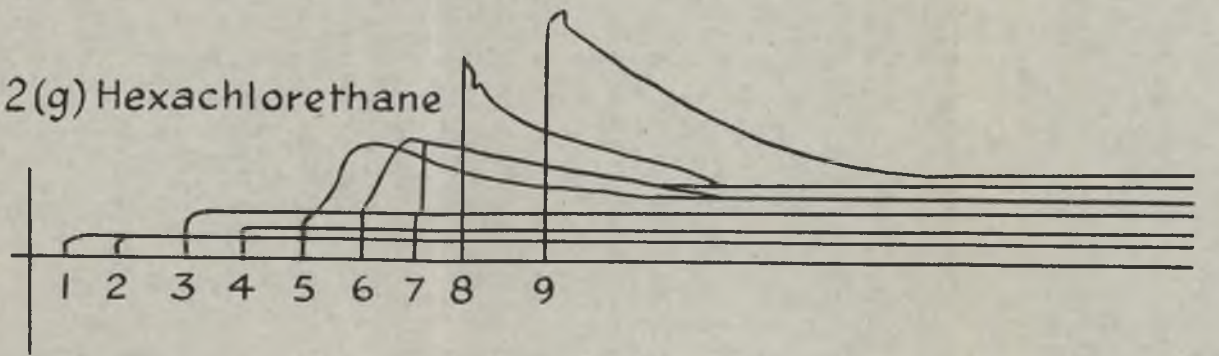
2(e) Trichlorethylene.



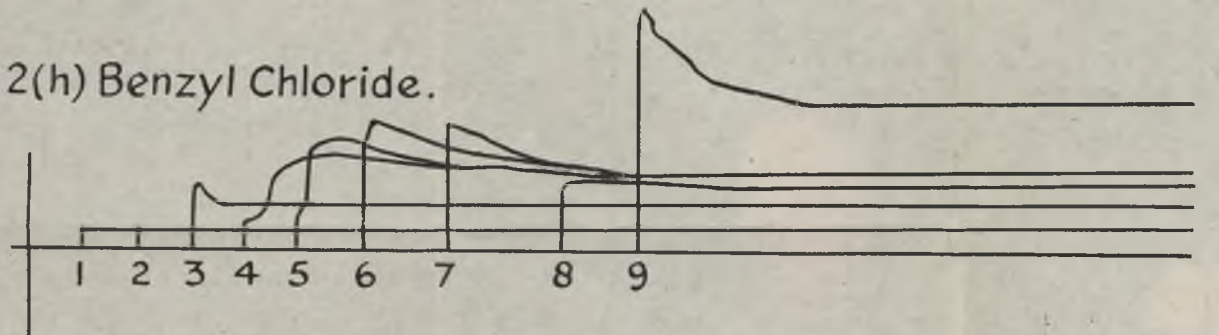
2(f) Tetrachlorethane.



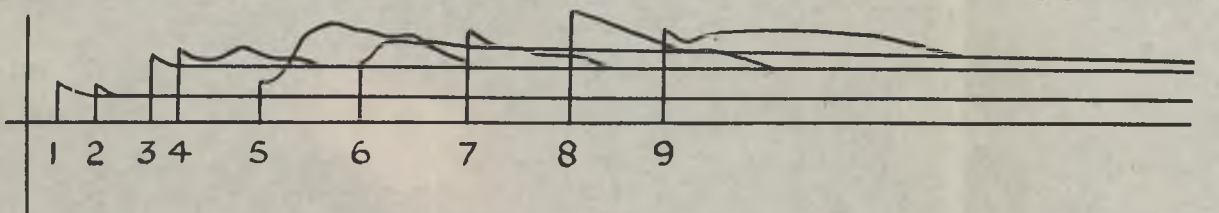
2(g) Hexachlorethane



2(h) Benzyl Chloride.



2(i) Benzo-Trichloride



These results indicate the very marked differences in E.P. properties of the materials tested, and serve as a basis for rating the performances of these compounds. The unique wear curves for benzo-trichloride and benzyl chloride indicate their marked superior E.P. properties.

The Friction/Time curves were all similar showing rapid seizure and recovery for the compounds exhibiting good E.P. properties. The non-active compounds gave diagrams resembling those of straight mineral oil.

SECTION 3.

5 per cent. Weight Blends in Penna 150 Neutral.

Load (kg.).	Mean Wear Diameter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.	
					Before Seizure.	After Seizure.		
3 (a). Anglamol 40.								
56	0-35	No seizure : smooth wear throughout.	—	—	0-05	—	Smooth wear.	
70	0-51	12-5	6-5	0-08	0-05	0-09	"	"
85	0-65	3-0	6-0	0-10	0-06	0-09	"	"
119	0-74	1-0	7-5	0-09	0-06	0-11	"	"
170	1-60	Almost instant.	10-0	0-20	0-06	0-09	Irregular wear.	
210	2-05	Instant.	8-0	> 0-25	—	0-09	"	"
270	2-45	"	8-5	> 0-25	—	0-09	"	"
310	2-69	"	11-5	> 0-25	—	0-09	"	"
410	Instant welding.						"	"
3 (c). Carbon Tetrachloride.								
56	0-35	No seizure : smooth wear throughout.	—	—	0-03	—	Smooth wear.	
70	0-40	"	—	—	0-03	—	"	"
85	0-60	" 4-0 "	3-3	0-08	0-03	0-09	"	"
119	0-73	1-3	5-0	0-11	0-03	0-09	"	"
170	0-88	Almost instant.	6-6	0-12	0-02	0-09	"	"
210	1-80	Instant.	6-6	0-14	—	0-07	Irregular wear.	
270	2-20	"	6-6	> 0-25	—	0-08	"	"
310	2-50	"	7-2	> 0-25	—	0-08	"	"
410	3-10	"	13-5	> 0-25	—	0-07	"	"
	Slight welding.						"	"
3 (g). Hexachlorethane.								
56	0-35	No seizure : smooth wear throughout.	—	—	0-04	—	Smooth wear.	
70	0-43	"	—	—	0-04	—	"	"
85	0-63	" 6-3 "	3-3	0-09	0-06	0-10	"	"
119	0-70	1-0	6-0	0-07	0-05	0-09	"	"
170	0-85	Almost instant.	3-3	0-03	0-05	0-08	"	"
210	2-13	Instant.	10-0	> 0-25	—	0-10	Irregular wear.	
270	2-60	"	6-6	> 0-25	—	0-09	"	"
310	2-75	"	7-5	> 0-25	—	0-09	"	"
410	Instant welding.						"	"
3 (h). Benzyl Chloride.								
56	0-35	No seizure : smooth wear throughout.	—	—	0-04	—	Smooth wear.	
70	0-50	5-3	2-6	0-03	0-04	0-07	"	"
85	0-58	1-3	5-0	0-07	0-08	0-09	"	"
119	0-65	< 0-5	3-3	0-04	0-09	0-09	"	"
170	1-12	Almost instant.	2-6	0-13	0-07	0-09	"	"
210	1-80	Instant.	2-6	0-13	—	0-10	"	"
270	2-29	"	5-0	> 0-25	—	0-10	"	"
310	2-36	"	6-0	> 0-25	—	0-10	"	"
410	2-20	"	5-0	> 0-25	—	0-07	"	"
	Trace of welding.						"	"

{|| - Indicates welding occurs at higher loads.

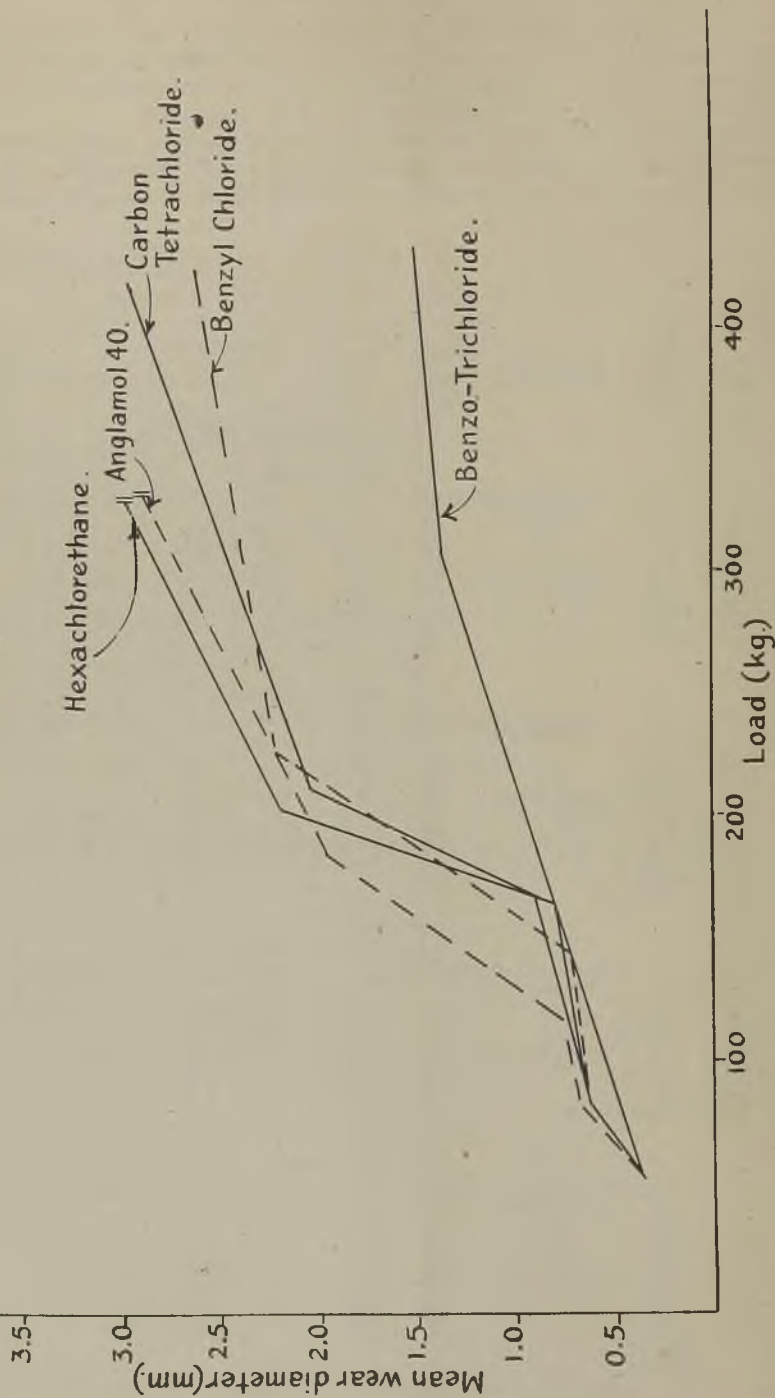


FIG. 3.
WEAR DIAGRAM—5% BLENDS IN PENNA 150 NEUTRAL.

SECTION 3—(continued).

Load (kg.).	Mean Wear Diameter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
3 (i). <i>Benzo-trichloride.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.05	—	Smooth wear.
70	0.40	" "	" "	—	0.05	—	" "
85	0.50	" "	" "	—	0.07	—	" "
119	0.55	" 1.0 "	" 1.2 "	0.03	0.07	0.07	" "
170	0.72	Almost instant.	7.5	0.06	0.06	0.07	" "
210	0.91	Instant.	5.0	0.09	—	0.07	" "
270	1.10	" "	6.5	0.11	—	0.07	" "
310	1.31	" "	7.5	0.11	—	0.07	" "
410	1.44	" "	8.0	0.14	—	0.06	" "

SECTION 4.

3 per cent. *Weight Blends in Penna 150 Neutral.*

Load (kg.).	Mean Wear Diameter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
4 (a). <i>Anglamol 40.</i>							
56	0.35	No seizure : smooth wear throughout	—	—	0.04	—	Smooth wear.
70	0.65	28.0	Rest of run.	0.05	0.03	0.05	" "
85	0.75	3.0	10.0	0.16	0.04	0.10	Irregular wear.
119	1.05	<0.5	3.5	0.14	0.04	0.09	" "
170	1.98	Instant.	8.2	> 0.25	—	0.10	" "
210	2.10	" "	10.0	> 0.25	—	0.10	" "
270	1.75	Instant seizure and recovery.	—	> 0.25	—	0.12	" "
4 (c). <i>Carbon Tetrachloride.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.03	—	Smooth wear.
70	0.45	24.0	Rest of run.	0.02	0.03	0.05	" "
85	0.61	6.6	8.0	0.09	0.03	0.08	" "
119	0.76	0.7	10.0	0.12	0.04	0.07	" "
170	2.00	Almost instant.	5.5	> 0.25	0.05	0.09	Irregular wear.
210	2.20	Instant.	6.6	> 0.25	—	0.09	" "
270	2.43	" "	8.2	> 0.25	—	0.09	" "
310	2.80	" "	9.2	> 0.25	—	0.09	" "
410	Welding.	" "	—	—	—	—	" "
4 (g). <i>Hexachlorethane.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.04	—	Smooth wear.
70	0.45	" "	" "	—	0.04	—	" "
85	0.68	" 5.0 "	" 9.5 "	0.13	0.04	0.09	" "
119	0.75	" 1.0 "	" 8.2 "	0.10	0.06	0.08	" "
170	1.65	Almost instant.	8.5	0.20	0.05	0.07	Irregular wear.
210	2.12	Instant.	8.5	> 0.25	—	0.09	" "
270	2.55	" "	10.0	> 0.25	—	0.09	" "
310	2.88	" "	13.0	> 0.25	—	0.09	" "
410	Welding.	" "	—	—	—	—	" "

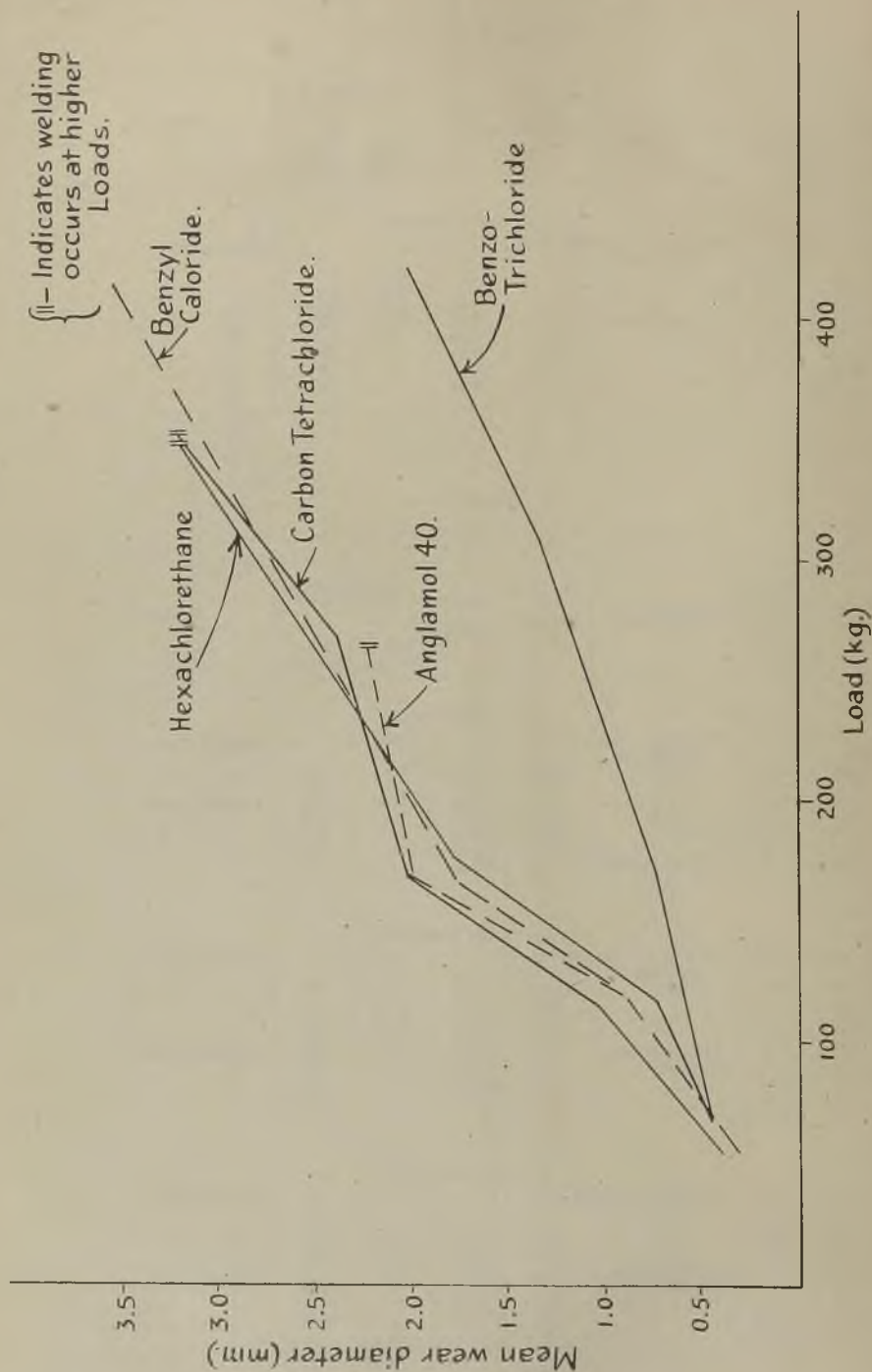


FIG. 4.
WEAR DIAGRAM—3% BLENDS IN PENNA 150 NEUTRAL.

SECTION 4—(continued).

Load (kg.).	Mean Wear Dia-meter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
<i>4 (h). Benzyl Chloride.</i>							
56	0-35	No seizure : smooth wear throughout.	—	—	0-03	—	Smooth wear.
70	0-45	" " "	—	—	0-03	—	" "
85	0-69	" " "	8-3	0-11	0-04	0-11	" "
119	0-90	<0-5	8-0	0-12	0-04	0-09	" "
170	1-88	Almost instant.	10-0	>0-25	0-05	0-09	Irregular wear.
210	2-05	Instant.	7-0	>0-25	—	0-09	" "
270	2-62	" "	8-5	>0-25	—	0-09	" "
310	2-72	" "	6-5	>0-25	—	0-10	" "
410	3-55	" "	5-0	>0-25	—	0-09	" "
<i>4 (i). Benzo-trichloride.</i>							
56	0-35	No seizure : smooth wear throughout.	—	—	0-05	—	Smooth wear.
70	0-45	" " "	—	—	0-05	—	" "
85	0-50	" " "	—	—	0-07	—	" "
119	0-60	" 0-7	5-0	0-06	0-05	0-09	" "
170	0-72	<0-5	7-5	0-06	0-06	0-09	" "
210	0-92	Instant.	7-5	0-09	—	0-09	" "
270	1-20	" "	7-0	0-10	—	0-08	" "
310	1-35	" "	6-5	0-09	—	0-07	" "
410	1-97	" "	6-0	0-10	—	0-07	Irregular wear.

SECTION 5.

1 per cent. Weight Blends in Penna 150 Neutral.

Load (kg.).	Mean Wear Dia-meter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
<i>5 (a). Anglamol 40.</i>							
56	0-35	No seizure : smooth wear throughout.	—	—	0-05	—	Smooth wear.
70	0-65	50	Rest of run.	0-12	0-04	0-17	" "
85	1-63	2-3	7-0	>0-25	0-07	0-14	Irregular wear.
119	1-80	<0-5	7-5	>0-25	0-07	0-11	" "
170	2-25	Instant.	7-2	>0-25	—	0-10	" "
210	2-50	" "	10-0	>0-25	—	0-11	" "
270	2-90	" "	7-0	>0-25	—	0-10	" "
310	(Slight welding.)	Instant welding.	—	—	—	—	" "
<i>5 (c). Carbon Tetrachloride.</i>							
56	0-35	No seizure : smooth wear throughout.	—	—	0-04	—	Smooth wear.
70	0-60	9-3	10-0	0-15	0-03	0-09	" "
85	1-55	2-0	7-0	0-22	0-05	0-10	Irregular wear.
119	1-77	<0-5	7-0	>0-25	0-07	0-09	" "
170	2-12	Instant.	7-2	>0-25	—	0-09	" "
210	2-46	" "	7-0	>0-25	—	0-09	" "
270	2-79	" "	5-0	>0-25	—	0-09	" "
310	3-01	" "	7-2	>0-25	—	0-09	" "
410	Instant welding.	Instant welding.	—	—	—	—	" "

{ — Indicates welding occurs at higher loads.

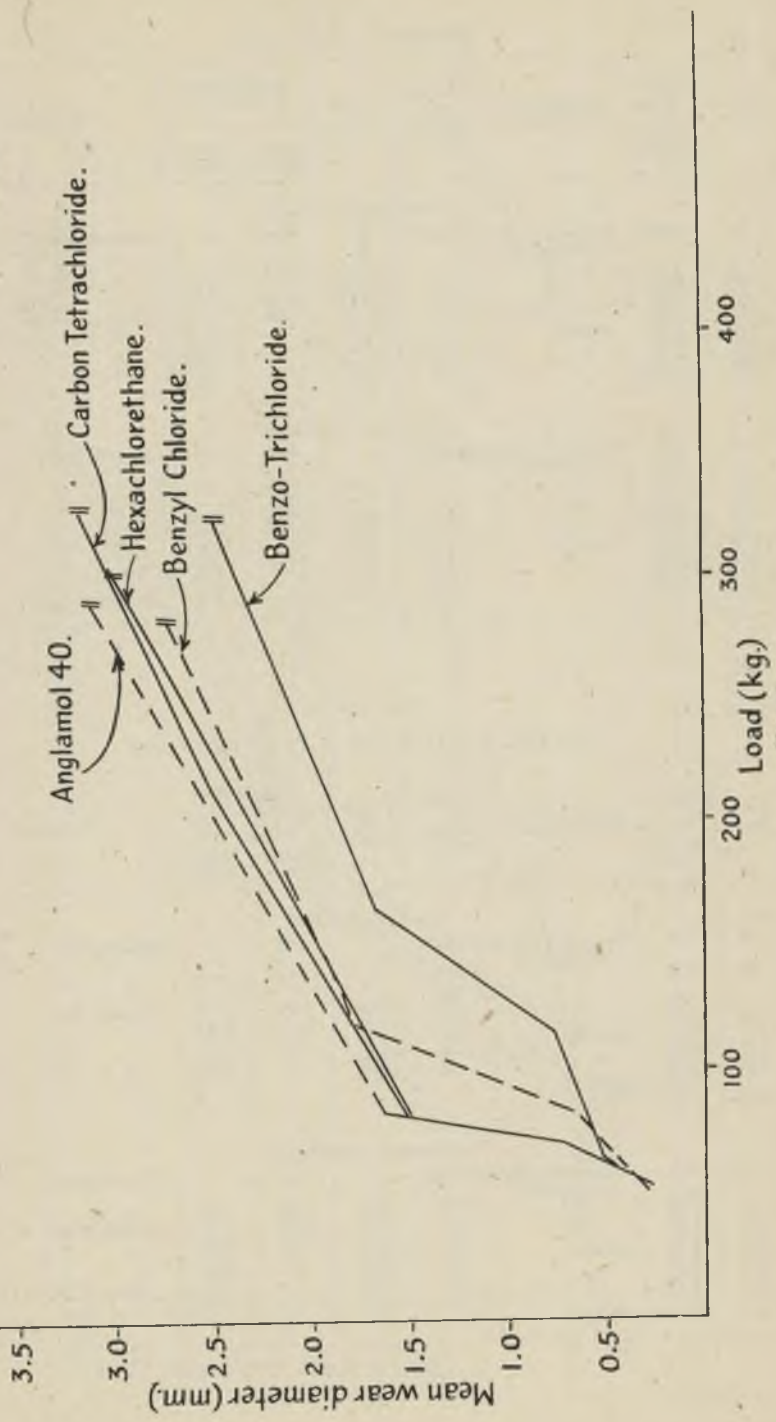
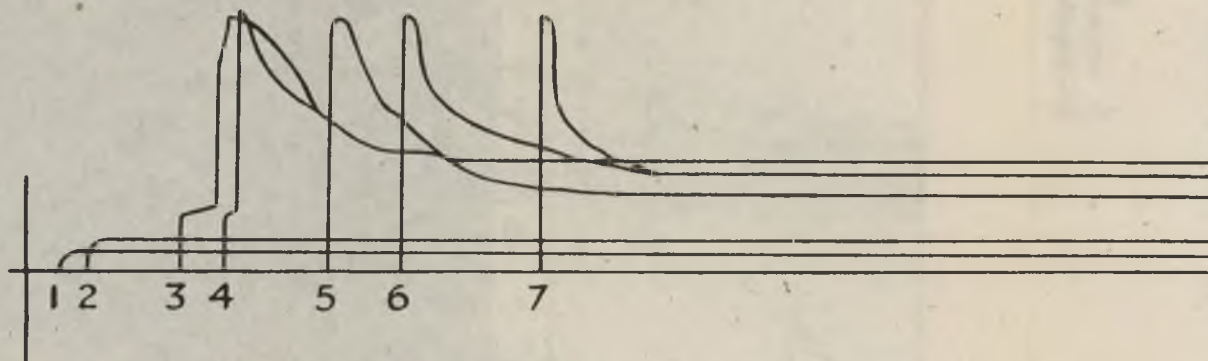


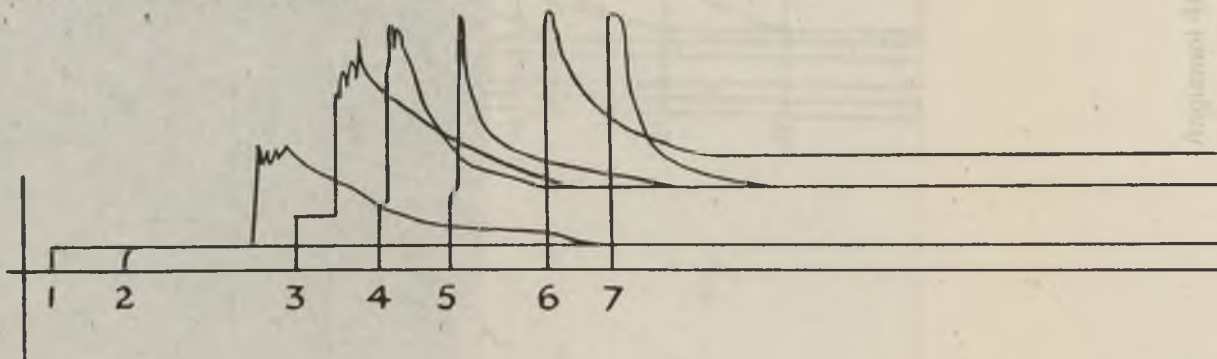
FIG. 5.
WEAR DIAGRAM—1% BLENDS IN PENNA 150 NEUTRAL.

SECTION 5. 1% BLENDS IN PENNA 150 NEUTRAL.

5(a) Anglamol 40.



5(g) Hexachlorethane.



[To face p. 87.]

SECTION 5—(continued).

Load (kg.).	Mean Wear Dia-meter (mm.).	Occurrence of Seizure (secs.).	Duration of Seizure (secs.).	Torque at Seizure.	Coefficient of Friction "f."		Remarks.
					Before Seizure.	After Seizure.	
<i>5 (g). Hexachlorethane.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.05	—	Smooth wear.
70	0.65	5.5	7.6	0.23	0.05	0.07	" "
85	1.48	3.5	10.5	0.21	0.05	0.09	Irregular wear.
119	1.75	0.7	4.3	0.20	0.07	0.08	" "
170	2.05	<0.5	3.5	> 0.25	0.07	0.10	" "
210	2.38	Instant.	8.0	> 0.25	—	0.11	" "
270	2.67	"	5.0	> 0.25	—	0.10	" "
	Slight welding.						
<i>5 (h). Benzyl Chloride.</i>							
56	0.35	No seizure : smooth wear throughout.	—	—	0.05	—	Smooth wear.
70	0.50	43.0	Rest of run.	0.07	0.05	0.12	" "
85	0.65	0.7	5.5	0.13	0.04	0.11	" "
119	1.78	<0.5	8.3	0.23	0.04	0.10	Irregular wear.
170	2.05	Almost instant.	6.0	> 0.25	0.04	0.10	" "
210	2.25	Instant.	5.5	> 0.25	—	0.10	" "
270	2.65	"	5.5	> 0.25	—	0.09	" "
310	Welding.						
<i>5 (i). Benzo-trichloride.</i>							
56	0.35	No seizure : smooth wear through.	—	—	0.05	—	Smooth wear.
70	0.55	8.2	5.8	0.09	0.05	0.09	" "
85	0.62	2.6	4.6	0.08	0.07	0.09	" "
119	0.78	0.5	4.0	0.09	0.08	0.09	" "
170	1.70	Instant.	4.6	0.17	—	0.09	Irregular wear.
210	1.85	"	10.5	0.18	—	0.09	" "
270	2.17	"	5.0	> 0.25	—	0.07	" "
310	2.42	"	4.3	> 0.25	—	0.09	" "
410	Instant welding.						

These results indicate the very marked superiority of benzo-trichloride in imparting E.P. properties. The other materials gave similar results, differing only in ability to carry high loads.

The Friction/Time curves were all similar, showing rapid seizure and recovery.

CONCLUSIONS.

The results may be summarized as follows :—

(1) The E.P. properties of chlorinated compounds are due to the liberation of atomic chlorine under extreme conditions.

(2) The liberated atomic chlorine forms an additive product with the metal surfaces yielding low wear ; the formation of ionic chlorine, e.g. from hydrogen chloride gives corrosion and high wear.

(3) A chlorinated compound will only possess good E.P. properties if its molecule

(a) contains chlorine atoms which become labile under the conditions of usage.

(b) is completely saturated with chlorine, i.e. there are no hydrogen atoms in the aliphatic chain which can give hydrogen chloride.

(4) A compound having chlorine attached to an aromatic nucleus will exhibit only slight E.P. properties.

Certain of the compounds tested have found some use in industry, but in general those compounds are too toxic to be of general application.

The author wishes to express his thanks to Messrs. "Shell" Refining & Marketing Co., Ltd., in whose laboratories the work was carried out, for permission to publish this work.

Bibliography.

¹ Boerlage, *Engineering*, 1933, **136**, 46.

² Clayton, "Lubrication and Lubricants," *Inst. Mech. Engrs*, 1937, **2**, 37 and 274.

IMPROVEMENTS IN LUBRICATING GREASES.*

By M. W. WEBBER.

THE manufacture of soap-thickened lubricating greases started round about 1860, and until about fifteen years ago development was rather more slow than steady. In fact for some time the technical qualities of the greases available were not fully equal to the demands made upon them and oils were used wherever possible. This position soon changed when the grease chemist began to exercise more control over the efforts of the rule-of-thumb grease-maker; although even now science has not by any manner of means eliminated the necessity for the art acquired from long experience.

The industry is now producing lubricants of uniform consistency, greater purity, wider temperature range, and greater load capacity. The point has almost been reached where further development will depend on the availability of new and improved ingredients and more efficient methods of test.

At the present time research and development proceed apace, but it must be remembered that while war conditions are a great incentive, at the same time shortages of materials and labour have a definite deterrent effect. This is particularly the case when so much technical ability is required for routine testing, for supervising unskilled labour, and for finding ways and means of using substitute and varying raw materials. The industry in Great Britain has also had to cope with interference caused by enemy action.

Until the outbreak of war, improvements in lubricating greases were to a considerable extent due to the initiative of the makers of ball and roller bearings. In particular this applied to practical tests, as the manufacturers could make use of the equipment designed and installed for testing the bearings themselves. In addition, we have the heat stability test developed by British Timken, Ltd., which has been modified and adopted by Government Departments and by such large users of greases as the London Passenger Transport Board. Great credit is also due to British Timken, Ltd., for their Wear and Lubricant Testing Machine, which is the only practicable apparatus for the determination of the load-carrying capacity and the wear and friction reducing properties of greases.

During the war period, considerable initiative has been shown by the Government departments, and their co-operation has been most helpful. Such co-operation is essential to deal efficiently with the many and complex problems involved in the production and use of greases. I would very much like to see it continued and extended by the formation of a British equivalent of the National Lubricating Grease Institute of America, preferably under the ægis of the Institute of Petroleum.

Let us consider in detail the development of improved and specialized greases.

* Paper read before the Northern Branch of the Institute of Petroleum on 25th April, 1944.

UNIFORMITY OF CONSISTENCY.

Uniformity of consistency has largely been achieved with the aid of the standard cone penetrometer, which has almost completely superseded the individual methods of test of manufacturers and users, and also reliance on the sense of touch. We do, however, need some equivalent of the classification of oils by viscosity, such as the S.A.E. and the British Standard systems. There is a useful basis in the classification adopted by the National Lubricating Grease Institute, which has been included in official specifications issued in the U.S.A. As in the case of oils, such classification would eliminate much confusion due to the marketing of different consistencies under the descriptions "soft," "medium," etc., and also the varying systems of numbering the different grades.

It would be necessary to make it quite clear that the classification was solely by an arbitrary measurement of penetration, and that only greases of similar type could be considered as interchangeable. The position will be vastly improved when we have available a standard method of determining the consistency of a grease in fundamental units which will be of real value in predicting service performance.

The cone penetrometer has been criticized as showing poor response to change in viscosity of the oil component and to differences in texture or structure. Also it requires a relatively large quantity of grease, and the apparatus is not suitable for use at temperatures which differ much from that of the surrounding atmosphere. In order to improve and control the temperature/consistency characteristics of special greases, use has been made of the cylindrical plunger type of penetrometer described in M.A.P. specifications D.T.D. 143C and D.T.D. 419 for low and high temperature greases. The apparatus is convenient for use over a very wide temperature range and the specifications mentioned require tests at from minus 50° C. to plus 100° C. This method of test has its drawbacks but it is capable of a higher degree of standardization.

Another cause of criticism is the fact that the range of usefulness of the standard cone penetrometer is by no means wide enough. Suggestions have been made for the use of a plastic cone with aluminium tip and plunger rod, giving a total moving weight of only 30 grams instead of the standard 150 grams, in order to facilitate the testing of very soft and semi-fluid greases. For the latter I prefer to use the Gardner or, preferably, the S.I.L. mobilometer. The S.I.L. mobilometer is fitted with a perforated cone instead of the perforated disc of the original Gardner instrument, and the S.I.L. consistency numbers, calculated by means of an arbitrary formula, are an approximate extension of the standard cone penetration figures. My reasons for preferring the mobilometer to the light-weight cone are that it is operated at a fairly constant rate of shear over a reasonable period of time, and that its scope extends to the testing of fluid greases having viscosities as light as 500 seconds Redwood No. 1 at 70° F.

Greater uniformity of consistency of greases has also been achieved in the manufacturing processes. Unless complication is caused by other stringent specification requirements, batches can readily be prepared of predicted penetration within very close limits. Also the consistency of the grease is

uniform throughout the containers, and it will not change appreciably during storage.

These results have been achieved by close control and careful selection of the ingredients, and by more complete laboratory supervision of the saponification and compounding. Difficulties are caused by the ever-present variations in the animal and vegetable fats supplied by nature, but it is hoped that during the next few years we shall have made available to us fatty acids of constant chemical composition. There is also the prospect of the production of synthetic saponifiable material of standard specification. As regards the mineral oil component, trouble is caused by variation in quality or type owing to war conditions, but in peace-time the grease-maker is able to select from the standard grades offered by the refiners and to compound his grease with paraffinic, naphthenic, or asphaltic oils, according to the requirements of the individual product.

Provided that the ingredients are of suitable quality, uniformity of consistency in the container and stability of consistency in storage are achieved by ensuring complete saponification during manufacture, and by strict control of the residual free acid and/or alkali. Excessive free acid usually results in soft centres in the containers and marked softening of the grease in storage and use. It is also imperative that the grease should receive sufficient agitation or working, and that it should not be drawn at too high a temperature. Saponification is readily completed in autoclaves in a short time, but equal results can be achieved in open kettles, provided that fatty acids are used. Manipulation of the grease is normally more easy in the open kettle, whether the soap is made as a concentrate or in the presence of the total oil content.

PURITY.

The greater degree of purity of the greases now produced is, in the first place, due to the elimination of fillers and excessive contents of water and free alkali. At one time the presence of such adulterants was far too common, largely due to the competition of greases imported from the Continent, which owed their cheapness to large proportions of such deleterious ingredients. Indeed, up to the outbreak of war it was quite common to meet such adulterated greases in France, Holland, and Belgium, and they were frequently marketed with the open declaration of "so much per cent. loading." However, it can safely be said that no lubricating grease marketed in this country for some years past has contained such fillers, unless it is of the cheap types specifically supplied for use in collieries, quarries, etc., or for wooden axles, where more is wasted or used for a protective coating than as a lubricant.

The need for the complete elimination of foreign matter has been emphasized by the demands of ball and roller bearings, of plain bearings with fine clearances, and of lubricating equipment which is easily choked. Great care is taken with the screening of greases through wire gauze on drawing from the kettle, but greater care is needed during the handling and application of greases. Also there is much scope for improvement in the containers and their closures, many of which do not completely prevent contamination of the contents.

STABILITY.

Improvements in the stability of greases require to be considered from several different aspects. There is stability of consistency, resistance to syneresis, resistance to oxidation, stability at high pressures, and stability to heat.

I have already referred to stability of consistency in storage, and provided that this is satisfactory, stability of consistency in service is concerned with resistance to mechanical breakdown. This may be anything from a slight softening of the grease to complete breakdown to an oily condition, with, perhaps, separation of the constituents. With lime soap greases any such trouble is usually due to incompatibility or faulty compounding of soap and oil, or to excessive free fatty acid content. The same factors also influence the stability of soda greases, while these are affected to a greater extent than lime greases by excessive contents of water and free alkali. Improved resistance to mechanical breakdown has been achieved by careful selection of soap stock and oil, by thorough working during manufacture, and by laboratory control of acidity, alkalinity, and water content. I have found it best not to endeavour to use too saturated a soap stock. The iodine value is a useful guide, and it should be maintained at about 40-60 for lime soap greases or about 55-75 for soda greases. As regards the mineral oil component, the best results are nearly always obtained with naphthenic base products.

The standard method of working the grease for sixty double strokes of the churn-dasher apparatus does not give sufficient information for many purposes of the resistance to breakdown of consistency of a grease. In the U.S.A., use is made of motorized workers, enabling the extension of the test to, say, 5000 strokes. It is of value to take the penetration of the grease at appropriate intervals and to plot it against the number of strokes of the worker. This method of test is being largely superseded by the development of breakdown tests based on the beating of the grease in ball and roller bearings. This is done at normal and high temperatures, and the stability of the grease is usually determined by torque tests made with a bearing filled with the grease before and after beating.

SYNERESIS.

Improvements in the resistance of greases to syneresis, or bleeding of oil, have been achieved by attention to the same factors as those mentioned in connection with stability of consistency. Particular attention must be paid to the selection of soap stock and oil, and to the mixing or compounding of the grease. Control of the rate of cooling of the finished grease is of importance, and in most cases it is found that syneresis is reduced by rapid cooling. The tendency to bleeding of oil increases with diminishing soap content, with reduction of the viscosity of the oil component, and with increase in storage temperature. Should trouble be experienced with the difficult conditions of small soap content and low oil viscosity, improvements can frequently be effected by the addition of polymers and/or polar materials. The use of stearines produced by pressing distilled wool grease

in the proportion of 30-50 per cent. of the soap stock will nearly always give greater resistance to bleeding.

Many specifications include accelerated tests to determine any tendency of the grease to bleeding of oil. The usual procedure is to weigh 10 grams of the grease into a cone made from 60-mesh wire gauze. The material should be carefully packed into the apex and finished with a convex surface, so that no separated oil may be trapped. The cone is suspended in a weighed beaker and placed in a constant temperature oven at 60° C. for from 8 hours to one week or more. With most greases 48 hours is a reasonable time for the test to give useful results. After heating, the cone and beaker are removed from the oven and the beaker is re-weighed. The weight of oil collected in the beaker gives a fairly accurate quantitative measure of the liability of the grease to syneresis. For purposes of research and development it is useful to prolong the test for two or three weeks and to determine daily the percentage loss of oil from the grease. The loss should be plotted against the total time of heating, and the curve obtained will amply demonstrate the stability or instability of the grease.

STABILITY TO PRESSURE.

Another form of syneresis is the separation of oil which tends to take place when soap-base greases are subjected to high pressures in greasing equipment. It must, however, be regarded as a distinct problem, as tests such as those described above do not give correlative information. Methods of test for stability at high pressure consist of applying pressure to the grease by means of a gun, or perhaps a spring or screw-down cup, and filtering off the separated oil through a porous thimble. Leather is also used as the filter medium, as it is to be found in some types of pressure lubricating equipment. The trouble with all filters is that they become choked with heavy grease or soap.

Improved resistance to separation at high pressures is achieved by attention to the factors mentioned in connection with syneresis. It is useful to maintain the viscosity of the oil component as high as possible and, in fact, the first "pressure gun greases" were ordinary cup greases made with oil of Pool No. 8 type instead of Pool No. 3.

RESISTANCE TO OXIDATION.

Improved resistance to oxidation in storage and service has been obtained by careful selection of ingredients and, more recently, by the use of anti-oxidants. The inhibitors employed comprise both those used for mineral lubricating oils and also those developed to prevent rancidification of fats and soaps. Most of them are amines or phenolic compounds—for example, diphenylamine and phenyl- β -naphthylamine.

The simplest method of test is to expose a thin film of the grease to the atmosphere and to examine it for any change in consistency or development of acidity. For purposes of research and standardization the conditions of temperature, humidity, and light should be controlled. It is desirable to expose the grease in contact with bearing metals, and tests are also carried out with ball-bearings packed with the lubricant.

Such tests with simple exposure to the atmosphere may require to be continued for weeks, unless the temperature is raised to the point where the results are affected by other factors, such as evaporation of oil and water, and even separation of the constituents. Accordingly, accelerated tests have been developed which involve exposure of the grease in an enclosed vessel to an atmosphere of oxygen, usually, even then, at fairly high temperatures and pressures. This type of test was developed by the Norma-Hoffman Bearings Corporation, and their apparatus and method have been included in official specifications. The apparatus consists of a stainless-steel bomb fitted with a suitable valve, for emptying and filling with oxygen, and a pressure-gauge. The grease sample is filled into five shallow trays, which are placed in the bomb on the racks of a special holder. The usual conditions of test are that the fall in pressure shall not be more than 5 lb. per sq. inch after 100 hours, commencing with the oxygen in the bomb at 110 lb. per square inch. The temperature is maintained at 210° F. for sodium and lithium greases and at 150° F. for calcium and aluminium greases.

This bomb method is not very convenient to use for routine testing, and great care and experience are needed to obtain reproducible results. It appears that saponification does not greatly affect the oxidation stability, and simpler tests may be devised for examination of the mixture of oil and soap stock in the liquid condition. A simple form of apparatus and method of test is described in *Industrial and Engineering Chemistry (Industrial Edition 1941)*, 33 (3), 339. The sample is placed in a modified Sligh flask, which is fitted by means of a ground-glass joint with an open-type mercury manometer. The flask is filled with oxygen at atmospheric pressure before attaching the manometer, which is fastened with springs to avoid leakage. The flask is immersed in an oil bath at 175° C., and the pressure is recorded at 5-minute intervals. It rises at first, owing to the thermometric effect, and after a time it begins to drop as oxygen is absorbed. The drop in pressure from the maximum is calculated at each time interval and recorded as a measure of the oxygen consumed. It remains to be seen whether the results thus obtained will show reasonable correlation with tests of the finished grease in the Norma-Hoffman apparatus.

STABILITY TO HEAT.

Stability to heat is frequently of more importance than is the drop point in determining the maximum safe working temperature of any grease, whatever its base. It is no good to say that a grease with a drop point of 150° C. is suitable for use at 100° C. if it separates at that temperature. Sometimes any tendency to separation may be observed when determining the drop point, but in many cases the period of heating is not long enough to give a true indication of the stability of the grease at high temperatures. Surprising differences in the consumption of two greases of apparently the same consistency and drop point can often be explained by heating samples for several hours either at the specific temperature of the particular application, or, if that is not definite or known, then, say, at 20° C. below their drop points. The good grease will only soften, but the faulty product will collapse, and flow usually with separation of oil.

Improved stability at high temperatures is obtained by careful selection of soap stock and oil, and by strict laboratory control of free acidity and alkalinity. Naphthenic oils usually give the best results, and if paraffinic oils are used, the addition of some polar material is helpful. The wool-grease stearines previously mentioned are of great value in obtaining heat-stable lime soap greases with the minimum of free acidity. The addition of small amounts of aluminium soap improves the stability to heat with most types of greases, whether of calcium, sodium, or lithium base. With greases of all types free alkali will cause trouble if the grease should be heated to its melting point or to any higher temperature.

The method of test for stability to heat as embodied in most British specifications is a modification of the original test developed by Messrs. British Timken, Ltd. It has been fairly well standardized at the heating of 10 grams of grease for 1 hour at 120° C. This is somewhat drastic for calcium soap greases, but the test does in many cases give useful indications of the stability of the grease when exposed to lower temperatures for long periods. It has been found that it is definitely desirable that greases for ball and roller bearings should pass the test, as, in addition to its value as an accelerated test for normal working temperatures, it does give some assurance of safety should the grease become locally overheated. Heating at 120° C. does give useful information concerning high-temperature sodium greases, but it is desirable to repeat the test at, say, 20° C. below the drop point of the particular sample, or at any specific temperature to which the grease may be exposed in service.

WIDE TEMPERATURE RANGE.

Wide temperature range is one of the most useful characteristics of soap-base greases. The global nature of this war has given added impetus to the development of greases with the widest possible temperature range. The lubricant in grease-lubricated bearings cannot readily be changed, and it is not possible always to anticipate the destination of equipment which has to be packed with grease at the time of assembly. The development of high-flying aircraft, especially in the tropics, has created a very special need for grease of wide temperature range. Another point is that extension of the temperature range minimizes the number of greases which must be carried in service conditions. However, the work done in this direction is not solely for war-time conditions, as aviation will continue in peace, and in many countries extreme temperature variations may be experienced in very short periods of time. For example, the President of Canadian National Railways has stated that, in the middle of winter, along the 3000-mile stretch from coast to coast, the temperature may range from 50° F. or more above zero to 30 or 40° F. below zero.

The great improvements which have been effected in the temperature range of greases of all types are principally due to the use of oils of lower viscosity and pour point and higher viscosity index. As regards pour point, it is noteworthy that oils containing pour-point depressants are of little value in low-temperature greases. Although the characteristics of the oil content have by far the greatest influence on the temperature range of a grease, improvements can also be effected by careful selection of the soap

stock. As regards the soap base, calcium has so far given the best low-temperature greases, but their value is strictly limited at the upper end of the scale, and sodium, or, if water resistance is important, mixed sodium and calcium or aluminium soaps, gives the best wide-temperature range products. It is probable that sodium will be displaced by lithium, which gives greases of good low-temperature performance and exceptionally high drop point. Lithium greases retain their consistency remarkably well over a very wide range of temperature, and they are water resistant.

EXTREME PRESSURE GREASES.

Parallel with the development of extreme pressure oils much work has been done on the production of greases with greater load-carrying capacity. The most important demand for extreme pressure greases is for anti-friction bearings in rolling mills, and they are also usefully employed for the lubrication of steering-gears, wheel-bearings, and, in fact, all bearings subjected to heavy and/or shock loading. Extreme pressure greases are employed with success to facilitate drawing and pressing operations. The additives employed in greases include sulphurized fatty and petroleum oils, chlorinated waxes, esters and soaps of chlorinated fatty acids, lead soaps, and even such materials as lead oxide, metallic lead, and elemental sulphur. In general, the combinations are similar to those used in oils. Thus lead soap and sulphurized fatty oil are usually employed together, and this combination gives high load capacity and shock resistance, but friction and wear are liable to be high. Chlorine compounds are frequently less effective in greases than in oils, and the best results are obtained when sulphur compounds are also present.

Most of the development work, as well as routine testing has been carried out with the aid of the Timken Wear and Lubricant Testing Machine. This machine, when fitted with the large screw-down lubricator, is the only practicable apparatus for the testing of greases as distinct from oils. It could further be improved by the fitting of a small mechanical grease lubricator. One great advantage of this machine is that the test-blocks and rings can readily be obtained, and are of consistent quality. In addition to the load capacity, the Timken machine also provides useful information concerning friction and wear. If the machine is used to test greases not having definite extreme pressure properties, it is helpful to reduce the speed of the test ring from 800 to 400 r.p.m., as this will give information of greater value for purposes of comparison.

BALL AND ROLLER BEARING GREASES.

Probably the largest "special" use of grease is for the lubrication of ball and roller bearings. Consideration of the requirements involved are a good example of why this paper changed from a discussion of individual special greases to a more general *résumé* of improvements in lubricating greases of all types and of some of the developments which we may expect in the future.

Thought will show that in many instances of so-called "special greases" we are still dealing with the requirements of the anti-friction bearing. This

applies to high- and low-temperature greases, to extreme-pressure greases, to high-speed greases, and to such individual products as wheel-bearing greases and electric motor and dynamo greases. If we list the requirements of greases for anti-friction bearings, we find that we are specifying grease of high quality for nearly all purposes. The following are the more important properties required, and it will be observed that most of them have already been discussed.

1. Uniformity and stability of consistency and structure.
2. Resistance to oxidation.
3. Resistance to syneresis.
4. Purity.
5. Wide temperature range.

It will be noted that structure is linked with consistency, and this is definitely a most important point, especially for high-speed bearings. Present methods of determination of consistency by penetration are misleading, as they do not differentiate between greases of varying structure. This is most unfortunate, as the bearing certainly does so differentiate. This point will be appreciated by those who do the actual testing of greases by means of the standard cone penetrometer and worker. The operator cannot fail to be struck by the vastly greater effort needed to operate the worker when testing a fibrous sodium soap-grease as compared with a calcium soap-grease of the same penetration. The importance of this is obvious when it is considered that the worker is a crude form of pressure viscometer or rather mobilometer.

It is regrettable that so many specifications give the impression that greases of different bases and types, but having the same penetration, are interchangeable. The development of methods of test based on torque determinations using standard ball-bearings packed with the grease should greatly improve the position. The beating of the grease in ball and roller bearings, both at low and high temperatures, is also the only satisfactory method of determining stability of structure as well as consistency. This is usually referred to as mechanical stability or resistance to mechanical breakdown.

We have already discussed requirement number 2, resistance to oxidation. This is of particular importance in the case of ball and roller bearings, as oxidation products are practically always corrosive, and one of the main functions of the grease is to give protection. The necessity for stability is emphasized by the fact that the grease in anti-friction bearings is seldom renewed except at long intervals, and in some cases the initial charge of lubricant is destined or desired to last the life of the bearing. In addition to oxidation stability, these points illustrate the vital necessity of stability of consistency and structure and of wide temperature range.

Resistance to syneresis is of great importance when grease packed bearings are kept in storage, as well as during storage of the grease in the usual containers. It has been stated that slight separation of oil in service is helpful, but it is not possible to control this within the necessary limits.

Purity includes freedom from excessive free alkalinity and acidity and from excessive water content, as well as from foreign matter.

Wide temperature range is necessary to give low-starting torque as well as

satisfactory service at running temperatures. Also, as noted previously, the grease in an anti-friction bearing cannot readily be changed in order to cope with differences in atmospheric temperature.

For the development of satisfactory lubricants for ball and roller bearings, grease-makers need advice from the makers of the bearings, and British Timken, Ltd., have led the way in issuing definite specifications. It is interesting to note that these show a preference for lime-soap greases.

The necessity for closer collaboration between the makers of the bearings, as well as between them and grease manufacturers, is obvious from the contradictory views which they express. This was well illustrated at the "General Discussion on Lubrication and Lubricants" held under the auspices of the Institution of Mechanical Engineers during October, 1937.

For example, Kjerrman (S.K.F., Sweden) emphatically disagreed with the statement made by Cooper (Hoffmann Manufacturing Co., Ltd.) that a good ball-bearing grease should not channel. While Cooper stated that breakdown on working is not desirable, Kjerrman asserted that such breakdown in the bearing is even advantageous. According to Kjerrman, lime-soap greases do not give the best results when water is present, whereas Richardson (Ransome and Marles Bearing Co., Ltd.) in spite of a general preference for soda greases, advocates the use of lime soap in condition of extreme moisture.

The general question of the favouring of lime-soap or soda-soap greases for ball and roller-bearing lubrication frequently comes up for discussion. The British preference is for lime-soap and the American for soda-soap greases. In spite of the fact that the use of lime-base lubricants is strictly limited to those applications where the regular running temperature is below 160° F., it is probable that over 90 per cent. of the ball and roller-bearing grease used in this country is of this type. It is noteworthy that most of this lime-base grease conforms with the specification of Messrs. British Timken, Ltd., including the severe heat test, and I believe that grease of this quality is not regularly available in the U.S.A.

The manufacture of such heat-stable lime-soap greases calls for the use of wool-grease stearine if high free acidity is to be avoided, and it is probably lack of this material which has prevented their intensive development by American grease-makers. On the other hand, the American manufacturer has given more attention to the production of superior soda-base greases having the smooth texture and short fibre which are necessary for efficient service in antifriction bearings.

GREASES CONTAINING SOLID ADDITIVES.

An interesting class of "special" greases are those containing solid additives. The expression solid additive is used to distinguish those fillers which serve some useful purpose from materials which are only added to secure bulk and cheapness.

ASBESTOS can be obtained very finely divided, but still retaining its peculiar fibrous structure. It is limited in use, owing to its abrasive nature. Asbestos is sometimes added to high-melting-point soda greases in order to assist their retention in the bearing housing at exceptionally high temperatures. Lime-soap greases are only compounded with asbestos when the

product is required to act as a seal rather than as a lubricant. It gives mechanical strength and improves adhesion. In America tractor roller "greases" are made from asbestos and cylinder stock, with, sometimes, a little soap. Such a mixture should help prevent the entry of mud and grit but it is almost certain to cause increased wear.

WOOL YARN is mixed with greases used for the packing of shafting boxes in mills. Normally about 10 per cent. yarn is mixed with 90 per cent. high-melting point soda or mixed soda-lime grease. The grease is slowly fed by the yarn, rather like an oil syphon, and a properly packed journal box will run without attention for more than six months. Horsehair is sometimes added to make an "elastic" yarn grease which will not pack down or clog in the box.

MICA, TALC, and SOAPSTONE are used in greases, but they have little value as lubricants, except perhaps for heavy loads and slow speeds, and they are mildly abrasive.

ZINC OXIDE has frequently been suggested and used as an ingredient of lubricating greases. Owing to the fact that it is electropositive to iron and steel, zinc oxide gives excellent protection from electrolytic corrosion. Accordingly greases compounded with zinc oxide are used for parts subject to varying stresses, *e.g.*, gear wheels, friction gears, and roller bearings. It is stated that a very thin film of zinc is produced on steel parts, thus preventing wear as well as corrosion. Such greases are covered by the "Keenol" patents. Zinc oxide is also used in greases as a pigment, to improve water resistance, to improve lubrication, and to give protection from atmospheric corrosion.

METALLIC LEAD in finely powdered form is added to greases to increase their specific gravity, to give added protection from rusting and corrosion, and also to secure mild, extreme-pressure properties. Lead oxides are also used for similar purposes. Lead-containing greases are used as gear greases, wire-rope lubricants, plug-valve lubricants, rolling-mill greases, gland packing grease, and in general for all applications where non-floating and water-resisting properties are required.

GRAPHITE is the most important and most widely used solid additive. It is essential that the grease-maker should use care in selection, as many of the graphites offered by merchants as suitable for addition to greases are quite unsatisfactory. Samples have been submitted with as little as 40 per cent. carbon content, and with much abrasive matter present. Graphite for grease compounding should have an ash content of less than 15 per cent. and it should pass a 150-mesh sieve. These are minimum requirements, and I have always endeavoured to use graphite with a minimum 99 per cent. carbon content and with at least 95 per cent. passing a 200-mesh sieve and leaving no residue at all on a 150-mesh sieve. The addition of graphite to greases improves their ability to carry heavy and shock loads, their friction and wear-reducing properties, their water resistance, and their suitability for use at high temperatures. Suitable greases containing graphite are used for the lubrication of machinery, automotive chassis bearings, axles, gears, plug valves, and, in particular, for leaf-springs and brake cables. Graphited greases are also used as anti-seizing compounds, and to assist the drawing and pressing of metals.

Although the use of graphite powder in greases does not present any

suspension problem, the use of colloidal graphite does provide advantages, owing to its high degree of purity and its very fine state of subdivision. According to Klemgard (1937), greases containing colloidal graphite have been found useful for railway bearings, high-speed fans, dictating machines, worm-gears, pitman bearings on jaw crushers, ropes, chains, and gears. He goes on to say that "while graphite in general is not applicable to anti-friction bearings, there is some evidence to show that in three- or four-point contact ball and roller bearings, which develop end thrust, extreme pressure conditions may exist and the utilization of colloidal graphite may be found advantageous." It has also been my experience that colloidal graphited greases are frequently beneficial when used for ball and roller bearings carrying heavy loads or running at higher than normal temperatures. The use of even colloidal graphite has been condemned by the makers of anti-friction bearings on the grounds that the introduction of solid particles even as small as those of colloidal graphite would cause the formation of dents and consequent scaling. However, it is the case that the particles of graphite, apart from being comparatively soft and lubricative, are far smaller than the particles of foreign matter generally present in all greases. Thus M.A.P. specification D.T.D. 577 and U.S. specification AN-G-3a give the limits for foreign particles as up to 7500 per cubic cm. of 0.001-inch diameter and above, and up to 1600 per cubic cm. of 0.003-0.005-inch diameter. This applies to grease which is most carefully prepared and packed. The particle size of Acheson's colloidal graphite is of the order of 0.001 mm. (0.00025 inch) and less.

Colloidal graphited greases should not, however, be regarded as extreme-pressure lubricants.

DEVELOPMENT PROBLEMS OF THE FUTURE.

To conclude this talk, I think it would be interesting to discuss the problems which Klemgard listed under this heading in his book "Lubricating Greases", published by the Reinhold Publishing Corporation in 1937, and to see what progress has been made.

"Investigations of various ingredients for producing a higher degree of oiliness. A study of such materials in the presence of various soaps is greatly needed.

"Various agents for increasing film strength and imparting extreme pressure properties of soap base lubricating grease require further study. The effects of materials for reducing friction under high pressure conditions should be considered simultaneously."

On these points the development of greases has followed that of oils. Satisfactory extreme-pressure greases are being produced to meet present demands using the additives mentioned earlier in this talk. Little has been published on the subject, but it does appear that additives are more affected by acid, alkali, or water in the grease than by the nature of the soap.

"The improvement of lubricating greases from the standpoint of increased melting points and decreased yield values or internal friction."

These two properties hardly go together. Little has been done as regards increasing the melting points of lime and soda greases, but it appears that

the introduction of lithium is going to permit the production of a new range of high-melting-point greases. I disagree with Klemgard when he suggests that decrease of yield values would be an improvement. It is the possession of a yield value which from the rheological point of view distinguishes grease from oil. It is the property which governs the ability of the grease to "stay put."

"Improvement of lubricating greases with respect to service characteristics at sub-zero temperatures and simultaneous improvement of non-leaking ability."

As he has classed these two properties together, presumably Klemgard is thinking of the liability of low-temperature greases to leak at normal temperatures, rather than the general problem of grease retention in bearings which I would classify with the next problem on his list. It is definite that during the last seven years great improvements have been made in low-temperature greases. These improvements have been achieved largely by the development of formulae and technique to enable the use of light viscosity, low cold-test oils of high viscosity index. The grease-maker is indebted to the oil refiner for the production of such oils with suitable grease-making properties. Still further improvements can be secured by the reduction of the volatility and increase of the flash point of these light oils. As an example of what has been achieved, lime-soap greases are in production which do not harden unduly at minus 60° C., are stable on exposure for long periods at 60° C., and have drop points above 80° C. Soda-soap and mixed soda-lime greases are being manufactured which have a service temperature range of from minus 40° C. to plus 100° C., and drop points around 150° C. Still further improvements are in process of achievement with the aid of lithium soaps, which furnish low-temperature greases of high drop point and have the additional advantages of non-fibrous structure and complete water resistance. All these greases can be relied upon not to leak from bearings at normal temperatures. If by non-leaking ability Klemgard would imply resistance to syneresis, this has been achieved even with the very light oils used in the ultra-low temperature greases. This is, however, a point which requires constant supervision, and there is still room for improvement.

"The development of soap base greases of greater mechanical stability. Some greases appear to be broken down by the disruptive forces existing in various bearings."

Reference has been made to this point during the discussion of stability of consistency and of structure.

"Development of greases having soap bases which are stable and do not separate from the oil phase when subjected to temperatures sufficient to evaporate nearly all of the water content."

This suggestion is not quite clear, as in 1937 there was a large production, at least in this country, of lime-soap greases which passed the Timken heat test and which did not separate when almost completely dehydrated at 120° C. Also there were, and are, in production sodium and aluminium greases of complete stability when dehydrated as completely as possible by heating. This stability is also possessed by the new lithium base greases.

"The development of new types of non-soap base greases, such as those made with various organic polymers and cellulose derivatives."

There have been no important developments on the lines indicated, but there are distinct possibilities of the production of soap-free lubricating greases using some of the materials developed in the plastics industry.

"The discovery of greases made with new bases which will impart high melting points (above 275° F.) and which are not readily emulsified by or soluble in water. Soda soap greases may be satisfactory from the standpoint of melting point, but are not sufficiently water resistant. The greases made with 10 per cent. of the stearates of calcium, cobalt, lead, magnesium, nickel and strontium all have melting points of less than 215° F. : whereas 10 per cent. of mercury stearate will produce a grease having a melting point of only 225° F. It is, therefore, obvious that the search for superior grease bases, whether they are soaps or other compounds, must be continued."

The requirements specified are met by the new lithium soap greases. The use of barium soaps has also possibilities. It is probable that considerable improvements may also be effected by the development of synthetic saponifiable materials.

METHODS OF TEST REQUIRED.

As I mentioned earlier in this talk, I think that the greatest need of the industry for the further scientific development of lubricating greases, whatsoever their composition, is some practicable method of determining their rheological properties in fundamental units. This is a very difficult problem, as in addition to their enormous range of consistency and wide variation of structure, the apparent viscosity of greases varies greatly with change of rate of shear. It would appear that a suitable apparatus would be the constant shear pressure capillary viscometer, but although Arveson's pioneer work on this subject was published as far back as 1932, this type of apparatus is still only to be regarded as a tool for research. Rotation viscometers have been suggested, but they are only suitable for very soft greases. It may be that the industry can develop an improved penetrometer which will give more definite and useful information than the standard cone penetrometer. Whatever method of test may be developed for the more accurate determination of consistency, it is essential that it should be suitable for use over the widest possible range of temperature. It is possible that consistency determinations at high temperatures combined with suitable heat stability tests may enable the elimination of the old stumbling-block of the melting or drop point.

We are also in urgent need of some means of determining and specifying the structure of greases in order to give some definition to such terms as "smooth," "non-fibrous," and "short, medium, and long fibre." It is possible that this can be done by microscopic examination. Tests for the determination and distinction of the properties of adhesion and cohesion would be of great value.



THOMAS MIDGLEY.

1889-1944.

[To face p. 103.

OBITUARY.

DR. THOMAS MIDGLEY.

THOMAS MIDGLEY, Jr., who discovered the anti-knock properties of tetraethyl lead, died suddenly at his home in Worthington, Ohio, on 2nd November, 1944, at the age of 55.

Although Dr. Midgley had been an invalid for the past four years as a result of an attack of infantile paralysis, he was active up to the last as an officer of the Ethyl Corporation and Kinetic Chemicals, Inc., and as president of the American Chemical Society. Less than two months before his untimely death he presided at the meeting of the American Chemical Society in New York City. He had also taken a prominent part in the negotiations which led to the Trust agreement by which the American Chemical Society was the beneficiary of income from the Universal Oil Products Co., to be applied to the support of advanced scientific education and fundamental research in the petroleum field.

The scientific discoveries of Thomas Midgley gave important and vitalizing impetus to the oil, automotive, rubber, and refrigerating and air-conditioning industries.

His discovery of tetraethyl lead as an anti-knock agent was made after he and his colleagues in the General Motors Research Laboratories had tried thousands of other chemical compounds without success. With Dr. Albert L. Henne of Ohio State University, he developed organic chloro-fluorides, which have been widely used as non-inflammable, non-toxic refrigerants. In both these developments he used his special knowledge of the periodic classification of the elements.

Dr. Midgley also contributed largely to the knowledge of the chemistry of rubber and the methods of synthesizing rubber. He was associated with the developments connected with the recovery of bromine from sea water.

Dr. Midgley won many honours and medals from scientific societies and educational institutions. He held the Priestley Medal of the American Chemical Society, the Willard Gibbs Medal of the Society's Chicago Section, the William H. Nichols Medal of the Society's New York Section, the Perkin Medal of the Society of Chemical Industry, and the Longstreth Medal. Last June, Ohio State University conferred upon him the honorary degree of Doctor of Science. At the time of his death he was both president and chairman of the board of the American Chemical Society, vice-president of the Ohio State University Research Foundation, vice-president of Ethyl Corporation, vice-president of Kinetic Chemicals, Inc., and a director of the Ethyl-Dow Chemical Company.

Dr. Midgley was born on 18th May, 1889, at Beaver Falls, Pennsylvania. His father, Thomas Midgley, an inventor and manufacturing executive, came to the United States from London at the age of six. Dr. Midgley was educated in the public schools of Ohio and at Betts Academy, Stamford, Connecticut. He received the degree of mechanical engineer from Cornell University in 1911.

After his graduation he entered the employ of the National Cash Register Company, Dayton, Ohio. Later he was associated with his father in the

Midgley Tire and Rubber Company of Lancaster, Ohio. In 1916 he returned to Dayton and began work under Charles F. Kettering.

When Dr. Kettering moved to General Motors he took Dr. Midgley with him—and also the researches into anti-knock compounds in which he and T. A. Boyd were engaged at the time. From the discovery of tetraethyl lead as an anti-knock agent came the formation of the Ethyl Corporation in 1924, with Dr. Midgley serving as its first vice-president. His Freon refrigerants gave rise to Kinetic Chemicals, Inc. He held several important patents, and he contributed many technical papers to magazines.

Dr. Midgley was married in 1911 to Carrie M. Reynolds, of Delaware, Ohio, who survives with two children, Mrs. Jane M. Lewis of Washington, D.C. and Thomas Midgley III, of Hartford, Connecticut.