

ENCLOSURE (B) 2

STUDIES ON SYNTHESIS  
OF AERO-ENGINE OIL  
BY CONDENSATION METHOD

by

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## ENCLOSURE (B)2

LIST OF TABLES  
AND ILLUSTRATIONS

Table I(B)2	Viscosity Ratios .....	Page 57
Table II(B)2	Condensation Products .....	Page 57
Table III(B)2	Hydrogenation Products .....	Page 58
Table IV(B)2	Lubricating Oil Synthesized from Diphenylmethane Series Hydrocarbons and Cetylchloride .....	Page 58
Table V(B)2	Lubricating Oil Synthesized from Diphenylmethane Series Hydrocarbons and Cetene .....	Page 59

## ENCLOSURE (B)2

SUMMARY

Dibenzyl-diphenylmethane was prepared by the condensation of benzene and benzyl alcohol in the presence of aluminum chloride at 60-80°C for five hours. The hydrogenated product had a viscosity index of 139, viscosity of 118 S.U.S. at 210°F, and a Conradson's carbon residue of 0.002%.

Diphenylmethane series hydrocarbons, prepared by the condensation of benzyl alcohol and benzene in the presence of  $AlCl_3$ , were condensed with octene and then hydrogenated. The product thus obtained had a viscosity index of more than 100, Conradson's carbon of 0.1%, and freezing point below -20°C, but the oxidation stability as indicated by the viscosity ratio of 2.2 in the British Air Ministry Oxidation Test was not good. This defect was easily remedied by adding 0.1% of copper-oleate, which reduced the viscosity ratio from 2.2 to 1.4.

An aeroengine oil of similar nature was also obtained by reduction of the condensation products of olefines with diphenyl-methane series hydrocarbons which were formed by the interaction of benzene and formalin in the presence of concentrated sulphuric acid.

I. INTRODUCTION

Although extensive chemical studies on lubricating oils derived from the petroleum oils have been carried out, practically nothing is known concerning the relation between chemical structure and the viscosity and other properties of cyclic compounds. The authors, therefore, from 1927 to 1942, have undertaken the present study relative to the relation of chemical structures of cyclic compounds to lubricating properties.

II. DETAILED DESCRIPTION

Prior to this study, one of the authors, I. KAGEHIRA\*, derived an idea from the systematic investigation of the relation between the molecular structure and the chemical and physical properties of hydroaromatic compounds, that a molecule in which cyclohexane rings combine by single bonds in the para position, such as perhydro-1, 4-diphenyl benzene, ( $C_6H_{11}-C_6H_{10}-C_6H_{11}$ ), should have good lubricating qualities. Table I(B)2 shows the data for this series of hydrocarbons.

If this idea is extended to dicyclohexyl, its viscosity would be assumed to be of the order of 20-30 poises at 25°C. (See Table I(B)2).

Therefore, compounds of the diphenylmethane series,  $C_6H_{11}(CH_2)-C_6H_{11}$ , have been synthesized by the method of Huston and Friedmann\*\* as follows:

4.5kg of benzyl alcohol were added drop by drop to a benzene solution (18kg) of  $AlCl_3$  (0.61kg) while agitating for 15 hours at 30°C. The reaction products were obtained by distilling off the solvent, and fractionating. For each frac-

\* I. KAGEHIRA, the report of Imperial Naval Fuel Depot, No.128 June, 1938.  
(Reference Nav Tech Jap Document No. ND26-0007-77)

\*\* R. C. Huston and T. E. Friedmann, J. Amer. Chem. Soc., 38, 1916, 2527.

## ENCLOSURE (B)2

tion the properties were determined and are shown in Table II(B)2. From these it was considered that fraction 1 was composed mostly of benzene, fraction 2 was diphenyl methane, fraction 3 was dibenzylbenzene, and fraction 4 was dibenzylidiphenylmethane. These fractions were hydrogenated under high pressure of hydrogen at 200°C in the presence of reduced nickel, and the properties of the reduced compounds were determined and are given in Table III(B)2. Tetracosahydro-dibenzylidiphenylmethane was observed to have a viscosity comparable with commercial aircraft lubricating oils and to have a very low Conradson's carbon, although its viscosity index was extremely poor. Also, a large increase in viscosity and decrease in viscosity index was obtained when dibenzylidiphenylmethane was completely hydrogenated.

It has been observed that the diphenylmethane series of hydrocarbons can be prepared by the condensation of benzene and formalin in the presence of concentrated sulphuric acid.\*\*\*

It is a generally known fact that the change of viscosity with temperature of paraffin hydrocarbons is the lowest of all types of hydrocarbons, and therefore, a cyclic compound which has a long paraffinic side chain might be expected to be of adequate viscosity and less susceptible to change of the viscosity with temperature. In this connection, L. A. Mikeska\*\*\*\* has synthesized various high viscosity index compounds by reduction of the condensation products of aromatic hydrocarbons and fatty acids.

Based on these facts, the authors prepared the hexadecyl derivative of dicyclohexyl methane,  $C_6H_{11}(CH_2)_{16}C_6H_{11}-C_{16}H_{33}$ . The results are shown in Table IV(B)2. One mol. of cetylchloride was condensed at 50°C, in the presence of 5% aluminum chloride, with one mol. each of diphenylmethane, dibenzylbenzene or dibenzylidiphenylmethane and the products were hydrogenated at 200°C in the presence of reduced nickel under high pressure hydrogen and then purified by fractionation.

The crude reaction products, as will be seen in Table IV(B)2, show viscosities at 210°F of 49, 74 and 77 S.U.S., viscosity indices of 136, 109 and 108, and Conradson's carbon values of 0.04, 0.14 and 0.21, respectively. The substances, purified by distillation, which correspond to the hexadecyl derivatives, dodecahydrodiphenylmethane, octadecahydro dibenzylbenzene and tetracosahydro-dibenzylidiphenylmethane, have S.U.S. viscosities of 97, 197 and 260., viscosity indices of 98, 90 and 86, and Conradson's carbon values of 0.05, 0.20, 0.39, respectively.

Instead of cetylchloride, one or two moles of cetene were used for the condensation, and the reaction products which were obtained in a similar manner as in the above case, showed almost the same results. These results are shown in Table V(B)2.

The synthetic compounds prepared as mentioned above did not have good stability as measured by the viscosity ratio of the British Air Ministry Oxidation Test (Table V(B)2). This defect was easily improved by adding 0.1% of copper oleate, which decreased the viscosity ratio from 2.2 to 1.4 (Table V(B)2).

### III. CONCLUSIONS

Some homologous series of dicyclohexyl, dicyclo hexylmethane and hexadecyl dicyclohexylmethane were synthesized and their chemical and physical properties were studied in comparison with those of the natural lubricating oils derived

\*\*\* C. Ellis, the Chemistry of Synthetic Resins, Vol. 1, p. 263.  
 \*\*\*\* L. A. Mikeska, J. Ind. Eng. Chem., 28 (1936) 970.

## ENCLOSURE (R12)

From petroleum.

Since the synthetic compounds are superior in chemical stability and viscosity index, they may be used in a proper way in an automobile and aero engine which require a lubricating oil of constant viscosity with varying temperature and of high stability for oxidation.

Table I(B)2  
VISCOSITY RATIOS

	Cyclohexane	Dicyclohexyl	Perhydro-1. Diphenylbenzene
Experimental Formula	C <sub>6</sub> H <sub>12</sub>	C <sub>12</sub> H <sub>22</sub>	C <sub>18</sub> H <sub>22</sub>
M.W.	84	166	248
Viscosity in Poises at 25°C	0.008991	0.031467	0.614263
Ratio of Viscosity to C <sub>6</sub> H <sub>12</sub>	1	3.5	68.3
Vis. Ratio Diff.	2.5		64.8

Table II(B)2  
CONDENSATION PRODUCTS

Fraction	Yield (gm)	Properties of Fractions			
		d <sub>4</sub> <sup>25</sup>	n <sub>D</sub> <sup>25</sup>	Mol. Refr.	
				Found	Calc.
1 -200°C	14.520	0.8756	1.5023	26.32	26.31
2 -170°C/5mm	4.007	1.0042	1.5763	55.42	55.03
3 170-250°C/5mm	1.185	1.0467	1.6024	84.64	83.76
4 250-290°C/5mm	353	1.0683	1.6170	114.04	112.48
5 Residue	185				

ENCLOSURE (B)2

Table III(B)2  
HYDROCRACKING PRODUCTS

Compound	B.P.	$d_4^{25}$	$n_D^{25}$	M.W.		Viscosity in Poles at 25°C	Viscosity in S.U.S.		Viscosity Index	Conrad- son's Carbon
				Found	Calc.		100°	210°		
Diisopropylaliphatic aromatics	224-244.90/ 74.5mm	0.8773	1.4747	58.07	57.83	0.04914	-	-	-	-
Diisobutylaliphatic aromatics	169-177/2.2 mm	0.9127	1.4940	88.19	87.96	0.9499	-	-	-	-
Tetraethylaliphatic aromatics	210-260°/ 7mm	0.9492	1.5206	119.36	118.09	-	6773	117.6	-139	0.002

Table IV(B)2  
LUBRICATING OIL SYNTHESIZED FROM DIFFERENTIARAME SERIES HYDROCARBONS AND CETYLCHLORIDE

New Materials and Reaction Products	Yield Theor. (%)	Boiling Pt. (°C)	M. Pt. (°C)	Density $d_4^{25}$	$n_D^{25}$	Viscosity in S.U.S.		Conradson's Carbon (%)	Pour Pt. (°C)
						at 100°	at 210°		
1. Completely	-	165-216°/2mm	-	0.8996	1.4479	-	-	-	-
2. High/low	-	110	26	1.0010	1.2728	-	-	-	-
3. p-Substituted	-	214	81-86	-	-	-	-	-	-
4. m-Substituted	-	270-272	-	1.0691	1.6803	863	47.6	62	-
5. Substituted product of 3 and 2	90	-	-	0.8928	1.5083	122.4	44.3	154	3.8
6. Substituted product of 3 and 3	81	-	-	0.9214	1.9560	210.3	52.6	141	5.75
7. Substituted product of 3 and 4	75	-	-	0.9298	1.5990	303.5	31.0	137	7.35
8. Completely hydrogenated product of 5	100	-	-	0.8612	1.4770	188.5	49.2	136	0.04
9. Completely hydrogenated product of 6	100	-	-	0.8787	1.4862	164.0	74.0	109	0.14
10. Completely hydrogenated product of 7	100	-	-	0.8777	1.4815	67.5	77.0	108	0.21
11. The fraction over 200°/2mm of 8	54	200	-	0.8661	1.6901	1160.0	97.0	98	0.05
12. The fraction over 200°/2mm of 9	71	200	-	0.8946	1.4997	1228.5	197.4	90	0.20
13. The fraction over 200°/2mm of 10	67	200	-	0.8950	1.6900	78000	260	86	0.39

ENCLOSURE (B)

Table V(B)2  
LUBRICATING OIL SYNTHESIZED FROM DIPIHTERIMETHANE  
SERIES HYDROCARBONS AND CETERA

No.	Materials and Quantities Products	Flash Temp. (°C)	S.P. (°C)	V.P. (%)	42° sp	35 sp	Viscosity in S.U.S.		Viscosity Index	Conrad- son's Carbon Content (%)	Pour Pt. (°C)	After the British In- dustry Commission Test	
							100°F	210°F				Vis- Ratio	Acid Carbon Ratio
1	Gasoline	-	380-385°/5mm	-	0.7785	1.4407	-	-	-	-	-21	-	-
2	High-boiling base	-	100°/5mm	28	1.0010	1.5753	-	-	-	-	-	-	-
3	Distillate/Chemical	-	211°/5mm	84-86	-	-	-	-	-	-	-	-	-
4	Condensation product of one mol. of (1) & one mol. of (7)	61	-	-	0.8955	1.9055	125	45.6	162	-	10	-	-
5	Condensation product of two mol. of (1) & one mol. of (7)	71.6	-	-	0.8750	1.8911	307.9	60.8	136	0.91	+3	-	-
6	Condensation product of two mol. of (1) & one mol. of (5)	90.3	-	-	0.9096	1.5150	475.4	71.7	125	-	-4	-	-
7	The fraction of over 200° 5mm of (4)	51.7	200°/5mm	-	0.9070	1.5122	380.9	62.0	120	-	-5	-	-
8	The fraction of over 200° 5mm of (4)	66.1	200°/5mm	-	0.8768	1.4944	486.6	74.0	128	1.04	+4	-	-
9	The fraction of over 200° 5mm of (7)	71.2	200°/5mm	-	0.9044	1.5113	815.3	91.2	117	-	-4	-	-
10	Empirically hydrogenated product of (5)	62.7	-	-	0.8651	1.4808	754.5	90.6	121	0.13	+4	-	-
11	Empirically hydrogenated product of (4)	75.9	-	-	0.8750	1.4872	1756.4	136.6	108	0.11	-4	2.2	2.6
12	(11) + 0.25 wt. Copper oleate	-	-	-	-	-	-	-	-	-	-	1.40	0.6
13	(11) + 0.25 wt. Iron oleate	-	-	-	-	-	-	-	-	-	-	1.44	-
14	(11) + 0.25 wt. Copper oleate	-	-	-	-	-	-	-	-	-	-	1.88	-
15	(11) + 0.25 wt. Iron oleate	-	-	-	-	-	-	-	-	-	-	2.10	-
16	(11) + 0.25 wt. Tin oleate	-	-	-	-	-	-	-	-	-	-	2.36	-
17	(11) + 0.25 wt. Van oleate	-	-	-	-	-	-	-	-	-	-	3.00	-
18	(11) + 0.25 wt. Triphenylphosphite	-	-	-	-	-	-	-	-	-	-	2.0	-