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ON THE SYNTHETIC LUBRICATING OILS FROM PURE HYDROCARBONS

Haag and Zorn

"ON THE SYNTHETIC LUBRICATING OILS FROM PURE HYDROCARBONS"

1. Polymerization of pure aliphatic olefins with $AlCl_3$.
2. Mixed polymerization of pure aromatic olefins with aromatic and hydroaromatic hydrocarbons.
3. Extension of the experimental results obtained with the pure olefin, and their application to cracked paraffin olefins.
 - a. Cracked olefin polymerization.
 - b. Mixed polymerization of cracked olefins with tetralin.
 - c. Mixed polymerization of cracked olefins with coal hydrogenation oil.

In order to establish a definite relationship between the properties of the synthetic lubrication oils and their constitution, the oils were prepared from pure initial materials, by polymerization or condensation with $AlCl_3$. Above all, it was to be established what effect the length of the C-chain and the degree of branching has on the main properties of the oil, namely the viscosity index and the stability towards oxidation. In order to develop a proper experimental sequence, the initial materials selected consisted of olefins containing 3,4,5,7,8,15 and 18 C-atoms. These olefins were polymerized by themselves once; then they were also condensed together with naphthalin and tetralin in order to establish the effect of the chain length (and of the number of side chains).

It should be stated here that the polymerization-or condensation methods applied in these experiments did not include the optimum conditions for the reactions being studied. Rather, it was considered of importance to maintain as much as possible the same experimental conditions for all the oils to be compared with each other. It is for this reason that, for instance, the same stirring speed was maintained, and the same $AlCl_3$ was used throughout, even in the same percentage quantity, if possible. The dilution with solvents was also the same, with a few exceptions. The effect of the temperature, as long as one operates below $100^{\circ}C$, does not seem to be of decisive importance; in our experiments, temperatures between 60 and 80° were used. All the oil sediments were, after termination of the stirring, decomposed with water, then treated with steam up to 200° and distilled in vacuo at 1 mm pressure up to 150° . The residual oil boiling above 150° was then examined.

TABLE I

Exp. No.	Initial Olefin	Oil boil'g above 150° at				spec. wt.	Slight Ox.T.
		Yield %	E at 38°C	E at 99°C	visc. ind.		
PP 86	propylene $\text{CH}_3\text{CH}=\text{CH}_2$	71.5	126	4.34	744	0.851	0
78	α -Butylene $\text{CH}_3\text{-CH}_2\text{-CH}=\text{CH}_2$	43	74.6	3.34	744	0.857	0
5	β -Butylene $\text{CH}_3\text{-CH}=\text{CH}_3$	27	23.4	1.76	-83	0.865	0
4	1-Butylene $\text{CH}_3\text{CH}=\text{CH}_2$	25	25.6	1.77	-107	0.876	0
164	n-Amylene $\text{CH}_3\text{CH}_2\text{-CH}_2\text{-CH}=\text{CH}_2$	74	43.3	2.84	773	0.868	0
165	1-Amylene $\text{CH}_3\text{CH}=\text{CH-CH}_3$	63	170	4.47	76	0.851	0
166	1-Amylene $\text{CH}_3\text{CH}=\text{CH-CH}_3$	23	6.32	1.39	-25	0.844	0
157	1, 2 Heptene $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}=\text{CH}_2$	85	34.4	2.91	799	0.846	0
156A	3, 4 Heptene $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}=\text{CH-CH}_2\text{-CH}_3$	45	5.6	1.42	724	0.860	0
1	n-Oktylene $\text{C}_5\text{H}_{11}\text{-CH}_2\text{-CH}=\text{CH}_2$	70	38.7	3.56	7114	0.851	0
169	1-Oktylene $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}=\text{CH}_2$	ca 85	387	13.2	798	-	-
2c	1-Oktylene $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}=\text{CH}_2$	38	6.16	1.42	714	0.860	0
1 a	1-Oktylene $\text{CH}_3\text{CH}=\text{CH-CH}_3$	23	21.7	1.76	-60	0.847	0
167	7, 8 Pentadecylene $\text{CH}_3\text{-(CH}_2\text{)}_5\text{-CH}=\text{CH-CH}_3$	73	8.27	1.65	798	0.847	0
3	n-Oktaedecylene $\text{-(CH}_2\text{)}_6\text{-CH}_3$	64	10.78	1.94	7125	0.848	0

Propylene	from the butadiene factory Ludwigshafen.
-butylene	from the n-butyl alcohol, by dehydration over bauxite at 370°.
β -butylene	Main Laboratory, Ludwigshafen.
1-butylene	from Oppanolfabrik Dr. Otto (Lit: Oppanol plant, Transl).
n-amylene	from paraffin cracking product, fraction 35-45°.
iso-3-amylene	from iso-amyl alcohol by dehydration over bauxite followed by purification with 60% H ₂ SO ₄ . B.pt. = 20-25°.
Trimethyl-ethylene	From iso-amyl alcohol, by dehydration over bauxite; refined by addition to 60% sulfuric acid. B.pt. = 36-37°.
n-heptene	from Dr. Sönksen; initial material for knock-value heptene.
3,4-heptene	from n-butyric acid-butylene-hydrogenation into alcohol followed by dehydration.
n-octylene	from n-octyl alcohol (Deutsche Hydrierwerke), by dehydration over bauxite.
1-octylene	from iso-amyl iodide and allyl homide,
(6-methyl-hexene 1)	acc'g to Grignard.
1-octylene	From n-butylaldehyde-methylalheptene
(2-ethyl hexene 1)	hydrogenation into alcohol and dehydration with bauxite.
di-iso-butylene	from iso-butylene, by dimerization with H ₂ SO ₄ (Dr. Sönksen).
pentadecylene 7	from caprylic-acid - caprylene hydrogenation into alcohol, and dehydration over bauxite.
octadecylene	from octadecyl alcohol (from Soya oil, Dr. Sönksen) and dehydration over bauxite.

In Table I, the experimental results obtained with the polymerization of pure olefins by means of AlCl₃ are summarized. The method of preparation of the olefins is also given in Table I. The most striking fact that can be seen from this table is that the tendency of the various olefins to give highly polymerized oils with lubrication properties is remarkably variable, depending on the constitution of the particular olefin. The position of the double bond and the degree and kind of branching of the C-chain are mostly responsible for the yield and quality of the lubricating oil fraction boiling above 150° at 1 mm Hg. The straight chain olefins with terminal double bond are the ones which polymerize with the greatest ease⁽¹⁾, and at the same time they give the highest yields and the highest viscosity index (V.I.) values. Within this particular series of compounds, the V.I. values increase approximately with the chain length of the initial olefin.

(1) Cf also Laboratory Report No. 1101.

Number	Olefin	above 150°, 1 mm Hg Yield	V.I.
PP 86	Propylene	71%	44
78	α -n-butylene(x)	43%	44
164	n-Amylene	74%	73
157	n-Heptylene	85%	99
1	n-Oktylene	78%	114
3	Oktadecylene	63%	125

(x) Perhaps not entirely freed from β -butylene.

These results are in agreement with the work done by Standard Oil of Indiana (Ind. Eng. Chem., 23, 604-11 (1931)).

Branchings of the olefin chain make themselves felt by the decrease of the viscosity index values; this decrease is stronger, the closer the branch is to the double bond.

Number		Yield above 150°C at 1 mm Hg	V.I.
1	C-C-C-C-C-C=C	70%	114
169	C-C-C-C-C-C=C	85%	98
164	C C-C-C-C=C	74%	73
165	C C C-C=C	80%	6

If branching occurs at the C-atom next to the C-atom with the terminal double bond, the polymerization is very definitely disturbed, as indicated by poor yields and very poor V.I. values:

Number		above 150°	V.I.
78	C-C-C=C	43%	44
4	C C-C=C	25%	-107
1	C-C-C-C-C-C=C	70%	114
2c	C-C-C-C-C=C C-C	38%	19

The polymerization reaction is also inhibited by a shift of the double bond towards the center of the molecule; both yield and viscosity index drop, especially when there are, at the same time, branches near the double bond:

Oil Number	Chemical Structure	Yield above 150° at 1 mm Hg	V.I.	°E at 99°C
78	C-C=C=C	43	/44	4.34
5	C-C=C-C	27	-83	1.76
164	C-C-C=C	74	/73	2.84
165	C C-C=C	63	/6	4.47
166	C C C=C-C	23	-25	1.39
157	C-C-C-C-C-C=C	85	/99	2.91
156a	C-C-C-C=C-C-C	45	/24	1.42
1	C-C-C-C-C-C-C=C	70	/114	3.56
169	C C-C-C-C-C-C=C	85	/98	13.2
1a	C C C=C-C	23	-60	1.76
3	C ₁₆ -C=C	64	/125	1.94
167	C ₆ -C=C-C ₇	73	/98	1.65

Furthermore, the viscosity too depends on the constitution of the olefin. In Laboratory Report No. 1101 (p.3) it was stated that the viscosity was proportional to the degree of branching of the C-chain of the initial material. The experiments above show that the degree of viscosity of the polymerization product also depends, to a great extent, on the position of the side-chain with respect to the double bond. Thus for instance, one obtains products of very high viscosity and very good V.I. value, when both the branching as well as the double bond are in a terminal position (See hydrocarbon No. 165 and 169). If the side chain is fixed to the doubly linked C-atom, the viscosity of the polymerization product is very low and the V.I. value very bad (See hydrocarbons No. 4 and 2c, Table I).

Independently of the constitution of the polymerized olefins, the oxidation stability of the oil is very good. All values of the Sligh oxidation test are below 0, which means that under the artificial aging conditions which are applied, no asphalts are formed.

The low specific weights (around .85, with small variations) of the polymerized products, are rather remarkable. In the oils obtained from di-isobutylene (1a) and octadecylene, the specific weight is exactly the same, despite the fact that their viscosity index values differ by some 180 units. We may conclude that the specific weight cannot be taken as a standard for measuring the quality of a synthetic lubricating oil.

If mixed-base mineral oils are treated with selective solvents (phenol, etc.), the aliphatic hydrocarbons will be strongly enriched in the refined phase. This phase has a lower specific weight and a higher V.I. value than the initial oil. In the extract-phase, enrichment of the aromatic and the hydro-aromatic hydrocarbons takes place; they have a high specific weight (above .9) and a bad V.I. In this case one can speak of a certain dependence of the viscosity index on the specific weight. Due to the fact that the extract-phase, which contains the aromatics, has a high specific weight, we may assume in all probability that our polymerized oils with the low specific weight consist of aliphatic hydrocarbons.

Thus, the V.I. of the oils is a property determined by the structure. A certain amount of branching of the hydrocarbons is necessary to give the character of oiliness to the lubricating oils. Entirely straight-chain paraffinic hydrocarbons cannot be used for purposes of lubrication because, in the higher boiling ranges, their pour-and/or melting-point is too high. The highly viscous hydrocarbons prepared by the polymerization of aliphatic olefins are always branched. Therefore, the degree and type of branching are of importance. It may be assumed that during the polymerization, there forms a principal chain with side chains connected to it. The length of these side chains and their degree of branching depends on the structure of the initial olefins. Straight chain olefins with a terminal $-C=CH_2$ group will give straight-chained side chains; branched olefins with terminal double bond will give branched side-chains; olefins whose double bond is not at the end-position will give rise to very strongly branched side chains.

The longer and the straighter these side chains are, the higher will be the viscosity index of the oil. Shortening or branching of the chains will lead to a drop in the V.I. value; the stronger the branching, the greater will be the V.I. drop. (See: Rep. of Dr. Zorn and Dr. Nienburg on "The Relations Between Structure And Lubrication Properties In Uniform, Synthetic Hydrocarbons").

The same phenomenon is observed with the olefins condensed or polymerized with the aromatic hydrocarbons; in this case, the aromatic nucleus replaces, in a certain sense, the main chain, and here again the V.I. is determined by the length and the degree of branching of the side chains which have been introduced. (See Rep. of Dr. Zorn and Dr. Nienburg).

These experiments are presented in tabular form in Tables II and III.

Table II deals with the polymerization oils resulting from olefins and naphthalin. In each case, 1 Mol. of naphthalin was brought together with 2 molecules of olefin; (in those cases where the reactants were gaseous, the olefin component was somewhat higher).

Again it is found that the specific weight does not permit us to draw any conclusions as to the quality of the oil. However, the specific weights, in all cases, are higher than those of the pure olefin polymerization products.

Comparison of the viscosity indices will show at first glance that a decrease has set in with respect to the pure olefin polymerization products. Again, the V.I. depends on the length of the olefin C-chain and on its degree of branching. The relations can be formulated as follows:

1. The longer the olefin chain, the greater the viscosity index:

Number		V.I.
26	N / n-octylene	25.5
17a	N / octadecylene	113.5

2. The smaller the degree of branching of the olefin chain, the greater will be the viscosity index:

Number		V.I.
26	N / n-octylene	25.5
14b	N / 1-octylene	80.5
13	N / diiso-butylene	resinified

As to the resistance of these naphthalin oils towards artificial aging, especially under conditions such as prevail in the Sligh oxidation test and in the Conradson coking process, it can be said that the number of side-chains which are introduced is of decisive importance.

Number		Sligh Test	Coking
14	N / 1-octylene 1:1.3	97	1.72
14b	N / 1-octylene 1:2	6.4	.16
17	N / octadecylene 1:1.1	196	2.08
17a	N / octadecylene 1:2	2.6	.28

TABLE II

Exp. No.	Initial material Naphthalene / chlorides	Yield in %	Viscosities		Prod. above 150° at 1 mm Hg	Sp. wt.	Mol. wt.	Cok- ing	Sligh Ox.T.
			E ₃₈ ^o	E ₉₉ ^o	V.I.				
16	N / β -butylene 1:2,5	71	21.3	1.7	-102	.9438	306	1.05	42
16a	N / β -butylene 1:2,3	68	23.4	1.75	-90	.9476	305	1.37	56
15	N / i-butylene 1:2	resinified							
13	N / diisobutylene	60	sticky			.9379	326	0.72	16
14	N / i-octylene	34	23.8	1.74	-109	.9580	337	1.72	97
14b	N / i-octylene 1:2	50	20.01	1.77	-80.5		355	0.16	6.4
26	N / n-octylene 1:2	39	11.0	1.61	/25.5	.9105	392	0.15	1
17	N / octadecylene	75.5	15.68	2.02	/97.0	.9063	468	2.08	196
17a	N / octadecylene 1:2	86	7.5	1.63	/113.5		483	0.28	2.6

TABLE IIIa

Condensation and polymerization of pure aliphatic olefins with tetralin

Exp. No.	Initial reagents		Oil above 150° at 1 mm Hg						
	Tetralin	Olefin	Yield	E ₉₉ ^o	V.I.	Spec. wt.	Sligh Ox.T.	Mol. wt.	Coking
42	1 Mol	2, 4 Mol ϵ -butylene	59%	1.74	-212	.942	5.4	319	0.23
38	1 Mol	2 Mol n-octane-1	61%	1.56	-155	.906	3.4	354	0.22
39	1 Mol	2 Mol 2-ethyl hexene-1	55%	1.99	-112	.946	21.7	342	1:16
40a	1 Mol	2 Mol diiso-butylene	19%	2.62	-435	.940	1.2	354	1:12
41	1 Mol	2 Mol octadecylene-1	72%	1.68	-110	.878	0	468	0.35

TABLE III

Naphthalene-Condensation Salts

Exp. No.	Initial material 1 naphthalene / 2 chlorides	Yield in %	Product above 150° at 1 mm Hg			Spec. wt.	Mol. wt.	Cok- ing	Sligh Oxida- tion T.
			Viscosities						
			E ₃₈ ^o	E ₉₉ ^o	V.I.				
7	N / n-butylchloride	57.5	6.67	1.42	-18.9	0.9661	297	2.92	98
8	N / i-butylchloride	49	resinified						
18	N / n-octylchloride	65	8.76	1.57	56.7	0.9269	352	1.97	1.1
23	N / i-octylchloride	49	25.3	1.80	-84	0.9461	341	1.16	9.2
9	N / di-isobutyl- chloride	Resin resinified							
21	N / octadecyl- chloride	81.5	10.7	1.88	113	0.8887	538	0.72	0

Origin of the chlorides given in Table III:

n-butyl chloride	Methyl aniline plant, Dr. Schulze
i-butyl chloride	Methyl aniline plant, Dr. Schulze
diiso-butyl chloride	from diiso-butylene & conc. HCl; b.pt. = 42-45° 10 mm Hg, 99% pure.
n-octyl chloride	from n-octyl alcohol) (Deutsche Hydrierwerke)
i-octyl chloride	from 2-ethyl hexanol) (Dr. Sonksen)
octadecyl chloride	from octadecyl alcohol) (Dr. Sonksen)

By treatment of the alcohols with ZnCl₂ and gaseous HCl, under pressure and at 100°C.

The experimental results obtained from the condensation of naphthalin with the ethyl-chlorides corresponding to the olefins of Table II, are reproduced in Table III. Here again, the same observations can be made:

1. The longer the side chain, the better the V.I.

Number		V.I.	Sligh Ox.T.	Coking	Mol. weight
7	N / n-butyl chloride	-19	98	2.92	297
18	N / n-octyl chloride	56.7	1.1	1.97	352
21	N / octadecyl chloride	112	0	.72	538

2. The smaller the branching of the alkyl chloride, the better the V.I.

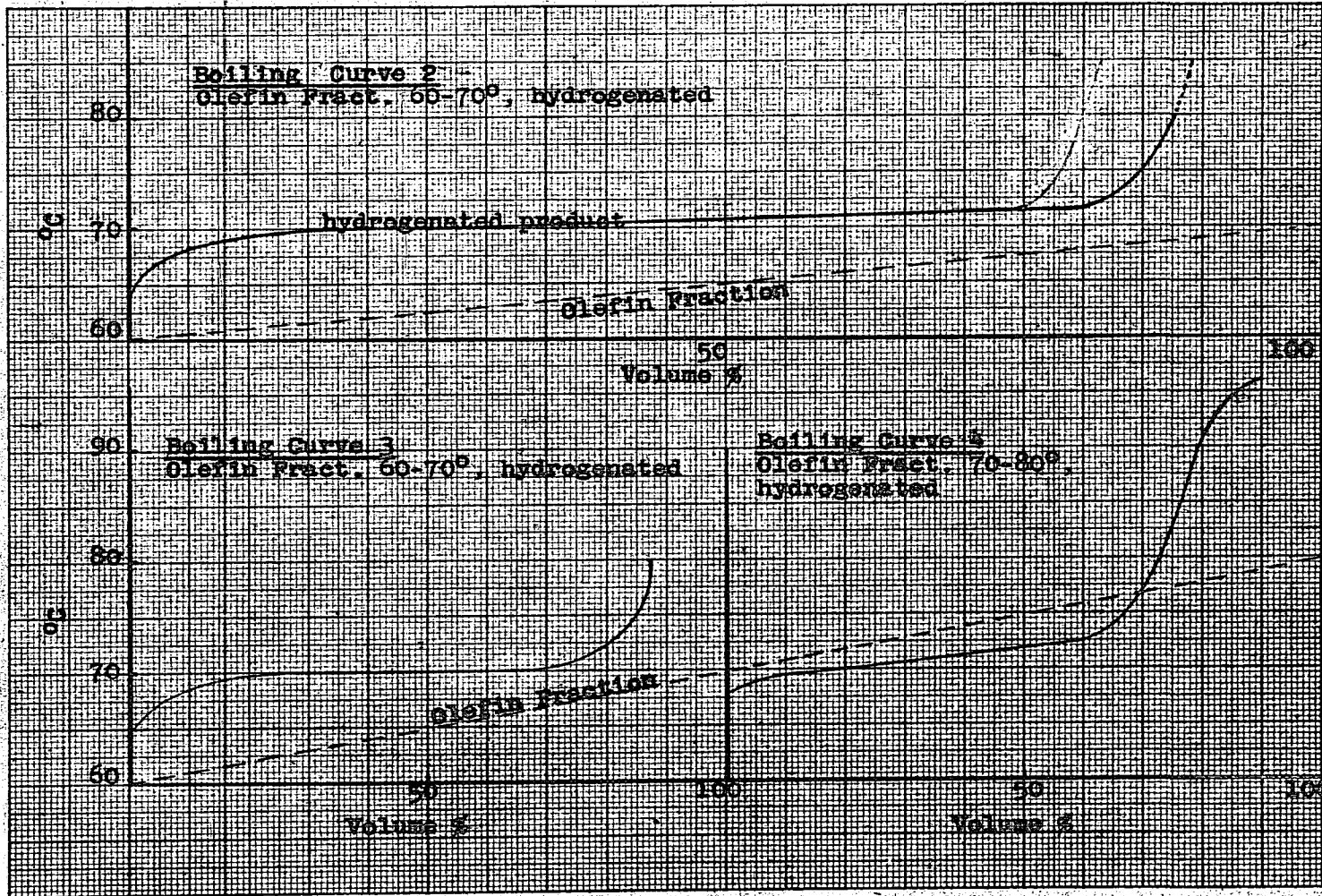
Number		V.I.	Sligh Ox.T.	Coking	Mol. weight
18	N / n-octyl chloride	56.7	1.1	1.97	352
23	N / i-octyl chloride	-84	9.2	1.16	341
9	N / diiso-butyl chloride resinified				

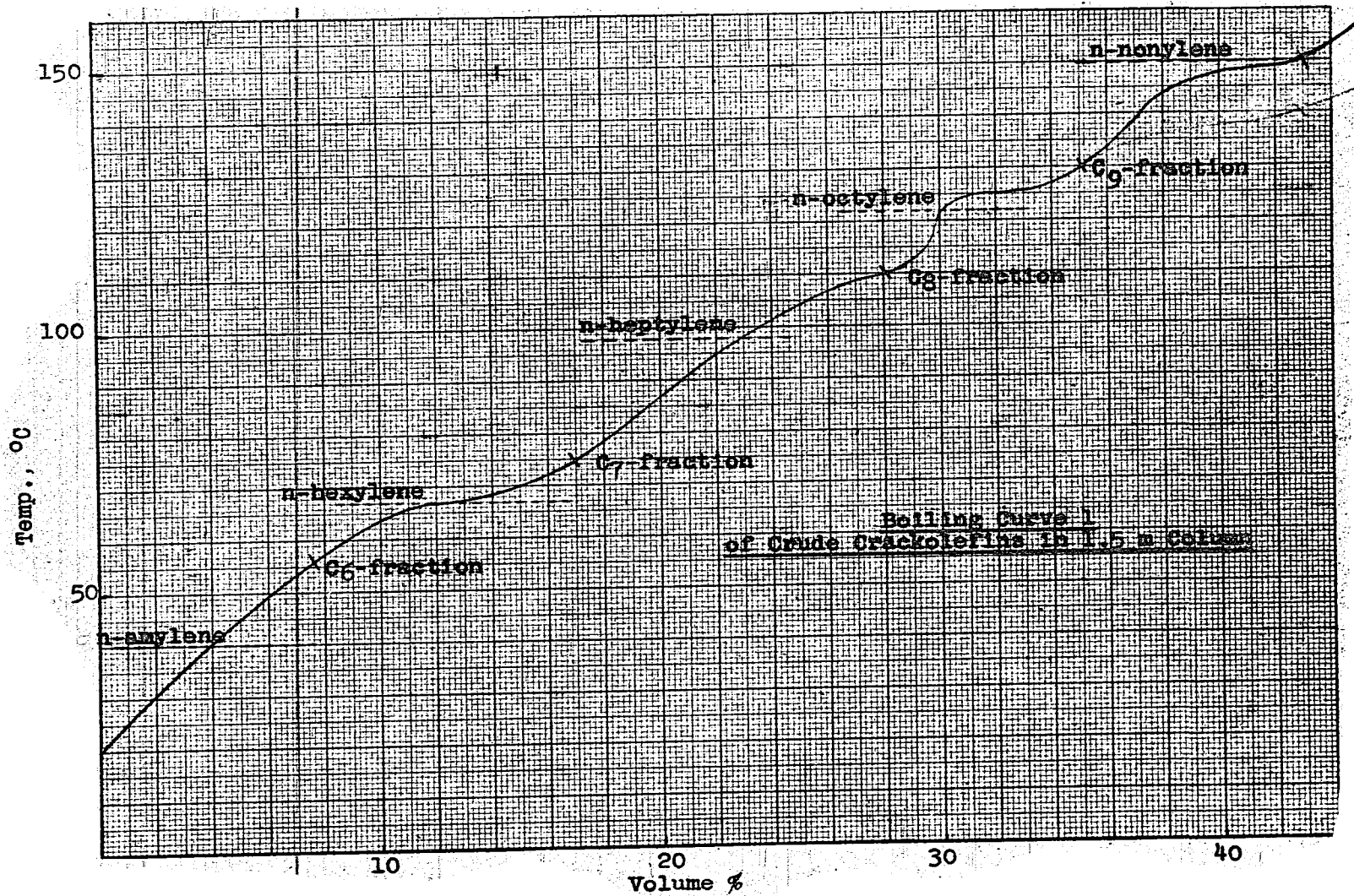
See Table III, opposite.

Following the polymerization of the pure aliphatic olefins with naphthalin, a corresponding series of experiments was repeated with tetralin (Table IIIa), opposite. Essentially, the experimental results are the same as those obtained with naphthalin; again, only the straight chain olefins with terminal double bond give positive V.I. values; these values increase with the chain length. The specific weights of the tetralin oils are, in all cases, higher than those of the corresponding oils obtained from the pure olefins.

Condensation experiments involving the condensation of tetralin with alkyl chlorides, did not lead to any useful result. The oils which were obtained were mostly sticky or completely resinified; besides, the yields were so bad, and therefore the possible sources of error so great, that no conclusions as to constitution and structure could be drawn.

The results obtained in the experiments with pure olefins, were now to be applied to an olefin mixture such as is obtained in the cracking of paraffins. The paraffin cracking product used for these experiments had been prepared by Dr. Hoffmann in Op. 36⁴, by the cracking of paraffins in the gas phase.





A rather remarkable feature of these liquid olefins was the exceptional ease with which they polymerized, and the good viscosity index of the oils derived from them. It was therefore quite logical to assume that either these cracked olefins consisted essentially of normal hydrocarbons with terminal double bond, or that the diolefins which are present in small amounts, strongly enhance the polymerization. The latter assumption seems to be wrong, as evidenced by the experimental results tabulated in Table IV.

The following procedure was used in this series of experiments: first of all, the cracking product was split into a low (0-80°) fraction and into a higher fraction (30-130° at 1 mm Hg); from both these components, the diolefins were removed by thorough stirring with 60% sulfuric acid. For purposes of comparison, lubricating oils were also prepared from untreated fractions (Exp. 30-33). For purposes of control a diolefin free olefin (iso-octylene) was polymerized with a 5% addition of isoprene, (Exp. 34 and 2). Furthermore, an olefin fraction boiling up to 120° was freed from its entire diolefin content by method developed by Dr. Stern. The results of these experiments can be seen from Exp. No. 35, 36 and 37. From this tabulation, it can easily be seen that the presence of diolefins improved neither the yield nor the viscosity index.

In order to clarify the problem of the structure of these cracked olefins, a careful fractionation was made in a 1.5 m high column. A single distillation was already sufficient (See boiling curve 1) to allow a distinct separation into fractions corresponding to the number of C-atoms in the olefin.

When the fractions, and/or the intermediate runnings, were subjected to hydrogenation, the boiling curve picture became still clearer. Boiling curve 2 represents a hexane fraction which was obtained by hydrogenation of an olefin component boiling between 60 and 70°. The curve shows that the hydrogenation product consists mostly of n-hexane, which can be separated with great sharpness from the first runnings and from the higher boiling components.

Curves 3 and 4 show the boiling behaviour of a hydrogenated olefin fraction (hexylene fraction) boiling between 60 and 80°. The hydrogenation product usually contains n-hexane and heptane, but it may be separated from them by fractionation.

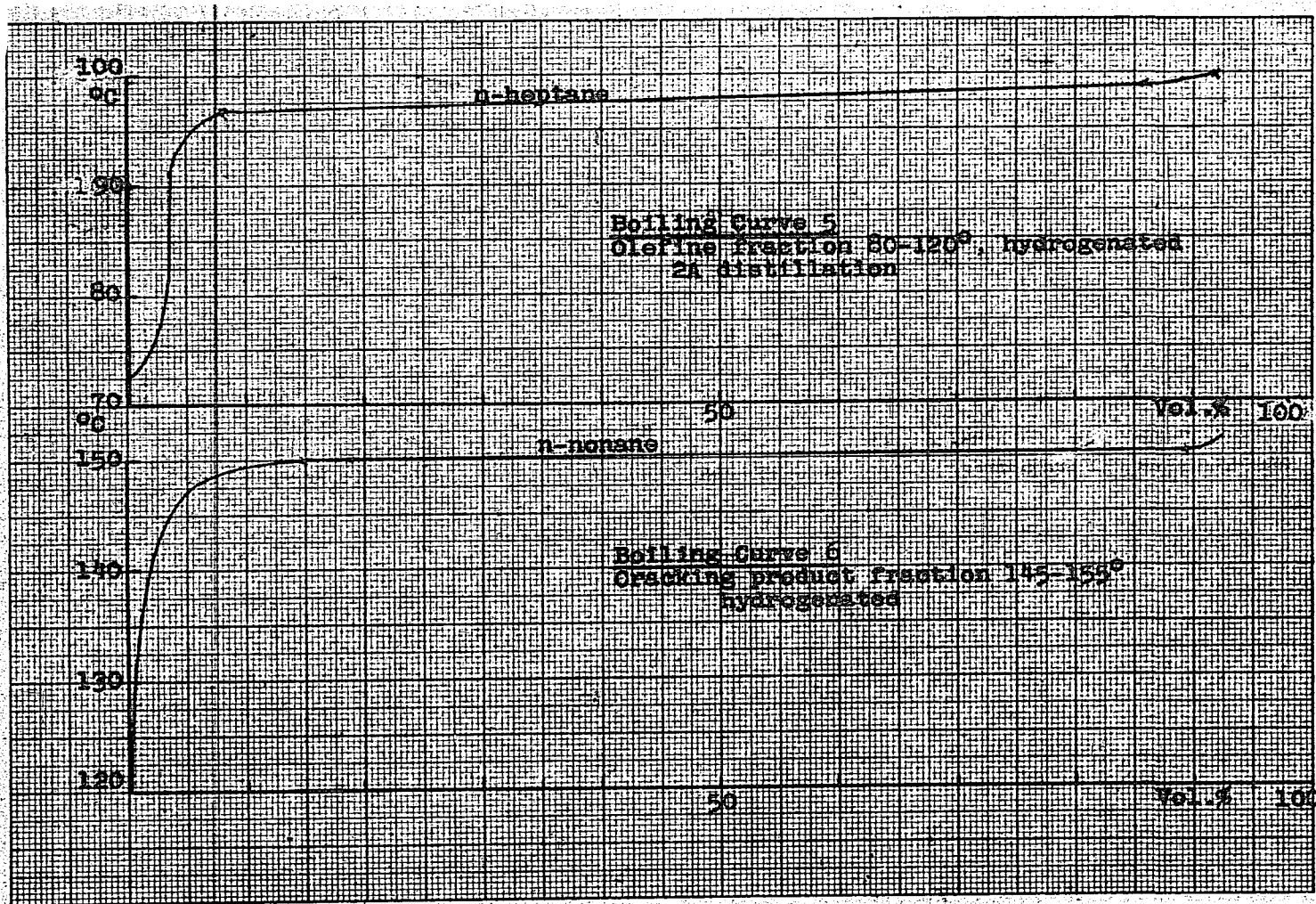
TABLE V
The Effect of Temperature of the Polymerization of Olefins

No.	Olefins	Time of stirring (hours)	Temp. °C	AlCl ₃ %	Lube oil fraction above 150° / 1 mm Hg					
					Yield wt. %	E ₃₈	E ₉₉	V.I.	Mol. wt.	spec. wt.
48	C ₇ /C ₈ , 80-130°	6	20	5	76.7	70.8	4.58	102	910	0.864
49	C ₇ /C ₈ , 80-130°	6	50	5	84	43.3	3.36	101	793	0.862
50	C ₇ /C ₈ , 80-130°	6	80	5	87	36.1	2.99	99.5	778	0.861
51	C ₇ /C ₈ , 80-130°	6	110	5	85	23.25	2.39	99	682	0.862
52	C ₇ /C ₈ , 80-130°	6	140	5	64	22.25	2.37	101	619	0.866
53	C ₁₄ /C ₁₅ /C ₁₆ 240-290°	6	20	5	82.5	77.5	7.10	125	1740	0.857
54	C ₁₄ /C ₁₅ /C ₁₆ 240-290°	6	80	5	86	49.3	4.71	123	1410	0.855
55	C ₁₄ /C ₁₅ /C ₁₆ 240-290°	6	140	5	71	46.6	4.47	123	1120	0.857

TABLE IV

No.	Initial Material			AlCl ₃ %	Temp. °C	Time hrs.	Yield %	Above 150° at 1 mm Hg					
	Olefin	Treatment	Addition					E38°	E99°	V.I.	Sligh Oxid.	Cok ing	Molec. Weight
30	Crack-olefin 30-70	-	-	5	60°	12	73	73.8	4.09	84	0	0.09	875
33	Crack-olefin 30-70°	Agitated with 60% H ₂ SO ₄	-	5	60°	12	87	43.4	3.04	84	0	0.07	818
31	Crack-olefin 30-130 @ 1 mm Hg	-	-	5	60°	12	88.5	44.8	4.31	122	0	0.10	1480
32	Crack-olefin 30-130 @ 1 mm Hg	Agitated with 60% H ₂ SO ₄	-	5	60°	12	91	57.5	5.24	123	0	0.07	1700
2	i-octylene 118-1210	-	-	5	60°	12	30	6.14	1.42	-7.9	10	0.14	407
34	i-octylene 118-1210	-	5% iso- prene	5	60°	12	33	6.40	1.44	16.2	0	0.04	395
35	Crack-olefin above 120°	-	-	5	60°	12	86.5	52.9	3.58	94	0	0.11	890
36	Crack-olefin above 120°	Cyclic diolefins extracted	-	5	60°	12	90	43.7	3.17	92	0	0.05	871
37	Crack-olefin above 120°	All diolefins extracted	-	5	60°	12	89	32.35	2.83	99	0	0.05	784

The effect of chain-length and diolefins



Curve 5 represents the course taken by n-heptane. The product was obtained by the hydrogenation of an 80-120° olefin fraction. The greater portion of the first runnings and of the residue were removed by a preliminary distillation. The main fraction 97-99° consists of a very pure n-heptane which, for instance, is sufficient to meet the severe requirements of the knocking value tests of gasolines in motor knocking tests. This product was found to be identical to the n-heptane prepared from butyric acid in coking plant-D.

See Table IV (opposite).

Curve 6 shows the boiling behaviour of n-nonane obtained by the hydrogenation of a 145-155° olefin fraction.

The results of the distillation allow the conclusion to the effect that the cracked olefins consist mostly of n-hydrocarbons (See Lab. Rep. 1101, p. 3).

Polymerization of the Cracked Paraffin Olefins

The polymerization of the cracked paraffin olefins had to be examined with greater accuracy because these products (in contrast to the other possible pure olefins) are available in relatively greater amounts and may be prepared with relatively greater ease, and might be considered for possible utilization as addition agents for mineral- and tar-oils; or, after hydrogenation, these products might be useful for the manufacture of automobile and airplane engine oils. (cf. O.Z. 6298)

The polymerization of all the olefins was examined, as well as that of individual fractions, so that the results could be compared with those obtained with the corresponding pure olefins. In contrast to our experiments with the pure olefins, where the conditions were maintained uniform as much as possible, the experimental conditions were now extensively varied. Above all, the effects of temperature, solvents and different amounts of $AlCl_3$ on the oils boiling above 150° at 1 mm Hg were studied. Furthermore, the effect of $AlCl_3$ additions, which could either enhance or inhibit the polymerization, was examined.

Influence of the Temperature

Two series of experiments were made in order to examine the effect of the temperature; the first series was made with a low olefin fraction boiling between 80-130 (at 760 mm Hg), and consisting of n-heptylene and i-octylene; the second series was made with a higher boiling fraction (240-290° at 760 mm Hg) containing n-olefins C_{14} - C_{16} . The results are tabulated in Table V, opposite.

Similarly to what had been found in our earlier experiments with n-octylene and octadecylene (Table I), it was again observed that, at corresponding reaction conditions (in this case at equal temperatures), the long chain olefins have a higher V.I. value. The degree of polymerization, i.e. the number of olefin molecules polymerized together to form a lubricating oil molecule, is apparently dependent on the temperature: the lower the temperature, the higher the degree of polymerization; this is shown by the average molecular weights. At equal temperatures, the higher olefins give correspondingly higher molecular weights.

The effect exerted by the temperature on the viscosity is worthy of note: the viscosity increases, within the series, with the degree of polymerization; in other words, the lower the temperature, the higher will be the viscosity of the oil.⁽¹⁾ However, the viscosity does not depend on the molecular weight, as evidenced by Exp. No. 48, 54 and 55.

Here, the V.I. is practically independent of the reaction temperature. This observation is in disagreement with Lab. Rep. 574, p. 4, where it was observed that the V.I. increases with increasing reaction temperature. The sharp drop of the yields, which sets in when one works above 120°, is due to the fact that at this temperature the AlCl₃ can have not only a polymerizing effect, but also a splitting effect. Therefore, excessively high temperatures are to be avoided.

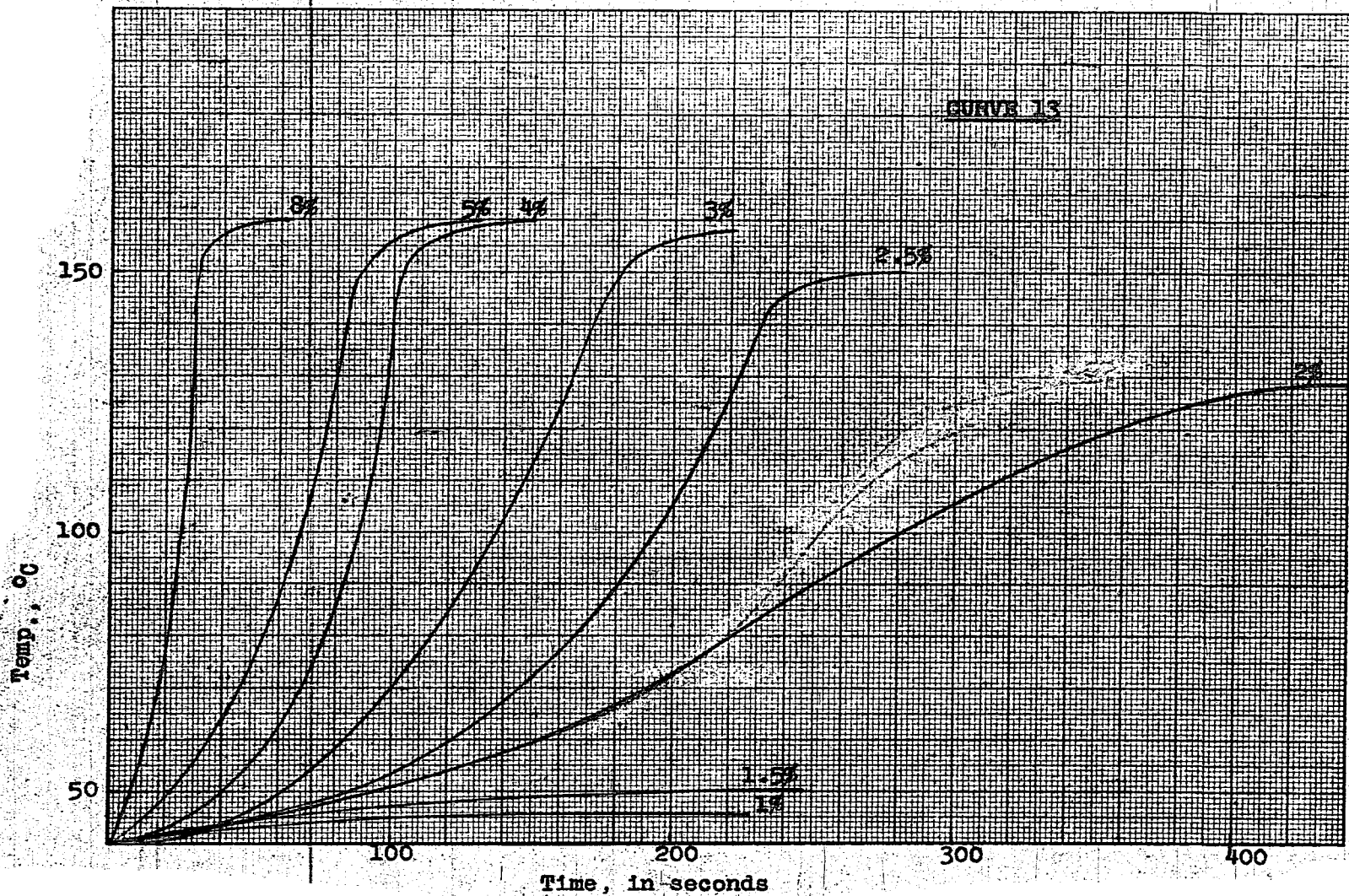
TABLE VI
TYPE OF SOLVENT AND AMOUNT OF SOLVENT

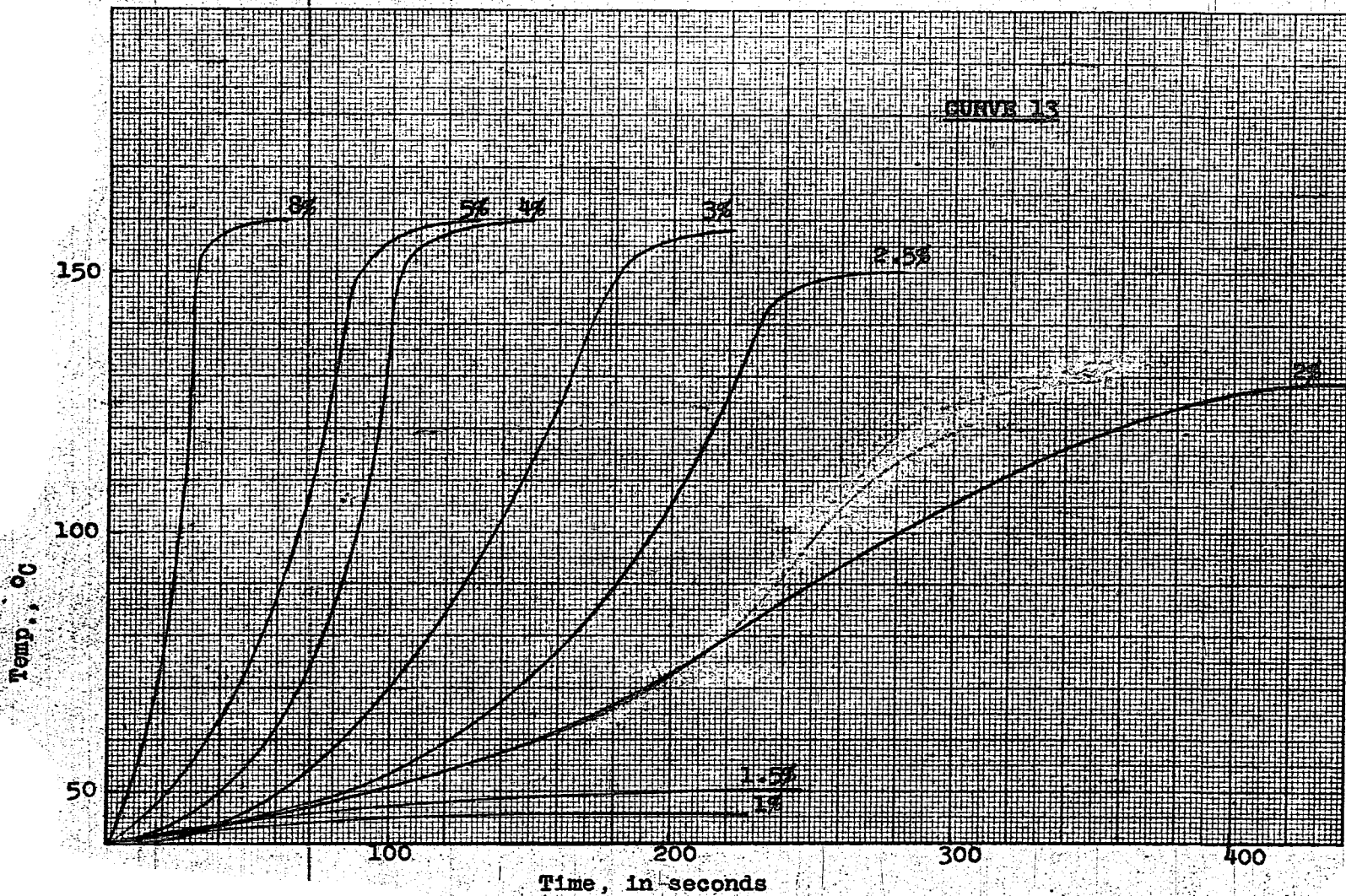
Exp. No.	Cracked Olefin Fraction 80-130° / Solvent 1:1	above 150° at 1 mm Hg			
		Yield	E38	E99	V.I.
49	None	84%	43.3	3.36	101
56	Ligroin	80%	25.75	2.47	95.5
57	Decalin	80.5%	27.15	2.65	103
59a	Hydrogenated crack prdct, fr. 200-225	82.5%	34.6	2.92	99.5
60	Tri-isobutylene	74.3	34.0	2.94	101.5

TABLE VII
TYPE OF SOLVENT AND AMOUNT OF SOLVENT

61a	Cr/hydrogen. crack prdct., 200-225°, (1:5)	80	55.2	3.85	101
59a	"	82.5	42.4	3.32	100
62	"	80.5	25.0	2.50	101
63	"	69.5	19.8	2.24	100

(1) This is in agreement with observations of Dr. Hartmann & Dr. Rabe, Lab. Rep. 574, p.4.





Tables IX and IXA show the influence exerted by AlCl_3 , in amounts varying from 2 to 16%.

Most noticeable, above all, is the strong yield increase which occurs up to about 5% AlCl_3 (we are speaking of yields in oil boiling above 150° at 1 mm Hg); after that, no further increase takes place. The V.I. values also increase strongly, and then remain stationary after 3% AlCl_3 has been reached. It therefore appears that 5% AlCl_3 would be the optimum amount with respect to V.I. and yield. Larger amounts of AlCl_3 lead only to an increase in the viscosity of the oil, without improving either the yield or the viscosity index (Cf. also Lab. Rep. 574, p.5).

The reaction temperature does not influence the effect of the AlCl_3 concentration on the yield and on the V.I. However, a lower reaction temperature (See Table IXA) causes the oils to be more viscous (as already mentioned earlier); the viscosity of such oils can then be further increased by adding larger amounts of AlCl_3 .

Before the results of the polymerization experiments with pure olefins and cracked olefins, either alone or with aromatics, could be applied to a cracked olefin / Leuna coal hydrogenation oil, further comparative experiments were made with cracked olefin / tetralin. Coal hydrogenation oil contains rather large amounts of semi-hydrogenated hydro-aromatic compounds, and therefore tetralin was chosen since it is the simplest representative of this class of compounds.

Examples of polymerization of cracked olefins (or fractions thereof), with tetralin are given in Table X, in the weight ratio 1:1. It was our purpose to show the effect exerted by the length of the side chains and by their number, on the V.I. and the Sligh oxidation test. The method of polymerization was the following: In series I, cracked olefins or their fractions were mixed directly with the tetralin, and then polymerized with 5% AlCl_3 . After termination of the main reaction, the polymerization was carried further by heating the mixture to 60° for 12 hours. In comparative series II, the olefins were in each case subjected to a preliminary half hour polymerization at 60°C , and only then the tetralin was added with the rest of the 5% AlCl_3 (total = 5%); then again, after the main reaction had subsided, the mixture was heated to 60°C for twelve hours. The conversion of the tetralin was determined by fractionation of the first running oil, and included in the computations. In series I, the olefins immediately add themselves to the tetralin, so that relatively short side-chains are formed. The V.I. values of these oils are between -22 and -97, and again it is lower olefin fractions which show exceptionally poor V.I. values. Furthermore, the viscosity of this oil

TABLE X
TETRALIN - CRACKED OLEFIN MIXED POLYMERIZATION

Exp. No.	Pre-polymerization	AlCl ₃	Initial reagents		Total AlCl ₃	Oil above 150° at 1 mm Hg					Percentage of initial tetralin converted
			Main polymerization	AlCl ₃		Yield %	Egg	V.I.	Mol. Wt.	SOF	
CFT 11	-	-	1 part tetralin 1 part olefin >130°	5	5	77	1.39	97.5	344	13.5	75%
CFT 14	-	-	1 part tetralin 1 part olefin <50°	5	5	35	1.81	-22	383	11.1	99%
CT 7	-	-	1 part tetralin 1 part cracking-product	5	5	55	1.44	87	-	4.6	77%
CFT 12	1 part olefin >130°	2.5	1 part tetralin	2.5	5	60	3.4	115	819	27.7	57%
CFT 13	1 part olefin <80°	2.5	1 part tetralin	2.5	5	40	4.1	48.5	605	36	73%
CT 5	1 part crack olefin	2.5	1 part tetralin	2.5	5	47	2.85	104	-	9.6	50%

series is very low. In contrast to this, series II shows that, due to the preliminary polymerization, longer chains are formed at first, which then add themselves to the tetralin. The viscosity indices are between 50 and 115. As usual, the short chain olefins give the poorer V.I. values. However, due to the preliminary polymerization, these oils are considerably more viscous than those of series I.

The preliminary polymerization improves the viscosity index but at the same time it hampers the Sligh Oxidation Test; this is probably due to the fact that the original number of molecules has been reduced (by the preliminary polymerization), which means that the side-chains which are introduced into the tetralin molecule are longer but fewer. The number of side chains, in turn, determined the stability towards oxidation, in the sense that the Sligh Oxidation Test values decrease with increasing number of side chains (See p. 7).

							Sligh
							O. T.
Tetralin/crack.	olefin	fract.	up to 180°	prel. polym.	VI.=48.5	36	
"	"	"	above 130°	"	"	115	
"	"	"	up to 80°	not"	"	-22	
"	"	"	above 130°	"	"	497	
						13.5	

When the experimental results were to be applied to the system consisting of cracked olefins and coal hydrogenation oil (K-oil), the problem was to achieve the maximum possible V.I. value with the smallest possible Sligh Oxidation Test (S.O.T.) value, while maintaining a ratio of 1:1 between the cracked olefins and the K-oil. On the basis of our previous observations, the polymerization process had to be as follows: first, a portion of the olefins had to be subjected to preliminary polymerization (in order to get a high viscosity index), and secondly, a portion of the olefins which had not been pre-polymerized had to be added later, in order to get a low oxidation test.

See Table X, opposite.

In a preliminary experiment, the procedure was such that 2/3 of the cracked olefin were mixed with the coal hydrogenation oil and then polymerized with 4/5 of the required amount of AlCl₃. After a reaction period of 1 and 1/2 hours, the last third of the olefin and the remaining 1/5 of the AlCl₃ were added and the polymerization was brought to termination. The yield of oil boiling above 150° at 1 mm Hg was 68% of the theoretical; the viscosity index = 60, SOT = 0. It is seen that, although a very good SOT value was obtained with this procedure, the viscosity index is definitely insufficient, owing to the introduction of short side-chains.

In a further experiment, 90% of the olefins were pre-polymerized with 1/3 of the required amount of $AlCl_3$ (total 5%) for one half hour; then the K-oil was added together with another third of the $AlCl_3$, and for one half hour, the mixed polymerization reaction was allowed to take place; only then, the rest of the $AlCl_3$ was added, and the remaining 10% of the olefins were added very slowly. Afterwards, the mixture was agitated for four hours at $100^\circ C$. The oil yield (above $150^\circ/1$ mm Hg) was 78%; V.I. = 104, Egg = 2.0, and the SOT = 2.4.

By using this method, it is seen that the viscosity index has been raised from 60 to 104 by the pre-polymerization. Although the oxidation test value is somewhat worse, it is still sufficiently small and will not cause any disturbances in the automobile motor. Thus, it is possible to obtain, from a properly guided mixed polymerization of coal hydrogenation oil with cracked olefin, a good yield of a lubricating oil which in viscosity, viscosity index and oxidation test, corresponds to the normal commercial automobile oils.

Summary.

The lubricating oil fraction boiling above $150^\circ C$ at 1 mm Hg, and resulting from the polymerization of pure aliphatic olefins with $AlCl_3$ under the reaction conditions applied in our experiments, is of a quality which depends largely on the structure of the initial olefins. In order to define the quality of the oils, mostly the temperature-viscosity behaviour (V.I.) and the behaviour under artificial aging (Slight Oxidation Test) were used as comparative standards.

It could be shown that:

1. The best V.I. values were obtained with olefins with terminal double bond, i.e. with a terminal $-C=CH_2$ group. Of these, the olefins with long and non-branched chains gave the highest viscosity indices; shorter and branched chains led to a drop in the V.I. value.
2. Olefins whose double bond is not terminal give lesser V.I. values than the corresponding olefins of the terminal double bond type.
3. The stronger the branching of the olefins, the poorer will be the V.I.
4. All the olefin polymerization products which were prepared are very stable under conditions of artificial aging, and they do not form any asphaltic components after oxidation in the Slight test.

5. All the specific weights are very low (around .85), and they show only small differences among each other. From this it may be concluded that no aromatic or hydro-aromatic rings have formed.
6. The olefins prepared by the cracking of paraffins consist mostly of straight chain aliphatic olefins with terminal double bond. The results of the experiments made with the corresponding pure olefins can be applied to both the individual fractions as well as to the entire cracked olefins.
7. When pure aliphatic olefins were polymerized with aromatic or hydroaromatic hydrocarbons, or when the latter were polymerized with the halogen-hydrocarbons corresponding to the olefins, the relationships as to temperature-viscosity behaviour were found to be analogous to those of the pure olefin polymerization products.
8. However, the specific weights of these oils are higher than those of the pure olefin oils, in proportion to their aromatic content; i.e. above .9.
9. Furthermore, the oxidation behaviour of these oils is, generally, considerably worse than that of the pure olefin oils. It depends on the number of side chains which are introduced, and also on the ratio of olefin:naphthalin or tetralin.
10. The experimental results obtained with the polymerization of aromatic and hydroaromatic hydrocarbons with pure olefins can also be applied to the corresponding polymerization with cracked paraffin olefins. Here too, the best V.I. values were obtained when using the higher fractions which contained the longer chain olefins. When the entire cracking product was used, the short chain olefins contained in it could be converted into longer chain olefins by a preliminary polymerization process; only then was the cracking product brought in contact with tetralin. However, due to this pre-polymerization, there was a diminution in the number of olefin molecules, so that the improved V.I. value was obtained at the expense of a diminished and insufficient number of side chains; this in turn caused poor oxidation behaviour. This disadvantage could be eliminated by pre-polymerizing only 90% of the olefins; the remaining 10% were added after the mixed-polymerization proper. By this method, the oxidation test value could be decreased down to a tolerable value.

The experimental results obtained with the cracked olefin - tetralin system can be applied without difficulty to

the cracked olefin - coal hydrogenation oil system. Here too, the V.I. value could be improved by preliminary polymerization, and the oxidation test could be improved by a follow-up polymerization with fresh cracked olefin.

This research was carried out in the years between August, 1933 and January, 1936, along with other topics, by the group under Dr. Zorn.

SIGNED:

/HAAG/

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