

THE ALKYLATION OF ISOPARAFFINS WITH OLEFINS IN THE PRESENCE OF SULPHURIC ACID. PART I. THE COMPOSITION OF AN AVIATION ALKYLATE.*

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SUMMARY.

An aviation alkylate has been submitted to repeated precise fractionation and the physical constants of the fractions determined. Infra-red spectroscopic analysis of a number of the fractions has been used to determine the composition of the alkylate.

INTRODUCTION.

THE product of the reaction between *isobutane* and mixed butenes in the presence of sulphuric acid, commercially known as "alkylate" ¹ consists essentially of 2:2:4-, 2:3:3-, and 2:3:4-trimethylpentanes. The reaction product contains some *isopentane* and varying amounts of hexanes, heptanes, octanes, and nonanes of undetermined structure. Higher boiling *isoparaffins* are also formed and these are removed from the commercial product by fractionation, the fraction b.p. 130° C–180° C is termed "Alkylate bottoms." The relative amounts of the three trimethylpentanes, *isopentane* and the minor constituents (hexanes, heptanes, etc.) are to a large extent dependent upon the reaction conditions and upon the composition of the olefin charging stock. Various analyses given in the literature ^{2, 3} are confined to the principal constituents (*isopentane* and the three trimethylpentanes) and no accurate information has yet been given of the amounts and structure of the hexanes, heptanes, octanes, and nonanes which normally accompany the principal constituents.†

The present work was undertaken to provide information concerning the nature and amounts of the various minor components. The mechanism by which these compounds arise and the effect of operating variables upon the composition of alkylates will form the subject-matter of subsequent communications.

EXPERIMENTAL.

An aviation alkylate (T.D. 91) which contained somewhat larger amounts of the minor constituents than a normal alkylate was chosen for investigation. The sample was produced from an olefin feed stock containing butene-1, butene-2, and 2-methylpropene. Details of the operating

* Part I and Part II of this series were originally read at the meeting of the Trinidad Branch of the Institute of Petroleum, October, 1944. Advantage has been taken of the delay in publication to bring the discussion and literature references up to date.

† Recently the analysis of a number of alkylates, codimers, etc., has been reported by Rossini *et al.*, *Refiner*, 1946, 25, 93–119.

conditions, feed-stock analysis, and preliminary inspection data on the sample are given in Table I. To illustrate the relatively large proportion

TABLE I.

*Inspection Data—Aviation Alkylate, T.D. 91.**Charge analysis:*

Total unsaturates (% by gas volume)	38.5
<i>iso</i> Butylene	9.4
C ₃ —	4.9
C ₅ +	0.6

Plant operating conditions:

Contact time, min.	75
<i>iso</i> Butane/olefin ratio	5.0
Fresh acid strength, % H ₂ SO ₄	98.6
Temperature, °F.	56, 49, 46
Circulating acid strength, % H ₂ SO ₄ :	
Reactor I	95.9
" II	92.7
" III	90.9

A.S.T.M. analysis:

I.B.P.	28° C
F.B.P.	132° C
Octane number clear (M.M.)	92.1

T.B.P. analysis, vol %:

C ₄ + <i>isopentane</i>	9.5
32°–97° C	15.5
2 : 2 : 4-Trimethylpentane	27.5
100°–112° C	17.0
2 : 3 : 4-, 2 : 3 : 3-Trimethylpentane	23.0
117°–130° C	7.5

of minor constituents in this sample (T.D. 91) the refractive index curve (n_D^{30}) of the sample is compared with the refractive index curve of a typical alkylate (T.D. 92) (Fig. 1).

A drum sample (163 litres) of T.D. 91 was subjected to batch fractionation in 4 feet of Stedman column, 25 mm in diameter, operated under adiabatic conditions.* The fractionation details are given in tabular form in the Appendix. The first series of distillations divided the charge into five cuts, the progress of the distillation being followed by both boiling point and refractive index change. No special precautions were taken to ensure constant pressure distillation nor are any of the boiling points corrected. Cut points were determined from a consideration of changes in refractive index.

The first five cuts were then redistilled at a higher reflux ratio and split into twenty-eight fractions which were subsequently re-blended into fifteen fractions. This process was repeated for a third series of fractionations resulting in forty blended fractions. At this stage certain of the fractions were becoming too small to handle in the 25-mm columns and, where necessary, a change to 4 feet Stedman columns $\frac{3}{8}$ inch in diameter was made. Series IV operation resulted in thirty-four blended samples, five of which were almost pure 2 : 2 : 4-trimethylpentane. In the fifth and sixth series it was not considered advisable (owing to the long time required for a distillation at the low throughputs and high reflux ratios required)

* Full details of the columns used have been given in a previous communication. *J. Inst. Petrol.*, 1943, **29**, 55–74.)

to distil the whole of a blend from the previous series. However, the material balance throughout has been computed as though the series had been carried to completion. Series V resulted in seventy-five samples, some of which were subjected to a sixth series of fractionation.

After every distillation the losses were carefully apportioned according to the boiling points of the various cuts. The losses during distillation were usually small (of the order of 1 per cent. or less) and their distribution was only complicated in the first two series. In the later series the boiling ranges were so small that losses were apportioned equally. However, in handling and blending and in analysis the losses were higher since most

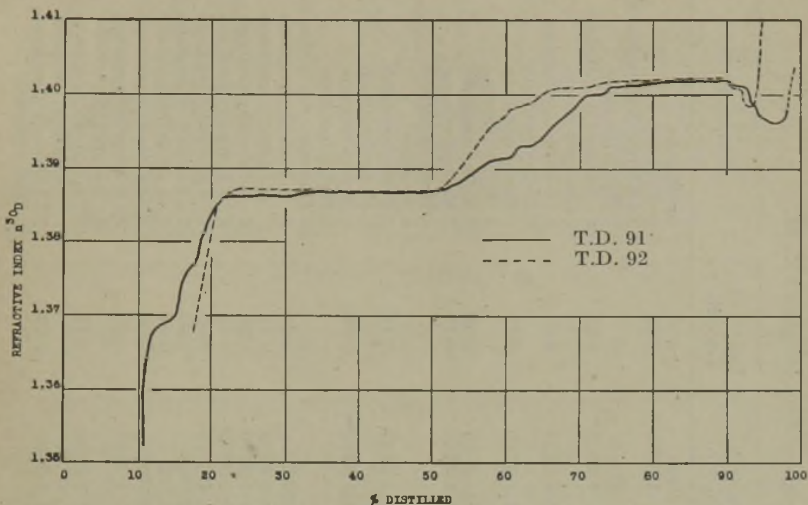


FIG. 1.

COMPARISON OF REFRACTIVE INDEX CURVES FOR TWO ALKYLATES.

samples were collected as 10-ml cuts; 0.4 ml was used for refractive index, 0.3 ml remained in the sample bottle and about 0.3 ml was lost in the receiver, in transference, and in evaporation, etc. Thus each series resulted in a loss of about 10 per cent of the material charged. These losses were apportioned systematically and the data in Table II, in Fig. 7, and in the Appendix have been corrected for losses throughout. The technique described above, although giving a quantitative knowledge of the composition of this alkylate, has little applicability as a routine method in the investigation of the alkylation reaction since it would not be feasible to apply so detailed an analysis to a series of samples drawn under different operating conditions.

RESULTS.

The final distillation resulted in a series of seventy-five fractions, five of which were pure 2:2:4-trimethylpentane. The physical constants, analysis, and relevant data concerning these fractions are given in Table II,

TABLE II
Analytical Data, Alkylate T.D. 91.

Fraction no.	Distillation series no.	Boiling range, °C.	Refractive index, n_D^{20} .	Vol % of T.D. 91.	Component.	Vol % of fraction.	Vol % of T.D. 91.
221	IV	28	<1.3500	8.81	<i>iso</i> Pentane	100	8.81
222	IV	58-59	1.3690-1.3699	3.46	<i>iso</i> Pentane	4.9	0.17
					2:3-Dimethylbutane	85.0	2.94
108	V	59-60	1.3680-1.3667	0.21	2-Methylpentane	10.1	0.35
109	V	60-60.5	1.3667-1.3667	0.09	2:3-Dimethylbutane	3.8	0.08
					2-Methylpentane	62	0.13
110	V	60.5-63.2	1.3667-1.3710	0.17	2:3-Dimethylbutane	12.0	0.01
					2-Methylpentane	88.0	0.08
111	V	63.2-63.4	1.3710-1.3710	0.06	2-Methylpentane	53.0	0.09
112	V	63.4	1.3710-1.3715	0.19	3-Methylpentane	47.0	0.08
					2-Methylpentane	100	0.06
155	V	63.0-63.0	1.3700-1.3702	0.13	2-Methylpentane	10.0	0.02
156	V	63.0-64.0	1.3708-1.3715	0.51	3-Methylpentane	85.0	0.16
					<i>n</i> -Hexane	5.0	0.01
276	V	<78.0	1.3764	0.01	2:4-Dimethylpentane	2.0	0.01
277	V	78.8-79.0	1.3768-1.3769	0.11	2:4-Dimethylpentane	100	0.01
278	V	79.5-80.0	1.3770-1.3770	1.95	2:4-Dimethylpentane	100	1.95
279	V	80.0-80.0	1.3772-1.3772	0.19	2:4-Dimethylpentane	100	0.19
280	V	80.0-80.0	1.3773-1.3778	0.05	2:4-Dimethylpentane	100	0.05
280R	V	80.0	1.3790	0.07	2:4-Dimethylpentane	100	0.07
121	V	80.0-80.0	1.3773	0.01	2:4-Dimethylpentane	100	0.01
122	V	80.0	1.3770	0.34	2:4-Dimethylpentane	100	0.34
137	V	81.0-81.0	1.3772-1.3780	0.20	2:4-Dimethylpentane	75.0	0.15
138	V	81.0-90	1.3792-1.3860	0.47	2:3-Dimethylpentane	25.0	0.05
139	V	88.0-89.5	1.3852-1.3860	0.75	2:3-Dimethylpentane	15.0	0.07
					2:4-Dimethylpentane	85.0	0.40
					2:3-Dimethylpentane	80.0	0.60
					2-Methylhexane	20.0	0.15

140	V	89.5	1-3854-1-3850	0.25	2:3-Dimethylpentane	20.0	0.05
151	V	90.0	1-3857-1-3858	0.06	3-Methylhexane	80.0	0.20
152	V	90.0-92.0	1-3856-1-3841	0.01	2:3-Dimethylpentane	66.6	0.04
160	V	88.0-90.0	1-3857-1-3858	0.07	3-Methylhexane	33.3	0.02
161	V	90.0-97.0	1-3856-1-3845	0.13	2:3-Dimethylpentane	20.0	0.02
162	V	97.0-99.0	1-3868-1-3870	33.45	3-Methylhexane	80.0	0.08
36	III	98.0-100.0	1-3870-1-3870		3-Methylhexane	43.0	0.03
45	III	99.0-100.0	1-3870-1-3870		2:2:4-Trimethylpentane	57.0	0.04
63	III	98.0-100.0	1-3870-1-3870		2:3-Dimethylpentane	7.7	0.01
117	IV	100.0	1-3868-1-3889		3-Methylhexane	77.0	0.10
127	IV	98-100	1-3862-1-3868	33.45	2:2:4-Trimethylpentane	15.3	0.02
164	V	95-104	1-3809-1-3868				
271	V	98-107	1-3871-1-3890		2:2:4-Trimethylpentane	100	
272	V	108-108.4	1-3891-1-3892				
165	V	104-109	1-3878-1-3902	0.24	2:2:4-Trimethylpentane	83.3	0.20
273	V	108.5-109	1-3897-1-3902	0.62	2:5-Dimethylhexane	16.7	0.04
286	V	109-109	1-3902-1-3906	0.62	2:2:4-Trimethylpentane	48.5	0.30
176	V	107-109.7	1-3900-1-3910	0.58	2:5-Dimethylhexane	51.5	0.32
274	V	109-109.2	1-3906-1-3909	0.23	2:2:4-Trimethylpentane	35.4	0.22
281	V	107-108.1	1-3903-1-3911	0.21	2:5-Dimethylhexane	48.4	0.30
285	V	109-109	1-3909-1-3909	0.16	2:4-Dimethylhexane	32.2	0.20
287	V	109-109.2	1-3903-1-3911	1.09	2:2:4-Trimethylpentane	16.8	0.06
					2:5-Dimethylhexane	27.8	0.10
					2:4-Dimethylhexane	55.6	0.20
					2:5-Dimethylhexane	31.0	0.60
					2:4-Dimethylhexane	69.0	1.35
					2:5-Dimethylhexane	47.0	0.29
					2:4-Dimethylhexane	53.0	0.33
					2:5-Dimethylhexane	40.0	0.23
					2:4-Dimethylhexane	60.0	0.35
					2:5-Dimethylhexane	13.0	0.03
					2:4-Dimethylhexane	87.0	0.20
					2:4-Dimethylhexane	100.0	0.21
					2:4-Dimethylhexane	100	0.16
					2:4-Dimethylhexane	100	1.09

TABLE II (contd.),
Analytical Data, Alkylate T. D. 91.

Fraction no.	Distillation series no.	Boiling range, °C.	Refractive index, n_D^{20} .	Vol % of T. D. 91.	Component.	Vol % of fraction.	Vol % of T. D. 91.
282	V	108.9-108.9	1.3911-1.3913	1.59	2: 4-Dimethylhexane	100	1.59
177	V	109.7	1.3914-1.3920	0.10	2: 4-Dimethylhexane	90.0	0.09
288	V	109.2-109.4	1.3912-1.3930	0.65	2: 2: 3-Trimethylpentane	10.0	0.01
283	V	108.9-108.9	1.3915-1.3931	1.38	2: 4-Dimethylhexane	91.0	0.60
					2: 2: 3-Trimethylpentane	9.0	0.06
					2: 2: 3-Trimethylpentane	87.6	1.21
					2: 2: 3-Trimethylpentane	8.0	0.11
247	V	104.5-108.5	1.3939-1.3925	0.09	2: 3: 4-Trimethylpentane	4.4	0.06
					2: 4-Dimethylhexane	78.0	0.07
275	V	Residue	1.3948	0.47	2: 2: 3-Trimethylpentane	11.0	0.01
					2: 3: 4-Trimethylpentane	11.0	0.01
248	V	108.8-108.9	1.3923-1.3921	0.51	2: 4-Dimethylhexane	66.0	0.31
					2: 2: 3-Trimethylpentane	19.0	0.09
					2: 3: 4-Trimethylpentane	15.0	0.07
249	V	108.9-113.0	1.3933-1.3999	0.75	2: 4-Dimethylhexane	88.0	0.45
					2: 2: 3-Trimethylpentane	6.0	0.03
					2: 3: 4-Trimethylpentane	6.0	0.03
289	V	109.4	1.3979	0.19	2: 4-Dimethylhexane	20.0	0.15
284	V	109.0	1.3990	0.35	2: 2: 3-Trimethylpentane	56.0	0.42
252	V	111.0-113.0	1.3990-1.3999	1.11	2: 2: 3-Trimethylpentane	24.0	0.18
253	V	113.0-113.0	1.4000-1.4001	2.83	2: 2: 3-Trimethylpentane	100.0	0.19
					2: 2: 3-Trimethylpentane	14.0	0.05
					2: 3: 4-Trimethylpentane	86.0	0.30
					2: 2: 3-Trimethylpentane	28.0	0.31
					2: 3: 4-Trimethylpentane	72.0	0.82
					2: 3: 4-Trimethylpentane	84.0	2.38
250	V	113.0-113.0	1.3999-1.4000	0.24	2: 3: 3-Trimethylpentane	15.0	0.42
					2: 3-Dimethylhexane	1.0	0.03
					2: 3: 4-Trimethylpentane	79.0	0.19
254	V	113.0-114.0	1.4001-1.4020	3.49	2: 3: 3-Trimethylpentane	17.0	0.04
					2: 3-Dimethylhexane	4.0	0.01
					2: 3: 4-Trimethylpentane	49.0	1.70
					2: 3: 3-Trimethylpentane	49.0	1.70
					2: 3-Dimethylhexane	2.0	0.09

256	V	113.0-113.6	1.4012	—	2:3:4-Trimethylpentane	53.5	0.30
257	V	113.6-114.0	1.4010-1.4013	9.59	2:3:3-Trimethylpentane	46.5	0.26
258	V	114.0-114.0	1.4015-1.4017	2.23	2:3:4-Trimethylpentane	50.1	4.80
258R	V	114.0	1.4012 1.4018	1.53	2:3:4-Trimethylpentane	79.0	4.79
259	V	114.0-115.0	1.4022-1.4022	0.37	2:3:3-Trimethylpentane	21.0	0.47
260	V	115.0-115.0	1.4022-1.4018	2.42	2:3:3-Trimethylpentane	78.5	1.20
261	V	Residue	1.4019	0.12	2:3:3-Trimethylpentane	15.0	0.23
261	V	115.0-115.0	1.4015-1.4009	0.94	2:3:3-Trimethylpentane	6.5	0.10
262	V	115.0-Residue	1.4000	0.37	2:3:3-Trimethylpentane	90.0	0.33
196	V	114.0-116.5	1.4000-1.3978	0.93	2:3:3-Trimethylpentane	10.0	0.04
197	V	116.5-117.5	1.3977-1.3968	0.86	2:3:3-Trimethylpentane	87.0	2.10
263	V	120-122	1.3980-1.3970	0.16	2:3:3-Trimethylpentane	13.0	0.32
264	V	122.0-122.0	1.3962-1.3962	0.16	2:3:3-Trimethylpentane	100.0	0.12
290	V	122.0-123.0	1.3961-1.3956	0.33	2:3:3-Trimethylpentane	80.0	0.75
291	V	123.0-123.0	1.3955-1.3955	0.57	2:3:3-Trimethylpentane	20.0	0.19
292	V	123.0-123.3	1.3952-1.3951	2.89	2:3:3-Trimethylpentane	100	0.37
268	V	123.3-123.9	1.3952-1.3952	0.41	2:3:3-Trimethylpentane	37.7	0.35
265	V	122.0-124.0	1.3962-1.3955	0.10	2:3:3-Trimethylpentane	45.2	0.42
266	V	124.0-124.0	1.3955-1.3955	0.45	2:3:3-Trimethylpentane	1.0	0.01
					3:4-Dimethylhexane	10.1	0.15
					4-Methylheptane	5.7	0.05
					3:4-Dimethylhexane	59.4	0.51
					3-Methylheptane	25.6	0.22
					2:2:5-Trimethylhexane	9.3	0.03
					3:4-Dimethylhexane	37.5	0.06
					3-Methylheptane	18.8	0.03
					2:2:5-Trimethylhexane	43.7	0.07
					3:4-Dimethylhexane	25.0	0.04
					3-Methylheptane	12.5	0.02
					2:2:5-Trimethylhexane	62.5	0.10
					3:4-Dimethylhexane	9.0	0.03
					3-Methylheptane	3.0	0.01
					2:2:5-Trimethylhexane	88.0	0.29
					2:2:5-Trimethylhexane	100	0.57
					2:2:5-Trimethylhexane	100	2.89
					2:2:5-Trimethylhexane	100	0.41
					2:2:5-Trimethylhexane	80	0.08
					2:2:5-Trimethylhexane	20	0.02
					2:2:5-Trimethylhexane	78	0.35
					2:2:5-Trimethylhexane	22	0.10

TABLE III.

Composition of Aviation Alkylate T.D. 91.

Hydrocarbon.	Vol % on alkylate.
2 : 2 : 4-Trimethylpentane	34.29
2 : 3 : 4-Trimethylpentane	14.11
2 : 3 : 3-Trimethylpentane	11.27
<i>iso</i> Pentane	8.98
2 : 4-Dimethylhexane	8.56
2 : 2 : 5-Trimethylhexane	4.84
2 : 3-Dimethylbutane	3.03
2 : 4-Dimethylpentane	2.96
2 : 5-Dimethylhexane	1.81
2 : 3-Dimethylhexane	1.53
2 : 2 : 3-Trimethylpentane	1.27
2 : 3-Dimethylpentane	1.16
3-Methylpentane	0.82
3 : 4-Dimethylhexane	0.79
2-Methylpentane	0.78
3-Methylhexane	0.41
3-Methylheptane	0.28
2-Methylhexane	0.17
4-Methylhexane	0.06
Normal hexane	0.02
2 : 3 : 5-Dimethylhexane	2.0
Remainder	0.86

Not found: *n*-Pentane, 2 : 2-dimethylbutane, 2 : 2-dimethylpentane, 2 : 2 : 3-trimethylbutane, 3 : 3-dimethylpentane, 3-ethylpentane, *n*-heptane, 2 : 2-dimethylhexane, 2 : 2 : 3 : 3-tetramethylbutane, 3 : 3-dimethylhexane, 2-methyl-3-ethylpentane, 2-methylheptane, 3-methyl-3-ethylpentane, 3-ethylhexane, 2 : 2 : 4 : 4-tetramethylpentane, *n*-octane, 2 : 2 : 4-trimethylhexane.

whilst Table III summarizes the final analytical figures. The Series V and VI distillations may be followed in the Figs. 2, 3, 4, 5, and 6, which show the refractive index, volume, and uncorrected boiling point relationships of the final fractions, with the exception of the bulk fractions containing 2 : 2 : 4-, 2 : 3 : 4-, and 2 : 3 : 3-trimethylpentanes.

The analysis of the final fractions was originally made on the basis of the physical constants (n_D^{30} , d_4^{30} , b.p., etc). However, during the course of the work, opportunity was taken to submit a number of Series IV and V fractions to Dr H. W. Thompson for analysis by infra-red spectroscopic methods. These results were then used to amplify and correct where necessary analyses made on the basis of physical constants. The derivation of the analytical results given in Table II is outlined in the following paragraphs.

*iso*Pentane.

Fraction 221, a blend of fractions 8 (Series II) and 98 (Series IV) (b.p. 28° C; $n_D^{30} > 1.3500$) was analysed by low temperature fractionation using a Podbielniak heligrid column. *n*-Pentane was not detected.

Hexane Fractions, b.p. 55° C–64° C (Fig. 2).

Eleven fractions were obtained in this boiling range, the refractive index, volume, and uncorrected boiling point relationships of which are shown in Fig. 2. In Table II the material boiling between 58° and 59° C is

shown as the bulk fraction 222 (IV), whilst in Fig. 2 the physical properties of the constituent fractions 99 (IV), 102 (IV), 10 (II), and 100 (IV) are given. Fractions 99 and 102 both contain traces of *isopentane*, but are essentially 2:3-dimethylpentane. Fraction 10 was analysed spectroscopically and contained 88 per cent 2:3-dimethylbutane and 12 per cent 2-methylpentane. The high refractive index of fraction 100 indicates the presence of traces of 3-methylpentane.

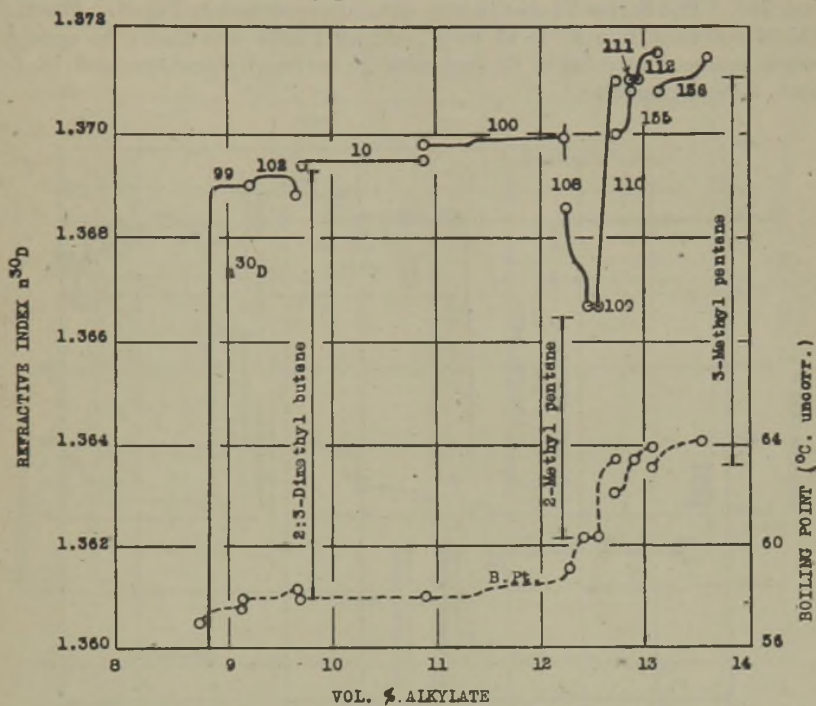


FIG. 2.

REFRACTIVE INDEX-BOILING POINT DATA, ISOMERIC HEXANE FRACTIONS.

The fall in refractive index of fraction 108 marks the appearance of 2-methylpentane. Spectroscopic analysis of fraction 109 showed 88 per cent of 2-methylpentane and 12 per cent 2:3-dimethylbutane.

Fractions 110, 155, 111, 112, and 156 contain 3-methylpentane, with small amounts of 2-methylpentane. Fractions 112 and 156 are of particular interest in that the physical constants of the fractions indicate the presence of *n*-hexane. Spectroscopic analysis of fraction 156 showed that the sample contained 2.0 per cent of *n*-hexane.

Heptane Fractions, 78° C-97° C (Fig. 3).

The isolation of 2:4-dimethylpentane from the fractions boiling between 78° and 82° C presented little difficulty. As noted above, *n*-hexane was virtually absent and no trace of 2:2-dimethylpentane was found in spectroscopic analysis. Likewise, 2:2:4-trimethylbutane and 3:3-di-

methylpentane were shown to be absent. Consequently the 2 : 4-dimethylpentane had only to be separated from 3-methylpentane boiling 17.5° lower and 2 : 3-dimethylpentane boiling 7.5° higher. Spectroscopic analysis of fraction 122 gave 100 per cent 2 : 4-dimethylpentane.

2:3-Dimethylpentane is present in fraction 137, and is the main constituent of fractions 138 and 139. These fractions were blended to give sample 243 and refractionated (Series VI) to yield fractions 244, 245, and 246. The Series VI distillation data are recorded in Fig. 3. Fraction 245 of constant b.p. 89.0° to 89.5°, and n_D^{20} 1.3859 was shown by spectroscopic analysis to contain 82 per cent 2:3-dimethylpentane and 18 per cent 2-methylhexane.

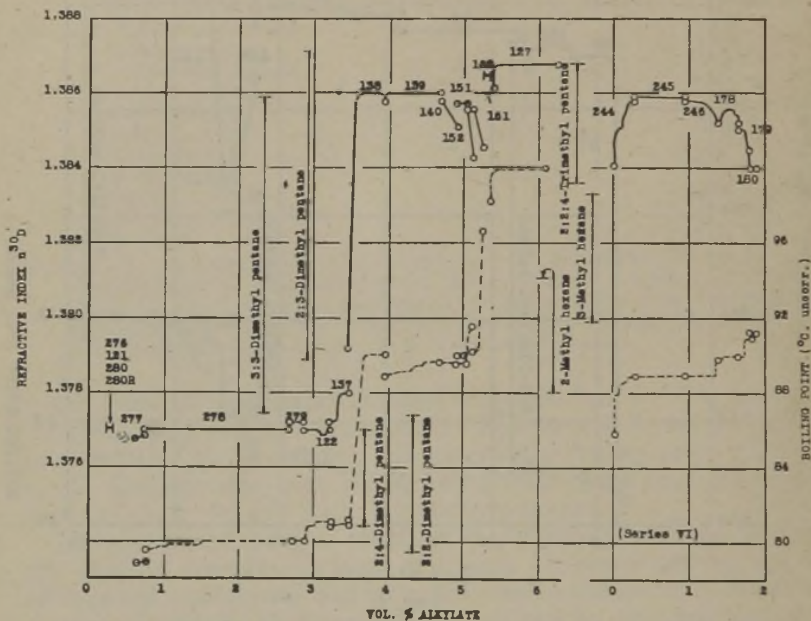


FIG. 3.

Fractions 140, 152, and 161 all show the presence of small amounts of 3-methylhexane. These fractions were blended (Sample 163, Series VI) and refractionated in Series VI to yield fractions 178, 179, and 180. The Series VI distillation data are given in Fig. 3 and show the increasing amount of 3-methylhexane in the fractions. Fraction 180 was examined spectroscopically and found to contain 98 per cent of 3-methylhexane and possibly 2 per cent of 2:3-dimethylpentane. The identification of the latter hydrocarbon in such small amounts is not absolute. Fractionation in this region was extremely difficult.

Octane Fractions, b.p. 98° C–116° C (Figs. 4 and 5).

The first fractions in this boiling range were 2:2:4-trimethylpentane (b.p. 99.2° C) and some 30 per cent of the total alkylate was finally isolated

(in five fractions) as material which was shown by spectroscopic analysis to be 100 per cent 2:2:4-trimethylpentane. Distillation data for two of these samples (127, 117) are given in Fig. 3.

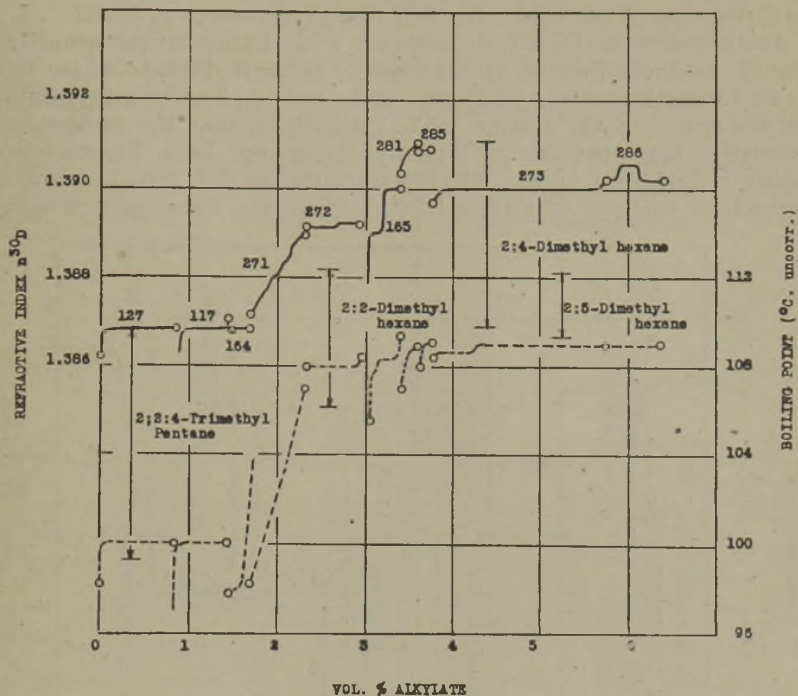


FIG. 4.

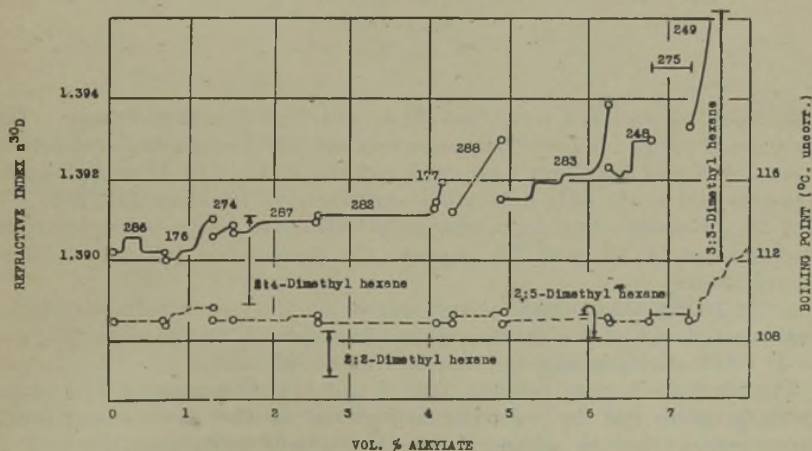


FIG. 5.

Fractionation of the material boiling between 108° and 110° C proved extremely difficult. Spectroscopic analysis of Series IV Sample 210 showed the presence of 2:4-dimethylhexane 42 per cent, 2:5-dimethylhexane 44 per cent, 2:2:3-trimethylpentane 10 per cent and 2:3:4-trimethylpentane 4 per cent. No 2:2-dimethylhexane was found.

Analysis of Series IV Sample 209 gave 2:2:4-trimethylpentane 13 per cent, 2:4-dimethylhexane 31 per cent, 2:5-dimethylhexane 52 per cent, 2:2:3-trimethylpentane 2.2 per cent and 2:3:4-trimethylpentane 1.8 per cent. In the absence of 2:2-dimethylhexane* the problem was essentially the separation of 2:5-dimethylhexane from 2:4-dimethylhexane boiling 0.8° C apart. The first fractions 164, 271, and 272 contained appreciable amounts of 2:2:4-trimethylpentane. Subsequent fractions

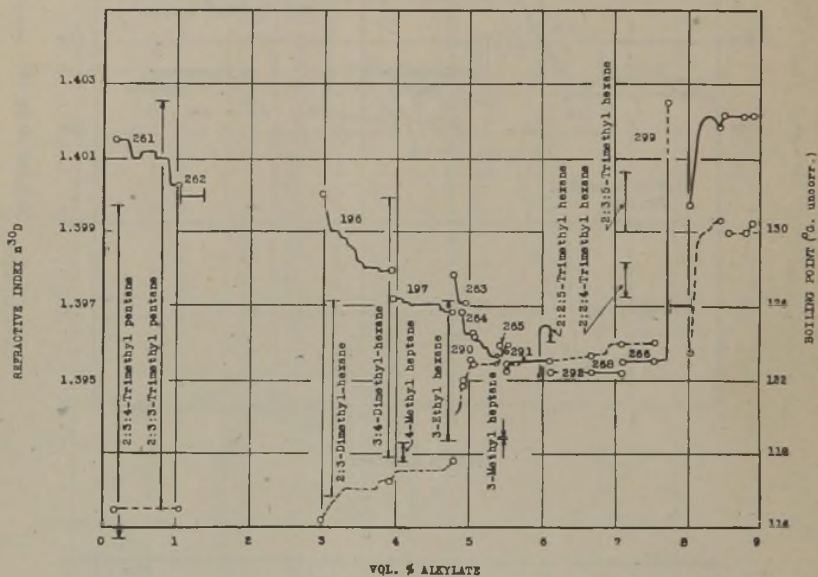


FIG. 6.

165, 273, 286, and 176 contained 2:4- and 2:5-dimethylhexanes. The isolation of pure 2:5-dimethylhexane was not possible although refractionation of fraction 271 might have achieved this end. 2:4-Dimethylhexane was obtained as the only detectable constituent of fractions 281, 285, 287, and 282, although the slight change of refractive index throughout the fractionation of 281 and 285 suggests the presence of traces of 2:5-dimethylhexane.

2:2:3-Trimethylpentane is responsible for the rise in refractive index towards the end of the fractionation of samples 177, 288, and 283, and 2:3:4-trimethylpentane first appears in sample 283.

The fractions boiling between 110° C and 115° C contained 2:3:4-trimethylpentane and 2:3:3-trimethylpentane as the main constituents. Spectroscopic analysis of the Series IV fractions containing the bulk of this boiling range gave the following figures:

that fractions 291, 292, and 268 are recorded as 100 per cent 2:2:5-trimethylhexane.

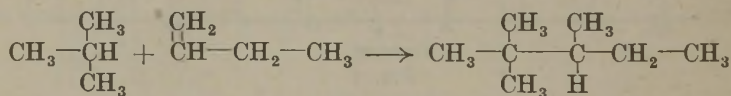
2:3:5-Trimethyl hexane was shown to be the principal constituent of fraction 188 (Series IV) and appears in fractions 265 and 266.

After the plateau (Fig. 6) corresponding to 2:2:5-trimethylhexane there is a sharp break in physical properties arguing the absence of *n*-octane and 2:2:4-trimethylhexane and confirming the spectroscopic data.

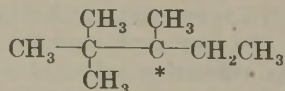
DISCUSSION.

Alkylates produced from feed stocks free from *isobutylene* under satisfactory operating conditions ¹ (high paraffin-olefin ratio, short contact time, high discard acid strength, etc) normally contain over 90 per cent of the three trimethylpentanes and *isopentane* (the major constituents). The large amounts of minor components in the sample under discussion may be ascribed to the presence of *isobutylene* in the feed stock and to a lesser extent to the rather long contact time and high reaction temperatures. The exact mechanism by which these factors affect the composition of the product is uncertain and discussion of this subject will be reserved for subsequent communications in this series.

There are a number of interesting points arising from a study of Table III. The three trimethylpentanes account for 59 per cent of the alkylate so that even under unsatisfactory conditions the formation of these hydrocarbons constitutes the major reaction. The presence of a 2:4-dimethylhexane in quantity equal to the amount of *isopentane* suggests that this hydrocarbon should be included among the "principal constituents." The presence of 2:2:3-trimethylpentane (1.27 per cent) is of considerable theoretical interest. This hydrocarbon should be the main product of the reaction according to the original classical reaction mechanism proposed by Ipatieff and Grosse.⁴



These authors suggested that isomerization of this product might account for the nature of the observed reaction products. More recently, Ciapetta ⁵ has proposed a reaction mechanism which would lead to the formation of a carbonium ion of this same structure, *i.e.* :



which according to the postulates of the carbonium ion theory would then rearrange. Birch and Dunstan ² have shown, however, that 2:2:3-trimethylpentane is less readily attacked by H_2SO_4 (98 per cent) than is 2:2:4-trimethylpentane and could not therefore be a precursor of 2:2:4-trimethylpentane.

With the exception of the small amounts of 2:2:3-trimethylpentane and 2:2:5-trimethylheptane the only hydrocarbon formed which contains the 2:2-dimethyl structure is the main component 2:2:4-trimethyl-

pentane. Assuming that the bulk of the hydrocarbons is formed in the first instance by a reaction involving isobutane and the olefin it follows that the subsequent breakdown or rearrangement involves a cleavage of the structure in the isobutane fragment. Ballard, McAllister, etc.,³ and Caesar and Francis⁶ have suggested that this cleavage actually takes place before the reaction with the olefin and that the so-formed fragments add to the double bond.

In view of the relative stability of isobutane to sulphuric acid this mechanism is unlikely. The results given in Table III, however, support the view that the overall reaction involves a cleavage of a carbon-carbon bond at the tertiary carbon atom at some stage during the reaction, with subsequent migration of the methyl group. The occurrence of hexanes, heptanes, and nonanes suggest that this may involve both inter- and intra-molecular migration.

The presence of traces of *n*-hexane is surprising. Although the evidence for this is satisfactory no trace of any other normal paraffin could be found. A particular search was made for *n*-pentane without success; *n*-heptane and *n*-octane were also shown to be absent.

The work reported herein illustrates the difficulties of analysis of a complex hydrocarbon mixture by fractionation technique. The recent advances in spectroscopic analysis⁷ and the development of the mass spectrometer⁸ will considerably simplify analyses of this nature.

ACKNOWLEDGMENTS.

Grateful acknowledgment is made to Dr H. W. Thompson for kindly undertaking the infra-red spectroscopic analyses of the samples, and to Messrs Trinidad Leaseholds Ltd. for permission to publish work carried out in the company's research laboratories.

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- ⁷ "The Application of Infra-Red Spectroscopy to Chemical Problems." General discussion held by the Faraday Society, Jan. 1945. *Trans. Faraday Soc.*, 1945, **41**, 171-297; cf. also Sweeney, W. J. *Industr. Engng Chem. Anal.*, 1944, **16**, 723-727.
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APPENDIX

Fractionation of Alkylate—T.D. 91.

SERIES I.

Fractionation on 4 feet of 25-mm Stedman packing at a reflux ratio of $7\frac{1}{2}$: 1.

Original material.	Fraction.	n_D^{30} range.	Volume, ml.	% on T.D. 91.
1	—	—	163,813	100.00
	2	1.3540–1.3863	42,078	25.7
	3	1.3864–1.3870	29,281	17.9
	4	1.3871–1.3990	46,577	28.4
	5	1.3991–1.4020–1.4000	30,479	18.6
	6	1.3999–1.3940	15,398	9.4

SERIES II.

Fractionation on 4 feet of Stedman packing at a reflux ratio of 34 : 1.

Original material.	Fraction.	n_D^{30} range.	Volume, ml.	% on T.D. 91.
2	8	—	6,479	—
	9	1.3485–1.3693	11,868	—
	10	1.3694–1.3695	2,019	—
	11	1.3695–1.3770	4,668	—
	12	1.3771–1.3778	459	—
	13	1.3779–1.3869	5,463	—
	14	1.3870–1.3870	9,540	—
	15	1.3871–1.3890	1,582	—
3	16	1.3645–1.3869	4,813	—
	17	1.3870–1.3870	23,135	—
	18	1.3871–1.3890	1,333	—
4	19	1.3862–1.3869	1,922	—
	20	1.3870–1.3870	11,509	—
	21	1.3871–1.3919	11,399	—
	22	1.3920–1.3990	8,028	—
	23	1.3990–1.4019	8,304	—
	24	1.4020–1.4020	3,574	—
	25	1.4000–1.4050	1,841	—
5	26 ¹	1.3940–1.3995	6,235	—
	27 ¹	1.3996–1.4002	2,767	—
	28 ¹	1.4003–1.4019	10,039	—
	29 ¹	1.4020–1.4020	7,566	—
	30	1.4019–1.3970	2,615	—
6	31	1.3970–1.4023	1,257	—
	32	1.3970–1.4000	243	—
	33	1.4000–1.3956	4,064	—
	34	1.3955–1.3952	6,440	—
	35	1.3953–1.4018	4,651	—

SERIES IIa.

Fractionation on 4 feet of 25-mm Stedman packing at a reflux ratio of 34 : 1.

Original material.	Fraction.	n_D^{30} range.	Volume, ml.	% on T.D. 91.
23	26 ²	1.3940-1.3995	1,192	—
	27 ²	1.3996-1.4002	1,082	—
	28 ²	1.4003-1.4019	4,236	—
	29 ²	1.4020-1.4020	1,794	—

Blend of Series II and IIa Cuts.

26 ¹ + 26 ² =	26	—	7,426	—
27 ¹ + 27 ² =	27	—	3,849	—
28 ¹ + 28 ² =	28	—	14,275	—
29 ¹ + 29 ² =	29	—	9,361	—

Blend of Series II.

Original material.	Fraction.	Boiling range, °C.	n_D^{30} range.	Volume, ml.	% on T.D. 91.
	8	I.B.P.-28	—	6,479	3.95
	9	I.B.P.-58	1.3485-1.3693	11,868	7.24
	10	58-59	1.3694-1.3695	2,019	1.23
	11	59-80	1.3696-1.3770	4,668	2.85
	12	80-81	1.3771-1.3778	459	0.28
13 + 16 + 19 =	42	81-100	1.3645-1.3869	12,198	7.45
14 + 17 + 20 =	36	98-100	1.3870-1.3870	44,184	26.97
15 + 18 + 21 =	37	99-99	1.3871-1.3919	14,314	8.74
22 + 26 + 32 =	38	110-114	1.3920-1.4000	15,697	9.58
27 =	39	113-114	1.3996-1.4002	3,849	2.35
28 =	40	114-115	1.4003-1.4019	14,275	8.71
24 + 29 =	41	115-115	1.4020-1.4020	12,935	7.90
30 + 33 =	43	115-124	1.4000-1.3970	6,679	4.08
	34	124-125	1.3955-1.3952	6,440	3.93
25 + 31 + 35 =	44	115-140	1.3953-1.3950	7,749	4.73

SERIES III.

Original material.	Fraction.	Boiling range, °C.	n_D^{30} range.	Volume, ml.	% on T.D. 91.
9	70	25-57	1.3680	8,564	—
	71	55-61	1.3681-1.3697	2,450	—
	72	61....	1.3697	854	—
11	73	55-62	1.3680-1.3699	1,554	—
	74	61-80	1.3700-1.3769	651	—
	75	80-81	1.3770-1.3770	1,968	—
	76	81....	1.3771-1.3800	495	—
42	60	(70)-84	1.3630-1.3799	1,597	—
	61	83-93	1.3800-1.3859	2,723	—
	62	91-99	1.3860-1.3869	1,922	—
	63	98-100	1.3870-1.3870	5,551	—
	64	100....	1.3871-1.3916	405	—

SERIES III (*contd.*).

Original material.	Fraction.	Boiling range, °C.	n_D^{30} range.	Volume, ml.	% on T.D. 91.
37	45	99-100	1.3870-1.3870	2,505	—
	46	100-108	1.3871-1.3899	1,547	—
	47	107-110	1.3900-1.3903	3,119	—
	48 ¹	109-110	1.3904-1.3909	2,695	—
	49 ¹	109-110	1.3910-1.3910	1,400	—
	50	109-110	1.3911-1.3990	2,378	—
	51	110....	1.3991-1.4012	670	—
38	48 ²	107-110	1.3904-1.3909	153	—
	49 ²	107-110	1.3910-1.3910	1,590	—
	52	108-110	1.3911-1.3922	3,275	—
	53	109-114	1.3923-1.3995	4,971	—
	54 ¹	112-114	1.3996-1.4002	1,148	—
	55	113-115	1.4003-1.4020	4,080	—
	56	115....	1.4008-1.4025	480	—
39	84	109-113	1.3958-1.3995	1,266	—
	85	112-113	1.3996-1.4002	464	—
	86	112-114	1.4003-1.4019	1,739	—
	87	113-114	1.4020-1.4020	207	—
	88	114....	1.4021-1.4040	173	—
40	54 ²	110-114	1.3991-1.4002	2,395	—
	57	113-115	1.4003-1.4019	7,480	—
	58	114-115	1.4020-1.4020	3,605	—
	59	116....	1.4018-1.4023	795	—
41 $\frac{1}{2}$ of charge	89	113-115	1.4015-1.4019	1,239	—
	90	115-115	1.4020-1.4020	2,254	—
	91	115....	1.4019-1.4010	176	—
$\frac{3}{4}$ of charge	225	113-115	1.4010-1.4023	7,810	—
	232	115-115	1.4023-1.4010	1,456	—
43	65	113-115	1.3992-1.4014	792	—
	66	114-115	1.4015-1.4015	1,856	—
	67	114-123	1.4014-1.3958	2,711	—
	68	123-124	1.3957-1.3950	1,092	—
	69	124....	1.3961-1.3970	228	—
44	77	114-116	1.3988-1.4015	1,736	—
	78	115-124	1.4009-1.3959	1,679	—
	79	123-125	1.3959-1.3952	479	—
	80	125-131	1.3960-1.4015	880	—
	81	131-135	1.4002-1.4019	963	—
	82	136-144	1.4002-1.4075	1,005	—
	83	144....	1.4074-1.4049	1,007	—
	8	28	—	6,479	3.95
	70	25- 57	1.3680	8,564	5.23
72, 74 = 60, 75, 12 =	71	55- 61	1.3681-1.3697	2,450	1.50
	73	55- 62	1.3680-1.3699	1,554	0.95
	10	58- 59	1.3694-1.3695	2,019	1.23
	92	61- 80	1.3697-1.3769	1,505	0.92
	93	(70)- 84	1.3630-1.3799	4,024	2.46
	76	81....	1.3771-1.3800	495	0.30
	61	83- 93	1.3800-1.3859	2,723	1.66
	62	91- 99	1.3860-1.3869	1,922	1.17

SERIES III (contd.).

Original material.	Fraction.	Boiling range, °C.	n_D^{20} range.	Volume, ml.	% on T.D. 91.
36, 45, 63 =	*	98-100	1.3870-1.3870	52,240	31.89
46, 64 =	116	100-108	1.3871-1.3916	1,952	1.19
	47	107-110	1.3900-1.3903	3,119	1.90
48, 49 =	*	107-110	1.3904-1.3910	5,838	3.57
50, 52, 53, 84 =	*	108-114	1.3911-1.3995	11,890	7.25
54 ¹ , 54 ² =	54	110-115	1.3911-1.4014	3,543	2.16
65, 85, 51 =	166	110-115	1.3911-1.4014	1,926	1.18
57, 55 =	*	113-115	1.4003-1.4020	11,560	7.04
86, 56, 89 =	183	115....	1.4008-1.4025	3,458	2.12
58, 87, 90, 225 =	*	113-115	1.4015-1.4020	13,816	8.49
78, 59, 88, 91, 232 =	153	114-116	(1.3988)-1.4040	4,279	2.62
66, 77 =	182	114-116	(1.3988)-1.4015	3,592	2.19
67 =	*	114-124	1.4014-1.3959	2,711	1.65
68, 79 =	154	123-125	1.3959-1.3950	1,571	0.96
	69	124....	1.3961-1.3970	288	0.14
	34	124-125	1.3955-1.3952	6,440	3.93
	80	125-131	1.3960-1.4015	880	0.54
	81	131-135	1.4002-1.4019	963	0.59
	82	136-144	1.4002-1.4075	1,005	0.61
	83	144....	1.4074-1.4089	1,007	0.61

* Not blended, but tabulated together in this table due to similarity of physical constants.

SERIES IV.

Original material.	Fraction.	Boiling range, °C.	Approx n_D^{20} range.	Vol % on charge.	% on T.D. 91.
70 * b	98	<31	<1.3500	93	4.86
	99	58...	1.3690	7	0.37
71 * b	100	58-59	1.3693-1.3699	90	1.35
	101	59-60	1.3691-1.3680	10	0.15
73 * b	102	58	1.3690	53	0.51
	103	59-61	1.3690-1.3678	31	0.29
	104	61...	1.3678-1.3710	16	0.15
92 *	105	60-61	1.3690-1.3700	30	0.28
	106	61-(70)	1.3700-1.3750	30	0.28
	107	(70)-80	1.3750-1.3768	40	0.36
93 *	113	79-80	1.3727-1.3771	7	0.17
	114	80...	1.3771-1.3773	86	2.12
	115	80...	1.3773-1.3779	7	0.17
76 * c	119	—	—	13	0.04
	120	—	—	87	0.26
61 *	123	83- 89.5	1.3790-1.3853	30	0.50
	124	89.5- 89	1.3898	60	1.00
	125	89- 90	1.3856-1.3842	10	0.16
62 *	126	(90)- 98	1.3860-1.3850	25	0.29
	127	98-100	1.3862-1.3868	75	0.88
116 *	117	100	1.3868-1.3889	50	0.59
	118	110	1.3889-1.3910	50	0.60

SERIES IV (contd.).

Original material.	Fraction.	Boiling range, °C.	Approx n_D^{20} range.	Vol % on charge.	% on T.D. 91.
47 ^d	128	105-(108)	1.3877-1.3891	10	0.19
	129	110	1.3891-1.3904	70	1.33
	130	110	1.3905-1.3910	10	0.19
	131	110	1.3911-1.3929	10	0.19
48 ^d	132	110	1.3895-1.3904	70	1.22
	133	110	1.3905-1.3912	24	0.42
	133A	110	1.3912-1.3930	6	0.10
49 ^d	134	(100)-110	1.3880-1.3902	55	1.00
	135	110	1.3905-1.3911	20	0.37
	136	110	1.3912-1.3929	25	0.46
50 ^d	146	108-108 ^s	1.3910	47	0.68
	147	108 ^s -109	1.3910-1.3930	53	0.77
52 ^d	141	108-110	1.3900-1.3911	75	1.50
	142	110-113	(1.3912)-1.3999	25	0.50
84 ^d	143	107-109	1.3912	20	0.15
	144	109-112	(1.3912)-1.3999	30	0.23
	145	112-113	(1.3999)-1.4011	50	0.39
54 ^c	157	110-112	1.3950-1.3999	30	0.65
	158	112-113	1.3999-1.4011	40	0.86
	159	113-114	1.4011-1.4022	30	0.65
166 ^c	198	109-114	1.3945-1.3999	25	0.30
	199	114-115	1.3999-1.4011	20	0.24
	200	115-115 ^s	1.4011-1.4022	40	0.46
	201	115 ^s -116	<1.4022	15	0.18
57* ^c	223	113-114	1.3998-1.4011	55	2.51
	224	114-115	1.4011-1.4023	45	2.04
55 ^c	189	114-115	1.3999-1.4011	65	1.62
	190	115....	1.4011-1.4022	35	0.87
183 ^c	202	113-114	1.4000-1.4011	40	0.85
	203	114-115	1.4011-1.4022	40	0.85
	204	115	1.4023-1.4025	15	0.31
	205	115	<1.4023	5	0.11
58 ^c	238	113-115	1.4018-1.4027	70	1.54
	239	115-	1.4028	14	0.31
	240	115-116	1.4025-1.4010	16	0.35
87 ^c	233	113-114	1.4020-1.4025	90	1.35
	234	114	1.4019-1.4016	10	0.15
225 ^c	235	114-115	1.4012-1.4024	83	3.98
	236	115-5	1.4025	5	0.24
	237	115-5-116	1.4025-1.4008	12	0.57
153 ^c	167	115-116	1.4018-1.4000	60	1.57
	168	116-122	1.4000-1.3970	30	0.79
	169	122-125	1.3970-1.3950	10	0.26

SERIES IV (contd.).

Original material.	Fraction.	Boiling range, ° C.	Approx n_D^{30} range.	Vol % on charge.	% on T.D. 91.
182 °	191	112-114	1.3990-1.4011	9	0.20
	192	114	1.4011-1.4020	10	0.22
	193	114	1.4020	50	1.09
	194	114-114 ⁵	1.4019-1.4000	25	0.55
	195	114 ⁵ -115	1.4000-1.3983	6	0.13
67 °	170	116-118	1.4018-1.4000	55	0.91
	171	118-123	1.4000-1.3970	35	0.58
	172	123-125	1.3970-1.3950	10	0.16
154 °	173	120-123	1.3964-1.3952	10	0.10
	174	123-124	1.3952-1.3950	80	0.77
	175	124....	1.3958	10	0.09
34 °	184	121-122	1.3961-1.3953	12	0.47
	185	122-123	1.3952	84	3.30
	186	123....	1.3965	4	0.16
80 * c	187	122-124	1.3950-1.3960	25	0.13
	188	124-131	(1.3972)-1.4020	75	0.41
81 * c	226	129-131.5	1.4018-(1.4000)	60	0.35
	227	131.5-135	(1.4000)-1.3988	28	0.17
	228	135	1.4020	12	0.07
82 * c	229	133-135	1.4000-(1.4008)	32	0.19
	230	135-136	1.4010-1.4074	26	0.18
	231	136-140	1.4078-1.4090	42	0.24

* Whole of charge not subject to Series IV fractionation.

^a Fractionation on 4 feet of 25-mm Stedman packing at a reflux ratio of 34 : 1.

^b Fractionation on 4 feet of $\frac{3}{8}$ -in Stedman packing at a reflux ratio of 59 : 1.

^c Fractionation on 4 feet of $\frac{3}{8}$ -in Stedman packing at a reflux ratio of 119 : 1.

^d Fractionation on 4 feet of 25-mm Stedman packing at a reflux ratio of 43 : 1.

^e Fractionation on 4 feet of 25-mm Stedman packing at a reflux ratio of 85 : 1.

Blend of Series IV.

Original material.	Blend.	Vol % on T.D. 91.
8 + 98	221	8.81
10 + 99 + 100 + 102	222	3.46
101 + 103 + 105	206	0.72
104 + 106 + 113 + 119	207	0.64
107	208	0.36
114 + 120	241	2.38
115 + 123	220	0.67
124	—	1.00
125	—	0.16
126	—	0.29
36 + 45 + 63 + 117 + 127	—	33.36
118	—	0.60
128 + 129 + 132 + 134 + 143	209	3.89
146	—	0.68
130 + 133 + 134 + 141 + 144	210	2.71
131 + 133A + 136 + 142 + 147 + 148	211	3.53

Blend of Series IV (contd.).

Original material.	Blend.	Vol % on T.D. 91.
149 + 157 + 198	212	1.71
145 + 150 + 158 + 189 + 191 + 199 + 202 + 223	213	7.43
{ 159 + 190 + 192 + 193 + 200 + 203 + 204 }	214	13.91
(224 + 235 + 236 + 238 + 239)		
167 + 170 + 194 + 234 + 237 + 240	215	4.10
168 + 171 + 195 + 201 + 205	216	1.79
169 + 172 + 173 + 184	217	0.99
174 + 185	218	4.07
69 + 175 + 186 + 187	219	0.52
188	—	0.41
226	—	0.35
227 + 229	255	0.36
228 + 230	242	0.25
231	—	0.24
83	—	0.61

SERIES V.

In no case was the whole of the charge subject to distillation. All distillations on 4 feet of $\frac{3}{8}$ -in Stedman packing at a reflux ratio of 119:1.

Original material.	Fraction.	Boiling range, °C.	n_D^{20} range.	Vol % on charge.	Vol % on T.D. 91.
206	108	59-60	1.3680-1.3667	30	0.21
	109	60-60.5	1.3667-1.3667	12	0.09
	110	60.5-63.2	1.3667-1.3710	24	0.17
	111	63.2-63.4	1.3710-1.3710	8	0.06
	112	63.4	1.3710-1.3715	26	0.19
207	155	63-63	1.3700-1.3702	20	0.13
	156	63-64	1.3708-1.3715	80	0.51
208	121	80.0	1.3773	6	0.02
	122	80.0	1.3770	94	0.34
241	276	< 78	1.3764	0.5	0.01
	277	78.8-79	1.3768-1.3769	4.5	0.11
	278	79.5-80	1.3770-1.3770	82	1.95
	279	80-80	1.3772-1.3772	8	0.19
	280	80-80	1.3773-1.3778	2	0.05
	280R	—	1.3790	3	0.07
220	137	81-	1.3772-1.3780	30	0.20
	138	81-90	1.3792-1.3860	70	0.47
124	139	88-89.5	(1.3852)-1.3860	75	0.75
	140	89.5	1.3854-1.3850	25	0.25
125	151	90-	1.3857-1.3858	40	0.06
	152	90-92	1.3856-1.3841	60	0.10
126	160	88-90	1.3857-1.3858	25	0.07
	161	90-97	1.3856-1.3845	45	0.13
	162	97-99	1.3868-1.3870	30	0.09
118	164	95-104	1.3869-1.3868	40	0.24
	165	104-109	1.3878-1.3902	60	0.36

SERIES V (contd.).

Original material.	Fraction.	Boiling range, °C.	n_D^{20} range.	Vol % on charge.	Vol % on T.D. 91.
209	271	98-107	1.3871-1.3890	16	0.62
	272	108-108.4	1.3891-1.3892	16	0.62
	273	(108.5)-109	1.3897-1.3902	50	1.95
	274	109-109.2	1.3906-1.3909	6	0.23
	275	Residue	1.3948	12	0.47
146	176	107-109.7	1.3900-1.3910	85	0.58
	177	109.7	1.3914-1.3920	15	0.10
210	285	109-109	1.3909-1.3909	6	0.16
	286	109-109.0	1.3902-1.3906-1.3903	23	0.62
	287	109-109.2	1.3903-1.3911	40	1.09
	288	109.2-109.4	1.3912-1.3930	24	0.65
	289	109.4	1.3979	7	0.19
211	281	107-108.9	1.3903-1.3911	6	0.21
	282	108.9-108.9	1.3911-1.3913	45	1.59
	283	108.9-108.9	1.3915-1.3931	39	1.38
	284	—	1.3990	10	0.35
212	247	104.5-108.5	1.3939-1.3925	5	0.09
	248	108.8-108.9	1.3923-1.3921-1.3930	30	0.51
	249	108.9-113.0	1.3933-1.3999	44	0.75
	250	113.0-113.0	1.3999-1.4000	14	0.24
	251	Residue	1.4019	7	0.12
213	252	111.0-113.0	1.3990-1.3999	15	1.11
	253	113-113.0	1.4000-1.4001	38	2.83
	254	113.0-114.0	1.4001-1.4020	47	3.49
214	256	113.0-113.6	1.4012	4	0.56
	257	113.6-114.0	1.4010-1.4013	69	9.59
	258	114.0-114.0	1.4015-1.4017-1.4012	16	2.23
	258R	Residue	1.4018	11	1.53
215	259	114-115	1.4022-1.4022	9	0.37
	260	115-115	1.4022-(1.4018)	59	2.42
	261	115-115	1.4015-1.4009	23	0.94
	262	Residue	1.4000	9	0.37
216	196	114-116.5	1.4000-1.3978	52	0.93
	197	116.5-117.5	1.3977-1.3968	48	0.86
217	263	120-122	1.3980-1.3970	16	0.16
	264	122-122	1.3962-1.3962	16	0.16
	265	122-124	1.3962-1.3955	10	0.10
	266	124-124	1.3955-1.3955	46	0.45
	267	Residue	1.4049	12	0.12
218	290	122.8-123	1.3961-1.3956	8	0.33
	291	123-123	1.3955-1.3955	14	0.57
	292	123-123.3	1.3952-1.3951	71	2.89
	293	—	1.3970	7	0.28
219	268	123.3-(123.9)	1.3952-1.3952	80	0.41
	269	123.9-124	1.3958-1.3959	11	0.06
	270	Residue	1.4067	9	0.05
188	294	120.0-130.0	1.4118-1.3972-1.4018	24	0.10
	295	130.0-130.0	1.4020-1.4021	51	0.21
	296	130.0-130.5	1.4021-1.4021	25	0.10

SERIES V (*contd.*).

Original material.	Fraction.	Boiling range, ° C.	n_D^{20} range.	Vol % on charge.	Vol % on T.D. 91.
226	297	114.0-114.0	1.4060-1.4026	95	0.03
	298	114.0-115.0	1.4021-1.4018	21.5	0.08
	299	115.0-129.5	1.4016-1.3981-1.4009	22.0	0.08
	300	129.5-130.4	1.4020-1.4022-1.4020	47.0	0.16
255	301	130.8-132.9	1.4017-1.4002	14	0.05
	302	133.0-133.0	1.4002-1.3996	79	0.07
	303	133.4-134.5	1.3992-1.3989	67	0.24

SERIES VI.

Original material.	Fraction.	Boiling range, ° C.	n_D^{20} range.	Vol % on charge.	Vol % on T.D. 91.
163	178	89.6-90.0	1.3853-1.3856-1.3853	47	0.23
	179	90.0-91.0	1.3851-1.3842	30	0.14
	180	91.0-91.5	1.3840-1.3840	7	0.03
	181	Residue	1.3878	16	0.08
243 (138 + 139)	244	86.0-89.0	1.3839-1.3853	19	0.26
	245	89.0-89.6	1.3859-1.3860	50	0.68
	246	89.6-89.7	1.3858-1.3854	31	0.42

ALUMINIUM STEARATE GELS FOR USE AS FLAME-THROWER FUELS.*

By C. M. CAWLEY,[†] J. H. G. CARLILE,[†] J. G. KING,[‡] and
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SUMMARY.

(1) An account is given of the work at the Fuel Research Station (D.S.I.R.) concerning the invention and development up to full-scale manufacture of flame-thrower fuels consisting of aluminium stearate gels in petrol peptised with cresylic acid or mixed xlenols.

(2) Descriptions are given of the investigation and control of the manufacture of the aluminium stearate, and the results of studies of the effects of peptisers and of various grades of petrol are recorded.

(3) Manufacture was developed at the Fuel Research Station to a stage where a mobile mixing plant (750 gallons) was designed, built, and operated.

(4) Studies of the following physical and chemical properties of the fuels are described :

- (a) Anomalous viscosity.
- (b) Variation of viscosity with temperature ("temperature" sensitivity").
- (c) Stability of gels on storage at various temperatures.

(5) Although the service fuel was highly satisfactory, attempts were made to effect improvements, mainly by the use of peptising agents other than xlenols. Thus, it was shown that the lower aliphatic alcohols decreased the temperature sensitivity of the fuels, while a considerable economy in the amount of aluminium stearate required, together with increased stability at high temperatures, was effected by the use of ethyl cellosolve as a peptising agent. The latter compound was of particular promise. Certain desirable properties of the gels, however, appeared to be conferred on them only by xlenols and it is probable that mixtures of the peptising agents, chosen according to the properties required in the fuel, would afford the best solution to the problem of producing improved flame-thrower fuels.

INTRODUCTION.

THE Mixtures Committee, an advisory committee of the Petroleum Warfare Department from 1940 to 1946, was concerned with the devising, investigation, and development of incendiary mixtures for use in a wide variety of munitions of war. The Committee was formed in the summer of 1940 under the chairmanship of Dr F. S. Sinnatt, Director of Fuel Research, Dept. of Scientific and Industrial Research. After his death in January 1943 Sir Alfred Egerton became chairman and retained that position until the Committee was disbanded in 1946.

Research and development work on different projects was carried out

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by various members of the Committee, each of whom had the benefit of the advice and help of the Committee as a whole. From 1940 to 1945, at least one group, and often two or more groups of workers at the Fuel Research Station were engaged continuously on work for the Committee and in addition a considerable amount of work was carried out directly for the Petroleum Warfare Department.

Experimental investigations concerned with the devising and study of incendiary mixtures for various purposes were carried out at the Station and an account of this work is to be given in a paper entitled "Incendiary Fuels for Various Purposes."¹ The most important work, however, was the study of the preparation and properties of flame-thrower fuels, and in particular the creation and development of aluminium stearate petrol gels* peptised with xylenols, known as FRAS flame-thrower fuels. A brief history of the development and use of this fuel has already been published.²

A general study of aluminium stearate gels in light hydrocarbon oils is described in a separate paper,³ and the present paper gives a survey of the work carried out in the development of the fuel from the laboratory scale to large-scale production for use as a service munition of war. It deals in particular with the part played by the Fuel Research Station in the invention of the fuel, and the effects of the nature of the raw materials on the properties of the fuel.

In the early investigations on incendiary mixtures for various purposes,¹ a solution of rubber in petrol or kerosine had been an important constituent in many of the mixtures developed, particularly for the purposes of controlling the rate of burning and of imparting to mixtures the necessary physical characteristics. The fall of Malaya in February 1942 led to a serious deterioration in the rubber supply position; work had already been commenced in January 1942 with the object of preparing substitutes for rubber-petrol solution, and it appeared that soap gels formed a promising substitute. Some examination was first made of sodium stearate gels, but sodium stearate alone does not form a satisfactory gel for this purpose in petrol or kerosine. Lawrence⁴ had shown that sodium stearate gels in Nujol were peptised by the addition of cresol which lowered the gelation point and reduced the viscosity of the gel, and it was thought that modification of sodium stearate gels in petrol in this manner might give a suitable product. It was found, however, that although cresol did have a peptising action in the gelation of sodium stearate in petrol, the gels produced were unsatisfactory and rapidly exhibited syneresis and crystal separation.

Attention was therefore directed to the use of aluminium soaps, and since it was understood that stearic acid was the only soap acid which would be available in sufficient quantities, the work was concentrated on aluminium stearate. It was found that aluminium stearate alone (5 g soap per 100 ml petrol) gelled at about 55° C giving a viscous material which set to a soft gel on cooling to 30° C. This gradually became rigid at room

* NOTE.—Various workers in colloid science have assigned different meanings to the terms "gel", "jelly", and "sol", and when aluminium stearate is dispersed in a hydrocarbon solvent with the addition of a peptiser to give a viscous liquid, the product is perhaps more properly termed a "sol." The term "gel," however, was adopted in the early stages of this work and in view of the lack of definition of such terms no change was made, and the process has been termed "gelation" throughout.

temperature and set to a solid gel which finally showed syneresis. The addition of cresol lowered the temperature of gelation and produced a transparent viscous gel which remained mobile and showed no great change in viscosity even after prolonged storage at room temperature. Moreover, it resembled solutions of rubber in petrol in possessing the property of anomalous viscosity, and also of forming long threads and adhering to surfaces; it thus appeared to be a highly promising substitute for rubber-petrol.

When, therefore, it was found that rubber-petrol gave a highly improved performance as a flame-thrower fuel as compared with unthickened fuels, such as fuel oil, and as the anomalous viscosity of rubber-petrol solution was a vital factor in its performance, the peptised aluminium stearate gel was tested and found to give even better results. As compared with the unthickened fuels, rubber-petrol and aluminium stearate gels more than doubled the effective range of the flame thrower and also produced a much greater target effect, *i.e.*, they enabled four or five times the amount of fuel to be deposited on the target as had been found possible with the fuels previously used. Furthermore, as these new fuels were made up with petrol as a base fuel the ease of ignition was greatly increased. The work on aluminium stearate gels peptised with cresol was therefore developed at the Fuel Research Station to the point where fuel production was taken over by the Ministry of Supply. The Fuel Research Station afterwards continued to serve as technical advisers on the large-scale production of the service fuels, of which some 9,000,000 gallons were manufactured and used in the European theatre of operations. This report gives a brief account of the work carried out at the Station, together with some details of the properties of the fuels and certain developments in the production of improved fuels.

The extension to full-scale production involved the development of the manufacture of aluminium stearate to produce a soap of constant gelling properties, in which the major part of the development work was done by A. Boake, Roberts and Co. Ltd. It also included the examination of commercial grades of xlenols, used in place of the cresol employed in the initial laboratory experiments. Investigations were also carried out in connexion with the large-scale production of the fuel itself, in which the "Shell" Refining and Marketing Co. Ltd. were mainly responsible for the final extension to full-scale manufacture. The Sandoz Chemical Co. Ltd. also made a large contribution to this development and carried out a great deal of other investigational work. In the full-scale production of the soap and fuel, acknowledgement must also be made of the part played by the Anglo-American Oil Co. Ltd., Barnfield Colour Co. Ltd., Burrell and Co. Ltd., Burt Boulton and Haywood, Ltd., J. Crosfield and Sons Ltd., and Tytpe and King Ltd.

In the early stages of the production programme the specifications for the raw materials and finished fuels were formulated for the Mixtures Committee by the Fuel Research Station who also carried out test work necessary to control supplies. After the adoption of the fuel as a munition of war the production and supply were taken over by the Ministry of Supply and the testing of materials and products by the Chief Chemical Inspector of that Ministry.

DEVELOPMENT OF PROCESS.

As already stated, supply considerations led to the concentration of the work on aluminium stearate although the other aluminium soaps were not neglected. In particular, aluminium naphthenate, without any added peptiser, was found to give gels in petrol which resembled rubber-petrol in appearance and properties. However, apart from the difficulty of the scarcity of naphthenic acids, the use of the aluminium naphthenate then available would have entailed certain disadvantages, namely, that (1) the manufacture of aluminium naphthenate was more difficult than that of the stearate, especially in the drying operations, in view of the tough and rubbery-like nature of the former compound, (2) aluminium naphthenate required a higher temperature and a longer time for dispersion than the stearate. It should be mentioned here that more recent developments in the manufacture of the naphthenate, by Alchemy Ltd., have produced an improved grade of aluminium naphthenate in granular or powder form, by a process in which the difficulties previously associated with the manufacture of aluminium naphthenate have been eliminated.

Production of Aluminium Stearate.

Aluminium stearate, as available commercially, is a white powder, obtained by the reaction between sodium stearate and aluminium sulphate in aqueous solution. The sodium stearate is prepared from commercial "stearic acid" which is of somewhat variable composition, a typical sample containing approximately 40 per cent stearic acid, 8 per cent oleic acid, and 52 per cent palmitic acid. The composition of the stearate indicates that it normally contained 1.5 mols acid to each atom of aluminium; the precise nature of the compound or compounds is uncertain, but some free fatty acid is present.

All the early work was done on a grade of aluminium stearate prepared by A. Boake, Roberts and Co. to meet a Ministry of Supply specification for other uses of the material. It was found, however, that for the production of flame-thrower fuels the material was not entirely suitable since different batches gave gels of widely different viscosities and storage stability.* As a result of a considerable amount of work carried out by A. Boake, Roberts and Co. Ltd. (in collaboration with the Fuel Research Station), certain modifications were introduced into the process of manufacture of the soap in order to ensure a greater uniformity of the product. Apart from a general tightening-up in the control of the factors governing the quality of the soap, the major modifications introduced were (a) the control of pH to a value not exceeding 7 and preferably not exceeding 5.3 at the termination of the reaction, and (b) the addition of a protective colloid, such as glue, during the reaction. The modified method of production of aluminium stearate has been covered by a patent.⁵ As a result of this work, Boake, Roberts were able to produce soaps of reasonably uniform and high gelling power. It then became possible to draw up a specification to control the supply of aluminium stearate for the production of flame-thrower fuels, which with certain minor modifications was afterwards adopted by the

* By storage stability is meant the capacity of a gel to retain its viscosity on storage.

Ministry of Supply when the manufacture of flame-thrower fuel was taken over by them. The main features of the final form of the specification (C.S. 2086B.) are given below :

SPECIFICATION C.S. 2086B. TO GOVERN SUPPLY AND INSPECTION OF
ALUMINIUM STEARATE P.W.4.

1. *Description.* The Aluminium Stearate P.W.4 must consist of aluminium stearate of high gel-forming power, free from foreign matter and visible impurities. The material is preferably supplied in granular form complying with the requirements of para. 3 (b).

2. *Examination.* Samples taken from any portion of the supply must comply with the following requirements :

(i) *Size of Granules.* Not more than 2 per cent of the material must be retained on a $\frac{1}{8}$ -inch mesh sieve and not more than 20 per cent must be retained on a $\frac{1}{16}$ -inch mesh sieve.

(ii) *Moisture Content.* The moisture content of the material must not be more than 1.3 per cent nor less than 0.5 per cent.

(iii) *Inorganic Acidity or Alkalinity.* The material must not be

(a) acid to methyl orange

(b) alkaline to bromocresol purple.

(iv) *Acidity to Phenolphthalein.* The acidity of the material to phenolphthalein must not exceed 5 per cent calculated as stearic acid.

(v) *Insoluble Ash.* The material must not yield less than 9.1 per cent nor more than 9.8 per cent of insoluble ash.

(vi) *Soluble Ash.* The material must not yield more than 1.0 per cent of water soluble ash.

(vii) *Gel-forming Power.*

(a) Material having a moisture content of 0.7 to 1.3 per cent must give a gel, when prepared by the method described below, with a "ball-drop viscosity" of not less than 60 seconds nor more than 120 seconds, determined 21 ± 1 hours after preparation.

(b) Material having a moisture content of 0.5 to 0.7 per cent must give a gel with a "ball-drop viscosity" of not less than 120 seconds nor more than 150 seconds, determined 21 ± 1 hours after preparation.

Method of Test. The materials required for this test are (1) pure benzol (to the current approved specification for Benzene Grade I), (2) Pure redistilled phenol (m.p. $>40^{\circ}\text{C}$), and (3) aluminium stearate as received, care being taken that this material, which is hygroscopic, is not allowed to absorb moisture in handling.

A mixing apparatus is required and this consists of a cylindrical glass jar ($3\frac{1}{4} \pm \frac{1}{8}$ inch in diameter, and 7 ± 1 inch in height) fitted with a cork carrying a sleeve for a stirrer shaft and a thermometer, the stirrer is made of glass and carries two blades ($1\frac{3}{4} \pm \frac{1}{8}$ inch in diameter) inclined at an angle of 45° to the shaft and at right angles to each other. The stirrer is driven by a motor and is regulated to rotate in the direction producing an upward swirl at 600 ± 100 r.p.m.

The test is carried out as follows : Measure 298 ml of pure benzole into the mixing jar and add 15 g of aluminium stearate. Start the stirrer and run continuously throughout the whole operation. By means of an external electric heater raise the temperature of the mixture to 45°C in the course of 30 minutes ; at 40°C add 9 g of molten phenol, wash in with 5 ml benzole. (This gives a total of 303 ml of benzole to allow for a loss of one per cent.) Raise the temperature of the mixture from 45°C to 50°C in the course of a further 60 minutes. Seal the jar (or transfer the gel to a storage jar and seal) and allow to stand 21 ± 1 hour at a temperature of $15-25^{\circ}\text{C}$ before determining the viscosity.

The viscosity ("ball-drop" viscosity) is expressed as the time of fall (in sec) of a $\frac{1}{16}$ -in steel ball through 5 cm of the sample, and is equal to $0.1 \times$ apparent viscosity (in poises) of the sample at the rate of shear in the determination.

Most of the clauses of the specification require no explanation; the insoluble ash was a measure of the aluminium content of the soap, and the soluble ash a measure of the efficiency of washing and of the amount of undesirable impurity (mainly sodium sulphate) retained.

Originally the soap was supplied as a finely ground powder in order to ensure rapid and easy dispersion of the soap in the solvent. Some difficulties were experienced in the milling of the soap and it was found that equally good results could be obtained with the granular material specified.

The value of moisture content determined by measuring the loss in weight of a 1-g sample on heating to $105 \pm 2^\circ \text{C}$ in an air oven for 3 hours, was one of the important factors affecting the gel-forming power of the soap, since moisture acts as a powerful peptising agent. The general effect of the water content of the soap on the viscosity of the gels produced is illustrated by the curves in Fig. 1, showing the viscosity of gels made

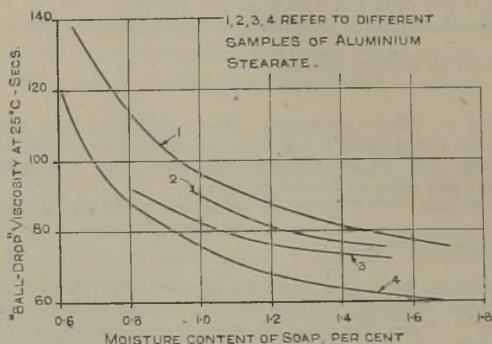


FIG. 1.

RELATION BETWEEN GEL-FORMING POWER AND MOISTURE CONTENT OF ALUMINIUM STEARATE.

according to the gel-forming-power test with four soaps, samples of each of which had been prepared with varying moisture contents. It was obviously undesirable to use soaps of unduly high moisture content since the gel-forming power would be low, though, providing the moisture content was not above 2 per cent, there was little effect on the stability of the gels produced. It was almost equally, though less obviously, undesirable to use soap of moisture content much below 1 per cent, for the following reasons:—

(1) Ultra-dry soaps are extremely hygroscopic and apart from handling difficulties a soap of high gelling power as determined by the laboratory test might easily absorb sufficient moisture under large scale gel manufacturing conditions to give an inferior result.

(2) To produce gels of the required viscosity with a dry soap of high gelling power with a fixed concentration of soap would involve adding additional xylenols to compensate for the absence of the peptising action of the moisture in the soap. It is true that the same result could be achieved by using a lower concentration of soap and peptiser, but

this was known to be undesirable, since for gels of any given viscosity the storage stability increases with increasing concentration of soap and peptiser.

For these and other reasons it was therefore considered that the aluminium stearate for the production of flame-thrower fuels should ideally contain 1.0 per cent moisture and in this condition give a gel, which, under the conditions of the gel-forming test, should have a viscosity of 90 to 100 seconds. In order to simplify and expedite production, Specification C.S. 2086 originally permitted the acceptance of soaps having moisture contents ranging from 0.7 to 1.3 per cent and giving gel-forming values of 60 to 120 seconds. This latter range was based on the observations that a soap giving a gel value of 90 seconds at 1.0 per cent moisture content would give values of approximately 60 and 120 seconds at moisture contents of 1.3 and 0.7 per cent respectively. Since, however, the specification allowed acceptance of soap giving gels of 60 seconds viscosity at 0.7 per cent moisture and also of soaps giving gels of 120 seconds at 1.3 per cent moisture, the tolerance permitted was considerable and was only justified by the paramount necessity of maintaining production at the highest possible level. This consideration led later to a further extension of this tolerance in that where manufacturers produced soaps with a moisture content between 0.5 and 0.7 per cent, such samples were accepted providing that the gel-forming value was between 120 and 150 seconds.

Investigations Relating to Gel-forming Test.

Although the actual flame-thrower fuels were made up in petrol with a commercial grade of mixed xylenols as the peptising agent, neither of these materials was considered suitable for the standard test for the assessment of the gel-forming power of the stearate, as it would have been difficult, if not impossible, to specify standard grades of these materials for use by all the manufacturers. Assessment of the stearate was therefore carried out by measuring the "ball-drop" viscosity of a gel prepared in benzene using 5.0 per cent wt/vol (*i.e.*, g per 100 ml benzene) of aluminium stearate and 3.0 per cent of phenol. This test gave reproducible results and provided a simple method of controlling the quality of the stearate produced by the various manufacturers.

Unfortunately the results of the test could not be correlated accurately with those obtained in the large-scale manufacture of gels for flame-thrower fuels using pool petrol and mixed xylenols. It was therefore of little assistance to the fuel manufacturers in the production of a fuel of a specified viscosity. It was suggested that the benzene-phenol test should be replaced by a petrol-xylenols test using special samples of petrol and xylenols, stocks of which would be laid down for use by all concerned. An examination of the practicability of this modification, carried out jointly with the "Shell" Refining and Marketing Co. Ltd. is recorded here.

As it was essential that the petrol should be stable in storage the special boiling point spirit No. 4 (S.B.P. 4) modified so as to remove the fraction below 55° C was used; the properties of this spirit are given below:—

Sp. gr. at 15° C	0.733
Aromatic content (% by vol)	12.3
Bromine No.	2

Distillation :

1 B.P., ° C.	.	.	.	57.5
Distillate to 70° C, % by vol	.	.	.	5
100° C, "	.	.	.	52
F.B.P., ° C.	.	.	.	159

The other materials used were :—

- (1) Benzene ("pure benzole," N.B.A. Specification No. 1, 1938);
- (2) Pure phenol (as in specification C.S. 2086B.);
- (3) Mixed xyenols (Sample A.293, supplied by P.R. Chemicals Ltd.);
- (4) Samples of aluminium stearate supplied by A. Boake, Roberts and Co. Ltd. and Messrs Burrell and Co. Ltd.

The benzene was used as supplied, without further drying; the effect of the moisture content of the benzene on the benzene-phenol test for a particular soap was as follows :—

Benzene.	"Ball-drop" viscosity at 25° C of benzene-phenol gel, sec.
As supplied	91
Dried over sodium	101
Saturated with water, 0.04%	83

The results obtained in the two laboratories for benzene-phenol and petrol-xylenol gels prepared from a series of soaps are shown in Table I.

TABLE I.

Comparative Gelation Data in Benzene and Special Petrol.

Stearate no.	Benzene-phenol gel (5/3).		Petrol-xylenols gel (5/1.5).	
	"Ball-drop" viscosity at 25° C after 21 hours, sec.		"Ball-drop" viscosity at 25° C after 21 hours, sec.	
	Lab. A.	Lab. B.	Lab. A.	Lab. B.
B.R. 121	78 79	82 —	175 188	207 183
B.R. 556	86 88	— —	199 222	203 210
B.R. 570	94 95	— —	218 232	224 —
B.R. 594	101 102	— —	207 —	— —
B.A. 141	72 75	76 —	220 —	218 —

The benzene-phenol gels were made up in the proportions (5/3) used in the standard test, but the petrol-xylene gels were prepared with 5 per cent wt/vol aluminium stearate and 1.5 per cent xylenols, in order to give a higher range of viscosities.

The results show that :—

(a) the error in duplication of results was greater in the petrol-gel test than in the benzene-gel test,

(b) the order of relative gelling strength of the soaps given by the benzene-gel test was different from that given by the petrol-gel test.

TABLE II.

Viscosity Data for Aluminium Stearate Gels in Benzene and Various Petrols.

Solvent :	Petrol.					Benzene.		
Grade :	Special petrol.	Pool non-leaded.	Pool leaded.	72 octane number leaded A.	72 octane number leaded B.	“ Pure benzole ”— N.B.A. Spec. No. 1 (1938).		
Peptiser :	Xylenols. Sample A. 293.					Phenol.	Xylenols A. 293.	Xylenols 74C.
Formula :	5.0/1.5					5.0/3.0.		
Stearate no.	“ Ball-Drop ” viscosity at 25° C, seconds.							
B.R. 121 .	175 188	143 147	127 141	87 89	79 79	78 79	58 60	103 105
B.R. 556 .	199 222	122 122	115 116	68 69	56 56	86 88	51 56	103 105
B.R. 570 .	218 232	147 161	131 142	90 94	75 78	94 95	59 64	115 116
B.R. 594 .	207 —	151 147	138 140	96 97	90 92	101 102	63 63	120 122
B.A. 141 .	220 —	144 140	141 149	104 106	96 102	72 75	61 66	100 105
	Order of relative gelling power of soaps.							
B.R. 121 .	5	3	4	4	3	4	4	} 3
B.R. 556 .	3	5	5	5	5	3	5	
B.R. 570 .	1	1	3	3	4	2	3	2
B.R. 594 .	4	2	2	2	2	1	2	1
B.A. 141 .	2	4	1	1	1	5.	1	5

It would appear from these results that in spite of poorer duplication of results, the petrol-gel test was preferable as giving more guidance for large scale manufacture. However, indications given by other work suggested that the order of relative gelling strength of soaps might vary for different petrols, in addition to the possibility that it might depend on the sample of xylenols used. Tests were therefore carried out using the same five

samples of soap, two samples of xyenols (A. 293 and 74C, the latter being supplied by the Monsanto Chemical Co. Ltd.), and various petrols. These included a non-leaded petrol and three different samples of the leaded Pool petrol as supplied for production of flame-thrower fuel in 1944-45 as well as the special petrol already used. The results are given in Table II.

The results show that the relative gelling power depended largely on the petrol used; the three leaded petrols gave similar but by no means identical results, while the two non-leaded petrols gave results different both from

TABLE III.
Comparison of Peptising Powers of Cresols, Xyenols, etc.

Peptising agent.	Benzene gel (5/3).	Petrol gel (5/1.5).
	" Ball drop " viscosity at 25° C after 21 hours, sec.	
Phenol	72	125
<i>o</i> -Cresol	360	340
<i>m</i> -Cresol	88	155
Xyenols as used during 1942	44	155
" " " 1943	24	132
" " " 1944	42	177
<i>Xyenols from P.R. Chemicals, Ltd. :</i>		
A. 291 (30% <i>o</i> -cresol)	147	220
A. 292 Mixed xyenols with <i>m</i> -5-xyenols removed	58	188
A. 293 { 80% xyenols } { 20% <i>o</i> - and <i>p</i> -cresols }	68	173
A. 294 { 52% <i>m</i> -cresol 35% <i>p</i> -cresol } { 3% <i>o</i> -cresol }	74	157
A. 289 } Xyenols delivered end of 1944 {	85	173
A. 290 } {	109	190
A. 307 } Xyenols supplied for fuel manu- {	86	160
A. 312 } facture, 1945 {	—	157
High-boiling tar acids	—	<1

the leaded petrols and from each other. It is clear, therefore, that any given sample of petrol, arbitrarily adopted as a " standard " petrol for the gelling test, would not necessarily give results which could be correlated with plant practice.

The benzene-phenol gels gave results quite different from the petrol-xyenols gels. On the other hand, the benzene-xyenols tests using A. 293 sample, gave results, practically identical with those for leaded petrols. This might suggest that it would be an advantage to use a benzene-xyenols test instead of the benzene-phenol test, but when a different grade of xyenols (74C) was used the order of gel-forming power of the soaps was practically the same as that given by the benzene-phenol test. Different batches of xyenols could therefore show at least as wide a variation as that between xyenols and phenol.

In view of these results it was decided not to change either the solvent or the peptising agent in the gel-forming test.

Peptising Agents.

As already stated, the peptising agent used in the original laboratory experiments was cresol or cresylic acid, but development to a large scale resulted in a change in the peptising agent to commercial grades of mixed xylenols, the choice being dictated mainly by reasons of supply. A full account of the peptising action of various compounds of this type has been given in another paper;³ the work recorded here was carried out as part of the control of the large-scale manufacture. Some results for phenol, cresol, and various batches of xylenols and high-boiling tar acids are given in Table III.

The peptising power of different grades of cresylic acid and xylenols differed greatly according to the composition of the particular grade used; the most important factor in determining the peptising power appeared to be the extent to which high-boiling acids and polyhydric phenols were present, since these have a very high peptising power as shown by the results quoted for high-boiling acids in Table III. This was of considerable importance in practice since during the period of manufacture of flame-thrower fuel the peptising power of the xylenols gradually decreased due to a reduction in the content of high-boiling tar acids, resulting from a relaxation of the order issued by Coal Tar Control which originally required that tar acids should be recovered from all high-boiling tar fractions. Attempts were made to formulate an assessment test of the peptising power of xylenols, but as the values obtained differed according to the grade of petrol used, it was decided that this would be of little service to the manufacturer whose needs could be better met by continuous consultation and co-operation between the fuel manufacturers, the producers of the xylenols, and the Fuel Research Station. During 1944-45 the peptising power was maintained at a fairly constant level by the addition of small proportions of high-boiling tar acids to those batches of xylenols deficient in peptising power.

Effect of Variations in Concentration of Gelling Agents on Gel Viscosity.

This can be illustrated by some results of early work with (a) a sample of soap with a moisture content of 1.4 per cent (gelling value 82 seconds) and (b) the same soap after drying to a moisture content of 0.6 per cent. The effect (i) of increasing the proportion of xylenols with a soap concentration (wt/vol) of 4.5 per cent, and (ii) of increasing the soap concentration with a fixed soap/xylenols ratio, are shown respectively in Figs. 2 and 3. Within the range studied the viscosity of the gel increased with increase in soap concentration and for a given soap concentration, decreased with increasing proportion of xylenols. The effect of such variations on gel stability is dealt with more fully later.

Effect of the Composition of the Petrol.

The fact that the viscosity of a petrol gel could vary considerably according to the composition of the petrol was illustrated by the data recorded in

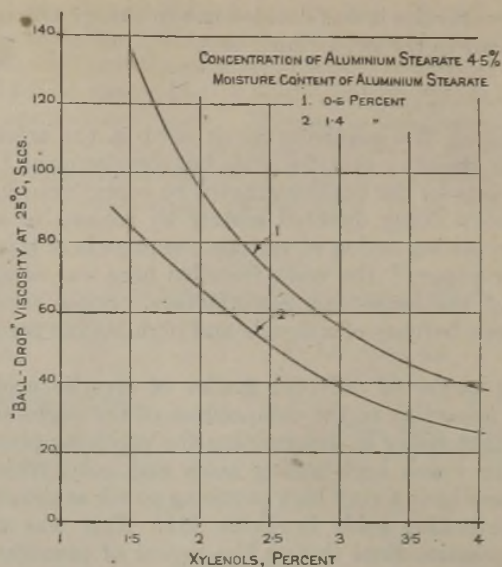


FIG. 2.

EFFECT OF CONCENTRATION OF XYLENOLS ON GEL VISCOSITY.

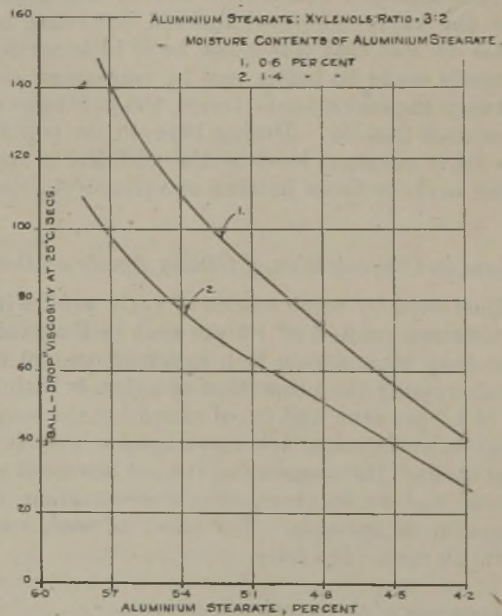


FIG. 3.

EFFECT OF CONCENTRATION OF ALUMINIUM STEARATE ON GEL VISCOSITY.

Table II, which also showed that the relative order of gelling power of various batches of soap was dependent on the nature of the petrol.

In the early stages of the work on these gels, it was found that lead tetraethyl in the quantities normally used in petrol caused a reduction in the initial viscosity of a gel, and though this effect was only slight and there was no effect on the stability of the gels, it was deemed advisable to use non-leaded petrol. As the scale of production was expanded, however, and it became necessary to use leaded petrol for reasons of supply, troubles at once arose owing to the low viscosity and reduced stability of the resultant fuels. It was found that these results were due, not to lead tetraethyl, but to the presence of reactive unsaturated hydrocarbons. This is illustrated by the data in Table IV which shows the effect of refining the petrol on the

TABLE IV.

Effect of Refining the Petrol on the Storage Stability of Aluminium Stearate Gels.

Treatment given to petrol.	" Ball-drop " viscosity at 25° C, sec after :					
	1 day.	1 week.	3 weeks.	8 weeks.	12 weeks.	16 weeks.
None	31	30	21	17	11	9
Washing with water	34	32	24	17	—	—
Washing with 10% H_2SO_4	28	28	22	17	—	—
Washing with 75% H_2SO_4	29	32	33	27	23	23

stability of the gels produced. It must be noted that these gels, while prepared according to normal service fuel specification, were small-scale preparations stored in glass jars exposed to light. Under these conditions the rate of deterioration of all the samples was much greater than that of bulk samples stored in steel drums.

It will be seen that the refining with strong acid which would remove reactive unsaturated hydrocarbons considerably increased the storage stability of the gels. The effect was still more clearly shown by tests on a petrol received from a fuel manufacturer who complained that it had given more unsatisfactory fuels and was unpleasant to work with on account of its objectionable odour. The petrol as received for examination was pale yellow in colour and had the odour associated with unrefined petrol containing unsaturated compounds and mercaptans. Analysis gave the results shown in Table V.

TABLE V.

Analysis of Petrol.

(Sample received April 28, 1945.)

Sp. gr. at 15° C	0.746
<i>Boiling Range :</i>	
I.B.P., ° C	33
Distillate to 100° C, % by vol	34
F.B.P., ° C	190
Total distillate, % by vol	95
<i>Composition :</i>	
Aromatic hydrocarbons, % by wt.	18
Unsaturated "	23
Saturated "	59

Gelling tests were made with the petrol, as received, and after various refining treatments, using a 5/1.5 formula. The results of the tests, including the effect of storage in the dark at room temperature and also at 104° F are shown in Table VI.

TABLE VI.
Effect of Refining of Petrol on Viscosity and Storage Stability of Gels.
(Sample of petrol received April 28, 1945.)

Refining treatment.	Loss in weight by acid extraction, per cent.	Storage temp., ° F.	"Ball-drop" viscosity at 77° F (25° C) of gel, sec after storage for :			
			1 day.	1 week.	2 weeks.	3 weeks.
1. None.	—	R.T.D.* 104 †	143 153	116 113	100 45	86 32
2. Water wash.	—	R.T.D. 104	150 146	119 115	103 59	89 31
3. Steam distillation.	—	R.T.D. 104	139 114	125 121	— 54	— 26
4. Wash with NaOH (20% solution).	—	R.T.D. 104	128 107	117 93	104 46	87 24
5. As 4 and steam distillation.	—	R.T.D. 104	167 157	153 144	133 66	110 38
6. Wash with conc. HCl and steam distillation.	—	R.T.D. 104	168 179	158 154	133 12	109 2
7. Wash with 70% H ₂ SO ₄ and steam distillation.	4.0	R.T.D. 104	201 178	208 181	195 106	177 69
8. Wash with 80% H ₂ SO ₄ (1 minute) and steam distillation.	6.1	R.T.D. 104	182 176	176 175	167 114	148 85
9. Wash with 80% H ₂ SO ₄ (10 minutes) and steam distillation. ‡	9.0	R.T.D. 104	209 219	214 210	202 141	178 105
Unleaded pool petrol for comparison.	—	R.T.D. 104	140 151	137 136	134 90	121 63

* Room temperature, not exposed to light.

† Storage at 104° F commenced after 1 week's storage at room temperature.

‡ Analysis of refined petrol :—

Aromatic hydrocarbons	17%
Unsaturated	„	15%
Saturated	„	68%

The results show that the removal of the most reactive unsaturated hydrocarbons by refining with sulphuric acid, resulted in gels of higher viscosities and greatly increased storage stability. The results of washing with hydrochloric acid to remove the small amount of bases used as inhibitors was also of some interest as the stability at 104° F was reduced to

a value much lower than that of the untreated petrol; the effect of basic substances on gel stability obviously merits further study.

Results for gels prepared in a series of pure organic solvents are given elsewhere,³ but the results for *cyclohexene* may be briefly mentioned here. They showed that this hydrocarbon in the pure state gave results similar to those obtained with paraffin hydrocarbons, but that the presence of peroxides and polymers formed from *cyclohexene* resulted in a marked reduction in the viscosity of the gel. Gels in *cyclohexene* had a low storage stability particularly at higher temperatures (104° F), due presumably to the effect of peroxides and polymers formed on storage.

The effect of the composition of suitable non-leaded petrols on the initial viscosity of the gels may be shown by the results for two petrols of different composition shown in Table VII.

TABLE VII.
Effect of Composition of Petrol on Gel Viscosity.

	Petrol A.		Petrol B.	
<i>Analysis of petrol :</i>				
Sp. gr. at 15° C	0.752		0.723	
Aromatics, per cent by weight	21.3		10.4	
Bromine No.	49		23	
<i>Distillation :</i>				
I.B.P., ° C	40		34	
Distillate to 100° C, % by vol.	41		42	
Distillate to 140° C, % by vol.	78		92.5	
F.B.P., ° C	184		153.5	
<i>Composition of gels (g per 100 ml petrol) :</i>				
Al stearate	5.0	7.5	5.0	7.5
Xylenols	1.5	3.0	1.5	3.0
“ Ball-drop ” viscosity of gels at 25° C, seconds	140	240	220	365

The more saturated petrol B gave gels of higher viscosity than the less saturated petrol A. Further data on the effect of the petrol on gel stability are given later in Table XIV.

PRODUCTION OF FUELS.

The laboratory-scale method of preparing fuels was the same as described in the gel-forming power test, except that to allow for the higher gelation temperature in petrol the final temperature to which the gel was heated was increased to 55° C. The apparatus employed and the procedure are described fully elsewhere.³

In the expansion of the work to a manufacturing scale certain problems, such as the effect of metals on the gel, had to be investigated. It was shown that while glass, tinned steel, and steel appeared to have no effect on the gels, zinc and solder had a slightly deleterious effect, while copper and lead had to be excluded from any plant manufacturing or handling the gel since they both caused a fairly rapid and irreversible loss of viscosity.

From the laboratory preparations (300–400 ml), the scale was increased to 8-gallon, 100-gallon, 400-gallon batches and finally to a mobile mixing unit

for the manufacture of 750-gallon batches, over 20,000 gallons being produced at the Fuel Research Station in the course of this work. At this stage production on a full scale was taken over by the "Shell" Refining and Marketing Co. Ltd. who encountered and overcame many difficulties involved in the development to the full industrial scale; much work was also carried out by the Sandoz Chemical Co. Ltd. and later by the Anglo-American Oil Co. Ltd. In general, the full-scale work gave results similar to those obtained in the laboratory-scale investigations though it was necessary for each manufacturer to determine for each batch of raw materials his own "correlation factor" connecting the viscosity as obtained in laboratory-scale experiments with that obtained on the full scale. The correlation factor depended on such factors as the difference in the method and rate of stirring, but was not far removed from unity. In general, the fuels produced showed uniformity in quality which was noteworthy in view of the nature of the product.

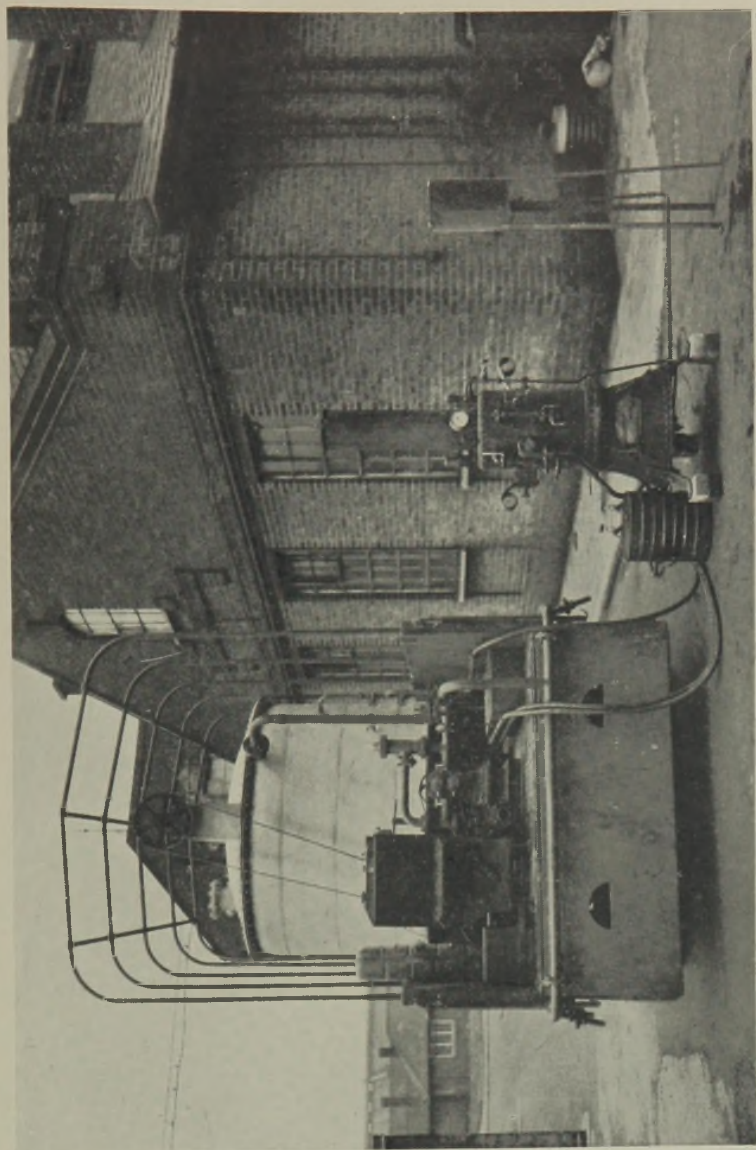
Mobile Mixing Plant.

This plant was designed to permit of batches of fuel (750 gallons) being made near the scene of operations, the main mixing device being mounted on a standard 3-ton Army lorry; a steam boiler was carried on a second lorry together with supplies of raw materials, spares, etc. Fig. 4 shows the unit ready for operation except that for convenience in photographing, the boiler is placed closer to the mixer than in normal working.

The unit consisted essentially of a 750-gallon mixing tank fitted with internal coils for steam heating, a paddle stirrer, a gear pump driven by a petrol engine together with the steam boiler.

The mixing tank, internal diameter 6 feet and capacity 850 gallons, was made of $\frac{3}{8}$ -inch mild steel plate and tested to a pressure of 40 p.s.i. There were two heating coils of 1-inch diameter pipe, one 178 feet long in the form of a cylindrical spiral round the vertical walls of the tank, and the other, 72 feet long, a flat spiral in the base of the tank; the coils were tested at a pressure of 200 p.s.i. The stirrer consisted of three paddles 3-inches wide and 5-feet diameter mounted on a vertical shaft, with the blades slightly twisted to form a propeller; baffles were fitted between the moving blades to increase the efficiency of stirring. The shaft was driven at 50 r.p.m. At the top of the tank were two 6-inch outlets, a flanged manhole cover (through which the stearate was changed), a vent cock, relief valve and a 1-inch opening for a dipstick. The pump used for charging petrol and xlenols and discharging the fuel had a capacity of 3000 gallons per hour, and the discharge line was fitted with ten 1-inch outlets so that the fuel could be discharged simultaneously into ten containers. The stirrer and pump were driven by a petrol engine (Willys Overland, as used in the "jeep" runabout). The steam for the heating coils was supplied from a small portable boiler (Merryweather Ltd., Greenwich, No. 2 portable boiler). The general layout is illustrated by the diagram shown in Fig. 5.

When operating the mixer, petrol was charged to the tank by means of the pump and the aluminium stearate added. The mixture was heated to 45° C and the xlenols added. Heating was continued for a further hour, the temperature being raised to a maximum not exceeding 55° C, and the



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FIG. 4.
MOBILE MIXING PLANT READY FOR OPERATION.

value for use as flame-thrower fuels could be assessed by the simple "ball-drop" viscosity test, which was therefore used throughout this work.

Storage Stability.

All the gels produced in this work were normally stable so far as absence of syneresis or other fundamental change in structure was concerned, and the term "storage stability" refers to the constancy of the viscosity of the fuels. Since the fuels had to be stored at temperatures possibly varying from 0° to 100° F it was essential that they should have a storage stability of a high degree not usually found in systems of this nature. A great deal of work was therefore carried out to determine the stability of fuels of different composition during storage at varying temperatures.

It was stated in the Introduction that cresylic acid or xlenols not only lowers the gelation temperature and viscosity of aluminium stearate but also confers on them a high degree of stability even at temperatures as low as - 10° F. Early work on the grades of stearate containing no protective colloid had shown that in order to achieve this stability it was necessary to have xlenols present to the extent of not less than 40 per cent by weight of the soap. Results with the improved grade of stearate, however, indicated that such a high proportion of peptiser was not necessary, and this was obviously a matter of considerable importance from the supply point of view, since for a gel of given viscosity, reduction in the proportion of peptiser enables a corresponding reduction in the concentration of soap to be made.

Experiments were carried out on the storage stability of 5, 6, 7, and 8 per cent aluminium stearate gels peptised with varying proportions of xlenols, and possessing "ball-drop" viscosities varying from 100 to 1500 seconds; the results for storage for one month at temperatures of 10° F and 104° F as well as at room temperature, are given in Table VIII and shown graphically in Figs. 6 to 8.

From these results the following conclusions were drawn :—

(1) The improved grade of aluminium stearate gave gels of very high stability at temperatures from room temperature down to 10° F, but the rate of loss of viscosity was relatively high at 104° F.

(2) For a given soap concentration the stability of the gel increased with increasing proportion of xlenols.

(3) An increase in soap concentration appeared to increase the stability of the gel, but this effect was somewhat difficult to assess, since for a gel of given viscosity any increase in the concentration of soap necessarily involved an increase in the proportion of xlenols which may have been the controlling factor in determining gel stability. What could most certainly be deduced was that for a gel of given viscosity the most stable gel was that containing the highest concentrations of soap and peptisers.

From the results given above, and other data not quoted, as well as from corresponding results for fuels of lower viscosity, specifications for fuel supply were drawn up in which a balance was maintained between the service requirements for the fuels and considerations of supply of the raw materials.

TABLE VIII.

Storage Stability of Aluminium Stearate Gels of Varying Composition.

Composition of gel, g per 100 ml petrol :		Storage tempera- ture, ° F.	“ Ball-drop ” viscosity at 77° F (25° C) in sec after storage for :				
Aluminium stearate.	Xylenols.		1 day.	1 week.	2 weeks.	3 weeks.	4 weeks.
5.0	2.0	R.T.*	110	115	100	95	90
		104	110	83	69	—	43
		10	110	100	100	100	90
„	1.75	R.T.	145	150	150	135	125
		104	145	125	95	—	55
		10	140	140	140	135	120
„	1.5	R.T.	200	195	205	185	180
		104	195	155	130	—	78
		10	200	195	—	190	175
„	1.25	R.T.	260	290	280	245	210
		104	260	185	135	—	69
		10	255	260	270	285	260
6.0	2.4	R.T.	210	205	195	190	160
		104	210	—	145	—	100
		10	210	215	195	190	195
„	2.1	R.T.	270	255	225	205	—
		104	280	—	160	—	105
		10	255	240	230	235	230
„	1.8	R.T.	395	405	390	375	325
		104	385	320	275	—	175
		10	405	400	385	370	305
„	1.5	R.T.	605	—	595	570	500
		104	620	520	430	—	270
		10	640	615	630	—	610
7.0	2.8	R.T.	325	320	300	300	280
		104	335	—	230	—	200
		10	350	360	340	340	335
„	2.45	R.T.	455	420	390	360	330
		104	450	—	310	—	205
		10	480	470	455	445	485
„	2.1	R.T.	590	540	495	510	500
		104	615	—	440	—	350
		10	630	625	590	650	530
„	1.75	R.T.	950	870	—	780	730
		104	950	—	700	—	560
		10	1000	1080	980	1020	1020
8.0	3.2	R.T.	535	540	525	505	460
		104	545	—	440	—	395
		10	510	540	515	—	—
„	2.8	R.T.	640	630	600	520	—
		104	660	—	530	—	450
		10	440	460	445	425	—
„	2.4	R.T.	900	—	850	870	—
		104	910	—	720	—	545
		10	810	850	—	830	800
„	2.0	R.T.	1500	1450	1350	1150	—
		104	1500	—	860	—	750
		10	1150	1250	1200	1150	1100

* R.T. = Room temperature.

Storage Stability of Service Fuels.

The results for storage stability quoted so far are exclusively those for laboratory-scale preparations, and it is therefore of interest to give results for fuels of the various types prepared by manufacturers for service use. For this purpose 8-gallon samples of service fuels prepared by various manufacturers were sent to the Fuel Research Station and stored in a covered

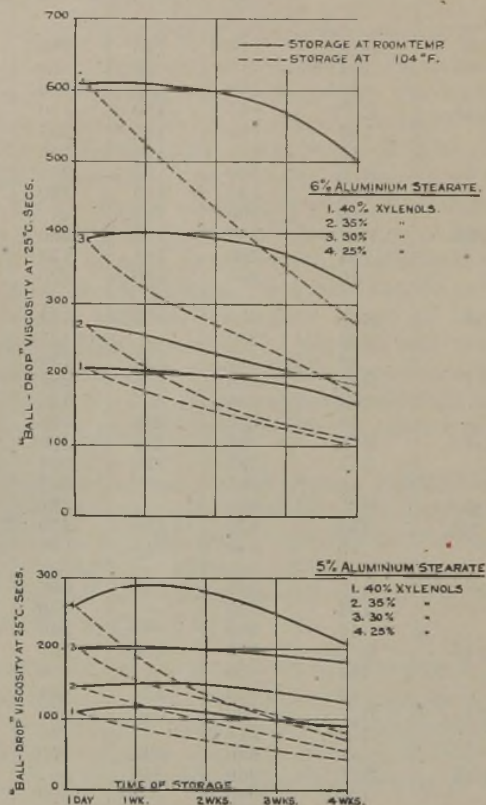


FIG. 6.

EFFECT OF SOAP AND XYLENOLS CONCENTRATIONS ON STABILITY OF HIGHLY VISCOUS FUELS. I.

trench the temperature of which during the period of the experiments did not differ materially from 60° F. Small samples were removed from the drums at monthly intervals and their "ball-drop" viscosities measured at 25° C (77° F). Results for some of these tests are recorded in Table IX and indicate the rate of loss of viscosity to be expected under service conditions in western Europe during the period from autumn to spring.

Storage stability trials were also carried out in the laboratory in sealed glass bottles stored in the dark at four temperatures, viz. 104° F (water-bath), 60–70° F (room temperature), 32° F, and 10° F (alcohol bath cooled

with solid carbon dioxide). As can be seen from the results in Table IX, storage of small laboratory samples gave a much higher rate of decrease in viscosity than that shown by samples stored in bulk in sealed steel drums,

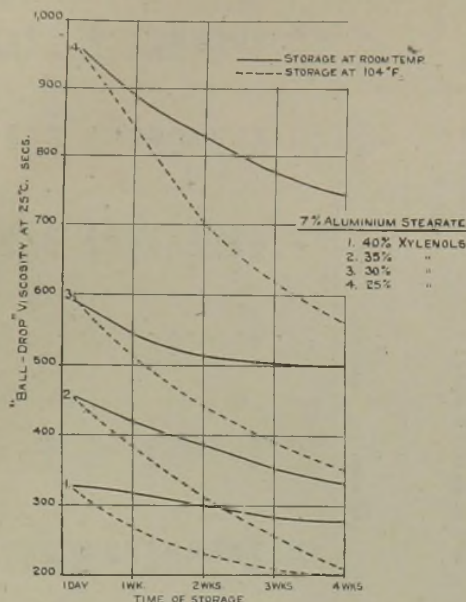


FIG. 7.

EFFECT OF SOAP AND XYLENOLS CONCENTRATIONS ON STABILITY OF HIGHLY VISCOUS FUELS. II.

but the data obtained give some idea of the probable "service" life of such fuels. Under the conditions of the test it was found that the viscosity of good fuels as measured by the "ball-drop" method at 77° F should show:—

(a) A decrease of not more than 5 per cent after storage for one month at 40° to 60° F.

(b) A decrease of not more than 10 per cent after storage for one month at 32° F.

(c) A decrease of not more than 50 per cent after storage for one month at 10° F (see Note below).

(d) A decrease of not more than 50 per cent after storage for one month at 104° F.

Note.—Later work showed that the tests at 10° F had given artificially high rates of loss of viscosity and results obtained using a thermostatically controlled refrigerator, indicated that the reduction in the viscosity of service fuels at 10° F was often negligible and never exceeded 20 per cent even when the petrol used was known to give fuels of low stability.

Stability of Fuels at Low Temperatures.

The introduction of a protective colloid during the manufacture of aluminium stearate increased the gel stability to storage at low tempera-

TABLE IX.
Storage Stability of Service Fuels.

Fuel no.	" Ball-drop " viscosity at 77° F. after 24 hours, seconds.	Age of fuel at start of storage tests.	" Ball-drop " viscosity at 77° F. seconds:								Samples stored in glass at :			
			Samples taken from drum stored at ca 60° F after :										60° F.	
			1 day.	1 month.	2 months.	3 months.	6 months.	8 months.	1 week.	1 month.	1 week.	1 month.	1 week.	1 month.
1	14	3 weeks	11	7	6	4	5	—	9	6	3	—	3	<1
2*	18	3 "	17	19	16	13	3	—	14	11	8	—	8	1
3	197	2 weeks	180	165	145	140	100	84	175	150	105	—	105	55
5†	195	2 "	150	125	93	64	52	—	140	87	76	—	76	37
6†	231	1 week	220	175	125	90	59	—	200	125	93	—	93	40
7†	197	2 weeks	145	125	95	90	70	—	120	80	99	—	99	48
8	—	1 week	235	215	195	190	140	135	210	175	175	—	175	87
9	240	1 "	255	240	225	205	160	135	240	195	165	—	165	80
10†	384	3 weeks	220	160	115	96	—	—	155	82	—	—	—	36
11†	233	3 "	160	115	82	67	—	—	130	72	92	—	92	20
4*	218	3 "	200	—	185	155	110	—	200	160	120	—	120	67
12	402	3 weeks	405	315	270	265	200	—	330	235	310	—	310	200
13	366	2 "	405	395	340	330	—	—	390	315	380	—	380	—
14	—	—	400	410	405	365	—	—	400	370	380	—	380	280
15	—	—	340	345	345	325	—	—	340	250	310	—	310	200
16	—	—	385	410	410	390	—	—	380	315	320	—	320	230
17	359	3 months	17	265	235	220	190	—	260	230	215	—	215	160
18	590	1 week	420	385	385	370	—	—	420	340	390	—	390	270
19†	—	4 weeks	470	320	245	235	—	—	360	230	300	—	300	165
20	440	3 "	375	290	270	245	210	—	310	250	300	—	300	135

* Made up in special petrol (see Table VII).

† Made up in 72 O.N. leaded petrol.

tures. The grade of aluminium stearate used before this modification was introduced, produced gels which on cooling to 10° F became rigid and failed to regain their normal properties on returning to room temperature. The final grade of aluminium stearate, on the other hand, produced gels with a greatly improved structural stability at low temperatures, as shown by results obtained on cooling gels made with this stearate in baths held at temperatures from 10° to -70° F in 10° F steps for 6 hours. The results are summarized in Table X.

TABLE X.

Stability of Aluminium Stearate Gels at Low Temperature.

Formula wt/vol.	Temperature at which gel became rigid, ° F. *	Temperature at which syneresis was observed, ° F.	Temperature from which gel failed to recover normal properties, ° F.
4/0.25	10	0	0
4/0.5	0	-20	-40
4/0.75	-20	-30	-50
4/1.0	-30	-40	-50
4/1.25	-30	-40	-60
4/1.5	-40	-50	-70
4/2.0	-40	-50	*
5/0.5	0	-20	-30
5/1.0	-30	-30	-50
5/1.25	-30	-40	-60
5/1.5	-30	-40	-60
5/1.75	-30	-40	-70
5/2.0	-40	-70	*
5/2.5	-40	-70	*
6/1.0	-10	-30	-60
6/1.5	-30	-40	-70
6/1.75	-30	-40	*
6/2.0	-30	-50	*
6/2.25	-40	-60	*
6/2.5	-40	-60	*
6/3.0	-50	-70	*

* Gradual recovery of normal stringy properties after 3-4 days even of sample cooled to -70° F, with reabsorption of synerized liquid.

As the temperature was lowered the gels became more viscous and less stringy and finally the latter property disappeared. The temperature at which this occurred is recorded as the "temperature at which gel became rigid"; syneresis was usually observed at a temperature about 10° F below this point. Most of the gels recovered their normal properties on returning to room temperature, in many cases even when they had been cooled to -70° F, the lowest temperature used. Within the limits examined the stability of the gel increased with the xlenols/soap ratio and to a smaller extent with the concentration of the soap. The effect of low temperatures on the gel depended both on the actual temperature and the time for which the gel was held at that temperature; thus syneresis and permanent break-

down were observed at higher temperatures than those shown in Table X when the gel was cooled for longer periods.

The stability of FRAS gels was thus so great that there was rarely any question of the structural breakdown of a gel. The viscosity stability of these fuels was such that they were still serviceable after a period of storage

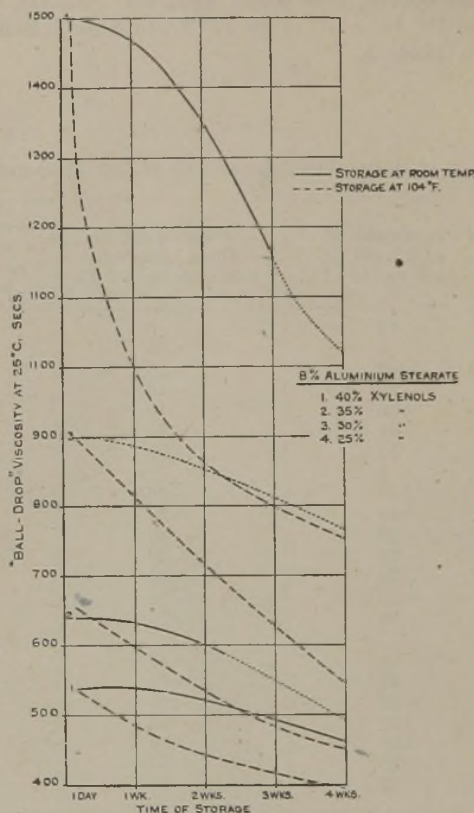


FIG. 8.

EFFECT OF SOAP AND XYLENOLS CONCENTRATIONS ON STABILITY OF HIGHLY VISCOUS FUELS. III.

at temperatures of 40° to 60° F of at least 1 year, and usually after several years.

It was also a requirement of these fuels that their viscosity stability should not be affected unduly by low temperatures so that they could be stored in the open during the winter, and results already quoted show that this requirement was met at temperatures down to 10° F. Nevertheless, when in the winter of 1944-45 some samples of the fuel deteriorated in a period coincident with a spell of very cold weather, further investigation of the possible effect of low temperature storage on the stability of the fuels was asked for. Some experiments were therefore carried out on the storage of three selected service fuels in glass tubes at temperatures of - 10°, 0°, and

+ 10° F, as well as at room temperature. Large Dewar flasks containing mixtures of solid carbon dioxide and alcohol were used as the low-temperature baths, and to economize in space the samples were contained in narrow tubes of $1\frac{1}{4}$ -inch diameter. The "ball-drop" viscosity determinations in these tubes gave somewhat higher results than those in the standard test in view of the increased wall effect, but as the correction factor was constant

TABLE XI.

Effect of Storage at Low Temperatures on Gel Stability.

Fuel number.	"Ball-drop" viscosity * of fuel at 77° F before storage, seconds.	Storage temperature, ° F.	Period of storage.	"Ball-drop" viscosity * at 77° F after storage, seconds.
SW 1028	204	R.T.D.	1 day	205
			3 days	207
			1 week	205
			2 weeks	183
			4 weeks	176
		10	1 week	157
			2 weeks	136
		0	1 day	202
			3 days	193
			1 week	150
			2 weeks	138
			4 weeks	122
		-10	1 day	143
			3 days	198
			1 week	117
			2 weeks	113
			4 weeks	52
WH 62	240	R.T.D.	4 weeks	—
		10	"	138
		0	"	162
		-10	"	133
KT 48	265	R.T.D.	4 weeks	211
		0	"	121
		-10	"	120

R.T.D. = Stored at room temperature in the dark.

* Determined in $1\frac{1}{4}$ -inch diameter tubes.

for all samples the relative results were not affected. The results are given in Table XI. It was found that after cooling to -10° F the hysteresis in the recovery of the viscosity to the normal value on return to room temperature markedly affected the results obtained 24 hours after removal from the cold bath, but an investigation of the results after one, two, and seven days showed that the hysteresis effect was eliminated after 48 hours; the results quoted for the viscosity at 77° F after storage were all obtained after this interval.

The results showed that the rate of reduction of viscosity increased as

the temperature was decreased, but there was no tendency to structural breakdown, and the loss of viscosity was not excessive. It may be concluded, therefore, that these fuels could be stored in the open during the winter in western Europe without deterioration even if exposed to very low temperatures for short periods.

Temperature Sensitivity of Fuels.

Although different grades of fuel had been provided for use under widely different temperature conditions, it was obviously still necessary that any given fuel should be usable over a fairly wide range of temperature, and

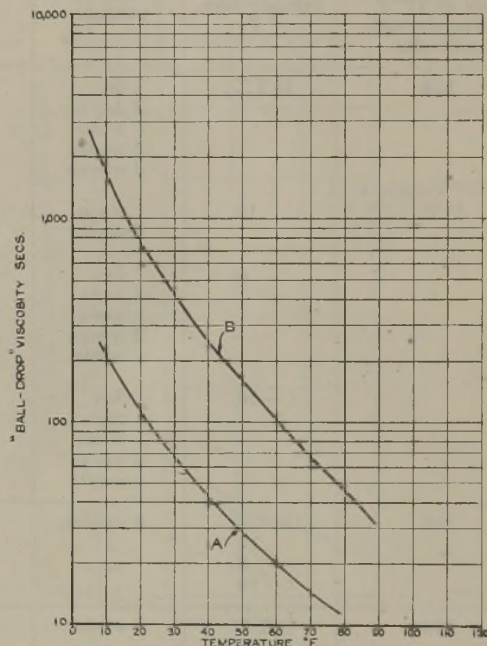


FIG. 9.

VISCOSITY-TEMPERATURE RELATIONSHIPS OF FUELS. I.

hence the change of viscosity of these fuels with temperature was of considerable importance. Aluminium stearate gels peptised with xylenols unfortunately show a high rate of change of viscosity with temperature as shown in Figs. 9 and 10 by the curves for four fuels with "ball-drop" viscosities at 77° F ranging from 14 to 350 seconds; the "temperature sensitivity" (*i.e.*, rate of change of viscosity with temperature) increased with increasing viscosity of the fuels.

Work carried out in attempts to produce fuels of lower temperature sensitivity is described in the following section.

EXPERIMENTAL FUELS.

Alcohol-peptised Fuels.

Investigations were made of the use of different peptising agents on the temperature sensitivity of the fuels. The first step was to determine the effect of reducing the acidity of the peptising agent by comparing the peptising action of *cyclohexanol* with that of phenol. *Cyclohexanol* had as high a peptising action as phenol though the stability of the gel produced was low. The next logical step was the use of the aliphatic alcohols and

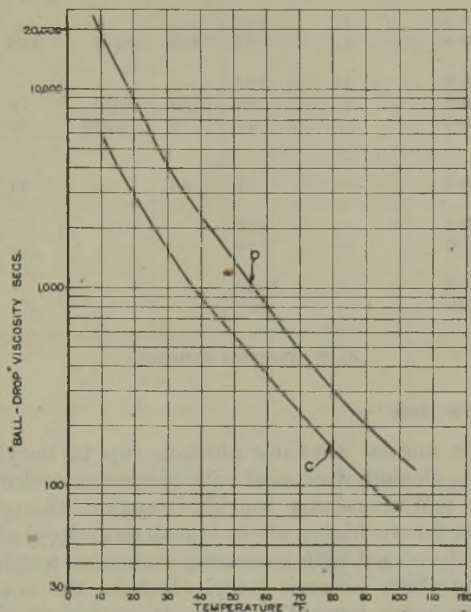


FIG. 10.

VISCOSITY-TEMPERATURE RELATIONSHIPS OF FUELS. II.

it was found that these compounds, and more particularly the higher members of the series, were extremely powerful peptising agents. Phenols did not reduce the gelling temperature to the same extent. Alcohols were the most important feature of the peptising action of aliphatic compounds. A fact that they produced gels of much lower temperature sensitivity. A preliminary survey of the effect of various alcohols showed that the peptising power decreased with increasing molecular weight and that the higher alcohols (such as tertiary amyl and dodecyl) produced gels of lower stability. A series of experiments was therefore carried out on the production of gels using methyl, ethyl, *n*-propyl, and the three isomeric butyl alcohols as peptisers with 5 per cent aluminium stearate (wt/vol). The results are recorded in Table XII.

TABLE XII.

Comparison of Various Alcohols as Peptising Agents.

Alcohol.	Amount of alcohol, g per 100 ml petrol.	Gelling temperature, ° C.	" Ball-drop " viscosity, secs.					
			As made.		After 18 hours at 10° F.		After 1 week at 10° F.	
			77° F.	40° F.	10° F.	77° F.	10° F.	77° F.
Methyl	0.3	—	79	138	opaque	72	solid. s.	66
	0.4	43	32	56	550	27	solid	26
Ethyl	0.3	47	145	—	—	—	—	—
	0.4	47	63	105	solid	105	s.	—
<i>n</i> -Propyl	0.3	48	193	—	—	—	—	—
	0.4	47	88	140	solid	76	—	—
	0.5	—	41	75	2300	38	solid. slight s.	48
<i>n</i> -Butyl	0.5	—	57	85	—	41	solid. s.	43
<i>sec.</i> -Butyl	0.5	—	403	—	—	—	—	—
	1.0	—	148	—	—	—	—	—
<i>tert.</i> -Butyl	0.5	—	1620	—	—	—	—	—
	2.0	—	217	—	—	—	—	—

s. = syneresis occurred.

The results show that :—

(1) For the normal aliphatic alcohols (up to butyl) the peptising activity (per g alcohol) decreased with increasing molecular weight, the activity per mol remaining roughly constant though other results indicated that for the higher alcohols such as dodecyl alcohol the molar activity also decreased with increasing molecular weight.

(2) For the three isomeric butyl alcohols, the activity decreased rapidly in the order, normal alcohol → secondary alcohol → tertiary alcohol.

(3) From room temperature down to 40° F the temperature sensitivity of the gels was very much less than that of the corresponding gels peptised with xylenols. Thus, on cooling from 77° to 40° F the " ball-drop " viscosity of a gel peptised with ethyl alcohol only increased from 25 to 41 seconds, whereas for a corresponding gel peptised with xylenol it increased from 25 to 127 seconds.

(4) As a viscosity increased from 25 to 127 seconds. enormously gels were cooled below 40° F the viscosity increased storage at 10° F the result of incipient solidification, and on prolonged storage at 10° F the gels solidified completely and syneresis took place.

It was clear, therefore, that while the use of alcohols as peptisers greatly reduced the temperature sensitivity of aluminium stearate gels, the gels thus produced had a lower structural stability than those peptised with xylenols, particularly at low temperatures. Experiments were accordingly carried out using mixtures of alcohols and xylenols as peptising agents to determine

if it would be possible to increase the stability of the gels to a sufficient degree without causing too great an increase in the temperature sensitivity of the gels.

The work was carried out with gels having viscosities of the order of 20 seconds, and it was shown that using a xynol : alcohol ratio of 2 : 1 it was possible to increase the stability of the gels so that there would be no syneresis after 1 month storage at 10° F and the sample stored at room temperature showed no appreciable change in viscosity. The increase in temperature sensitivity was not excessive; the ratio of the viscosity at 40° F to that at 77° F was increased from 1.7 to 2.6 by the addition of the

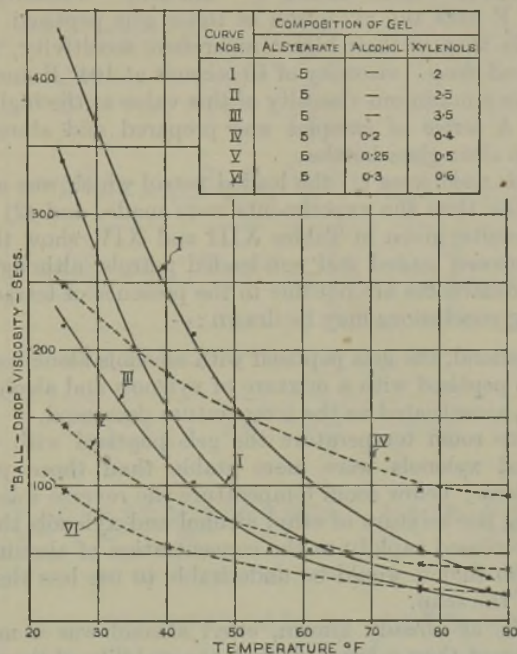


FIG. 11.

EFFECT OF PEPTISING AGENTS ON VISCOSITY-TEMPERATURE RELATIONSHIPS OF GELS.

xynols whereas for a gel of similar viscosity peptised with xynols alone the ratio was 5.0. Curves illustrating the effect of the nature of the peptising agent on the temperature sensitivity are given in Fig. 11, showing the results for gels peptised respectively with mixtures of xynols and alcohols and with xynols.

Most of these early results were obtained with gels of low viscosities (20 to 30 seconds); later the work was extended to fuels use at least of about 200 seconds. It was found that it was possible to obtain a stability at temperatures of about 8 per cent aluminium stearate (with 0.3 per cent alcohol and 0.6 per cent xynols) in order to obtain gels of similar stability to the gels of much inferior stability below 40° F, and that even with

stability to those peptised with xyenols alone, *e.g.*, they were only stable for 4 to 6 days at 32° F. On the other hand, the stability at 104° F was superior to that of the xyenols-peptised gels.

In view of these results, work on alcohol peptisers for high viscosity fuels was suspended, but as the gels of low viscosity appeared to show greater promise from the point of view of low-temperature stability further work was carried out on the production of this type of fuel using mixtures of xyenols and alcohol as a peptiser.

Experiments were made on gels peptised with ethyl alcohol, *n*-butyl alcohol, xyenols, and mixtures of each alcohol with xyenols. The gels were all made to give fuels having a "ball-drop" viscosity of 15 to 30 seconds at 77° F with the exception of those gels peptised with xyenols alone; these, in view of their high temperature sensitivity, were made so as to give a "ball-drop" viscosity of 10 seconds at 104° F since all fuels are required to have a minimum viscosity of this value at the highest operating temperature. A series of samples was prepared and stored at various temperatures in clear glass bottles.

The base fuels used were (1) the leaded petrol which was available on a large scale at the time the experiments were made, and (2) a non-leaded petrol. The results, given in Tables XIII and XIV, show the differences often found between leaded and non-leaded petrols, although, as already explained, the differences are not due to the presence of tetraethyl lead.

The following conclusions may be drawn :—

(1) In general, the gels peptised with alcohols alone were less stable than those peptised with a mixture of xyenols and alcohol, the difference being accentuated as the temperature decreased.

(2) Above room temperature the gels peptised with a mixture of alcohol and xyenols were more stable than those peptised with xyenols alone; below room temperature the reverse was the case.

(3) Using the mixture of ethyl alcohol and xyenols the stability of the gels decreased rapidly as the concentration of aluminium stearate decreased so that it would be undesirable to use less than 5 per cent (wt/vol) of the soap.

(4) While, as already known, ethyl alcohol was a more powerful peptising agent than *n*-butyl alcohol, the stability of the gels produced was in general similar except that with butyl alcohol the gels were rather less stable at high temperatures and more stable at low temperatures.

(5) The effect of the grade of petrol was in agreement with the conclusions already reached in the earlier section.

Fuels suitable for portable flame throwers, having a low temperature sensitivity and reasonable storage stability could thus be prepared using a mixture of ethyl alcohol and xyenols as peptising agent, and would be particularly suitable for summer or tropical use as they were more stable at it was at temperatures than the normal service fuel, although they would be required to be stable at low temperatures. Owing to their low temperature sensitivity viscosity curves in the low temperature range as shown by the temperature-together with that for a typical xyenol-peptised fuels (A and B), containing a mixture of ethyl alcohol

TABLE XIII.
Storage Stability Tests.

Alcohol.	Composition of fuel, g per 100 ml petrol.			"Ball- drop" viscosity at 77° F., seconds.	Storage tempera- ture, ° F.	"Ball-drop" viscosity, seconds, after storage for :											
	Al stearate.	Alcohol.	Xylenols.			1 week.		2 weeks.		4 weeks.		8 weeks.		3 months.			
						S.T.	77° F.	S.T.	77° F.	S.T.	77° F.	S.T.	77° F.	S.T.	77° F.	S.T.	77° F.
Ethyl .	5	0.4	—	R.T.	17	—	8	13	—	9	11	—	9	—	11	—	9
	"	"	—	104	17	—	74	7	262	7	8	—	8	13	12	15	14
	"	"	—	32	24	—	—	23	solid	29	94D	—	—	—	—	—	—
	"	0.3	—	R.T.	21	—	—	17	—	21	—	—	—	—	—	—	—
	"	"	—	104	24	—	9	14	8	11	19	—	19	11	17	8	18
	"	"	—	32	23	—	126	20	114	14	14	77	14	64	15	67	12
	"	"	—	10	26	—	950	27	480	20	20	—	—	solid	4D	—	—
	"	"	—	R.T.	23	—	—	19	—	19	16	—	16	—	13	—	11
	4.5	0.25	—	104	18	—	7	5	4.5	4D	—	—	—	—	—	—	—
	"	"	—	32	17	—	50	15	68	14	14	46	14	48	14	—	7
	"	"	—	10	19	—	250	6	96	<1D	—	—	—	—	7	—	5
	"	"	—	R.T.	24	—	—	18	—	11	8	—	8	—	—	—	—
	4	0.14	—	104	16	—	4	3	4	2D	—	—	—	—	—	—	—
	"	"	—	32	16	—	59	19	131	58	180D	—	—	—	—	—	—
	"	"	—	10	21	—	solid	135	syneresis solid	6D	—	—	—	—	—	—	—
	n-Butyl	5	0.7	—	R.T.	22	—	—	17	—	15	14	—	14	—	15	—
"		"	—	104	19	—	12	10	12	11	21	20*	21	22	22	23	24
"		"	—	32	23	—	83	15	76	15	15	220	15	12,000	181D	—	—
"		"	—	10	22	—	585	6	syneresis D	—	—	—	—	—	—	—	—
5		0.5	0.6	R.T.	28	—	—	—	—	25	23	—	23	—	17	—	14
None .	"	"	—	104	26	—	12	17	10	14	12	9	12	4	5	4	4
	"	"	—	32	23	—	62	20	67	19	18	56	18	48	16	64	19
	"	"	—	10	26	—	400	24	400	21	14	506	6	420	6	10,000	6
	"	"	—	R.T.	37	—	—	36	—	31	28	—	28	—	18	—	12
	5	—	4	104	35	—	7	22	4	11	2	—	2	—	—	—	—
	"	—	—	32	37	—	281	33	218	34	29	325	27	230	27	114	22
	"	—	—	10	34	—	1380	25	740	18	14	424	6	135	6	60	3
	"	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

D = Sample discarded. S.T. = Storage temperature. R.T. = Room temperature. * Thickening due to loss of petrol by evaporation.

TABLE XIV.
Effect of Petrol on Storage Stability.

Alcohol.	Composition of gel, g per 100 ml petrol.		Storage tempera- ture, ° F.	Petrol.	"Ball- drop" viscosity at 77° F., seconds.	"Ball-drop" viscosity, seconds, after storage for :										
						1 week.		2 weeks.		4 weeks.		8 weeks.		3 months.		
	Al stearate.	Alcohol.				Xylenols.	S.T.	77° F.	S.T.	77° F.	S.T.	77° F.	S.T.	77° F.	S.T.	77° F.
Ethyl .	5	0.3	0.6	104	24	9	14	8	11	8	11	8	11*	17	8	13
	"	"	"	"	31	14	19	12	16	—	—	—	13	18	17*	25
n-Butyl	5	0.5	0.6	104	26	12	17	10	14	9	12	9	4	5	4	4
	"	"	"	"	32	16	23	15	20	18*	25	20	20	28	26*	28
None .	5	—	4	104	35	7	22	4	11	2	4D	—	—	—	—	—
	"	—	"	R.T.	27	9	29	6	18	4	10	4	2	4	1	3
				"	37	—	36	—	31	—	28	—	—	18	—	12
				"	29	—	28	—	27	—	23	—	—	12	—	12
			32	32	37	281	33	218	34	325	29	230	27	114	22	22
			"	10	32	313	28	294	36	351	33	290	30	147	26	26
			"	"	34	1380	25	740	18	424	14	135	6	60	3	3
			"	"	32	1220	33	1200	32	905	20	460	16	210	10	10

R.T. = Room temperature.

S.T. = Storage temperature.

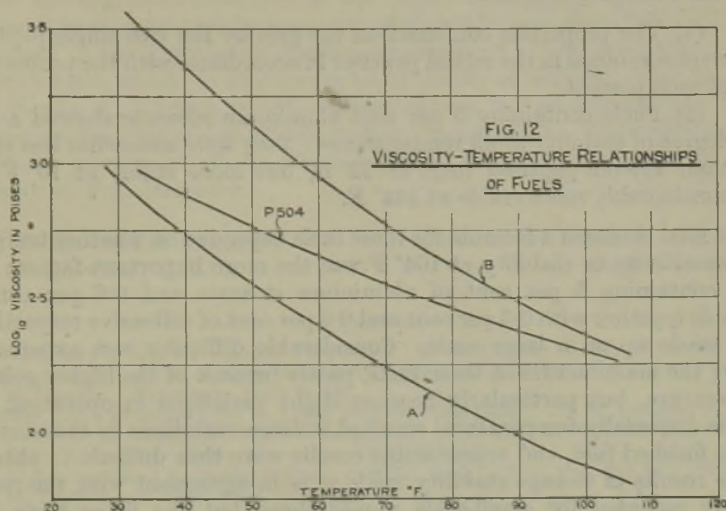
D = Sample discarded.

* Thickening due to loss of petrol by evaporation.

and xyenols as peptiser. The latter fuel had a viscosity not less than B at 120° F and not greater than A at 30° F and therefore covered the whole range for which the two fuels A and B were otherwise required.

Cellosolve-peptised Fuels.

The suggestion that ethyl cellosolve (the mono-ethyl ether of ethylene glycol) should be used as a peptising agent was originally made by Dr H. G. Williams (Anglo-American Oil Co.) who pointed out that its use would effect considerable economy in aluminium stearate since it was possible to make stable gels of high viscosity with a smaller proportion of aluminium stearate



than that required when xyenols were used. Unfortunately his results also showed that while the cellosolve-peptised gels were stable at room temperature their stability at low temperatures was inferior to that of the corresponding gels peptised with xyenols. At the time the suggestion was made, gel stability at low temperatures was considered to be of paramount importance and cellosolve-peptised fuels were not considered suitable for service use.

Later, the question of economy in the use of aluminium stearate assumed major proportions, and further work was carried out, initially on the use of cellosolve as a peptiser for the preparation of thick fuels, using 4 to 5 per cent aluminium stearate and 0.5 to 1.5 per cent cellosolve. The gelation temperature was higher (50° to 53° C) than for xyenol-peptised fuels (44° C) and the mixtures were therefore heated to 55° to 65° C instead of 45° to 55° C.

Results of storage and firing tests on these fuels showed that :—

- (1) The fuels were less stable than xyenol-peptised fuels at low temperatures (10° F and 32° F) but more stable at high temperatures (104° F).

- (2) The fuels had a higher elasticity modulus than xynol-peptised fuels and hence were more difficult to handle.
- (3) The fuels had a much higher temperature sensitivity than xynol-peptised fuels.
- (4) The use of cellosolve would enable a substantial reduction to be effected in the proportion of soap required to give a stable gel.

The results suggested that a combination of the best properties of cellosolve and xynols would give a superior fuel to any previously made (except from the point of view of temperature sensitivity). Tests were therefore carried out on gels containing mixtures of cellosolve and xynols with the following results :—

- (1) The properties conferred on the gels by the two single peptisers were combined in the mixed peptiser in accordance with the proportions of each present.

- (2) Fuels containing 5 per cent aluminium stearate showed a high degree of stability at all temperatures; they were somewhat less stable than xynol-peptised fuels at 32° F, but more stable at 10° F and considerably more stable at 104° F.

The final choice of a formula for these fuels depended on whether temperature sensitivity or stability at 104° F was the more important factor; two fuels containing 5 per cent of aluminium stearate and 0.6 per cent of xynols together with 0.3 per cent and 0.6 per cent of cellosolve respectively were made up on a large scale. Considerable difficulty was experienced during the manufacture of these fuels, partly because of the higher gelation temperature, but particularly because slight variations in operating conditions (especially temperature) resulted in large variations in the viscosity of the finished fuel, and reproducible results were thus difficult to obtain.

The results of storage stability trials were in agreement with the results already recorded for small-scale preparations, but the firing tests were somewhat less satisfactory, so that further work on these fuels would be necessary before full-scale manufacture could be adopted. Nevertheless, it was considered that the introduction of cellosolve as a peptising agent gave promise of the production of fuels considerably superior to the standard service fuels particularly for use in tropical zones.

Comparison of Peptisers.

The results described in this paper show that the properties of aluminium stearate gels may be profoundly affected by the use of various peptising agents, and that the effect of these agents may be specific to the class of compound employed.

Thus for conferring stability at low temperatures, low elasticity and maximum lowering of gelation temperature, and the less easily defined but no less important properties of ease of manufacture and reproducibility of results, the xynols are by far the most effective peptising agent employed.

The use of cellosolve enables a much smaller proportion of aluminium stearate to be used and also confers a high degree of stability at high temperatures. The temperature sensitivity of the gels is higher than for the xynol-peptised gels.

The lower aliphatic alcohols reduce the temperature sensitivity to a marked extent by comparison with the value obtained with the other two peptising agents. The stability of the gels produced is slightly superior at 104° F to the xyleneol-peptised gels but inferior to the cellosolve-peptised gels.

With a mixture of peptising agents all the effects described above are additive, so that, given the requirements for any specified fuel, it is possible to select the most suitable mixture of peptising agents in order to obtain fuels with the desired properties.

ACKNOWLEDGMENT.

The investigations described in this paper were carried out at the Fuel Research Station of the Department of Scientific and Industrial Research on behalf of the Petroleum Warfare Department. The work was carried out by a team which, in addition to the authors, at different times included C. C. Noaks, A. G. Lowe, and W. J. Sparkes; the last-named was responsible for the engineering design of the mobile mixing plant. The paper is published by permission of the Chief Scientist, Ministry of Supply, and the Director of Fuel Research.

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September 1946.

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