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AUTHOR: R.H.Mettivier Meyer,
AMSTERDAM

TITLE: Improvement of the oxidation stability of synthetic Bright Stocks and aviation oils by polymerizing vapour phase cracked distillate along with aromatics or fractions rich in aromatics. -

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N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, THE HAGUE

003855 16104 V

REPORT NO. S 7169.

TITLE: Improvement of the oxidation stability of synthetic Bright Stocks and aviation oils by polymerizing vapour phase cracked distillate along with aromatics or fractions rich in aromatics.

AUTHOR: R. H. Mettivier Meyer.

SUMMARY AND CONCLUSIONS:

Synthetic oils, prepared by polymerizing vapour-phase cracked distillate with $AlCl_3$ as catalyst do not meet the B.A.M. specification as regards the viscosity ratio before and after the oxidation; the Ramsbottom Coke Number, as well as its increase after oxidation, is very satisfactory with these oils.

We have now found that special aromatics, such as naphthalene and its homologues, if polymerized together with the cracked distillate, have a very favourable effect on the viscosity ratio, while neither the Ramsbottom Coke Number, nor its increase after oxidation, are appreciably raised.

We also tried aromatic products obtained from practice, such as Pernis Coking Gas Oil, Woodriver Coking Gas Oil, Balik Papan Kerex and Anthracene Oil, but only Pernis Coking Gas Oil proved to be suitable.

In further experiments the addition of aromatics was studied after the cracked distillate had been wholly or partially polymerized at a low temperature. They were carried out with naphthalene, but were not reproducible. For reasons stated in the report it is, however, highly probable that by carrying out such experiments in a continuous polymerization apparatus, reproducible results will be obtained.

The addition of aromatics will undoubtedly also tend to keep the sludge in the engine in suspension, which will promote cleanliness.

An aviation oil made by polymerizing vapour-phase cracked distillate, to which about 10 % of naphthalene had been added before polymerization, met the B.A.M. specifications, and was the best oil as regards tendency to ringsticking and coke formation ever tested in the Deutz benzine motor at Delft.

IMPROVEMENT OF THE OXIDATION STABILITY OF SYNTHETIC BRIGHT STOCKS AND AVIATION OILS BY POLYMERIZING VAPOUR PHASE CRACKED DISTILLATE ALONG WITH AROMATICS OR FRACTIONS RICH IN AROMATICS.

Introduction.

Synthetic oils, both Bright Stocks and aviation oils, have been found not to meet the B.A.M. oxidation test as regards the viscosity ratio before and after the oxidation (<2), but readily to answer the requirement that the Ramsbottom Coke number of the oil itself shall be less than 0.7 % and that it shall not increase by more than 1.0 % during oxidation.

Purely olefinic cracked distillates, obtained by vapour-phase cracking of pure paraffin wax, give oils with the highest viscosity ratio. However, there is a relation between the boiling limits of the olefinic base material and the value of the viscosity ratio. Thus, aviation oils, made from low-boiling fractions show a ratio of 3.0, which drops to about 2.0 for the polymerizate from the high boiling fractions (e.g. cetene fraction).

The increase in Ramsbottom Coke is very slight for all these oils made from purely olefinic fractions (e.g. 0.26 for the fr. <175°C.), especially for the polymerizates from low-boiling fractions.

A similar influence of the boiling limits of the base material, on the viscosity ratio as well as on the increase in coke, has been observed in the case of Bright Stocks.

Starting from a technical base material, such as vapour-phase cracked distillate (fr. up to 280°C.) ex Balik Papan Wax cakes, which contains cracked products rich in rings especially in the higher boiling fractions, polymerization gives synthetic oils which do mot meet the B.A.M. viscosity ratio either, while the Ramsbottom Coke increase is comparatively unfavourable (usually 0.6 - 0.7 for S 505). A marked improvement in Ramsbottom increase is possible by removing the highest boiling fractions from the cracked distillate (to 0.45 - 0.50, for the aviation oils from fr. <250°C. and <160°C. ex B.P. cracked distillate). The viscosity ratio, however, remains far above 2.0.

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Graph 1.

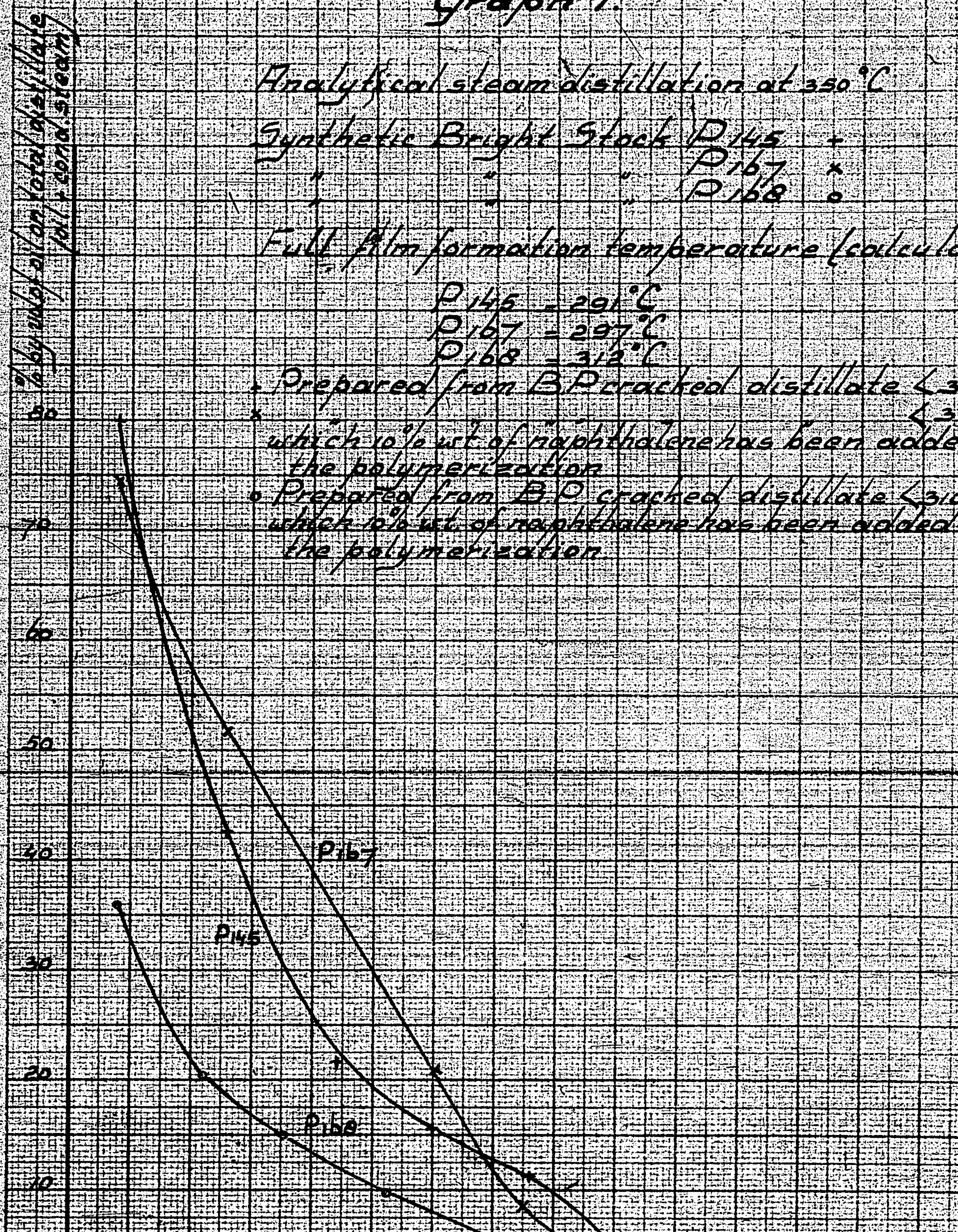
Analytical steam distillation at 350 °C

Synthetic Bright Stock P145 +
" " " P167 ×
" " " P168 o

Full film formation temperature (calculated):

P145 – 291 °C
P167 – 297 °C
P168 – 312 °C

+ Prepared from B.P. cracked distillate < 310 °C
× " < 310 °C to which 10 % wt of naphthalene has been added during the polymerization
o Prepared from B.P. cracked distillate < 310 °C to which 10 % wt of naphthalene has been added after the polymerization



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These cracked aromatics therefore had an unfavourable effect. On the contrary, naphthalene, when polymerized together with the cracked distillate, imparted to the Synthetic Bright Stock a low viscosity ratio as well as a comparatively low coke increase, without impairing the other properties.

This result led to a more extensive investigation into the possibility of polymerizing the cracked distillate together with naphthalene and other aromatics or strongly aromatic fractions. Special attention was paid to the addition of naphthalene after the complete or partial polymerization of the cracked distillate, so as to saturate the high-polymer olefine with an aromatic nucleus. In this way a saturated and very highly molecular Bright Stock might be formed (with high film formation temperature and high viscosity).

It has been found that it is actually possible to prepare a higher molecular Bright Stock by adding 10 % of naphthalene after the cracked distillate has practically been polymerized. The naphthalene nucleus has then reacted with the polymerization product (about 5 % passed over unaltered as naphthalene in the subsequent distillation). The viscosity (Saybolt U. 210°F.) consequently rose from about 200 to about 240 sec., while the full film temperature was 312°C., i.e. about 20°C. higher than that of an oil made from B.P. cracked distillate (without naphthalene) and steamed off at 300°C. (see graph 1).

In subsequent experiments, in which naphthalene was added after the cracked distillate had been more or less polymerized, this result has not been fully realized. It was invariably noticed that only a small portion of the naphthalene takes part in the reaction, the rest being separated unaltered or in the volatile tops, even when an additional amount of $AlCl_3$ was added and the temperature was raised.

The reproducibility of the procedure is not very great. It is assumed that the polymerization reaction takes place in such a way that the high-polymer compounds are formed <u>at once</u> owing to the very rapid growth of an activated molecule. In the case of "incomplete" polymerization the reaction product therefore chiefly consists of the high-polymer oil, the unaltered base material and a small quantity of tops. It depends on the exact moment of addition whether the required reaction takes place, or whether the unaltered base material reacts with the naphthalene to mainly low-molecular tops.

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Table 1.

Polymerization of Balik Papan cracked distillate <310°C. (TMC 8130) with the addition of naphthalene.

Experiment	P 145	P 168	P 167	P 169
10% of naphthalene added	none	after 4 h. (B.V.=1)	After 75 min. (B.V.=40)	At once (B.V.=91)
Polymerization temp., °C.	20	20	20	20
Duration of the polymerization before the addition	4 h.	4 h.	$1\frac{1}{4}$ h.	-
Duration of the polymerization after the addition	-	2 h.	$2\frac{3}{4}$ h.	4 h.
B.V. of the tops	9.6	5.1	13.8	32.6
Yields.				
% top layer/CD + N	91.8	92.0	93.0	92.0
% conc./top layer	76.6	72.5	74.9	67.3
% conc./CD + N	70.3	66.7	69.6	61.9
Properties.				
E/50	32.2	50.4	34.9	27.8
Saybolt viscosity/210°F.	173	237.2	171.5	141
V.I.	119	114	109	104.5
Flash point PM cl.c.	235	263	249	263
Conradson Carbon	0.19	0.34	0.24	0.34
Colour	$2\frac{1}{2}$	$3\frac{1}{2}$+	$2\frac{1}{2}$+	3
d 15/4	0.873	0.878	0.887	0.889
Ring analysis.				
d 20/4	0.8690	0.8738	0.8835	0.8855
n_D^{20}	1.4858	1.4898	1.4982	1.4995
r_D^{20}	0.3303	0.3308	0.3319	0.3319
A.P., °C.	138.6	130.2	125	116.7
Mol. wt.	1007	1124	842	785
Estimated % aromatic ring	abt. 8	abt. 12	15	18
B.A.M. test.				
Visc. 100°F. (poises)	4.01	6.64	4.71	3.73
Ditto after oxidation	9.0	11.25	7.68	6.47
Ratio	2.25	1.70	1.64	1.73
Ramsbottom coke	0.25	0.28	0.28	0.31
Ditto after oxidation	0.80	0.80	0.82	0.86
Increase	0.55	0.52	0.54	0.55

The right moment of addition can only be found by means of a continuous polymerization apparatus, where this addition can be made at a given and fixed moment.

EXPERIMENTS.

3 Fractions of a Balik Papan vapour-phase cracked distillate ex wax cakes (TMC 8130) were polymerized together with aromatics:

a. Fraction <310°C.
b. " <280°C.
c. " <250°C.

The fractions a and b were exclusively polymerized to Bright Stock, c was also polymerized to aviation oil.

a. Balik Papan vapour-phase cracked distillate <310°C.

Three tentative experiments were made first, wherein 10 % of naphthalene was added:

immediately to the cracked distillate (B.V. = 91); P 169
after 75 minutes' polymerization (B.V. = 40); P 167
" 4 hours' " (B.V. = 1); P 168

The polymerizations were carried out at about 20°C.

In Table 1 the results have been compared with those of Bright Stock made from the same fraction without the addition of naphthalene (P 145). It is clear that in P 169 and P 167 the naphthalene molecules reacted with low-molecular olefines, so that strongly substituted aromatics were formed with a comparatively low molecular weight. These evidently act as anti-oxidant in the B.A.M. test: the viscosity ratio drops to 1.64 and 1.73, respectively, while the coke increase is not higher than that of the Bright Stock ex fr. <310°C. without naphthalene.

Bright Stock P 168, on the contrary, is higher molecular, and the viscosity ratio is also very satisfactory (1.70). The naphthalene molecule has therefore evidently condensed with the Bright Stock molecule to a higher molecular Bright Stock with a high full film temperature (312°C.; see graph 1).

Table 2.

Polymerization of B.P. cracked distillate <280°C. (ex TMC 8130) with the addition of Kerex and naphthalene.

Experiment	P 205	P 208	P 209	P 226
Base stock	fr.<280°C. ex B.P.crack.dist.	Ditto	Ditto	Ditto
Substance added	-	10% naphthalene	10% kerex fr. 200-250°C.	10% naphthalene
Polymerization temp., °C.	20	20	20	20
Duration of the polymerization before the addition	4	4(B.V.=1)	4(B.V.=1.3)	1¾(B.V.=2.4)
Duration of the polymerization after the addition.	-	2	2	2¼
Bromine value of tops	9.1	2.9	5.1	7.9
Yields.				
% Supernatant layer/C.D.+sub.added	92.5	91.7*	91.6*	94.5*
% conc./supernatant layer	77.4	71.9	72.4	76.7
% conc./C.D.+subst.added	71.6	66.0	66.3	72.5
Properties.				
Visc. E/50	33.6	44.1	40.6	44.2
" Saybolt U 210°F.	180.5	216	206	213.5
V.I.	117	115	115	112
Flash point P.M. closed cup °C.	260	268	257	254
Conradson	0.16	0.19	0.22	0.16
Colour Union	2+	2½	2+	2
d 15/4	0.869	0.875	0.874	0.879
Ring analysis.				
d 20/4	0.8563	0.8590	-	-
n_D^{20}	1.4743	1.4754	-	-
r_D^{20}	0.3284	0.3280	-	-
A.P., °C.	150.6	151.2	-	-
Mol. wt.	1099	1061	-	-
Estimated % aromatic ring	abt.6	abt.8-9	-	-
B.A.M. test.				
Visc. 100°F. in poises	4.12	5.08	5.20	5.78
Ditto after oxidation	9.40	10.4	11.45	11.0
Ratio	2.28	2.06	2.20	1.91
Ramsbottom coke number	0.19	0.22	0.25	0.20
Ditto after oxidation	0.57	0.66	0.67	0.64
Increase	0.38	0.44	0.42	0.44

* As referred to total naphthalene consumption.

b. Balik Papan vapour-phase cracked distillate <280°C.

The following polymerizations were carried out, also at 20°C.:

P 208, fr. <280°C., to which 10 % of naphthalene was added after 4 hours' polymerization (B.V. = 1), upon which the polymerization was continued for 2 hours.

P 209, fr. <280°C, to which 10 % of kerex (fr. 200-250°C.) was added after 4 hours' polymerization (B.V. = 1.3), which was also continued for another 2 hours.

For comparison, fr. <280°C. was polymerized to Bright Stock without the addition of aromatics (P 205).

The results are given in table 2.

The addition of kerex causes the B.S. to become slightly thicker, but the B.A.M. viscosity ratio remains practically unaltered (2.2). The experiment with naphthalene (P 208) shows a slightly more favourable viscosity ratio (about 2.05). Only about 3 % of naphthalene has been absorbed in the oil; the rest has been steamed off unaltered and in the tops. (See also d_4^{15} and V.I.). Possibly, the reactivity of the $AlCl_3$ with which the cracked distillate had already been polymerized for 4 hours, was too slight to effect complete adsorption of the naphthalene molecule.

To ascertain this, an experiment was made (P 226) in which the naphthalene was added earlier (after 1¼ hours; B.V. abcut 2.5); the polymerization was subseqüntly carried out for 2¼ hours at a higher temperature (60°C.). The naphthalene adsorption is actually better now ($d_4^{15} = 0.879$; V.I. = 112), for the B.A.M. viscosity ratio is about 1.90. Yet even in this case the absorption of naphthalene proved to be incomplete.

c. Balik Papan vapour-phase cracked distillate <250°C.

1. Polymerization at room temperature (15-20°C.).

More extensive examinations were carried out relative to the addition of aromatics and aromatic fractions to the cracked distillate fraction <250°C., before as well as after polymerization (see table 3). In the first place it was attempted to polymerize 10 % of naphthalene together with the cracked distillate, after this had been partly polymerized (B.V. of the reaction mass = 6). After the addition of the naphthalene 1 % of $AlCl_3$ was supplemented. It is, however, 8 7169.

Table 3.

Preparation of Bright Stocks in some cases with the addition of various aromatics or aromatic fractions.

Polymerization run	P 233	P 258	P 295	B 269	B 270	B 292	B 293
Base stock	B.P.crack. dist. fr.<250°C.	ditto	ditto	ditto	ditto	ditto	ditto
Substance added	none	10% naphthalene	10% naphthalene	10% Kerex fraction 200-250°C.	10% Anthracene oil <380°C.	10% Pernis coking cycle stock <320°C.	10% Wood river coking cycle stock
Time of polymerization before the addition.	4	1½	5	0	0	0	0
Time of polymerization after the addition.	-	4	2	4	5¼	5½	5
Polymerization temp., °C.	15	20	20	20	20	20	20
Time of polymerization	4	6½	7	4	5	5½	5
% $AlCl_3$	4.0	3 + 1 %	4.5	4.0	6.0	5.0	4.0
Decrease in bromine value.							
Initial B.V.	107.4	107.4	107.4	abt.96	abt.96	abt.96	abt.96
After 1 hour	7	abt.16	24.5	3	51	37	23
" 2 hours	4	(1½ h) 6 (+N)	5	1.5	47.5(+1%)	30(+1%)	6
" 3 "	1.5	<1(+1%)	2(+½%)	<1	37	4½	1.5
" 4 "	1	-	(5 h) 0.5 (+N)	-	33(+1%)	<1	1
Final B.V.	1	-	-	<1	<1	<1	<1
Bromine value tops	11.7	7.3	(2.8)	28.2	11.1	17.2	17.5
Concentration temp., °C.	280	285	285	290	285	285	285
% Supernatant layer/C.D. + subst.added	89.2	92.0	90.5	90.8	86.0	86.9	90.0
% conc./supernatant layer	80.8	76.8	77.7	72.9	79.5	75.8	75.4
% conc./C.D.+subst.added	72.1	70.6	71.2	66.2	68.4	65.9	67.9
Properties conc.							
Visc. E/50	45.5	40.5	43.9	34.8	37.7	29.2	25.8
" Saybolt U 210°F.	230.5	200.5	215.0	178.0	181.5	152	139
V.I.	116	115	115	113	109	112	112
Flash point P.M. closed c., °C.	260	257	266	257	260	254	241
Conradson	0.07	0.12	0.14	0.16	0.60	0.14	0.09
Colour Union	1½	1½	1½+	1½-	3½+	1½+	1½
d 15/4	0.865	0.871	0.8685	0.8715	0.879	0.874	0.8705
B.A.M. oxidation test.							
Abs. visc. 100°F. in poises	5.83	5.09	5.40	4.45	5.00	3.65	3.17
Ditto after oxidation	14.0	10.35	12.28	10.3	9.54	7.60	7.60
Visc. ratio	2.40	2.03	2.28	2.32	1.91	2.09	2.21
Ramsb.coke number % by wt.	0.12	0.15	0.15	0.14	0.34	0.15	0.13
Ditto after oxidation	0.45	0.57	0.47	0.56	0.91	0.70	0.70
Increase	0.33	0.42	0.32	0.42	0.57	0.55	0.57

clear from the constants of the polymerizate that a large part of the naphthalene has <u>not</u> taken part in the reaction. The B.A.M. viscosity ratio is 2.00 - 2.05. A negative result was obtained in an experiment (<u>P 295</u>) in which 10 % of naphthalene was added after complete polymerization (B.V. 0.5), upon which the reaction was continued at 60°C. (Viscosity ratio about 2.25 - 2.30).

In some experiments other aromatic products (see Addendum I) were added to fr. <250°C. ex B.P. cracked distillate:

10 % of Kerex (fr.200-250°C.), polymerization Exp. <u>P.269</u>.
10 % of Anthracene Oil (fr. <380°C.) " <u>P 270</u>.
10 % of Woodriver Coking Cycle Stock (TMC 8911)" <u>P 293</u>.
10 % of Pernis Coking Cycle Stock fr. <320°C. " <u>P 292</u>.
(TMC 9046)

To ensure complete polymerization of these additions, the aromatic fractions were dissolved in the cracked distillate <u>before</u> polymerization.

As appears from table 3, the addition of the <u>kerex</u> fraction has hardly any influence on the properties of the oil in the B.A.M. oxidation test. The addition of the Anthracene oil fraction <380°C. causes a very high Conradson (0.60) and a poor colour (3½+); the viscosity ratio, however, drops to 1.91. As regards the <u>aromatic Coking Cycle Stocks</u> from Wood river and Pernis fr.<320°C.), in spite of the high aromatic content (d_4^{20} = 0.9228 and 0.996, respectively), only the Pernis Coking Cycle Stock has some influence on the B.A.M. viscosity ratio (about 2.10), while the coke increase is rather high (0.55 - 0.57).

Upon the whole, it may therefore be said that (if the addition is 10 % wt.) only the most aromatic fractions such as Anthracene oil and to a certain extent the Pernis Coking Cycle Stock (fr. <320°C. contains more than 60 % of C in aromatic ring), have an appreciable influence on the B.A.M. viscosity ratio. <u>This is, however, accompanied by a greater coke increase, which is not the case when naphthalene is added</u>. (See also sub 2)

2. <u>Polymerization to aviation oil.</u>

For the preparation of a 100 sec. aviation oil the Balik Papan cracked distillate should be polymerized at about 85°C.

At this temperature the polymerization takes place extremely quickly. The addition of aromatics <u>after</u> the

Table 4. Polymerization experiments at different temperatures with Balik Papan
and 25 % naphthalene was added before polymerization.

Polymerization run	P 237(II)	P 235	P.
Base stock	B.P. crack dist. fr. <250°C.	Ditto	Di
% wt. naphthalene added.	10%	10%	10%
Time of polymerization, h.	4½	2¾	
Polymerization temp., °C.	5	abt. 60°	abt
Decrease B.V.:			
After 1 hour	5.5	1	<
" 2 hours	3.5	1	
" 3 "	2	-	
" 4 "	1		
B.V. tops	9.7	10.6	9
% supernatant layer/C.D.+naphthalene	91.8	90.5	83
% conc./supernatant layer	79.3	78.8	80
% conc./C.D.+naphthalene	72.8	71.4	67
Properties:			
Visc. E/50	44.6	27.2	20
" Saybolt U 210°F.	206.5	137.5	11
V.I.	109	106	10
Flash point P.M. closed c., °C.	246	246	24
Conradson	0.26	0.21	0.
Colour Union	2	1½	2
d 15/4	0.885	0.882	0.
Ring Analysis:			
d 20/4			0.
n_D^{20}			1.
r_D^{20}			0.
A.P.			11
Mol. wt.			
Complete hydrogenation.			
d 20/4			0.
n_D^{20}			1.
r_D^{20}			0.
A.P.			13
Mol. wt.			6
Prediction			
% C in aromatic ring			
% C in naphthenic ring			5
% C in paraff. chain			80
B.A.M. oxidation test.			
Abs. viscosity in poises/100°F.	6.07	-	2.
Ditto after oxidation	10.4	-	4.
Visc. ratio	1.71	-	1.
Ramsbottom coke number in % by wt.	0.23	-	0.
Ditto after oxidation	0.61	-	0.
Increase	0.38	-	0.
% Tops >300°C./C.D.	4.5	5.9	6
Properties of the tops >300°C.			
Partially hydrogenated.			
d 20/4	0.8608*	-	0.
n_D^{20}	1.4731	-	1.
r_D^{20}	0.3260	-	0.
A.P., °C.	96.3	-	67
Mol. wt.	311	-	3
Prediction:			
% C in aromatic ring	39.5	-	
% C in naphthenic ring	0	-	
% C in paraff. chain	60.5	-	

* Completely hydrogenated. % C in aromatic ring computed from the rise in anil

th Balik Papan cracked distillate ≤ 250°C. (TMC 8130) to which 10 %

235	P.221	P 273	P 241	P 238	P 222
tto	Ditto	Ditto	Ditto	Ditto	Ditto
	10%	25%	25%	25%	10%
¾	4	4	4	4	1 + 3
,60°	abt.100°	40	60	abt.120°	abt.82.5°
1	<1	0.5	0.9	0.5	<1.0
1	-	-	0.5	-	Naphthalene added after one hour's polymerization
-	-	-	-	-	
	-	-	-	-	
.6	9.5		5.0	7.6	
.5	83.8	89.5	86.8	89.0	84.8
.8	80.8	72.9	72.8	66.1	75.0
.4	67.7	65.3	63.2	58.8	63.6
.2	20.5	30.6	27.6	22.3	16.7
7.5	111.0	141	136	109	104.0
6	100	96	96	88	112
6	246	243	243	252	246
21	0.39	0.27	0.27	0.50	0.15
½	2	2-	2½-	2½+	1½+
882	0.882	0.897	0.897	0.898	0.866
	0.8778		0.8938		
	1.4958		1.5083		
	0.3327		0.3337		
	114.9		103.2		
	-		691		
	0.8597		0.8690		
	1.4749		1.4793		
	0.3274		0.3265		
	131.6		130.4		
	667		-		
	14		23		
	5.5		0		
	80.5		77		
-	2.62	-	4.00	3.05	
-	4.83	-	6.24	4.67	
-	1.84	-	1.56	1.53	
-	0.27	-	0.26	0.29	
-	0.72	-	0.67	0.81	
-	0.45	-	0.41	0.52	
.9	6.8	10.8	10.5	13.3	
-	0.8706	-	0.8702*	0.8895	
-	1.4948	-	1.4771	1.5075	
-	0.3348	-	0.3248	0.3348	
-	67.9	-	92.0	54.2	
-	310	-	301	304	
-	28	-	44.5	36.5	
-	0	-	0	0	
-	72	-	55.5	63.5	

e rise in aniline point.

polymerization has taken place will only be effective if these aromatics react with the polymerization product formed at the high temperature. As these high temperature polymers are formed under the influence of cyclization and saturation reactions, it is hardly to be expected that this reaction (between the added aromatics and the polymers) will take place to a satisfactory extent. Such a polymerization experiment (P 222) was carried out at 82.5°C. The resulting oil, however, contained hardly any naphthalene, judging from its constants.

It was therefore decided that in the next experiments the aromatics will be added at once to the cracked distillate. Though this will cause a complete change in the reaction diagram, it will ensure that the aromatics take part in the polymerization reaction. The experiments were carried out at different temperatures and also with different percentages of naphthalene.

a. <u>Addition of 10 % wt. of naphthalene</u> (see table 4 and graphs 2 & 3).

<u>P 237</u>, polymerization at 5°C.
<u>P 235</u>, " " abt. 60°C.
<u>P 221</u>, " " " 100°C.

The viscosities of these polymerizates are 200, 137,5 and 111 sec. Saybolt, respectively. The polymerizate P 237 possesses very good properties (Conradson 0.26; colour Union 2, V.I. 109) and meets the B.A.M. oxidation test (viscosity ratio 1.70 and coke increase 0.38). These constants become slightly less satisfactory at a polymerization temperature of 100°C. (Conradson 0.39, V.I. 100; coke increase in the B.A.M. test 0.45; viscosity ratio 1.84).

This shows at the same time that the addition of 10 naphthalene gives a comparatively thin Bright Stock at a low temperature and a comparatively thick aviation oil at a high temperature, in other words, the temperature susceptibility of cracked distillate decreases considerably under the influence of the naphthalene. A temperature of about 120°C. will be necessary for the preparation of a 100 sec. oil (see graph 3). The influence of the naphthalene addition on the yield of lubricating oil is not unfavourable (see graph 2). Calculated on cracked distillate + addition, the yields of Bright Stock (74 %) and aviation oil (67½ %) are about 1 % <u>higher</u> than when cracked distillate is polymerized without the addition of naphthalene.

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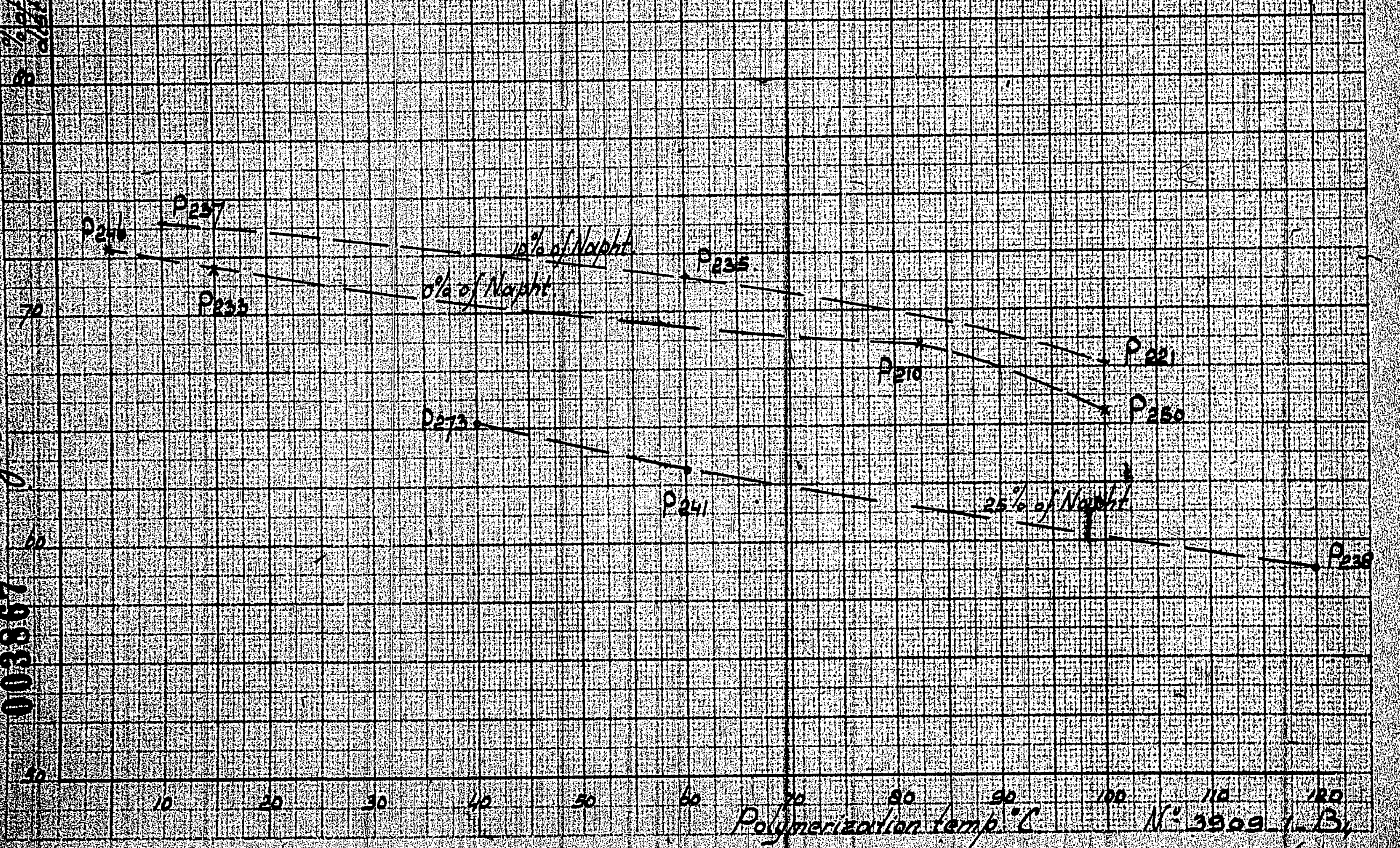
Graph 2.

Influence of the addition of naphtalene to B.P. cracked distillate <250°C on the oil yield



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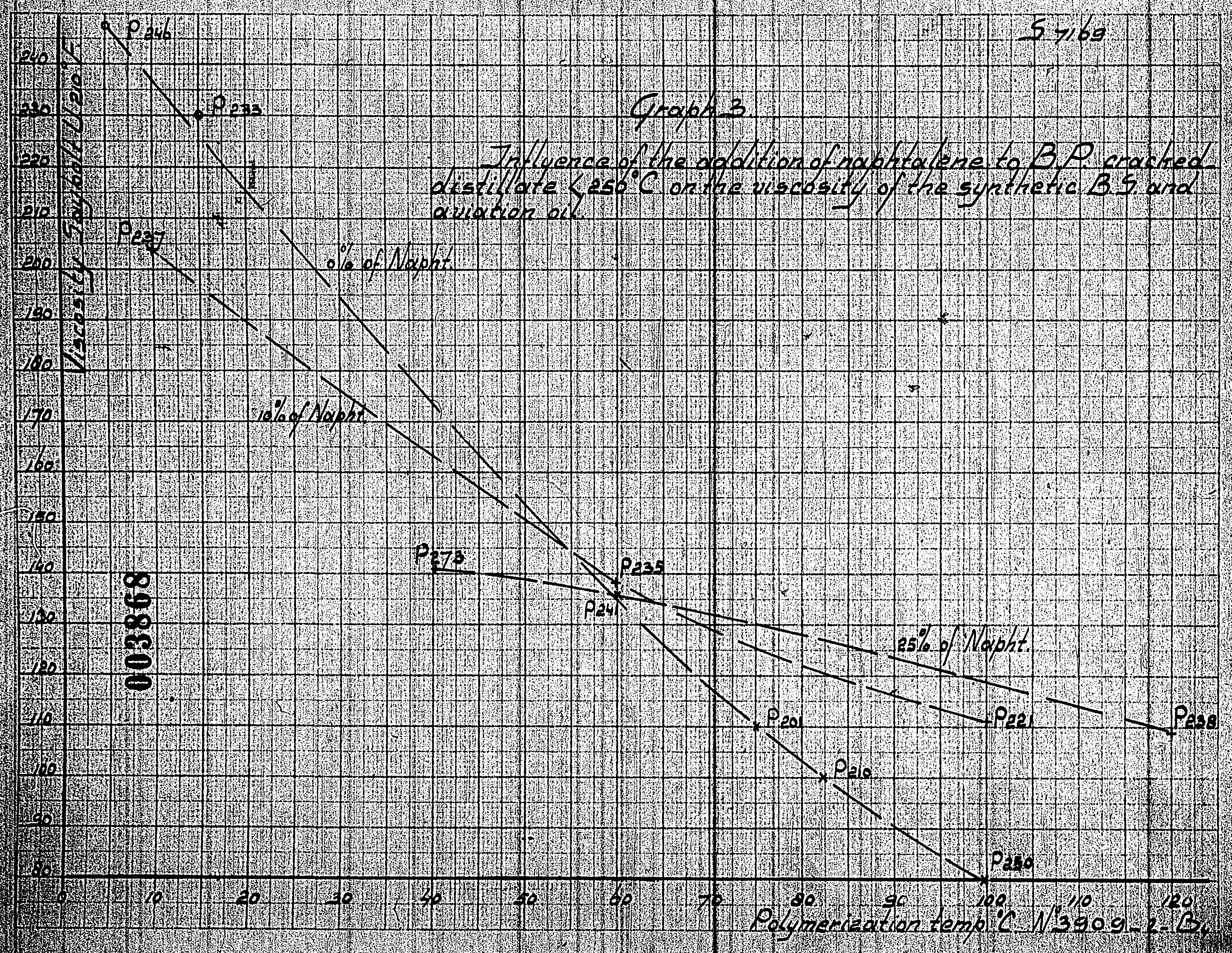

Graph 3.

Influence of the addition of naphtalene to B.P. cracked distillate < 250°C on the viscosity of the synthetic B.S. and aviation oil.

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b. Addition of 25 % of naphthalene (see table 4 and graphs 2 & 3).

P 273, polymerization at 40°C.
P 241, " " 60°C.
P 238, " " abt. 120°C.

The viscosities of these polymerizates are 141, 136 and 109 sec. Saybolt. As appears from table 4, the constants of the first two oils are highly satisfactory (Conradson 0.27; colour Union 2- and 2½-, respectively); the B.A.M. oxidation test gives a viscosity ratio of 1.56 and a coke increase of 0.41. At about 120°C. an aviation oil is produced, but its properties are not quite satisfactory (V.I. 88, Conradson 0.50; viscosity ratio 1.53; Ramsbottom increase 0.52). It is remarkable that the influence of the temperature on the viscosity of the polymerization product is very slight. A temperature of about 130°C. would, consequently, be required for the production of an aviation oil (see also graph 3).

Under the influence of the high percentage of naphthalene, the polymerization reaction has evidently been largely replaced by an "alkylation reaction", which is far less dependent on temperature. One can, consequently, hardly speak of a normal polymerization reaction. During the polymerization with 25 % of naphthalene many low-molecular products are formed, which lie outside the lubricating oil range. Owing to this, the oil yield is comparatively low (65 % and 58½ %, respectively).

The following has also been found: in the polymerization with 10 % of naphthalene all the naphthalene takes part in the reaction, partly forming volatile tops, which are highly aromatic (P 237 40 % of C in ring structure, P 221 about 28 % of C in ring structure, see table 4), but chiefly resulting in lubricating oil constituents. Thus, the analysis of oil P 221 shows 20 % of C in ring structure (an aviation oil made from B.P. cracked distillate <250°C. only contains about 10 % of C in ring structure). When polymerizing with 25 % wt. of naphthalene not all the naphthalene reacts, part of it being recovered unaltered when the reaction mixture is steamed off; moreover, the tops boiling above 300°C. are exceedingly aromatic (about 45 % of C in ring structure in P 241, about 36 % in P 238).

It is, therefore, hardly advantageous to polymerize more than 10 % wt. of naphthalene together with the cracked distillate (polymerizate P 241 contains 22.5 % wt. of C in ring structure, which is only 2.5 % more than polymerizate P 221, formed by the polymerization with 10 % of naphthalene).

The B.A.M. test of polymerizate P 241, too, is, comparatively, only little better than that of polymerizate 0 P 221.

Résumé and Conclusion.

Synthetic oils as such are known not to meet the B.A.M. specification as regards the viscosity ratio, but, on the contrary, to have a highly satisfactory Ramsbottom Coke increase; in particular the polymerizates from volatile olefines show a very low coke increase. The compounds rich in rings, which occur in the highest fractions of the technical vapour-phase distillate ex B.P. wax cakes have a very unfavourable influence on the Ramsbottom coke increase, although the B.A.M. specification (coke increase <1.0) is still met.

It has now been found that special aromatics (such as naphthalene and the simple homologues of naphthalene), if polymerized together with olefinic cracked distillate or Balik Papan cracked distillate <250°C., have a highly favourable effect on the B.A.M. oxidation test as regards the viscosity ratio, while the Ramsbottom coke increase is practically not raised.

A favourable effect was obtained with naphthalene and, though to less extent, with Pernis Coking Gas Oil <320°C. Woodriver Coking Gas Oil and a fraction ex B.P. kerex on the contrary proved to be too little aromatic. Anthracene oil <380°C., although affecting the viscosity ratio favourably, had a very bad influence on the Ramsbottom coke number as well as on its increase.

The polymerization of cracked distillate with naphthalene has been examined more extensively. Special attention was paid to the addition of naphthalene after the cracked distillate had completely or partly polymerized at a low temperature. In a few cases the resulting Bright Stock actually had a higher mol.weight, a very good B.A.M. test and a high full-film temperature. The procedure is not yet reproducible, however; this can only be effected by a continuous polymerization apparatus. By polymerizing cracked distillate to which about 10 % of naphthalene had previously been added a high yield of polymerizate was obtained (both Bright Stock and aviation oil) with highly satisfactory properties and B.A.M. test.

Undoubtedly, naphthalene derivatives are formed which act as anti-oxidant. An aviation oil P 221, made by polymerizing B.P. cracked distillate <250°C. + 10 % wt. of naphthalene at about 100°C. was tested in the Deutz gasoline engine at Delft. It was found that "it was the best oil as regards tendency to ringsticking and coke formation ever tested at Delft". Moreover, oils formed from good cracked distillates, to which the right aromatics have been added, will most probably be better than those made without aromatics in keeping sludge in the engine in suspension.

LABORATORY
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Amsterdam, 22nd April 1938.
He/S.

with two addenda.

ADDENDUM I TO REPORT S 7169.

Table 5. Analysis of different aromatic products polymerized together with Balik Papan cracked distillate.

	fraction 200-250°C. ex B.P. kerex	fr.<380°C. ex anthracene oil	Woodriver Coking Cycle stock TMC 8911	fr.<320°C. ex Pernis Coking Cycle stock TMC 9046
Bromine value	-	-	10.6	8.3
d 20/4	0.9098	1.0863	0.9228	0.996
n_D^{20}	1.5231	1.6440	1.5287	-
r_D^{20}	-	0.3334	0.3340	-
A.P., °C.	1.5	-	7.0	-15.0
Average mol, weight	155.5	172	163	-
A.S.T.M. I.B.P.	-	-	190	188
10 %	-	-	219	243
20 %	-	-	228	254
30 %	-	-	235	260
40 %	-	-	243	266
50 %	-	-	250	272
60 %	-	-	257	278
70 %	-	-	266	287
80 %	-	-	277	298
90 %	-	-	291	311
95 %	-	-	303	317
F.B.P.	-	-	320	327
% residue	-	-	1	1½
% loss	-	-	-	-

ADDENDUM II TO REPORT S 7169.

Analytical methods used:

Engler viscosity	54/36
Saybolt Universal	70/36
Viscosity Index	S.A.M.Book, page 116
Union Colour	5B/36
Flash point P.M. cl. cup	15/36
% of ash	"
acid value	26/36
density	1c/36
B.A.M. oxidation test	103S/36
Bromine value	8/36
Aniline point	101S/36
A.S.T.M. distillation	4/36
Ring analysis	E 18
