

TABLE II. PHYSICAL PROPERTIES OF PRODUCTS OBTAINED BY THE VACUUM FRACTIONATION OF EXTRACTS FROM BLENDS A, B, AND C

Cut No.	Weight, Grams	% of Blend	% of Crude	Centistokes		Viscosity		Kinematic index	50% B. P. at 10 Mm. Hg. ° C.	Sp. Gr. (20/20° C.)	Gravity, ° A. P. I.	Refractive Index, $n_D^{20}$	A. S. T. M. Color	Pour Point, ° F.
				100° F.	210° F.	Saybolt Sec. 100° F.	210° F.							
Extract from Blend A														
Blend A	25,880	100.0	1.6	97.4	8.67	449	54.7	45.5	282	0.9270	20.8	1.5160	8+	50
Ext.	13,160	50.7	0.8	164.3	10.40	757	60.6	1.4	286	0.9634	15.0	1.5423	8+	40
1	860	3.3	0.05	16.1	3.08	81.6	36.5	50.4	212	0.9225	21.4	1.5152	3	30
2	858	3.3	0.05	32.3	4.48	151	40.9	34.8	239	0.9346	19.4	1.5249	3	45
3	869	3.3	0.06	64.7	6.44	298	47.3	19.7	257	0.9463	17.6	1.5321	4	45
4	867	3.3	0.06	109.3	8.33	504	53.5	3.4	268	0.9555	16.2	1.5371	4	40
5	878	3.3	0.06	148.2	9.56	683	57.7	-10.3	278	0.9600	15.5	1.5403	4	35
6	874	3.4	0.06	179.8	10.52	827	61.1	-15.1	280	0.9630	15.0	1.5423	4	35
7	886	3.4	0.06	203.3	11.23	936	63.7	-15.4	285	0.9625	15.1	1.5429	4	35
8	872	3.4	0.06	229.1	11.96	1,053	66.4	-16.6	287	0.9638	14.9	1.5446	4	35
9	896	3.4	0.06	255.4	12.59	1,178	68.7	-20.0	290	0.9664	14.5	1.5452	4	35
10	888	3.4	0.06	280.9	13.25	1,297	71.3	-20.4	291	0.9670	14.4	1.5462	4	35
11	892	3.4	0.06	316.8	14.05	1,460	74.4	-23.3	295	0.9686	14.2	1.5480	4	35
12	901	3.5	0.06	361.4	14.95	1,662	77.8	-27.5	298	0.9711	13.8	1.5498	4	35
13	887	3.4	0.06	447.1	16.56	2,060	84.3	-33.0	300	0.9767	13.0	1.5530	7	35
Bottoms	1,360	5.3	0.08	884	23.30	4,070	112.7	-44.8	308	0.9905	11.0	1.5540	8	35
Extract from Blend B														
Blend B	30,600	100.0	2.0	163.6	12.35	755	67.8	59.5	307	0.9238	13.2	1.5140	8+	55
Ext.	15,630	51.0	1.0	260.6	14.17	1,200	74.8	13.3	306	0.9495	17.2	1.5328	3	35
1	805	2.6	0.05	31.6	4.87	148	42.3	83.8	252	0.8827	28.3	1.4900	4	5
2	832	2.7	0.05	61.7	6.94	285	48.9	62.3	275	0.9017	24.9	1.5035	4	10
3	835	2.7	0.05	149.2	10.75	688	61.9	34.2	293	0.9349	19.4	1.5232	4	35
4	869	2.8	0.06	194.0	12.22	894	67.3	27.0	298	0.9407	18.4	1.5288	4	40
5	853	2.8	0.05	214.0	12.82	986	69.6	24.2	302	0.9436	18.0	1.5310	4	35
6	859	2.8	0.06	230.4	13.29	1,060	71.4	22.3	302	0.9457	17.8	1.5321	4	35
7	857	2.8	0.05	245.0	13.70	1,128	73.0	20.8	304	0.9475	17.5	1.5330	4	35
8	843	2.8	0.05	260.0	14.06	1,197	74.4	17.4	305	0.9487	17.3	1.5339	4	35
9	855	2.8	0.05	288.2	14.77	1,327	77.1	15.3	306	0.9508	16.9	1.5363	5	35
10	910	3.0	0.06	303.4	15.11	1,397	78.4	13.3	306	0.9526	16.7	1.5376	5	35
11	870	2.8	0.06	312.4	15.32	1,438	79.3	12.3	307	0.9541	16.4	1.5382	5	35
12	873	2.8	0.06	337.9	15.98	1,556	81.9	11.3	309	0.9554	16.2	1.5400	5	35
13	874	2.8	0.06	347.1	16.10	1,598	82.4	9.2	310	0.9564	16.1	1.5405	5	35
14	866	2.8	0.06	364.9	16.62	1,680	84.5	10.4	313	0.9570	16.0	1.5411	6	35
15	841	2.7	0.05	395.2	17.33	1,820	87.5	9.5	314	0.9586	15.7	1.5426	7	35
16	872	2.8	0.06	434.0	18.04	1,998	90.4	5.5	326	0.9612	15.3	1.5440	8	35
17	874	2.9	0.06	598.0	20.81	2,753	102.1	-7.0	322	0.9688	14.2	1.5490	8	30
Bottoms	820	2.7	0.05	684.2	65.82	31,500	306.9	-76.0	328	1.005	13.0	....	8+	65
Extract from Blend C														
Blend C	28,800	100.0	1.8	212.0	14.85	976	77.4	66.5	323	0.9201	21.8	1.5121	8+	45
Ext.	15,890	55.2	1.0	478.0	20.20	2,200	99.5	23.8	323	0.9528	16.6	1.5331	8+	40
1	845	2.9	0.05	175.6	11.66	809	65.2	30.4	306	0.9389	18.7	1.5263	8+	40
2	897	3.1	0.06	272.4	14.93	1,254	77.7	28.5	311	0.9432	18.1	1.5300	5	45
3	848	2.9	0.05	290.3	15.50	1,336	80.0	29.4	314	0.9440	18.0	1.5308	5	45
4	875	3.0	0.06	306.5	15.94	1,411	81.8	28.5	317	0.9454	18.8	1.5313	5	45
5	846	2.9	0.05	320.3	16.41	1,475	83.7	29.4	316	0.9461	17.7	1.5321	4	45
6	850	2.9	0.05	336.0	16.86	1,547	85.5	29.5	317	0.9466	17.6	1.5329	4	45
7	831	2.9	0.05	346.1	17.13	1,593	86.6	29.2	319	0.9474	17.5	1.5333	5	45
8	885	3.1	0.06	357.7	17.44	1,647	87.9	29.0	320	0.9478	17.4	1.5334	6	40
9	870	3.0	0.06	372.9	17.86	1,717	89.6	29.0	321	0.9479	17.4	1.5341	6	40
10	864	3.0	0.06	392.6	18.43	1,809	92.0	29.5	323	0.9490	17.2	1.5348	7	45
11	847	2.9	0.05	411.4	18.86	1,894	93.8	28.5	324	0.9496	17.1	1.5351	7	40
12	838	2.9	0.05	440.7	19.47	2,029	96.4	26.4	328	0.9511	16.9	1.5361	7	40
13	854	3.0	0.05	478.3	20.32	2,202	100.0	25.3	329	0.9522	16.7	1.5380	7	45
14	890	3.1	0.06	538.6	21.62	2,480	105.5	23.8	...	0.9524	16.7	1.5397	7	35
15	887	3.1	0.06	617.2	22.94	2,842	111.1	18.7	...	0.9590	15.7	1.5420	7	40
16	904	3.1	0.06	727.0	25.00	3,347	120.2	17.0	...	0.9613	15.3	1.5425	7	35
17	395	1.4	0.03	865.8	27.31	3,986	130	14.0	...	0.9649	14.8	1.5465	7	35
Bottoms	1,765	6.1	0.11	2626	49.06	12,090	229	7.2	...	0.9782	12.8	1.5300	8+	40

mately 23 liters). Consequently, eight separate fractionations were performed. Cuts corresponding to the same volume per cent distilled were blended after physical tests showed them to be very similar. Eighteen overhead cuts of 2 gallons (7.6 liters) each were obtained. All of these were solid at room temperature. They were partially dewaxed by diluting with one volume of *n*-butanol, cooling, and filtering off the wax. After stripping the butanol from the oil, physical properties of all cuts were measured and are summarized in Table I.

The eighteen cuts were then blended into three fractions designated as blends A, B, and C. Blend A is composed of cuts 1 to 6, inclusive; blend B, cuts 7 to 12, inclusive; and blend C, cuts 13 to 18 and a sample of the bottoms. Each of these blends was then extracted with acetone to approximately the 50 per cent point at room temperature by a successive batch process and a solvent-oil ratio of one to one. Three extractions were necessary to cut blend A to the 50 per cent point; six were necessary for blend B, and eight for blend C. The extracts from any one blend were combined so that there were now six samples of oil of ap-

proximately 5 gallons (19 liters) each. Three of these were extracts and three were raffinates.

After the solvent was removed from the six oil samples, their physical properties were determined, and they were then fractionated in the vacuum column under the same conditions as the fractionations described earlier. Cuts of approximately 800 grams (4.4 per cent) were taken; their physical properties were determined and are summarized in Tables II and III. A selected number of the six series of fractions were then further separated in the efficient reflux extraction unit previously described by the authors (3). Acetone was used as the solvent, and the extractor was operated under total reflux until equilibrium was reached and the extract cut was then removed. Physical properties of the products were measured and are presented in Table IV.

All viscosities reported were measured by the simple, precise, modified Ostwald viscometers, developed by the authors (4), which are now in extensive use in the petroleum industry. Saybolt viscosities are those converted from the kinematic viscosities by means of the conversion tables recently published for infor-

TABLE III. PHYSICAL PROPERTIES OF PRODUCTS OBTAINED BY THE VACUUM FRACTIONATION OF RAFFINATES FROM BLENDS A, B, AND C

Cut No.	Weight, Grams	% of Blend	% of Crude	Centistokes		Viscosity		Kinematic index	B. P. at 10 Mm. Hg., ° C.	Sp. Gr. (20/20° C.)	Gravity, ° A. P. I.	Refractive Index, $n_D^{20}$	A. S. T. M. Color	Pour Point, ° F.
				100° F.	210° F.	Saybolt	Sec. 210° F.							
Raffinate from Blend A														
Blend A	25,880	100.0	1.6	97.4	8.67	449	54.7	45.5	282	0.9270	20.8	1.5160	8+	50
Raff.	12,712	49.2	0.8	62.1	7.45	287	50.6	84.0	285	0.8915	26.9	1.4911	6	55
1	824	3.2	0.05	13.2	2.98	70.5	35.9	113.0	219	0.8684	31.0	1.4796	1	50
2	826	3.2	0.05	30.2	4.85	142	42.1	93.7	244	0.8828	28.3	1.4874	1	55
3	844	3.3	0.05	45.8	6.08	212	46.1	76.4	260	0.8923	26.8	1.4921	1+	50
4	861	3.3	0.05	59.6	7.03	275	49.2	72.6	268	0.8974	25.8	1.4944	1+	50
5	882	3.4	0.06	68.9	7.62	318	51.1	71.4	272	0.8992	25.5	1.4953	1+	50
6	855	3.3	0.05	74.2	8.01	342	52.4	72.2	276	0.8986	25.6	1.4960	1+	50
7	840	3.3	0.05	77.4	8.24	357	53.2	73.4	279	0.8984	25.6	1.4955	2	50
8	837	3.2	0.05	79.2	8.38	365	53.7	74.2	281	0.8975	25.8	1.4948	2	50
9	845	3.3	0.05	80.4	8.53	370	54.2	76.4	285	0.8960	26.1	1.4941	2	50
10	837	3.2	0.05	80.7	8.59	372	54.4	77.8	286	0.8950	26.3	1.4935	2	50
11	843	3.3	0.05	81.4	8.73	375	54.9	80.8	290	0.8933	26.6	1.4922	2	55
12	851	3.3	0.05	81.3	8.79	375	55.1	83.0	294	0.8929	26.6	1.4916	2	55
13	830	3.2	0.05	81.1	8.91	374	55.5	86.8	297	0.8904	27.0	1.4905	2+	55
14	831	3.2	0.05	81.8	9.02	377	55.9	88.4	298	0.8899	27.2	1.4900	3	55
15	361	1.4	0.02	84.2	9.28	388	56.8	91.0	304	0.8873	28.0	1.4888	3+	55
Bottoms	790	3.1	0.05	129.8	12.29	597	67.6	91.2	308	0.8946	26.3	1.4900	8+	45
Raffinate from Blend B														
Blend B	30,600	100.0	1.95	163.6	12.35	755	67.8	59.5	307	0.9238	13.2	1.5140	8+	55
Raff.	14,980	49.0	0.95	77.4	8.83	357	55.2	91.6	303	0.8850	28.0	1.4880	5	55
1	801	2.6	0.05	25.7	4.54	122	41.1	109.0	254	0.8621	32.3	1.4752	1	10
2	819	2.7	0.05	44.4	6.23	206	46.6	94.5	275	0.8747	29.8	1.4825	1	20
3	835	2.7	0.05	72.0	8.16	332	52.9	83.4	288	0.8888	27.2	1.4900	1	45
4	849	2.8	0.05	81.4	8.78	375	55.1	82.3	294	0.8915	26.7	1.4910	1	45
5	828	2.7	0.05	84.5	9.01	390	55.8	82.8	294	0.8919	26.7	1.4912	1	50
6	842	2.7	0.05	85.8	9.11	395	56.2	83.5	299	0.8911	26.8	1.4912	1	50
7	836	2.7	0.05	86.3	9.26	398	56.7	86.5	299	0.8900	27.0	1.4909	1	55
8	837	2.7	0.05	86.9	9.35	400	57.0	87.7	302	0.8906	27.1	1.4902	1+	55
9	833	2.7	0.05	87.2	9.45	402	57.3	89.8	304	0.8882	27.3	1.4895	1+	55
10	823	2.7	0.05	87.6	9.46	403	57.4	89.4	304	0.8879	27.4	1.4893	2	55
11	829	2.7	0.05	88.0	9.53	405	57.6	90.3	304	0.8875	27.4	1.4891	2	55
12	830	2.7	0.05	88.4	9.58	407	57.8	90.8	307	0.8870	27.5	1.4883	2	55
13	827	2.7	0.05	89.0	9.68	410	58.1	92.2	306	0.8862	27.7	1.4882	2	55
14	827	2.7	0.05	89.5	9.75	412	58.4	92.9	310	0.8835	28.2	1.4879	2	55
15	831	2.7	0.05	90.4	9.86	416	58.7	94.0	310	0.8830	28.2	1.4875	2	55
16	821	2.7	0.05	91.1	10.01	420	59.2	96.2	314	0.8811	28.6	1.4870	3	60
17	793	2.6	0.05	93.8	10.22	432	60.0	96.7	318	0.8820	28.4	1.4866	4	60
Bottoms	973	3.2	0.06	108.9	11.27	502	63.8	96.5	321	0.8844	28.0	1.4865	8	50
Raffinate from Blend C														
Blend C	28,800	100.0	1.8	212.0	14.85	976	77.4	66.5	323	0.9201	21.8	1.5121	8+	45
Raff.	12,940	45.0	0.8	108.4	11.35	499	64.1	98.5	319	0.8841	28.2	1.4871	8+	60
1	840	2.9	0.05	89.6	9.55	413	57.7	88.2	308	0.8892	27.3	1.4890	3	50
2	839	2.9	0.05	98.0	10.20	451	59.9	90.1	309	0.8888	27.3	1.4887	2	50
3	835	2.9	0.05	98.4	10.26	453	60.1	90.8	310	0.8878	27.5	1.4879	2	55
4	837	2.9	0.05	98.1	10.36	452	60.5	93.3	313	0.8871	27.6	1.4875	2	55
5	846	2.9	0.05	98.5	10.40	454	60.6	93.7	314	0.8843	28.0	1.4875	2	55
6	836	2.9	0.05	98.1	10.52	452	61.1	96.4	317	0.8852	28.0	1.4870	2	55
7	841	2.9	0.05	98.8	10.63	455	61.5	97.7	318	0.8824	28.5	1.4866	2	55
8	825	2.9	0.05	98.6	10.68	454	61.7	98.8	320	0.8806	28.8	1.4859	2	55
9	820	2.8	0.05	100.2	10.77	461	62.0	98.4	323	0.8807	28.8	1.4855	2	55
10	813	2.8	0.05	101.2	10.87	466	62.3	99.0	322	0.8804	28.8	1.4853	2	55
11	820	2.8	0.05	103.4	11.07	476	63.1	99.8	326	0.8793	29.0	1.4852	2+	55
12	816	2.8	0.05	106.6	11.29	491	63.9	99.6	327	0.8801	28.9	1.4851	3	55
13	797	2.8	0.05	109.9	11.54	506	64.8	100.0	331	0.8798	28.9	1.4852	3+	55
14	464	1.6	0.03	115.3	12.05	531	66.7	101.9	334	0.8803	28.8	1.4854	3+	55
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Bottoms	1,565	5.4	0.10	19.12	16.30	880	83.2	96.4	342	0.8837	26.5	1.4880	8-	40

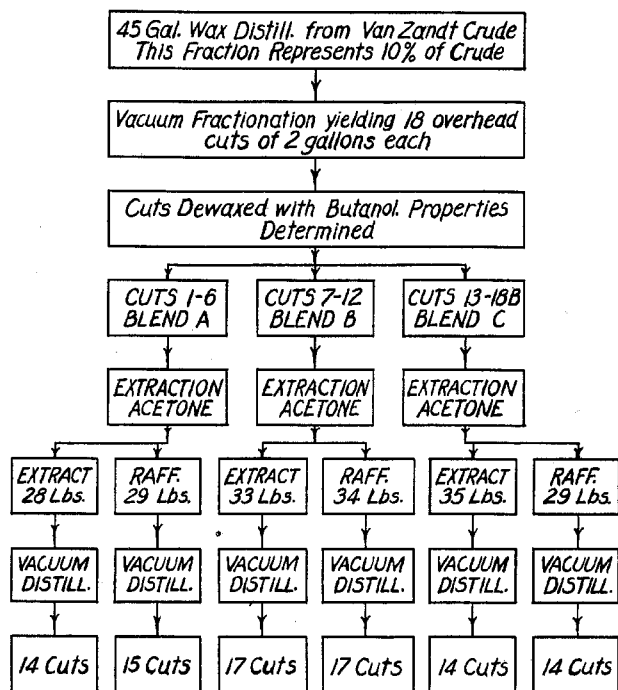
mation by Committee D-2 of the American Society for Testing Materials (1). Kinematic viscosity indices were calculated from the published tables of Hersh, Fisher, and Fenske (5). The use of kinematic viscosity for this purpose rather than Saybolt viscosity greatly increases the accuracy of the viscosity index and enables one to determine this property for light oils.

### Results of Vacuum Distillation

A flow sheet showing the sequence of the various operations is presented in Figure 1. The results obtained by vacuum fractionation of the Van Zandt wax distillate are shown in Table I, and for clearer presentation several properties are plotted in Figure 2. It is evident that the fractionation yielded products of widely different properties and that the types of molecules were quite different from fraction to frac-

tion. A sharp maximum is reached in the refractive index curve, and a sharp minimum exists in the viscosity index curve at the same point. This probably means that these particular fractions are rich in polynuclear compounds such as polynuclear aromatics or polynuclear naphthenes. This particular charge, with the exception of the first fraction, steadily increases in degree of paraffinicity as the molecular weight increases. This is clearly indicated by the kinematic viscosity index curve which increases from 32 to 72 in going from the second cut to the bottoms. It is interesting to point out that the fractionation of a coastal oil from Sugarland crude reported by Hersh (4) showed just the opposite trend; paraffinicity steadily decreased with increasing molecular weight, as evidenced by the fact that the kinematic viscosity index went from 28 to -28 from the first to the last

distilled fraction of this coastal crude. However, in the case of the Van Zandt crude, it appears that heavy oils of high viscosity index could be obtained in greater yields than would be possible for light oils of high viscosity index.



Selected cuts from the above six fractionations were further extracted in reflux extractor

FIGURE 1. FLOW SHEET

Tables II and III give the properties of the products obtained by the vacuum fractionation of the extracts and raffinates from blends A, B, and C. The blends were separated into approximately equal portions by extraction before being distilled. Several properties are plotted in Figure 3. The abscissas give the percentages referred to the over-all original blend, and since each extract and raffinate comprises 50 per cent of the original blend, it follows that the 50 per cent point represents the limit on the abscissas. This facilitates direct comparison of extract and raffinate fractions.

Within the limits of experimental error, the corresponding extract and raffinate cuts have the same 50 per cent boiling point at 10 mm. of mercury, absolute pressure. However, in practically every case there is a difference in viscosity of several hundred per cent. More striking is the rate at which the viscosity increases with molecular weight or boiling point. In going from a 50 per cent boiling point of 280° to 290° C. the extract cuts from blend A increase in 100° F. (37.8° C.) viscosity from 180 to 255 centistokes (41 per cent increase); the corresponding raffinate cuts increased in 100° F. viscosity from 79 to 81 centistokes (2.5 per cent increase). Apparently cyclization, which has an enormous effect on viscosity, increases consistently with increasing molecular weight in the extract fractions. In the more paraffinic raffinate fractions, on the other hand, the viscosity increase may be due to an increase in hydrocarbon chain lengths or an increase in the number of branches in the hydrocarbon chains since the molecular size may be increased by these methods with the least change in viscosity. These fractions at 210° F. (98.9° C.) increase by 20 and 3 per cent, respectively, for the same boiling range.

The kinematic viscosity indices of the various fractions from the fractionation of the extracts and raffinates increase

with boiling point. It is apparent that the viscosity index (V. I.) and the refractive index at 20° C. (R. I.) have shown consistently opposite trends. A rough empirical correlation exists between the refractive index and the viscosity index which may be expressed by the equation:

$$V. I. = 2920 - 1900 R. I.$$

This relation is not general but applies to the oils reported in this paper. It is of interest to point out that for a given viscosity index the only pure compounds prepared by Mikeska (8) with refractive indices at all close to those obtained from this oil are derivatives of cyclohexane and decahydronaphthalene. The derivatives of benzene, naphthalene, and tetrahydronaphthalene have refractive indices considerably higher than the above oil fractions of similar viscosity index. The close-cut fractions which are correlated by the above equation differ in 50 per cent boiling point as much as 100° C. and in viscosity by several hundred per cent so that comparison with the low-boiling, less viscous compounds is not unreasonable.

The specific gravities of the viscous fractions of low viscosity index were from 10 to 18 per cent higher than the fractions of high viscosity index. The color becomes darker with increasing molecular weight and is much darker for the extract fractions than it is for the raffinate fractions.

Table IV summarizes the properties of the products obtained by extracting selected cuts in the reflux extractor. Figure 4 is a plot of the viscosities and viscosity indices of the oils produced by one of these extractions. The oil samples charged to this unit had been refined to the extent where they represented only 0.05 per cent of the original crude. The most striking fact revealed here is that no materials of intermediate viscosity index exist in these samples to any appreciable extent, for the transition from the region of low viscosity index to that of high viscosity index is very sharp.

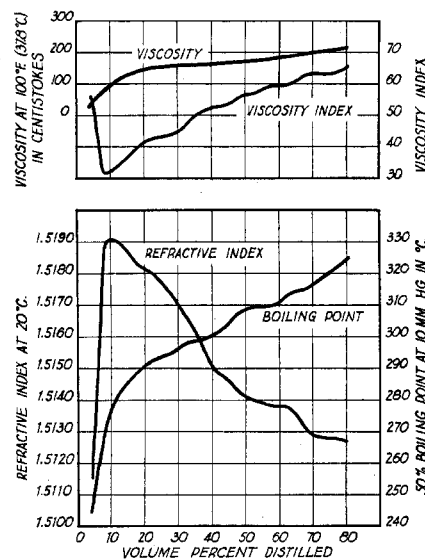


FIGURE 2. VACUUM FRACTIONATION OF VAN ZANDT WAX DISTILLATE

The products obtained from this unit represent approximately 0.01 per cent of the original crude or 0.1 per cent of the original wax distillate. Their wide variation in physical properties indicates the extreme complexity of this oil.

In the foregoing, comparison of viscosity indices of various fractions have been made although wax concentration varied. The effect of dewaxing on the viscosity index of this oil was to

TABLE IV. EXTRACTION OF HIGHLY REFINED CUTS IN THE REFLUX EXTRACTOR

Designation	Extn. Time, Hr.	Tower Temp., ° C.	Liters Acetone per Hr.	Weight of Sample, Grams	Per Cent Yield	Refractive Index, $n_D^{20}$	Sp. Gr. (20/20° C.)	Centistokes 100° F.	Centistokes 210° C.	Viscosity Saybolt Sec. 100° F.	Viscosity Saybolt Sec. 210° F.	Kinematic index	A.S.T.M. Color
Charged Cut 8 of Extract from Blend A													
Charge	..	..	..	300	..	1.5450	0.9652	224.9	11.71	1,035	65.4	-21	8
Extract 1	4.0	13	3.6	95	32	1.5670	0.9959	591	16.38	2,720	83.6	-114	8+
Extract 2	2.25	12	4.4	92	31	1.5609	0.9879	475	15.38	2,187	79.5	-84	8+
Extract 3	2.25	11	4.5	43	14	1.5513	0.9768	346	13.87	1,593	73.7	-51	8+
Holdup in solvent	..	..	..	36	12	1.4953	0.8965	74.7	8.14	344	52.9	76	4
Raffinate	..	..	..	10	3	1.4781	0.8684	52.3	7.08	233	49.4	101	2
Charged Cut 8 of Raffinate from Blend A													
Charge	..	..	..	340	..	1.4974	0.9040	88.5	8.70	408	54.8	63	3
Extract 1	2.75	13	4.4	66	19.2	1.5402	0.9694	384.3	14.76	1,769	77.1	-48	8+
Extract 2	3.0	13	4.4	40	11.6	1.5290	0.9717	269.5	13.16	1,241	70.9	-14	8+
Raffinate	..	..	..	194	56.4	1.4799	0.8748	57.1	7.27	264	50.0	92	3
Charged Cut 9 of Extract from Blend B													
Charge	..	..	..	370	..	1.5290	0.9483	168.4	11.17	775	63.4	24	8
Extract 1	3.75	13	4.2	90	24.4	1.5681	0.9966	1,050	22.61	4,834	109.7	-103	8+
Extract 2	2.25	12	4.3	95	25.6	1.5641	0.9931	962	22.09	4,429	107.5	-91	8+
Extract 3	2.50	13	4.8	51	13.8	1.5570	0.9834	802	21.10	3,692	103.3	-65	8+
Holdup in solvent	..	..	..	62	16.7	1.4976	0.8999	101	9.71	465	59.1	73	4.5
Raffinate	..	..	..	43	11.6	1.4732	0.8954	57.2	7.84	264	51.9	109	3
Charged Cut 9 of Raffinate from Blend B													
Charge	..	..	..	423	..	1.4909	0.8899	89.7	9.44	413	57.3	85	6
Extract 1	2.75	13	4.6	66	15.6	1.5348	0.9669	433	17.28	1,994	87.3	-5	8+
Extract 2	2.75	13	4.4	27	6.4	1.5253	0.9472	330	15.72	1,590	80.9	10	8+
Raffinate	..	..	..	280	66.3	1.4787	0.8709	64.9	8.22	299	53.2	105	3
Charged Cut 9 of Extract from Blend C													
Charge	..	..	..	380	..	1.5349	0.9526	358.3	17.23	1,650	87.0	25	8
Extract 1	3.25	13	4.0	98	25.8	1.5697	1.0026	2,252	33.56	10,368	158.5	-108	8+
Extract 2	2.25	12	4.0	82	21.6	1.5700	1.0056	2,397	34.48	11,036	162.7	-111	8+
Extract 3	2.25	13	4.6	45	11.8	1.5600	1.0031	1,729	31.44	7,960	148.9	-72	8+
Holdup in solvent	..	..	..	61	16.0	1.4989	0.9018	139.0	12.02	640	66.6	76	6
Raffinate	..	..	..	73	19.2	1.4739	0.8601	69.2	8.99	319	55.8	109	3
Charged Cut 9 of Raffinate from Blend C													
Charge	..	..	..	356	..	1.4880	0.8862	118.4	11.50	545	64.7	90	4
Extract 1	3.0	13	4.5	31	8.7	1.5360	0.9626	838	25.10	3,858	120.6	-6	8+
Extract 2	3.0	13	4.3	12	3.4	1.5238	..	472	20.75	2,173	101.8	33	8+
Raffinate	..	..	..	282	79.3	1.4808	0.8763	91.6	9.92	422	58.9	94	2

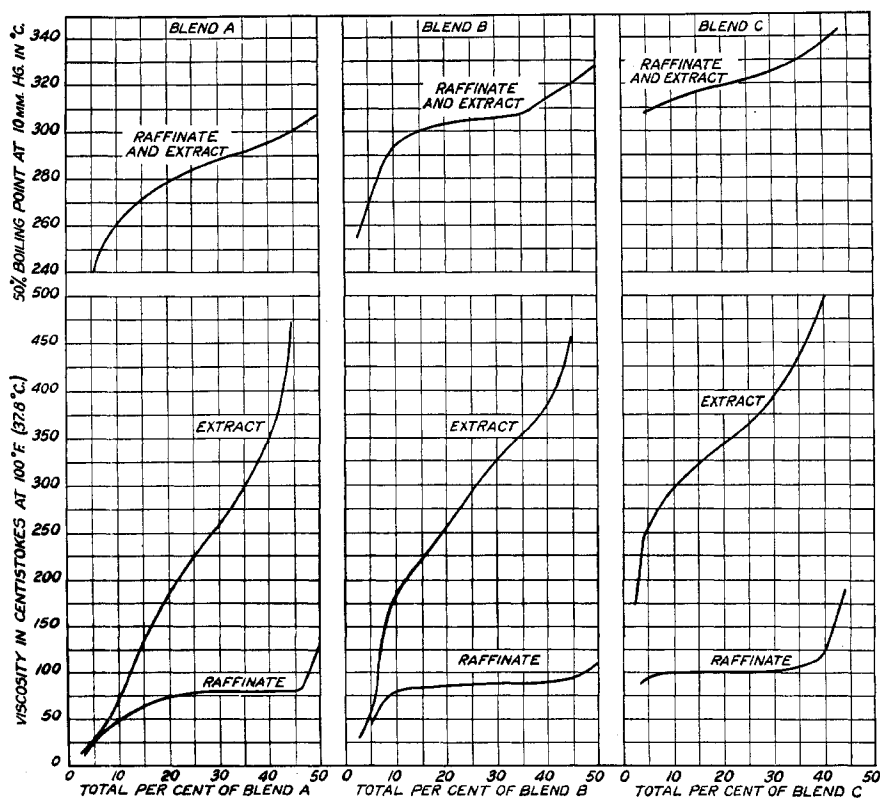


FIGURE 3. VACUUM FRACTIONATION OF EXTRACTS AND RAFFINATES FROM BLENDS A, B, AND C

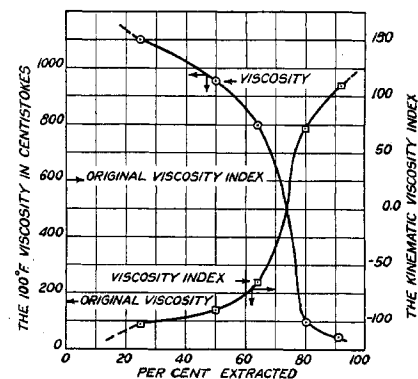


FIGURE 4. FURTHER SEPARATION OF CUT 9 OF THE EXTRACT FROM BLEND B IN THE REFLUX EXTRACTOR WITH ACETONE

lower the viscosity index approximately one point for every 6° F. (3.3° C.) change in pour point. Since the difference in pour points of the fractions was never more than 30° F. (16.7° C.), it is obvious that very little of the marked difference between comparable fractions can be due to differences in wax content.

### Summary

To summarize briefly, it was found that starting with a lubricating oil

distillate from Van Zandt crude having a viscosity index of 60 and a 100° F. viscosity of 169 centistokes (780 Saybolt Universal Seconds, S. U. S.) products ranging in viscosity index from -114 to 109 were obtained. Approximately half of this oil could be made into a product with a viscosity index of 100. The 100° F. viscosity of the various constituents ranged from 14 to 2400 centistokes (74 to 11,000 S. U. S.). The materials of low viscosity index are very viscous, whereas those of high viscosity index are relatively nonviscous. The 100° F. viscosity of the high-viscosity-index materials ranged from 13 to 190 centistokes (70 to 880 S. U. S.); the low viscosity index materials, from 200 to 2400 centistokes (920 to 11,000 S. U. S.). The spread in viscosity between materials of low and high viscosity index increases with increasing molecular weight.

Although the oil fractions charged to the reflux extraction unit had already been highly refined to the point where they represented only 0.05 per cent of the original crude, products of widely different properties were obtained but no appreciable quantity of intermediate viscosity index material (i. e., between 10 and 90) exists, for the transition from the negative to the highly positive viscosity index region is very sharp.

### Acknowledgment

The authors are indebted to the Standard Oil Company of Louisiana for furnishing the oil investigated and to A. T. Paik, R. M. McCormick, and J. H. Bresnowitz for their aid in securing many of the data. This paper is published by permission of the Graduate School of The Pennsylvania State College.

### Literature Cited

- (1) Am. Soc. Testing Materials, Standards on Petroleum Products and Lubricants, p. 20, Sept., 1936.
- (2) Balsbaugh, J. C., Larsen, R. G., and Oncley, J. L., *IND. ENG. CHEM.*, **30**, 287 (1938).
- (3) Cannon, M. R., and Fenske, M. R., *Ibid.*, **28**, 1035 (1936).
- (4) Cannon, M. R., and Fenske, M. R., *IND. ENG. CHEM., Anal. Ed.*, **10**, 297 (1938).
- (5) Hersh, R. E., Fisher, E. K., and Fenske, M. R., *IND. ENG. CHEM.*, **27**, 1441 (1935).
- (6) Mair, B. J., and Schickltanz, S. T., *Ibid.*, **28**, 1446 (1936).
- (7) Mair, B. J., and Willingham, C. B., *Ibid.*, **28**, 1452 (1936).
- (8) Mikeska, L. A., *Ibid.*, **28**, 970 (1936).
- (9) Rossini, F. D., *Proc. Am. Petroleum Inst.*, **III**, **18**, 36 (1937).
- (10) Rossini, F. D., *Refiner Natural Gasoline Mfr.*, **14**, No. 6, 255 (1935).

This paper is part of a thesis submitted by M. R. Cannon in partial fulfillment of the requirements for the degree of doctor of philosophy in chemical engineering at The Pennsylvania State College.

# NITRATION OF ISOPENTANE<sup>1</sup>

L. W. SEIGLE AND H. B. HASS

Purdue University and Purdue Research Foundation,  
Lafayette, Ind.

THE vapor-phase nitration of ethane, propane, and the two butanes was reported by Hass, Hodge, and Vanderbilt (4). Hass and Patterson (6) extended this process to *n*-pentane. These workers found evidence for the presence of each of the nitro compounds that would be expected by applying the free-radical theory of nitration (4, 8).

The present paper deals with the vapor-phase nitration of isopentane. Evidence was obtained for the presence of each of the expected nitro compounds as predicted by the free-radical theory of nitration. Since there is no reason to believe that any other nitro compounds were formed, this is further confirmation of this theory. McCleary and Degering (8) previously analyzed the exit gases from the nitration of isopentane and found each of the olefins that might be expected from a free-radical mechanism.

The free radicals which can be obtained, theoretically, from isopentane by the loss of hydrogen or by a carbon-to-carbon fission include 2-methyl-1-butyl, 3-methyl-1-butyl, 3-methyl-2-butyl, 2-methyl-2-butyl, 2-butyl, 2-methyl-1-propyl, 2-propyl, ethyl, and methyl. Every nitroparaffin has been obtained that is theoretically possible by adding a nitro group to these free radicals. These radicals correspond to the nitro compounds found, which were 2-methyl-1-nitrobutane, 3-methyl-1-nitrobutane (a mixture boiling at 164-165° C., not separated), 3-methyl-2-nitrobutane (boiling at 155° C.), 2-methyl-2-nitrobutane (boiling at 150.5° C.), 2-nitrobutane, 2-methyl-2-nitropropane (a mixture boiling at

140° C., not separated), 2-nitropropane (boiling at 120° C.) nitroethane (boiling at 115° C.), and nitromethane (boiling at 101° C.). The boiling points given were obtained by correcting the boiling points at reduced pressure to 760 mm. of mercury.

Nitromethane, nitroethane, 2-nitropropane, 2-methyl-2-nitrobutane, 3-methyl-2-nitrobutane, the mixture of 2-methyl-1-nitrobutane and 3-methyl-1-nitrobutane, and the mixture of 2-methyl-1-nitropropane and 2-nitrobutane can be separated from one another by careful rectification. It is not practicable, however, to separate the two mixtures into their components by rectification.

Isopentane was nitrated in the vapor phase in an apparatus developed in this laboratory and described previously (4, 6).

### Identification of Products

Acetone was obtained as one of the products from the nitration. It was identified by preparing the 2,4-dinitrophenyl hydrazone (melting point, 127° C.).

Nitromethane was identified by its boiling point (99-100° C. at 745.5 mm.) and by the formation of a red color due to the presence of the sodium salt of methazonic acid when treated with concentrated sodium hydroxide.

2-Nitropropane was identified by its physical constants. It gave the blue pseudonitrole color test.

2-Nitrobutane and 2-methyl-1-nitropropane were proved to be present by use of the nitrolic acid and pseudonitrole test and by the boiling point of the mixture. The phenylthiourea derivative (melting point, 100-101° C.) of 2-butylamine was obtained from the reduction product of the mixture.

<sup>1</sup> This article, which contains material abstracted from the doctoral dissertation of L. W. Seigle, is the ninth in a series on the subject of syntheses from natural gas hydrocarbons. The others appeared in *INDUSTRIAL AND ENGINEERING CHEMISTRY*, **23**, 352 (1931); **27**, 1190 (1935); **28**, 333, 339, 1178 (1936); **29**, 1335 (1937); **30**, 67 (1938); **31**, 118 (1939).

2-Methyl-2-nitrobutane was identified by its boiling point (149.8° C. at 752.3 mm.) and by its insolubility in a sodium hydroxide solution.

3-Methyl-2-nitrobutane, boiling at 154° C. (746.2 mm.), was identified by the fact that it formed a blue pseudonitrole when treated with an alcoholic solution of sodium hydroxide and sodium nitrite with subsequent neutralization of the solution.

The analysis of the mixture containing 2-methyl-1-nitrobutane and 3-methyl-1-nitrobutane involved the reduction of the mixture to the amines. The amine fraction of boiling range 94–97° C. was collected and converted to the hydrochlorides. The melting point of the hydrochloride mixture was compared to the melting point of known mixtures of the hydrochlorides of 2-methyl-1-butylamine and 3-methyl-1-butylamine.

### Mixture Containing 2-Nitrobutane and 2-Methyl-1-nitropropane

A fraction of the distillate within the range of the boiling point of 2-nitrobutane and 2-methyl-1-nitropropane was reduced to the amines with iron and hydrochloric acid. The amines were rectified and the fraction of boiling range 61–62.2° C. was collected. The phenylthiourea derivative melted at 100–101° C. This proves the presence of 2-nitrobutane in the original mixture.

Another portion of the nitrobutane mixture was rectified, and the fraction boiling at 77–81.6° C. (100 mm.) was collected. This material was dissolved in sodium hydroxide, and a slight excess of the calculated amount of sodium nitrite was added. The solution was made acid with sulfuric acid. The aqueous solution was blue. This color was due to the pseudonitrole of 2-nitrobutane which was known to be present. The aqueous solution was extracted with ether, and the ether extract shaken with an aqueous solution of sodium hydroxide. The ether layer remained blue in color, but the aqueous layer was orange-red. The orange-red color of the aqueous solution is characteristic of the sodium salts of the

and 2-methyl-1-nitropropane are present. The amounts of each component of the mixture could not be determined.

### Preparation of Amine Hydrochlorides

In order to determine the amounts of the hydrochlorides of 2-methyl-1-butylamine and of 3-methyl-1-butylamine present, a melting point-composition curve was prepared from the pure compounds.

*sec*-Butyl alcohol was converted to the bromide by the use of bromine in the presence of phosphorus (3) and purified by rectification. The *sec*-butyl bromide was converted to the nitrile according to the procedure of Hass and Marshall (5). The yield was very poor. The nitrile was purified by rectification. The fraction boiling at 123–125° C. was collected.

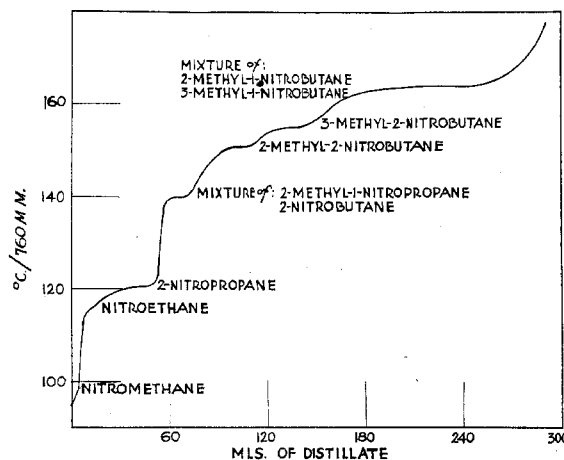


FIGURE 2. RECTIFICATION CURVE OF THE PRODUCT OBTAINED BY NITRATING ISOPENTANE AT 420° C.

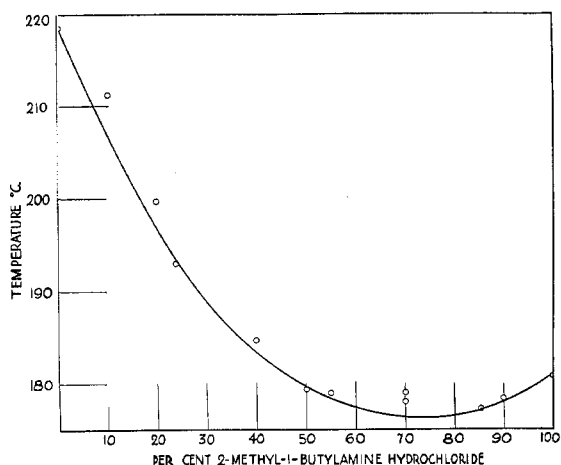


FIGURE 1. COMPOSITION-MELTING POINT CURVE FOR 2- AND 3-METHYL-1-BUTYLAMINE HYDROCHLORIDE

nitrolic acids. Demole (2) showed that the nitrolic acid derived from 2-methyl-1-nitropropane yields isobutyric acid upon treatment with sulfuric acid. Upon treatment with sulfuric acid the orange-red aqueous layer gave a distinct odor of isobutyric acid, which confirmed the presence of 2-methyl-1-nitropropane. From the boiling point of the fraction and the color reaction it is believed that 2-nitrobutane

The nitrile was reduced to the corresponding amine by the method of Adams and Marvel (1). After unreacted sodium was destroyed, the reaction mixture was steam-distilled. The distillate was made acid with hydrochloric acid and evaporated to dryness. The salt was taken up with a sodium hydroxide solution. The alkaline solution was extracted with ether, and the ether extract was dried over anhydrous potassium carbonate. The ether was stripped from the amine in a modified Podbielniak column, and the amine was rectified. The fraction of boiling range 94–96.5° C. was collected. The amine was dissolved in ether and treated with dry hydrogen chloride in the cold. The amine hydrochloride was filtered off and dissolved in a small amount of anhydrous butyl alcohol. The solution was filtered, and the 2-methyl-1-butylamine hydrochloride was reprecipitated by the addition of dry ether. The melting point of the salt was 180–181° C. The melting point given in the literature is 176° C. (9).

The hydrochloride of isoamylamine (3-methyl-1-butylamine) was prepared in a manner similar to that just described. The conversion of the isobutyl bromide to the nitrile was less than that obtained in the previous preparation. The phenylthiourea derivative of the isoamylamine was prepared. Its melting point was 103.6° C. The melting point in the literature is 102° C. (10). The remainder of the amine was converted to the hydrochloride by the method previously described. The melting point of the isoamylamine hydrochloride was 218–219° C.

Ten samples of mixtures of the two amine hydrochlorides were weighed out and mixed, and five melting points of each mixture were taken with calibrated Fisher short-stem thermometers (7). The curve shown in Figure 1 was obtained