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Relationship between temperature and vapor pressure of light oils

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RELATIONSHIP BETWEEN TEMPERATURE

AND VAPOR PRESSURES

OF LIGHT OILS

BY- W. O. Keeling.

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Thesis: Relationship between temperature and vapor pressures of light oils.
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INTRODUCTION

There are a few data scattered through the literature on the vapor pressures of pure hydrocarbons, but the author has never seen a systematic study of the relationship between temperature and vapor pressures of complicated mixtures such as the various light oils encountered in refinery practice.

Such data would be useful in designing equipment for distillation, steam stilling, vacuum distillation and in calculating heat balance, etc.

An attempt has been made to link the vapor pressure of a light oil, at various temperatures, to the average boiling point of the oil.

Apparatus Used

The apparatus used was an ordinary mercury barometer, jacketed by a two inch Pyrex tube. An electric heating coil was placed in the space between the barometer and Pyrex tubing. A meter stick was placed behind the barometer. One end of a small metal rod was inserted into one end of this stick, the other end of the rod passing through the cork which held in the bath oil. THe distance from the end of the meter stick to the end of the rod was measured. The free end of the rod was made to barely touch the surface of the mercury in the barometer well by raising or lowering the latter.

Agitation of the bath oil was accomplished by introducing air into the lower part of the annular space. By regulating the electric current in the heater and the amount of air used for stirring, the temperature was maintained at the desired point.

Kind of Oils Used

The oils selected for the experimental work were:-

1. Light, Straight-Run gasoline
2. Heavy, Straight-Run gasoline
3. 40-60 Blend of Cracked and Straight-Run gasoline
4. Pressure Distillate
5. Benzine
6. Crude Oil

These oils represent most of the light oils encountered in the average refinery practice. The vapor pressure of each oil was first measured at different temperatures. Each oil was then fractionated into 10% cuts and the vapor pressures of each cut were determined at different temperatures.

Procedure

The procedure used was to introduce the oil to be tested into the barometer by means of a curved medicine dropper. A sufficient amount of oil was introduced into the barometer as to insure some of the lighter ends remaining in a liquid form at the higher temperatures. At least 10 cc were used for each test. After the introduction of the oil, the electric current was turned on and the air jet started. As the bath warmed up, the height of the barometer was read at 20°F intervals. The results are tabulated in the following tables.

LIGHT GASOLINE

Ave. B.P. is 259

Gravity	61.2°Be'	Temp. °F	Vapor Pressures M.M. Hg.
I.P.	114	100	584
10	174	120	621
20	198	140	655
30	216	160	675
40	232	180	727
50	250	200	(Atm)
60	267	220	-
70	286	240	-
80	316	260	-
90	358	280	-
E.P.	438	300	-
Recovery	95%		

DISTILLATIONS ON 10% CUTS OF LIGHT GASOLINE

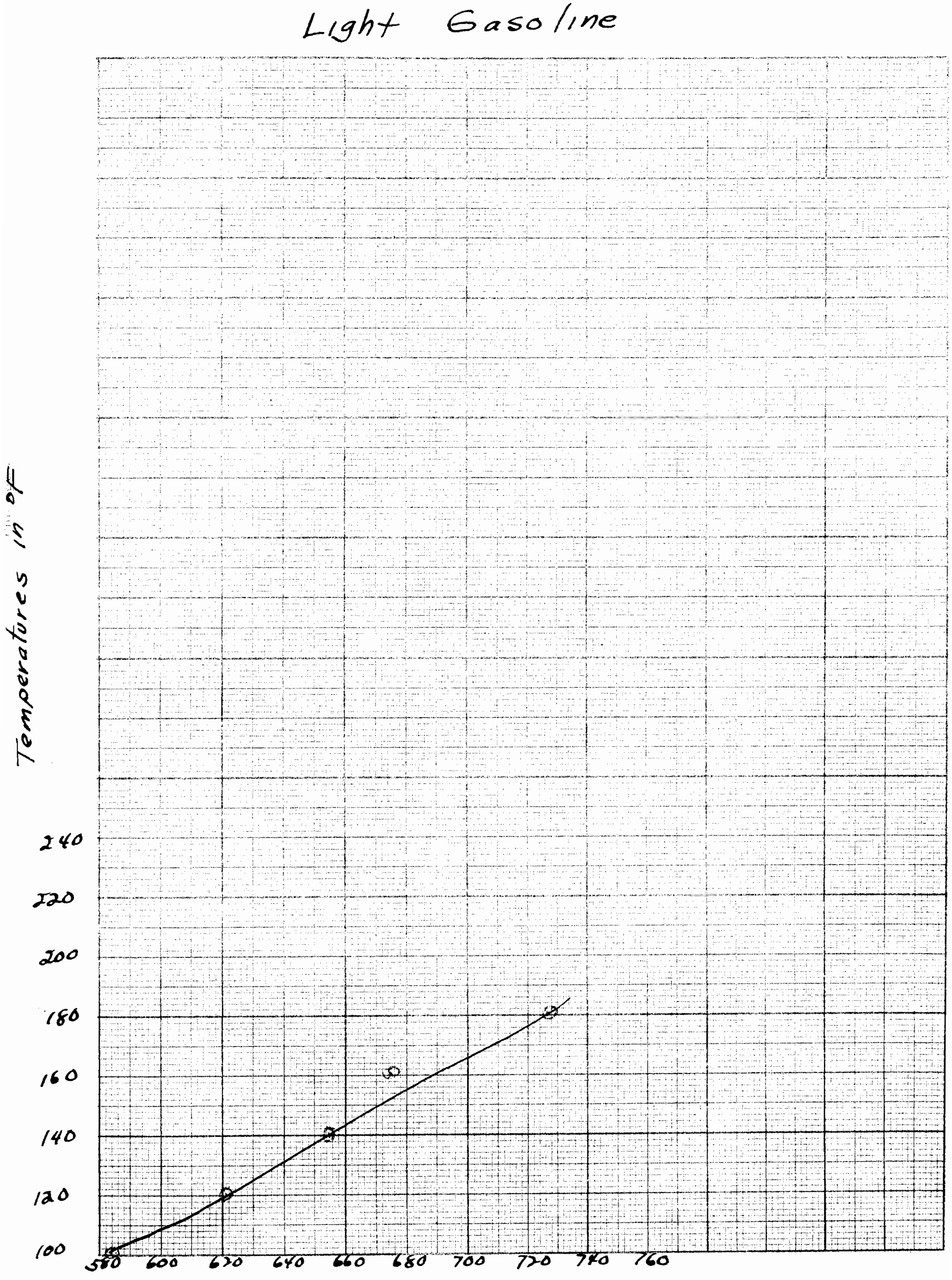
	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-100
Gravity	76.1	69.6	65.3	62.2	60.2	58.3	55.8	53.3	48.9	44.2
I.P.	106	130	162	187	207	229	251	260	308	350
10	126	152	179	202	220	239	260	288	330	377
20	132	158	184	206	224	242	263	292	332	382
30	135	162	188	210	228	245	267	295	336	387
40	142	168	192	212	230	248	270	299	341	392
50	148	172	196	216	234	252	274	301	345	398
60	154	176	200	220	238	256	278	306	350	404
70	160	180	205	224	242	361	283	311	354	411
80	168	188	211	230	250	268	288	317	363	420
90	179	199	222	242	260	279	298	327	378	438
E.P.	204	230	248	268	290	304	324	366	437	492
A.B.P.	150	174	199	219	239	257	278	306	352	405

CORRECTED VAPOR PRESSURES OF CUTS FROM LIGHT STRAIGHT RUN IN MILLIMETERS OF MERCURY

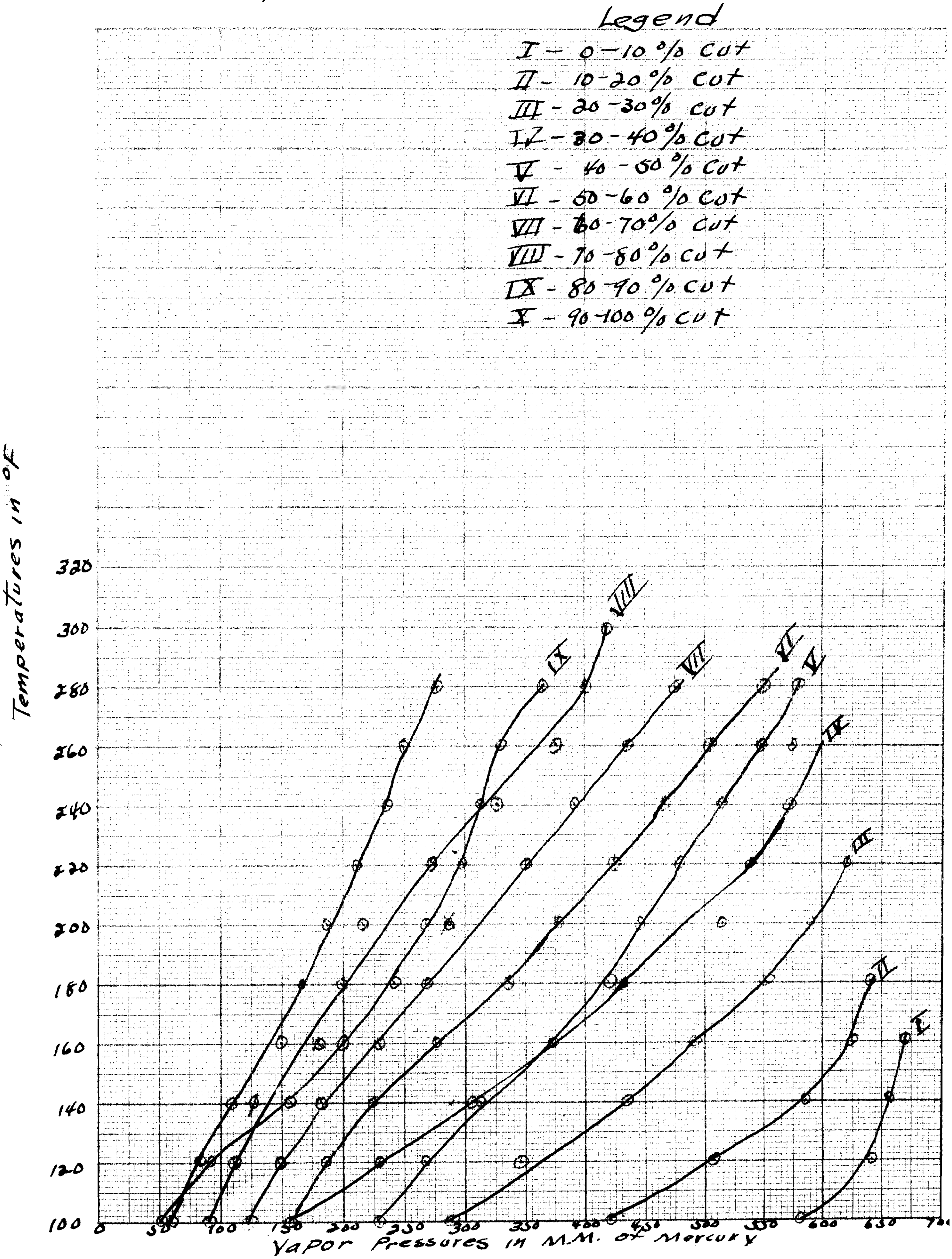
Fahr. Temp.	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-10
100	581	421	264	155	228	157	123	91	52	60
120	641	508	347	229	267	186	149	112	93	83
140	655	586	434	304	311	224	183	157	128	109
160	669	625	492	372	370	276	229	180	200	150
180	atm.	641	552	433	420	336	267	199	242	167
200	-	atm.	593	514	446	377	284	216	267	187
220	-	-	620	538	479	425	350	274	299	210
240	-	-	-	573	514	466	392	327	313	237
260	-	-	-	575	549	504	435	377	329	249
280	-	-	-	-	580	550	475	400	365	278
300	-	-	-	-	-	-	-	416	-	-
320	-	-	-	-	-	-	-	-	-	-

The following curves are plotted from the above figures:

Light Gasoline



10% Cuts From Light Gasoline



HEAVY STRAIGHT RUN

A.B.P. is 294

Gravity	56.5°Be'	Temp. °F	Vapor Pressures M.M. Hg.
I.P.	128	100	242
10	202	120	313
20	230	140	368
30	253	160	423
40	275	180	498
50	296	200	555
60	316	220	601
70	340	240	646
80	359	260	Atm.
90	389	280	-
E.P.	443	-	-

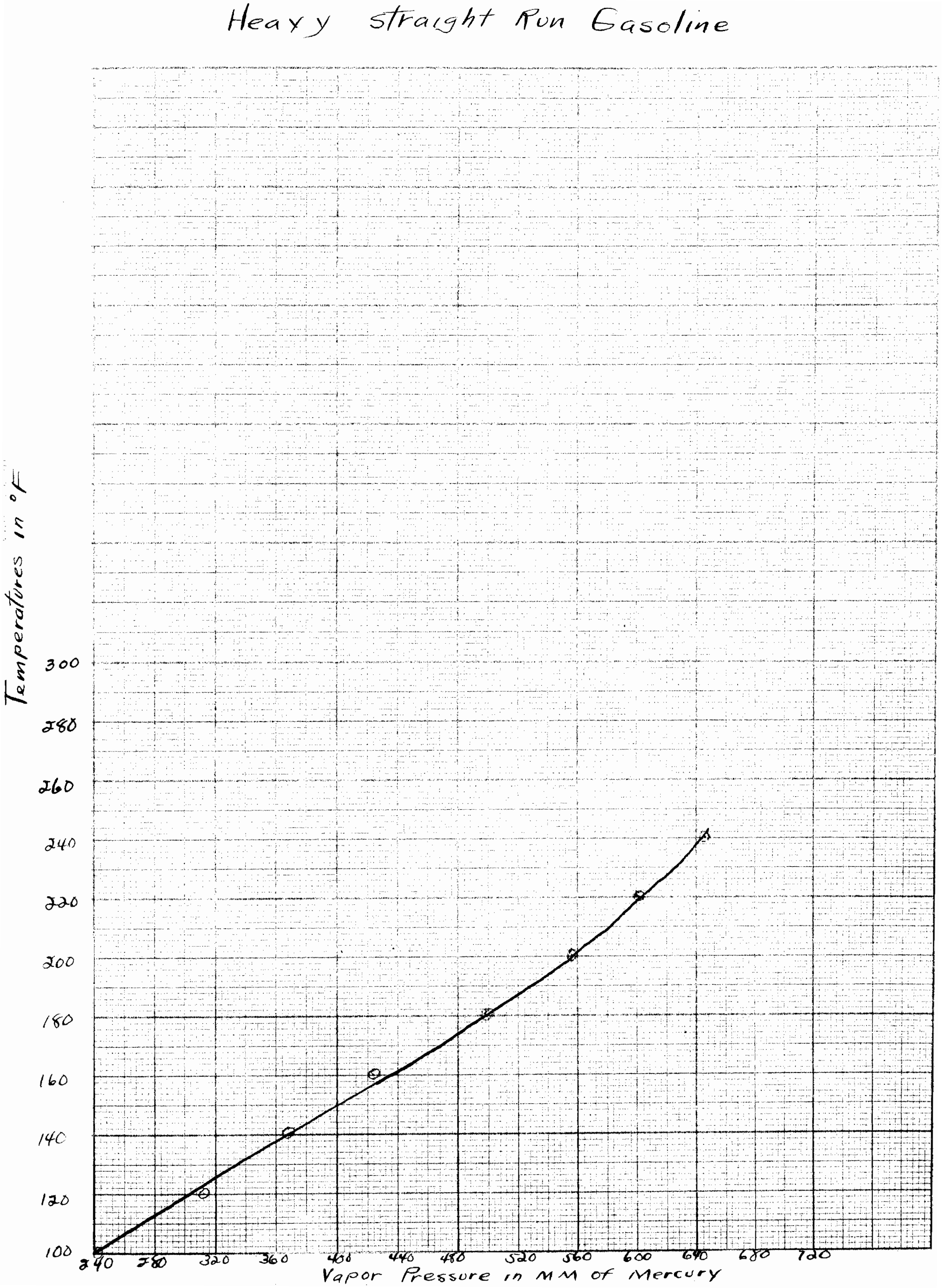
DISTILLATIONS ON 10% CUTS OF HEAVY STRAIGHT RUN

	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-100
Gravity	73.3	63.8	60.7	58.3	55.5	53.0	50.5	48.5	45.9	43.0
I.P.	118	150	200	220	242	270	302	319	356	381
10	133	166	212	232	256	286	311	330	363	395
20	141	173	215	238	260	289	314	334	366	399
30	146	180	218	241	264	292	317	337	369	402
40	153	186	221	245	268	296	320	340	372	405
50	160	192	225	249	273	301	323	344	375	408
60	166	199	229	254	278	305	327	347	378	412
70	173	206	235	259	284	310	332	351	382	417
80	181	214	244	266	290	316	337	356	387	424
90	193	225	256	277	300	326	346	364	396	435
E.P.	250	260	316	315	325	350	383	394	426	482
A.B.P.	165	196	234	254	276	304	329	347	380	415

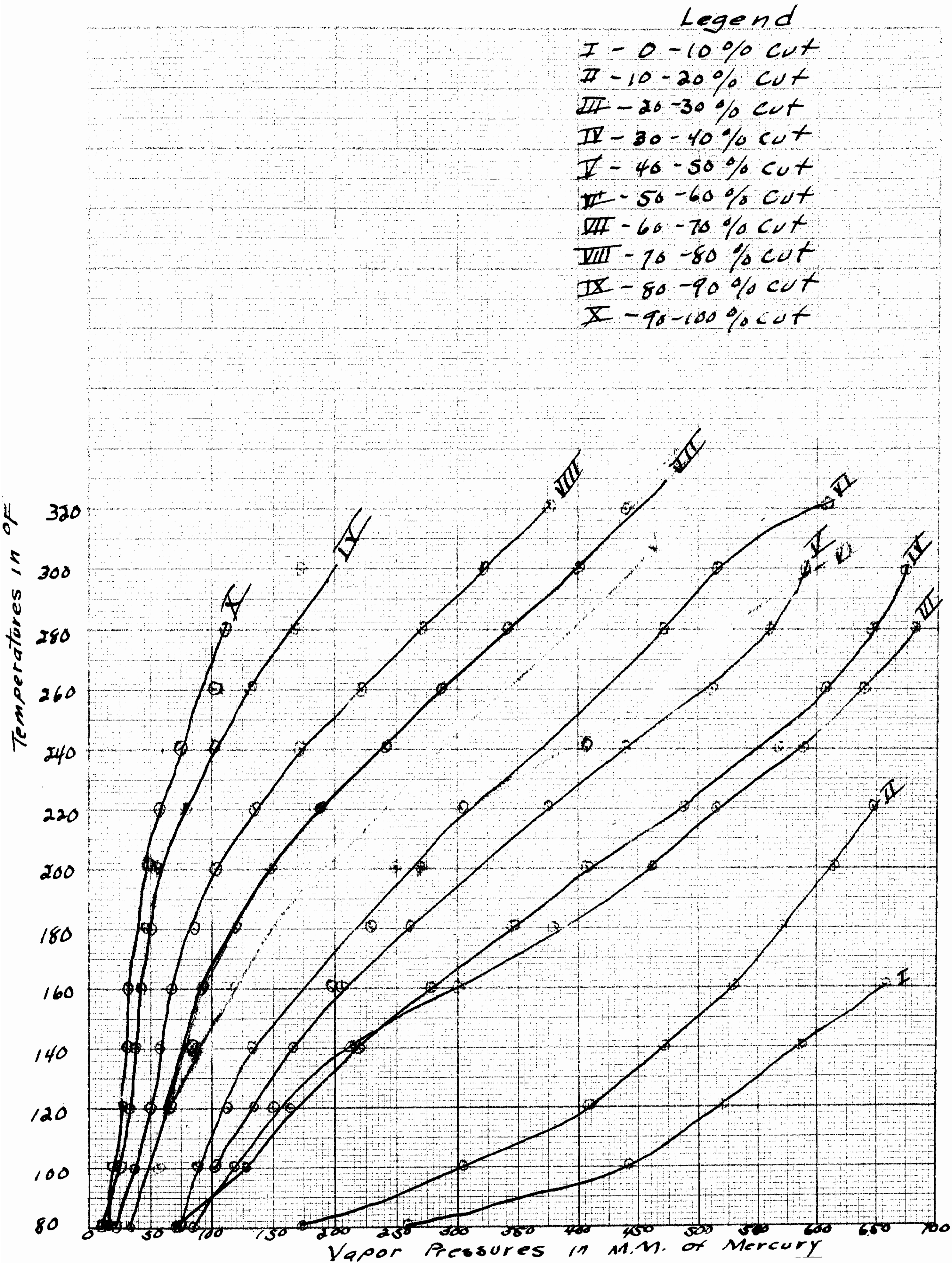
CORRECTED VAPOR PRESSURES OF CUTS FROM HEAVY STRAIGHT RUN IN MILLIMETERS OF MERCURY

Fahr. Temp.	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-100
80	258	173	85	70	-	74	34	23	10	15
100	441	304	117	127	101	89	57	39	25	21
120	519	408	150	162	134	113	66	50	33	28
140	586	471	212	219	166	132	81	57	37	31
160	657	530	300	278	205	198	92	68	42	34
180	Atm.	572	381	345	262	228	119	81	50	39
200	-	615	461	407	270	248	148	103	54	48
220	-	648	540	489	376	303	189	135	80	57
240	-	Atm.	590	568	440	407	242	173	101	75
260	-	-	640	608	511	-	283	222	132	101
280	-	-	683	648	560	471	343	271	168	110
300	-	-	Atm.	674	590	515	401	319	172	-
320	-	-	-	Atm.	-	606	440	377	-	-

The following curves are plotted from the above vapor pressures.


Heavy Straight Run Gasoline
Temperatures in °F
300
280
260
240
220
200
180
160
140
120
100
240
280
320
360
400
440
480
520
560
600
640
680
720
Vapor Pressure in MM of Mercury

10% Cuts From Heavy Straight Run Gasoline



PRESSURE DISTILLATE

Gravity	51.4°Be'	Temp. °F	Vapor Pressure M.M. Hg.
I.P.	118	100	375
10	195	120	427
20	247	140	482
30	288	160	520
40	324	180	558
50	342	200	588
60	378	220	622
70	414	240	655
80	435	260	Atm.
90	469	280	-
E.P.	516	-	-

A.B.P. is 339

DISTILLATIONS ON 10% CUTS OF PRESSURE DISTILLATE

	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-100
Gravity	78.3	64.9	56.8	52.0	48.6	42.8	41.4	39.4	36.0	32.5
I.P.	87	130	224	272	298	357	380	410	433	460
10	106	169	247	290	324	369	397	422	460	481
20	117	180	252	293	328	373	400	425	462	498
30	127	190	255	297	332	376	404	428	465	504
40	139	199	260	301	336	379	406	430	468	510
50	144	210	263	305	339	382	408	433	472	517
60	150	221	267	310	342	385	411	436	476	524
70	158	227	272	315	346	389	414	439	480	536
80	166	233	278	320	352	394	420	443	488	565
90	177	245	288	331	361	403	430	450	500	590
E.P.	282	305	328	373	390	430	460	468	542	640
A.B.P.	150	209	267	309	341	385	412	435	478	530

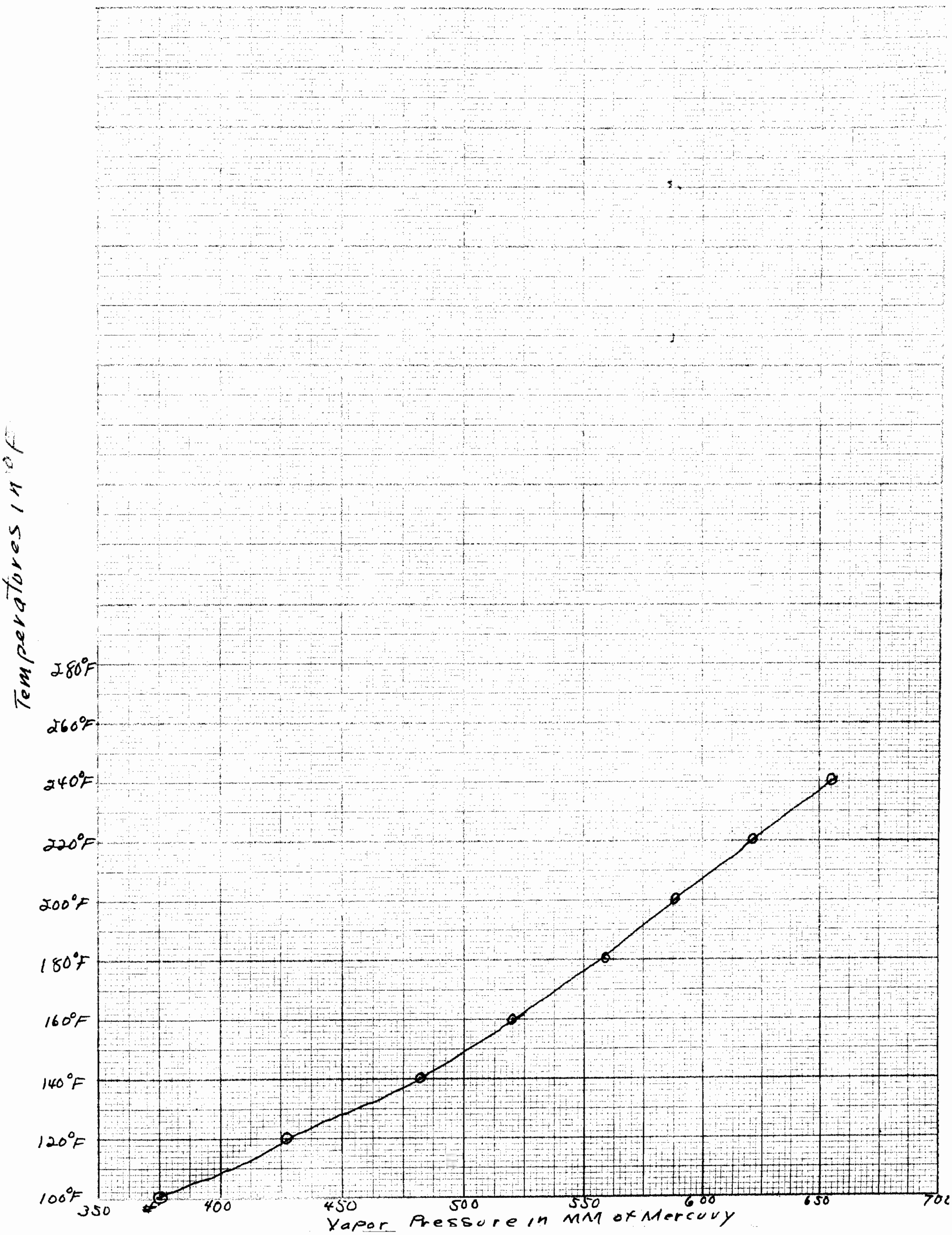
CORRECTED VAPOR PRESSURES OF CUTS FROM PRESSURE DISTILLATE IN MILLIMETERS OF MERCURY

Fahr. Temp.	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-100
80	637	445	-	-	-	-	-	-	-	-
100	Atm.	460	45	42	25	23	Broke Container	23	22	24
120	-	475	60	50	32	28		24	24	25
140	-	520	82	53	35	30		25	26	28
160	-	577	130	70	50	38		26	28	31
180	-	625	167	91	62	42		28	34	36
200	-	Atm.	241	121	77	52		33	38	38
220	-	-	367	172	106	70		35	44	42
240	-	-	495	232	147	94		40	48	47
260	-	-	630	346	222	110		48	55	55
280	-	-	Atm.	465	274	132		60	66	64
300	-	-	-	665	382	182		81	81	72
320	-	-	-	Atm.	480	260		112	102	81
340	-	-	-	-	-	362		154	-	96

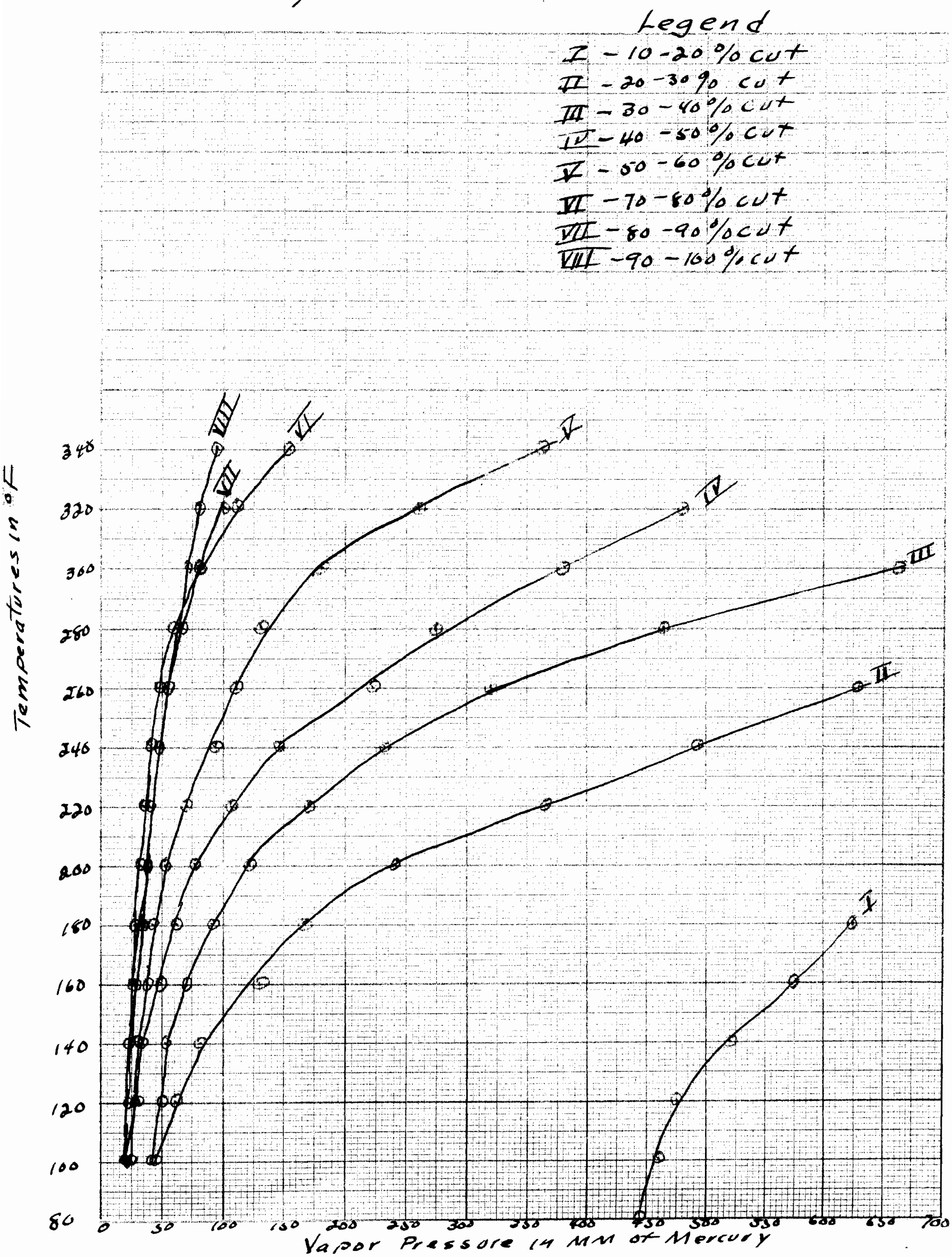
0-10% cut equalled atmospheric pressure at 92°F.
10-20% cut equalled atmospheric pressure at 132°F.

The following curves were drawn from the above pressures.

Pressure Distillate



10% Cuts From Pressure Distillate



BLEND OF PRESSURE AND STRAIGHT RUN GASOLINE

A.B.P. is 309

Gravity	55.2°Be'	Temp.°F	Vapor Pressures M.M. Hg.
I.P.	118	100	313
10	200	120	366
20	234	140	422
30	258	160	477
40	282	180	520
50	310	200	585
60	338	220	627
70	364	240	670
80	402	260	Atm.
90	430	280	-
E.P.	466	-	-

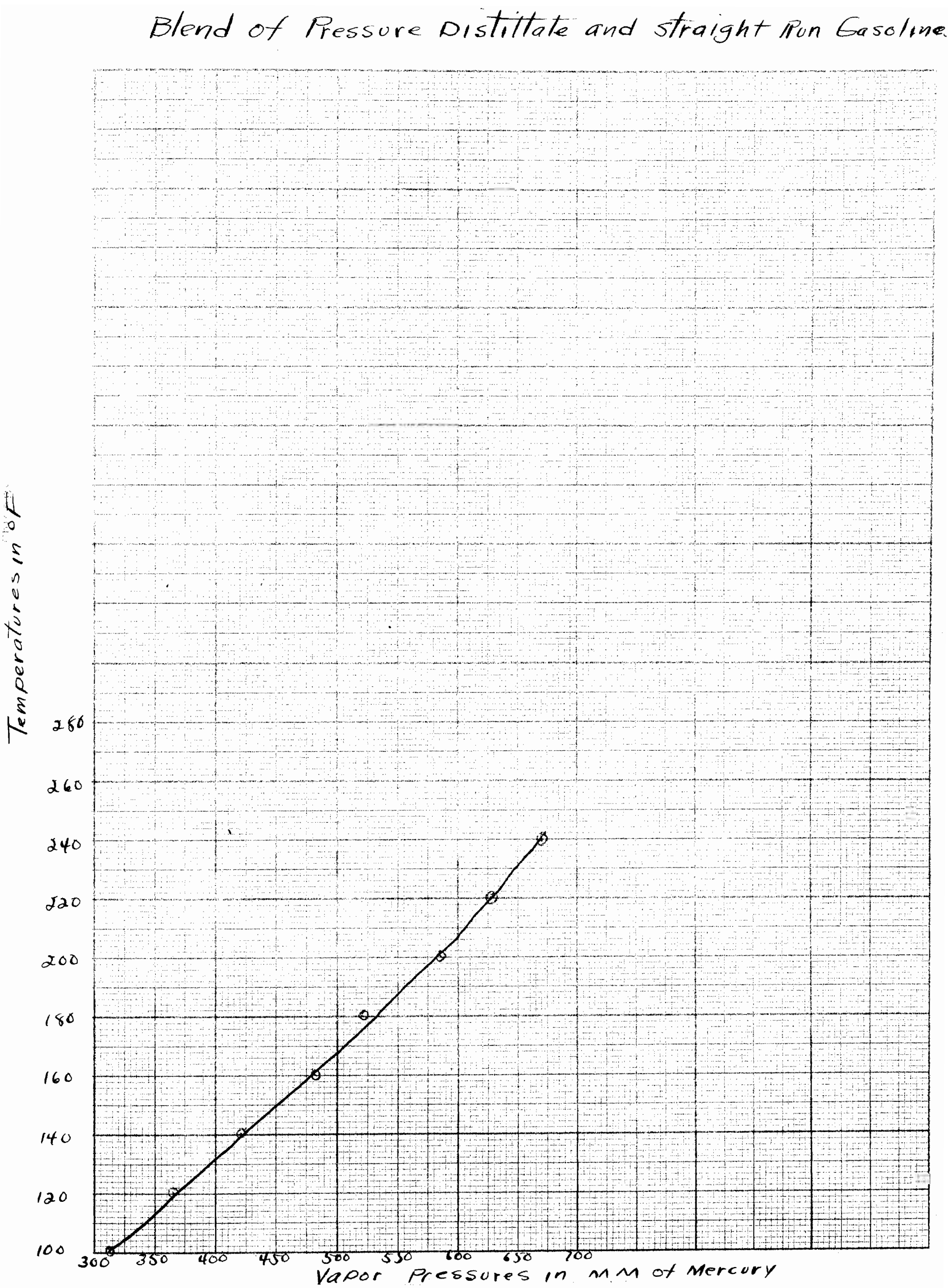
DISTILLATION OF CUTS FROM BLEND

	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-100
Gravity	74.0	64.4	58.0	54.7	52.1	48.8	46.7	43.8	39.7	36.0
I.P.	116	165	210	266	284	295	338	361	366	432
10	128	183	231	272	294	318	344	379	423	458
20	134	189	233	274	297	322	352	382	428	466
30	139	194	237	277	300	326	356	385	431	469
40	145	198	239	280	302	328	359	388	436	473
50	152	202	242	283	306	330	362	391	439	477
60	159	206	245	286	310	336	366	394	445	483
70	163	210	250	292	316	340	370	398	448	493
80	176	216	254	298	321	346	376	402	454	503
90	192	225	264	308	331	353	382	410	466	524
E.P.	232	257	318	364	373	385	410	430	506	597
A.B.P.	158	204	248	291	312	334	365	393	440	489

VAPOR PRESSURES OF CUTS FROM BLEND IN MILLIMETERS OF MERCURY

Fahr. Temp.	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70	% 70-80	% 80-90	% 90-100
80	293	-	-	-	-	-	-	-	-	-
100	440	111	34	32	31	27	31	24	22	23
120	527	164	112	43	38	30	40	37	24	25
140	608	247	148	64	46	35	45	38	26	27
160	Atm.	385	180	81	60	45	60	42	27	30
180	-	585	220	110	79	60	93	43	28	34
200	-	655	350	155	115	78	141	58	32	37
220	-	Atm.	485	234	166	106	183	75	36	41
240	-	-	615	335	240	156	224	91	40	45
260	-	-	Atm.	465	356	215	255	101	49	52
280	-	-	-	610	466	292	301	124	66	63
300	-	-	-	Atm.	622	388	345	143	89	74
320	-	-	-	-	Atm.	530	415	216	119	96
340	-	-	-	-	-	665	-	-	156	-

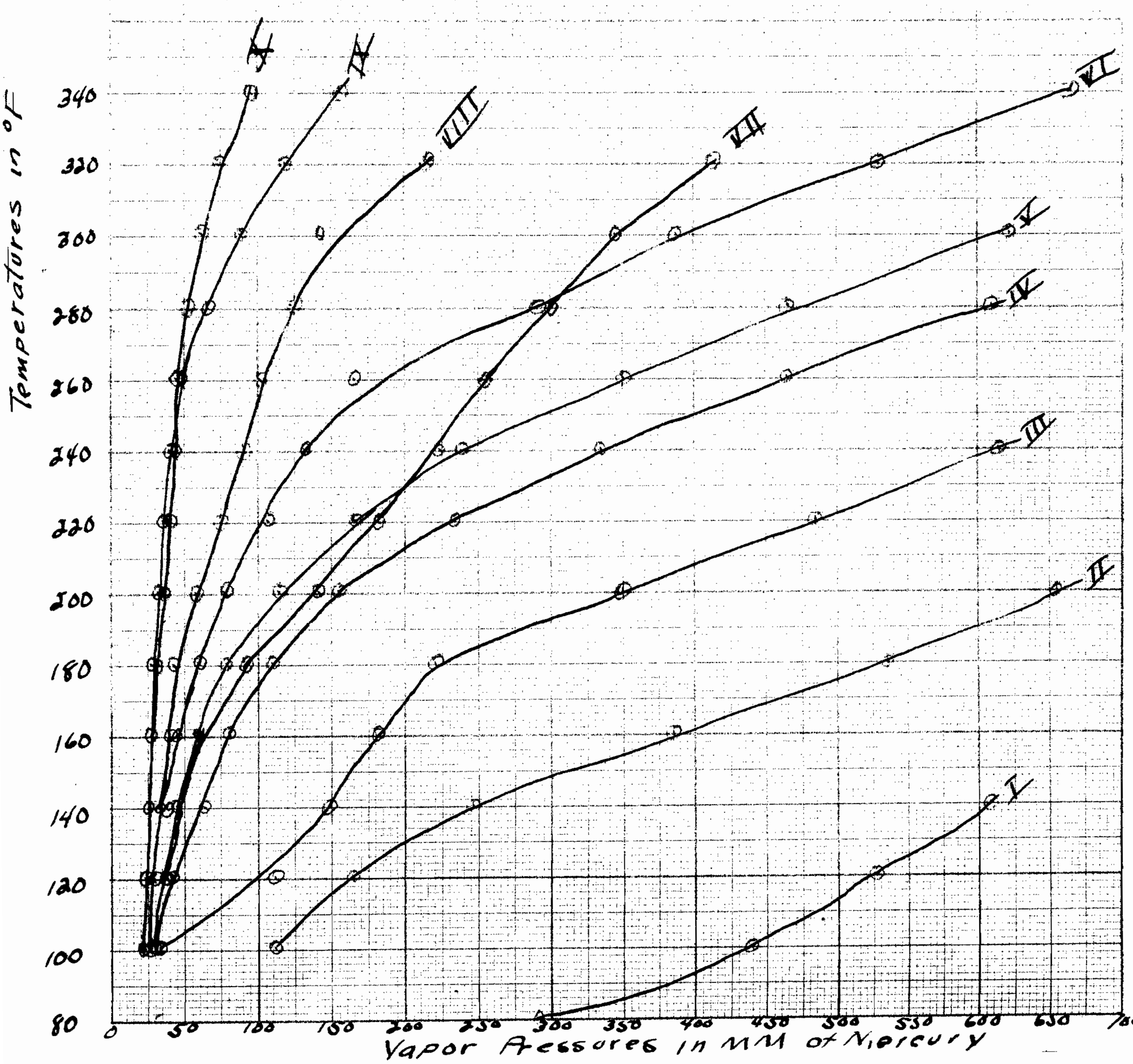
The following curves were drawn from above table.



Blend of Pressure Distillate and Straight Run Gasoline
Temperatures in °F
280
260
240
220
200
180
160
140
120
100
300
350
400
450
500
550
600
650
700
Vapor Pressures in M.M of Mercury

10 % Cuts From Blend

Legend
I - 0-10 % cut
II - 10-20 % cut
III - 20-30 % cut
IV - 30-40 % cut
V - 40-50 % cut
VI - 50-60 % cut
VII - 60-70 % cut
VIII - 70-80 % cut
IX - 80-90 % cut
X - 90-100 % cut



45°Be' BENZINE

DISTILLATIONS ON DIFFERENT FRACTIONS

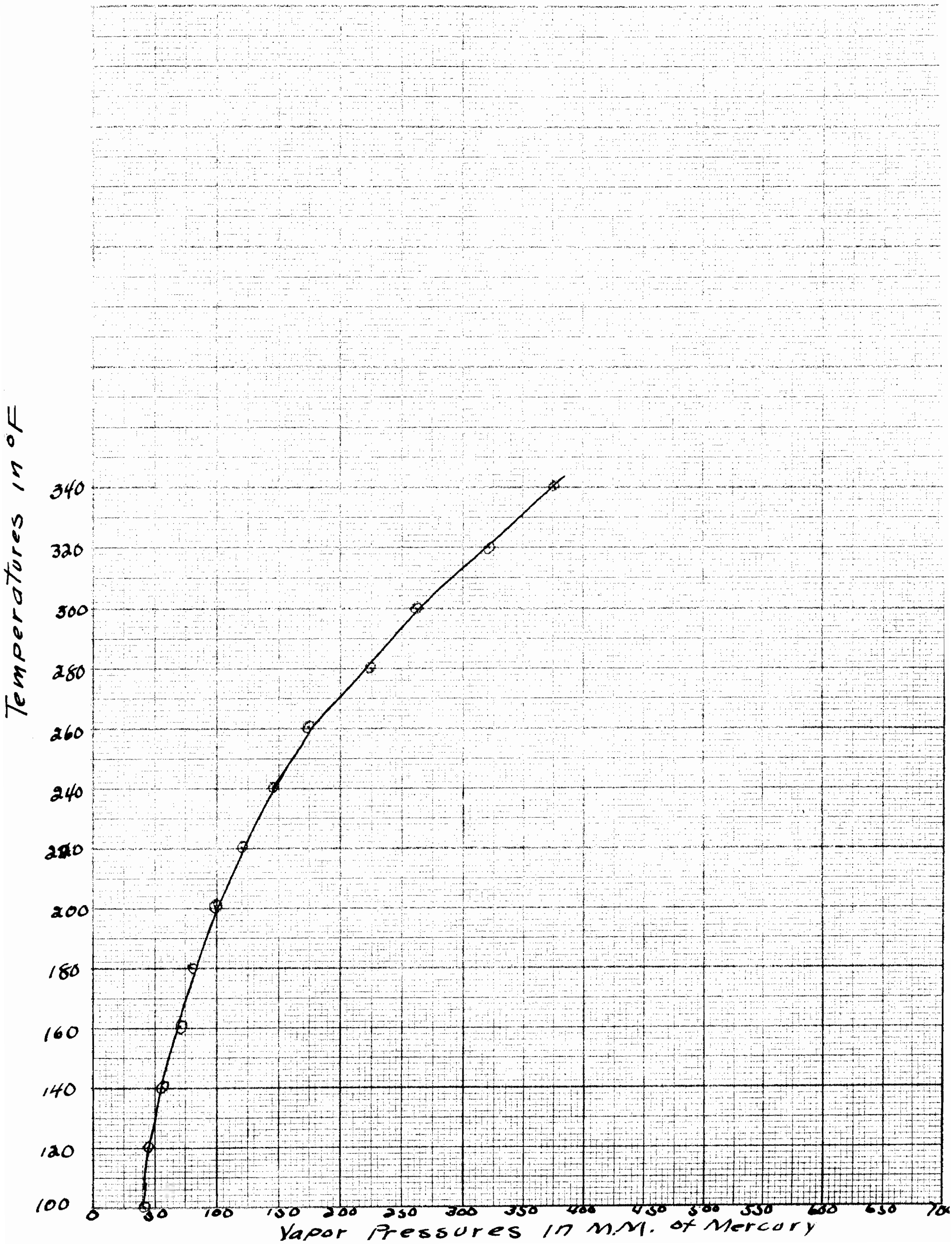
Original		% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70
I.P.	240	140	260	318	336	360	370	392
10	324	220	284	330	340	364	392	406
20	362	230	298	340	360	380	398	410
30	390	240	310	348	368	386	400	416
40	404	264	320	354	374	392	408	420
50	422	278	328	360	380	386	410	426
60	438	294	340	370	388	400	418	432
70	446	314	352	380	394	404	426	438
80	-	340	370	396	410	424	436	450
90	-	376	396	418	432	444	454	470
E.P.	-	390	408	460	466	476	478	514
A.B.P.	275	280	333	370	386	402	417	434

CORRECTED VAPOR PRESSURES OF FRACTIONS FROM BENZINE

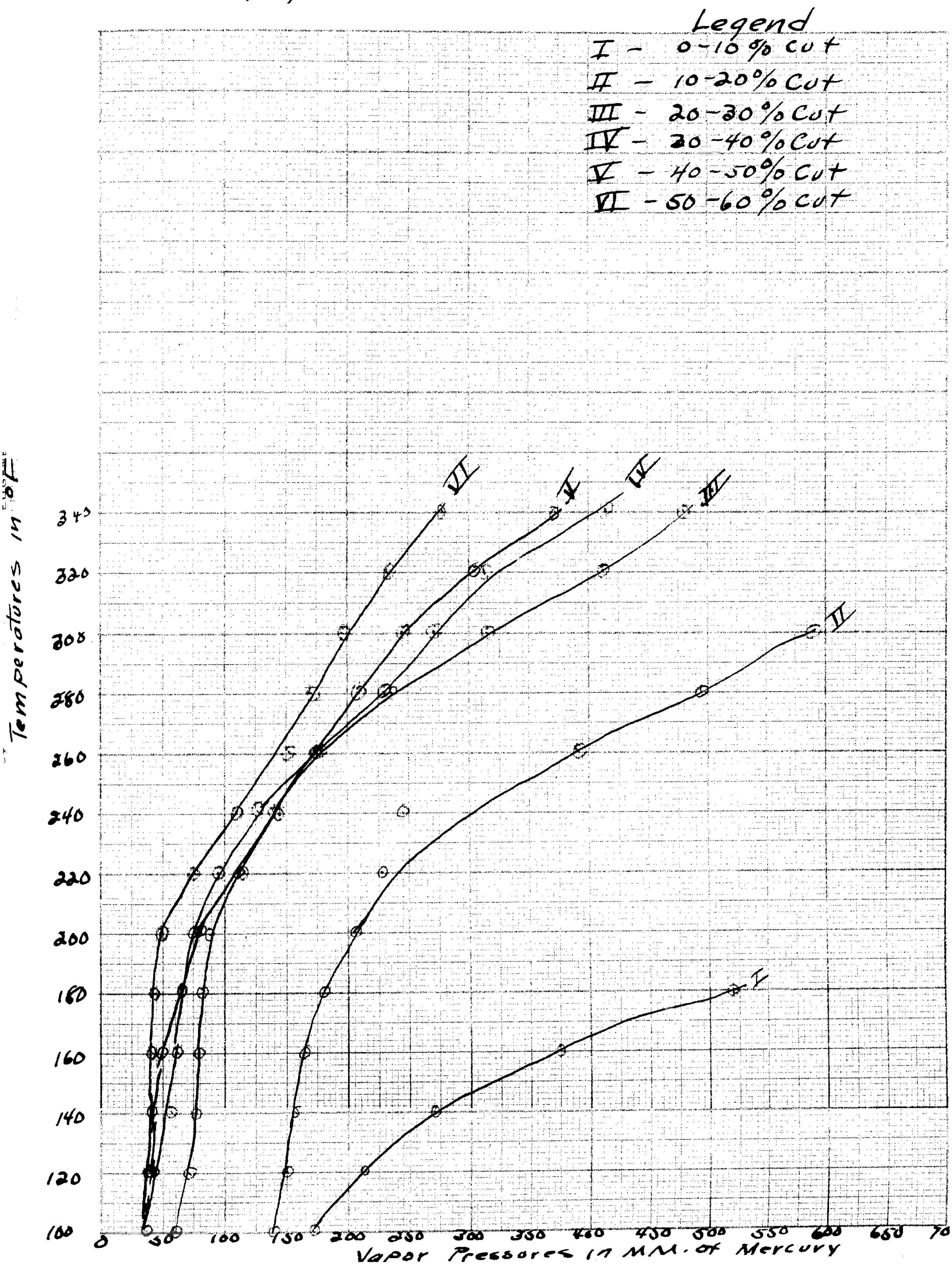
Fahr. Temp.	Benzine	% 0-10	% 10-20	% 20-30	% 30-40	% 40-50	% 50-60	% 60-70
100	42	173	138	60	37	37	35	
120	45	213	150	73	47	40	37	
140	56	270	157	76	56	42	39	
160	71	375	166	79	63	50	42	
180	80	520	180	83	66	65	44	
200	98	Atm.	206	89	76	84	50	
220	120	-	227	115	95	110	76	
240	145	-	245	140	128	145	110	
260	174	-	391	176	175	176	153	
280	224	-	495	236	230	208	170	
300	261	-	590	315	273	245	197	
320	321	-	Atm.	412	313	304	233	
340	376	-	-	480	415	374	279	

Below are curves plotted from the foregoing data.

Benzine


Temperatures in °F
340
320
300
280
260
240
220
200
180
160
140
120
100
0
50
100
150
200
250
300
350
400
450
500
550
600
650
Vapor Pressures in M.M. of Mercury

10% Cuts From Benzine



36.2° Gravity CRUDE OIL

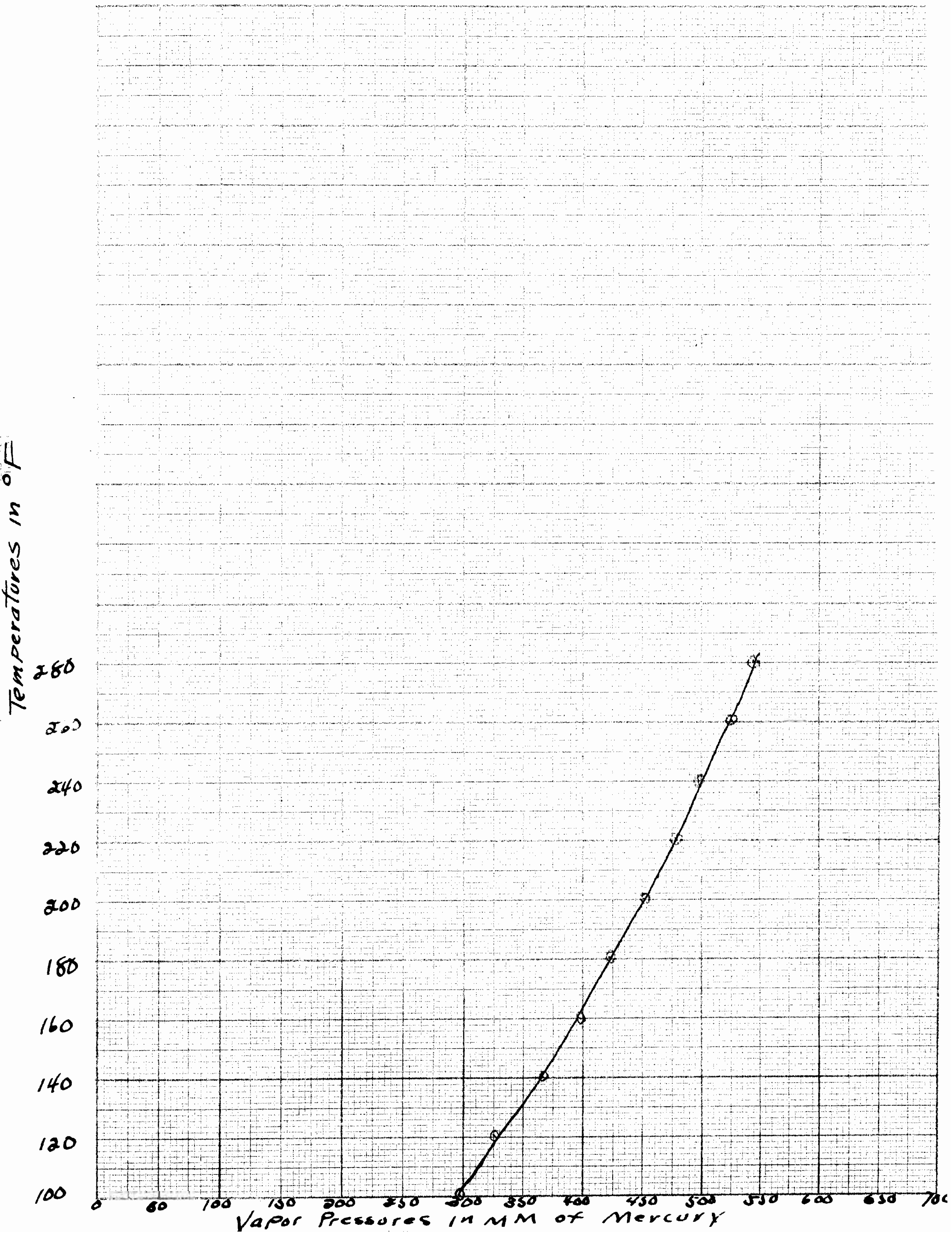
Temp.°F	Vapor Pressures M.M. Hg.
100	298
120	326
140	367
160	397
180	423
200	451
220	478
240	498
260	525
280	545

CORRECTED VAPOR PRESSURES OF 10% CUTS FROM CRUDE

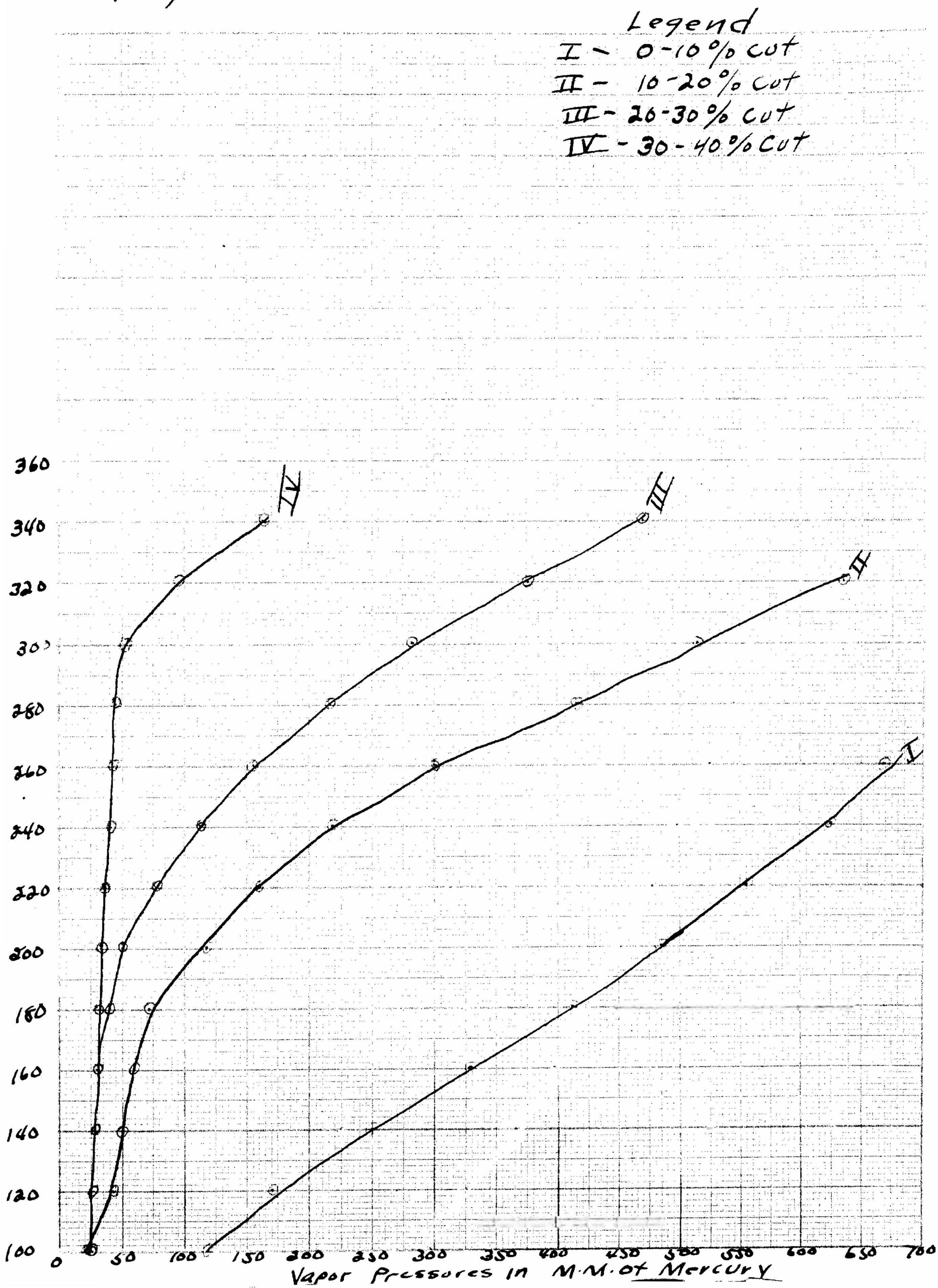
Temp. Fahr.	% 0-10	% 10-20	% 20-30	% 30-40
100	118	20	25	25
120	170	38	26	26
140	250	50	28	28
160	328	60	30	30
180	412	71	40	32
200	485	118	50	34
220	555	160	78	36
240	625	218	113	40
260	668	300	155	43
280	Atm.	415	216	45
300	-	515	283	54
320	-	635	376	96
340	-	Atm.	470	126
360	-	-	-	165

The following curves are plotted from the above data.

Crude oil


Temperatures in °F
280
260
240
220
200
180
160
140
120
100
0
60
100
150
200
250
300
350
400
450
500
550
600
650
700
Vapor Pressures in MM of Mercury

10% Cuts From Crude Oil



DISCUSSION

From the very nature of the substances worked with, the regularity of results can not equal the results to be obtained from pure substances. Gasolines of exactly the same gravity, or even the same initial and end points may differ from each other in vapor pressures at any given temperature, because of differences in composition. The author recognizes this and simply offers the data obtained in the hope that it will be useful for average engineering computations.

It will be observed that the first two or three cuts from each oil, particularly pressure gasoline, gives vapor pressures that seem to be a little out of line with the remainder of the cuts. This is probably due to one or two things - dissolved permanent gases, or wide variation in composition. This is shown also in the A.S.T.M. distillations of the 10% cuts from each oil. The tendency is for the difference in temperature between the initial point and end point to be greatest for the lightest cuts and least for the heaviest cuts even though the same fractionating column was used and the same rate of distillation maintained. Then, too, there is a tendency for the overlap between the end point of the first fraction and the initial point of the second to be larger than the overlap between two successive fractions of higher boiling cuts, although the difference shows less regularity than the difference in temperature between the initial and end points.

Rejecting the figures obtained for the first three cuts of each oil, excepting benzine and crude oil, the remaining data seems to show a general relationship between temperature and vapor pressure. By use of this relationship, this data can be extended from the particular products tested (with the incorrect figures thrown out in any case) to general use on all usual light oils and possibly the heavier. This relationship can be expressed mathematically as:

$$P = 600 \left\{\frac{t + 460}{T + 460}\right\}^9 \quad \text{Equation No. 1}$$

P = Vapor pressure in m.m. of mercury at temperature t in degrees Fahrenheit

t = Temperature Fahrenheit

T = Average boiling point of fraction in degrees Fahrenheit

The following comments are in order about this empirical equation:

1. It gives average figures for this data. On any one fraction from a particular oil it may show some error. Much of our engineering work covers average conditions, with the probable error within the accuracy of other factors, so this equation is available for use with judgement. Further work would probably permit the use of the equation for any kind of conditions with acceptable accuracy.

2. The equation applies with greatest accuracy to close cut fractions. Plant practice rarely has to do with close cuts, hence a modification is necessary for fractions of wide boiling point ranges.

Let,

T' = Value of T to be used in Equation No.1

T = Actual mean boiling point

D = Distillation range, or difference between initial and end points in degrees Fahrenheit

then,

$$T' = T - \frac{D^2}{2(T + 460)} \qquad \text{Equation No. II}$$

3. Even this modification will not give correctly the vapor pressure if there is an appreciable quantity of dissolved gas in the oil. This dissolved gas adds to the vapor pressure of the cut itself. In this case the vapor pressure of the gas must be considered separately and must then be added to that of the oil itself.

<u>Use of the Equations Illustrated</u>

Assume a close cut naphtha fraction with an A.B.P. of 375°F. The vapor pressure is required at 200°F.

$$t = 200^\circ F.$$

$$T = 375^\circ F.$$

$$P = 600 \frac{(200 + 460)^9}{(375 + 460)}$$

$$= 600 \times (.79)^9 = 600 \times .121 = 73 \text{ m.m. Hg.}$$

Checking over the data, temperatures at which this vapor pressure will be exerted by cuts of about this mean boiling point seem to vary within 10°F of 200°F.

If, instead of a close cut fraction, we have a naphtha of about 200°F I.P., 450°F E.P., 375°F A.B.P., as would be met with in actual practice, the correction for temperature will be required. Here t and T are as in above problem.

$$D = 450 - 200 = 250^\circ F. \text{ Then}$$

$$T_1 = T - \frac{D^2}{2(T+460)} = 375 - \frac{250^2}{2(375+460)}$$

$$= 375 - \frac{62500}{2 \times 835} = 375 - 37 = 338^\circ F, \text{ and}$$

$$P = 600 \left(\frac{t + 460}{T + 460}\right)^9$$

$$= 600 \left(\frac{200 + 460}{338 + 460}\right)^9 = 600 \left(\frac{660}{798}\right)^9$$

$$= 600 \times (.827)^9 = 600 \times .182 \doteq 115 \text{ m.m. Hg.}$$

instead of 73 m.m. for close cut fraction

Calculations for determining the degree of vacuum required in vacuum distillation of light oils would be determined by the same calculations as above, but it should be borne in mind that these data and equations should be used only for "flash" distillation and not for batch.

Use of Data for Steam Distillation Calculations For Light Gasoline

The following formula will give the theoretical amount of steam to use in steam distillation.

$$p = P \times \frac{18}{18 + aM}$$

$$\text{or } a = \frac{(P-p)\ 18}{pM}$$

where p Partial pressure of oil.

P Absolute pressure on surface of oil.

M Molecular weight of oil.

a Quantity of steam to one part of oil.

18 Molecular weight of water.

Take the light gasoline. This has an average boiling point of 259°F. This corresponds to Octane which has a boiling point of 259 and a molecular weight of 114.

Assume the oil is to be distilled with steam at atmospheric pressure at 240°F. Required the amount of steam to use.

p 675 M.M. at 240°F.

P 760 M.M., atmospheric pressure.

M 114, molecular weight of oil.

18 Molecular weight of water.

a Unknown.

$$a = \frac{(760-675)\ 18}{675 \times 114} = .15$$ lbs. steam, to one part of oil. Actual practice using open and closed coils shows about double the calculated amount of steam. Then .04 lbs. of steam per pound of oil, or 12 pounds of steam per barrel of gasoline will be necessary when steam stilling at 240°F.

In practice, distillation is usually carried on under pressures of from 5 to 10 pounds per square inch. Suppose we steam still under 10 pounds per square inch, gage pressure the other factors remaining the same. What amount of steam will be necessary?

$$a = \frac{(1340 - 675) \times 18}{675 \times 114} = .15 \text{ lbs. steam per lb. of oil theoretically.}$$

Actually .3 pounds of steam per pound of oil or 90 pounds of steam per barrel of oil.

Now let us take a heavier gas and see what the steam consumption will be. Let us take the 90-100 per cent cut of heavy straight-run gasoline. The average boiling point is 415°F. which corresponds to the boiling point of Dodecane which has a molecular weight of 170. Suppose the distillation is to be carried out at 280°F. and atmospheric pressure.

$$p = 110 \text{ M.M.}$$

$$P = 760 \text{ M.M.}$$

$$M = 170$$

$$a = \frac{(760 - 110)\ 18}{110 \times 170} = .6$$ pounds of steam per pound of oil theoretically or 1.20 pounds of steam or 360 pounds of steam per barrel of oil actually.

Now let us distill this oil at 10 pounds gage pressure at the same temperature.

$$a = \frac{(1340 - 110)\ 18}{110 \times 170} = 1.88$$ pounds of steam per pound of oil theoretically or 3.76 pounds of steam per pound of oil

or 1128 pounds of steam per barrel of oil under actual conditions.

Suppose that the distillation is carried on under a vacuum of 300 M.M., then,

$$a = \frac{(300 - 110)\ 18}{110 \times 170} = .18$$ pound of steam per pound of oil theoretically or .36 pounds of steam per barrel of oil or 108 pounds of steam per barrel of oil, actually.

CONCLUSIONS

1. There is a definite relationship between the vapor pressure of a light oil, at any given temperature, and its average boiling point.

2. This relationship is expressed in the Equation No. I for close cut oils, and in Equation No. II for oils of wide boiling point range.

3. An accuracy of about 5% can be had by use of these equations, which is accurate enough for most engineering calculations.

4. Examples have been given showing the use of the equations.