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NAVY DEPARTMENT

BUREAU OF ENGINEERING

Report

on

FR-1360

Acid Heat of Aviation Gasolines.

NAVAL RESEARCH LABORATORY
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WASHINGTON, D.C.

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INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Aeronautics letter Aer-E-46-MN JJ7G1 of 30 September 1936.

(b) Statement of Problem

2. Part of the problem as stated in letter of authorization is to "study the stability of aviation fuel blends under various conditions of use and storage." NRL Report No. P-1354 gives the results of a study entitled "Aviation Gasoline Storage at Naval Air Station, Pensacola, Florida." The gasolines made available from that study and from various commercial sources were used in this report on the "acid-heat" of aviation gasolines.

(c) Known Facts Bearing on the Problem

3. It has been determined that some unsaturated organic compounds cause the formation of gum in gasoline. Sulfuric acid, when shaken with these compounds, reacts with an evolution of heat. This fact has been used in specifications for aviation gasoline by means of the acid heat test. A good gasoline will give a temperature rise of about 2°F. The specification limit is 20°F. Several gasolines, which have been reported in NRL Report No. P-1354, have passed this test and have later been proven unsatisfactory.

(d) Theoretical Discussion

4. The work herein reported is based on the fact that strong acids react with unsaturated compounds and generate heat. As was shown in NRL Report No. P-1354, several gasolines known to be unsatisfactory passed the present specifications. The reaction of nitric acid with unsaturates is much more vigorous than sulfuric and a higher temperature rise can be obtained by using a mixture of the two. In Appendix A is given the details of a study of various mixtures of these two acids and it is shown that a mixture of 90% sulfuric and 10% nitric gives results which show a greater differentiation between good and doubtful gasolines. There are, however, certain limitations to this method.

(e) Narrative of Original Work Done at this Laboratory

5. No previous work has been reported from this Laboratory on the acid heat of gasolines or unsaturated hydrocarbons. In this report it is shown that the use of sulfuric acid for determining a temperature rise does not give satisfactory differentiation between gasolines that were satisfactory in service and those that were not. Therefore, mixed acids were studied using the beaker test with 75/25% sulfuric and nitric acid first studied by Mr. Beall of the Wright Aeronautical Corporation. Since heat radiation from an unprotected beaker is great and exceedingly

variable, a one pint thermos bottle was substituted. As may be noted in Appendix A, Figure I, this method gave high and greatly scattered results. This led to a study of the various acid ratios. As a result, a selection of the 90/10 ratio was made because at that point, the desirable and undesirable gasolines were grouped and so arranged that the gasolines could be easily classified.

6. A further study of the 90/10 acid mixture was made to determine the effect of the addition of mixed aromatics to a gasoline of the border-line variety. It may be noted in Figures III and IV of Appendix A, that the addition of aromatics depresses the acid heat value of a gasoline. This depression is so marked that the inclusion of 15% aromatics in a gasoline of questionable stability may be sufficient to cause it to pass a specification limit of 45°F. without improving the storage stability.

METHODS

7. Appendix A of this report gives the various details of the method employed. The method is very similar to that specified in previous specifications.

8. A number of commercial gasolines were tested by the several acid ratios and that data are as follows:

	Temperature Rise °F.*		
No.	100% Sulfuric Acid	90% Sulfuric Acid 10% Nitric Acid	75% Sulfuric Acid 25% Nitric Acid
N200	2	36	70
N201	2	33	72
N202	3	40	48
N203	4	34	74
N204	2	37	80
N205	1	36	62
N206	3	34	82
N214	3	36	77
N215	2	36	78
N216	2	34	77
N217	6	49	67
N218	10	73	126
N219	7	50	89
N220	2	34	83
N221	2	39	73
N222	3	34	78
N223	28	80	132

* 150 ml fuel and 30 ml acid in a thermos bottle used in all cases.

CONCLUSIONS AND RECOMMENDATIONS

(a) Facts Established

9. From the above table, the mean acid heat value and average deviation for the commercial gasolines has been calculated:

Method	Mean Value	Average Deviation
100% sulfuric acid	2	± 0.6
90% sulfuric, 10% nitric	36	± 1.6
75% sulfuric, 25% nitric	73	± 6.1

In this calculation, samples N217, N218, N219, and N223 have been excluded, since they fail to pass the 45° limit using 90/10 acid. The accuracy of the 90/10 acid method is very close to that of the 100% sulfuric. The 75/25 method is obviously subject to many variables.

(b) Opinions

10. As has been previously noted, the addition of aromatics to a gasoline carrying unsaturates, will lower the acid heat value (90/10). This fact destroys the value of the test as a permanent specification method. However, the test may be of value if it is considered as a stop-gap and only employed until further tests are devised which will predict the stability of aviation gasolines.

(c) Recommendations

11. Since more precise results can be obtained by the use of the revised method, it is recommended that the use of a mixed acid consisting of 90% concentrated sulfuric acid and 10% concentrated nitric acid be used in the specification. The modified procedure is given in Appendix C. However, due consideration must be given to the above noted limitations to this test.

SUMMARY

12. In this report and in Appendix A is given the data obtained for the development of an "acid-heat" test using 90% sulfuric and 10% nitric acid. This test is recommended temporarily for aviation gasolines. The temperature rise recommended is 45°F. as described in detail in Appendix C.

APPENDIX A

THE ACID HEAT TEST

Many investigators have written on the mechanism of the formation of gum in gasoline, and it is reasonably well agreed that the cause lies in the absorption of oxygen by various types of unsaturated hydrocarbons. The rate of gum formation depends upon the structure of the molecule as well as the degree of unsaturation. Cassar[1] reports simple olefins to be comparatively stable, but that di-olefins and mono-olefins attached to the benzene ring form gum with great ease. This contention is supported by Flood, Hladky, and Edgar[2] who also state that even aliphatic mono-olefins will form appreciable amounts of gum in some cases.

Aviation gasoline purchased by the U.S. Navy must be able to withstand long storage periods under the most adverse conditions. The fuels may be stored above ground in tropical regions for two years or more. These conditions make high stability a quality of primary importance. It is for this reason that discrimination against unsaturated hydrocarbons has been included in the specifications by the use of the acid heat test.

The acid heat test is a modified form of the Maumene number determination sometimes used in the testing of turpentine and fatty oils. Dean and Hill[3], in a study of the methods of determining unsaturates in gasoline, investigated this test. According to their data, the use of a thermos bottle and vigorous shaking will yield higher results than other methods. They are of the opinion that no errors can increase the temperature rise and therefore the method giving the highest result is probably the most accurate. However, they also conclude that the test is of value only in connection with a gasoline of moderately low concentration of unsaturates, since with high percentages a large portion of the heat is used in vaporizing the gasoline and not in raising the temperature of the system. Marden and Dover[4] also used a thermos bottle in determining Maumene numbers of fats by a modified procedure. They further conclude that the strength of the acid largely effects the results.

In a determination of unsaturated and aromatic hydrocarbons in a hydrocarbon mixture, Manning[5] found that the aromatics were attacked by sulfuric acid of 80% or higher concentration. His method made use of an acid mixture of 10% concentrated nitric in concentrated sulfuric. By this means, the unsaturates are oxidized and the aromatic content is determined from the nitro-derivatives.

The methods used in this report are essentially the same as those specified in the Navy specification for aviation gasolines. The

1. Cassar, Ind.Eng.Chem. 23, 10, 1132 (1931).
2. Flood, Hladky, and Edgar, Ind.Eng.Chem. 25, 11, 1234 (1933).
3. Dean and Hill, Bur.Mines Tech. Paper 181 (1917).
4. Marden and Dover, Ind.Eng.Chem. 9, 9, 858 (1917).
5. Manning, J.Chem.Soc. 1929, 1014-20.

modified procedure is as follows:

Apparatus:

Bottle - A one-pint thermos bottle of the type commonly used in lunch kits and provided with a metal cap.

Cork stoppers - Two tapered cork stoppers were used (2" long and 1" in diameter at smaller end). One was vented with a 1/8" hole. Both were impregnated with hard paraffin of 140°F. melting point.

Thermometer - A general thermometer of the range 0 - 220°F. was used.

Reagents - Commercial 66° Be sulfuric acid having a specific gravity of 1.835 - 1.840 (94% acid). Commercial nitric acid having a specific gravity of 1.415 - 1.420 (68 - 70% acid).

Procedure:

Step (1) - 150 ml of the fuel to be tested was measured into the bottle at approximately room temperature. The temperature of the fuel was observed after two minutes and recorded.

Step (2) - 30 ml of the acid having the same temperature as the fuel as observed in Step (1), was poured into the bottle, the vented cork inserted and the mixture gently shaken with a rotary motion for one minute.

Step (3) - The vented cork was removed and the thermometer inserted with its bulb in the acid layer. The maximum temperature is recorded. (This preliminary reading is taken as a precautionary measure.)

Step (4) - The thermometer was removed and the unvented cork inserted which is held in place by means of the metal cap and a spacer. The bottle was shaken with an up and down motion for two minutes at the rate of 130-160 up-and-down motions per minute.

Step (5) - The cork was removed and the thermometer again inserted into the acid layer, recording the maximum temperature.

Step (6) - The differences in degrees between the initial temperature as determined in Step (1) and final temperature as determined in Step (5) was recorded as the acid heat value of the fuel.

This method may be varied at four principal points:

1. Acid used.
2. Fuel/acid ratio.
3. Type of container used.
4. Initial temperature.

As previously noted, Dean and Hill have shown that the use of a thermos bottle gives the most consistent results.

Acid heat values have been determined for several gasolines using increasing amounts of nitric acid. These results have been tabulated in Table 1 and plotted in Figures 1 and 2. Samples 1 and 2 are known to contain simple olefinic hydrocarbons in addition to those found in normal aviation gasoline. Sample 1 has deteriorated to the extent that it deposited a gummy residue in the induction system and on the intake valves of an airplane motor, although the gum content as determined by A.S.T.M. method D381-34T, was only 4 mg/100 ml. Samples 3 and 4 are commercial aviation gasolines, the former being leaded and the later unleaded. Number 5 is natural gas heptane and 6 is commercial iso-octane.

It will be observed that the spread of values when using concentrated sulfuric acid alone is very small and no definite division between good and bad can be made. An acid heat specification using sulfuric acid of 20°F. maximum would pass all of these gasolines. The addition of nitric acid in increasing amounts raises the acid heat value until a maximum point is reached. The drop is probably due to the fact that at the maximum point, sufficient nitric acid is present to just nitrate all of the aromatic hydrocarbons and that past that point, excess nitric acid forms oxidation products. At the 75/25 point the spread is so great that again no sharp differentiation can be made. However, in all cases samples 1 and 2 have an acid heat value which greatly exceeds the other gasolines. It may be further noted that sample 1, which is in a more advanced state of deterioration than sample 2, has the higher acid heat.

A variation in the fuel/acid ratio was made by comparing 150 ml fuel/30 ml acid with a 50/20 ratio or a doubling of the acid quantity. The only effect is the proportionally raising of the acid heat values. The general characteristic of the curves remains the same.

The initial temperature of the fuel and acid was lowered below room temperature to ascertain the effect on the final acid heat value.

(a) Commercial Iso-octane.

Initial Temperature °F.	Acid Heat Value °F.*
40	17.5
45	18
72	20.5
98	24

(b) Natural Gas Heptane.

39	40
45	39
74	38
104.5	40.5

* 10% nitric acid in sulfuric acid; 150/30 fuel acid ratio.

It is evident from these data that initial temperature has very little influence on the final result. While commercial iso-octane had a 6.5° rise, it was over quite a range of initial temperature and the normal variation in room temperature would bring this discrepancy within experimental error.

An acid mixture containing 10% nitric and a fuel/acid ratio of 150/30 was selected to further investigate the effect of increasing percentages of olefins, aromatics, and mixtures of the two in a saturated base stock. The base stock used was commercial iso-octane which had been washed with nitrating acid and redistilled. Its acid heat was 1°F. These data have been tabulated in Tables 2, 3, and 4 and plotted in Figure 3 and 4. Increasing the olefin content with either di-isobutylene or tri-isobutylene increases the acid heat value though the rate of increase tends to fall off, probably due to the decrease in excess acid.

The addition of aromatic hydrocarbons to the base stock shows that the nitric acid is used up with 2 to 3 per cent aromatics and the acid heat value remains practically constant with increasing percentages. The aromatics used consisted of a mixture of equal parts of benzene, toluene, and xylene.

If 2% di-isobutylene were added to the base stock and acid heat values determined with increasing aromatic content, a depression occurred reaching a minimum value at approximately 6% aromatics. The depression at this point amounted to 12°F. or from 54°F. for 2% di-isobutylene and 98% iso-octane to 42°F. for 2% di-isobutylene, 6% mixed aromatics, and 92% iso-octane. This fact is also reflected in the curve which shows a base stock containing 15% mixed aromatics and increasing percentages of olefins. The base point is 35°F. and only rises to 49°F. for the mixture of 4% di-isobutylene, 15% mixed aromatics, and 81% iso-octane. This corresponds to an acid heat value of 65°F. for 4% di-isobutylene in iso-octane.

The various test methods employed at the present time to evaluate the stability of ordinary gasoline do not have sufficient sensitivity to predict storage stability necessary for the Navy. While these data show that the acid heat test is of questionable reliability, its use in Navy specifications may be considered as a stop-gap until acceptable test methods are devised which will indicate with ease and accuracy small percentages of hydrocarbons that are detrimental to storage characteristics.

Table I (a)

Thermos Bottle
150 ml Fuel
30 ml Acid

Sample		1	2	3	4	5	6	7
% H_2SO_4	% HNO_3							
100	0	14	11	3	2	3.5	4	1
95	5	38	34	21	19	22	20	1.5
90	10	62	68) 62.5)	38	36	39	26	1
85	15	86	75	34.5	52	58.5	22	1
80	20	98	84	29	68	57	22	1
75	25	98.5	88	29	70	50	22	0.5

Table I (b)

Thermos Bottle
50 ml Fuel
20 ml Acid

Sample								
% H_2SO_4	% HNO_3							
100	0	12	8	3	2	5	3	1
95	5	40	38	23	22	22	17	2.5
90	10	70	73	19	40	48.5	20	2.0
85	15	95.5	81.0) 87.5)	18	64	49	18	2.0
80	20	110.0	86.0) 108.0)	18	68	35	16	2.0
75	25	112.0	108.0	21.5	61	34	14.5	1.0

Table II (a)

	90/10
Iso-octane (cleaned)	1
+ 1/2% DIB	18.0
+ 1% DIB	38.0
+ 2% DIB	52.5
+ 3% DIB	59.0
+ 4% DIB	65.0

Table II (b)

Iso-octane (cleaned)	1
+ 1/2% TIB	16.0
+ 1% TIB	28.0
+ 2% TIB	44.0
+ 3% TIB	47.0
+ 4% TIB	52.0

Table III

Iso-octane (cleaned)	1
+ 1% Mixed aromatics	22.5
+ 2% Mixed aromatics	33.5
+ 3% Mixed aromatics	37.0
+ 5% Mixed aromatics	34.0
+10% Mixed aromatics	34.0
+15% Mixed aromatics	35.0

Table IV (a)

Iso-octane (cleaned) + 2% DIB	52.5
+ 2% DIB + 5% Mixed aromatics	44.0
+ 2% DIB + 10% Mixed aromatics	42.0
+ 2% DIB + 15% Mixed aromatics	41.5

Table IV (b)

Iso-octane (cleaned) + 15% Mixed aromatics	35.0
+ 1/2% DIB + 15% Mixed aromatics	36.0
+ 1% DIB + 15% Mixed aromatics	39.0
+ 2% DIB + 15% Mixed aromatics	41.5
+ 3% DIB + 15% Mixed aromatics	47.0
+ 4% DIB + 15% Mixed aromatics	49.0

From the above data, it may be concluded that:

1. The present method employing ordinary concentrated sulfuric acid does not give sufficient spread to differentiate between desirable and undesirable aviation gasolines.

2. Sufficient spread can be obtained by using a mixed acid of 90% ordinary concentrated sulfuric and 10% concentrated nitric acids.

3. The inclusion of aromatic hydrocarbons will depress the acid heat value. This depression destroys the value of the acid heat test to the consumer who wishes to discriminate against all types of olefinic hydrocarbons.

APPENDIX B

Socony-Vacuum Oil Co.

N200 Aero-Mobil Gas, unleaded.
N201 RD-2-50 Light refinery gasoline, 315° E.P., unleaded.
N202 RD-2-51 Commercial aviation gasoline, leaded.
N203 RD-2-52 Commercial aviation gasoline, unleaded.
N204 RD-2-53 Commercial aviation gasoline, leaded.

- - - - -

N205 Richfield Combat aviation gasoline, 73 octane.
N206 Associated Oil Co., refer EES Report No. 6722.

- - - - -

Shell Oil Co.

N214 T.A.-1 from Los Angeles Basin crude.
N215 T.A.-1 from Los Angeles Basin crude plus 4% iso-octane, 95%.
N216 T.A.-1 from Dominquez Hill - Huntington Beach crude.
N217 Iso-octane, 98%.
N218 Iso-octane, 95%.
N219 T.A.-11 from Wilmington storage.

- - - - -

N220 Union Oil, 73 octane, aviation.
N221 Phillips Petroleum Corp., special aviation.
N222 Standard Oil of California, Sample #27377R.
N223 Standard Oil of California, Sample #27378R.

- - - - -

Sample
1 Bulk storage, Corry Field.
2 Power Plant 555.
3 Power Plant 558.
4 Aero-Mobil Gas (Socony-Vacuum).
5 Natural gas, heptane.
6 Commercial iso-octane.
7 Cleaned iso-octane.

APPENDIX C

The modified procedure is as follows:

Apparatus:

Bottle - A one-pint thermos bottle of the type commonly used in lunch kits and provided with a metal cap.

Cork stoppers - Two tapered cork stoppers are used (2" long and 1" in diameter at smaller end). One is vented with a 1/8" hole. Both are impregnated with hard paraffin of 140°F. melting point.

Thermometer - A general thermometer of the range 0 - 220°F.

Reagent - The acid consists of 90% commercial 66° Be sulfuric acid having a specific gravity of 1.835 - 1.840 (94% acid), and 10% commercial nitric acid having a specific gravity of 1.415 - 1.420 (68 - 70% acid).

Procedure:

Step (1) - 150 ml of the fuel to be tested is measured into the bottle at approximately room temperature. The temperature of the fuel is observed after two minutes and recorded.

Step (2) - 30 ml of the acid mixture consisting of 90% sulfuric and 10% nitric, having the same temperature as the fuel as observed in Step (1), is poured into the bottle, the vented cork inserted and the mixture gently shaken with a rotary motion for one minute.

Step (3) - The vented cork is removed and the thermometer inserted with its bulb in the acid layer. The maximum temperature is recorded. (This preliminary reading is taken as a precautionary measure.)

Step (4) - The thermometer is removed and the unvented cork inserted which is held in place by means of the metal cap and a spacer. The bottle is shaken with an up and down motion for two minutes at the rate of 130-160 up-and-down motions per minute.

Step (5) - The cork is removed and the thermometer again inserted into the acid layer, recording the maximum temperature.

Step (6) - The difference in degrees between the initial temperature as determined in Step (1) and final temperature as determined in Step (5) is recorded as the acid heat value of the fuel.

U. S. NAVAL RESEARCH LABORATORY
BELLEVUE, D. C.

DATE

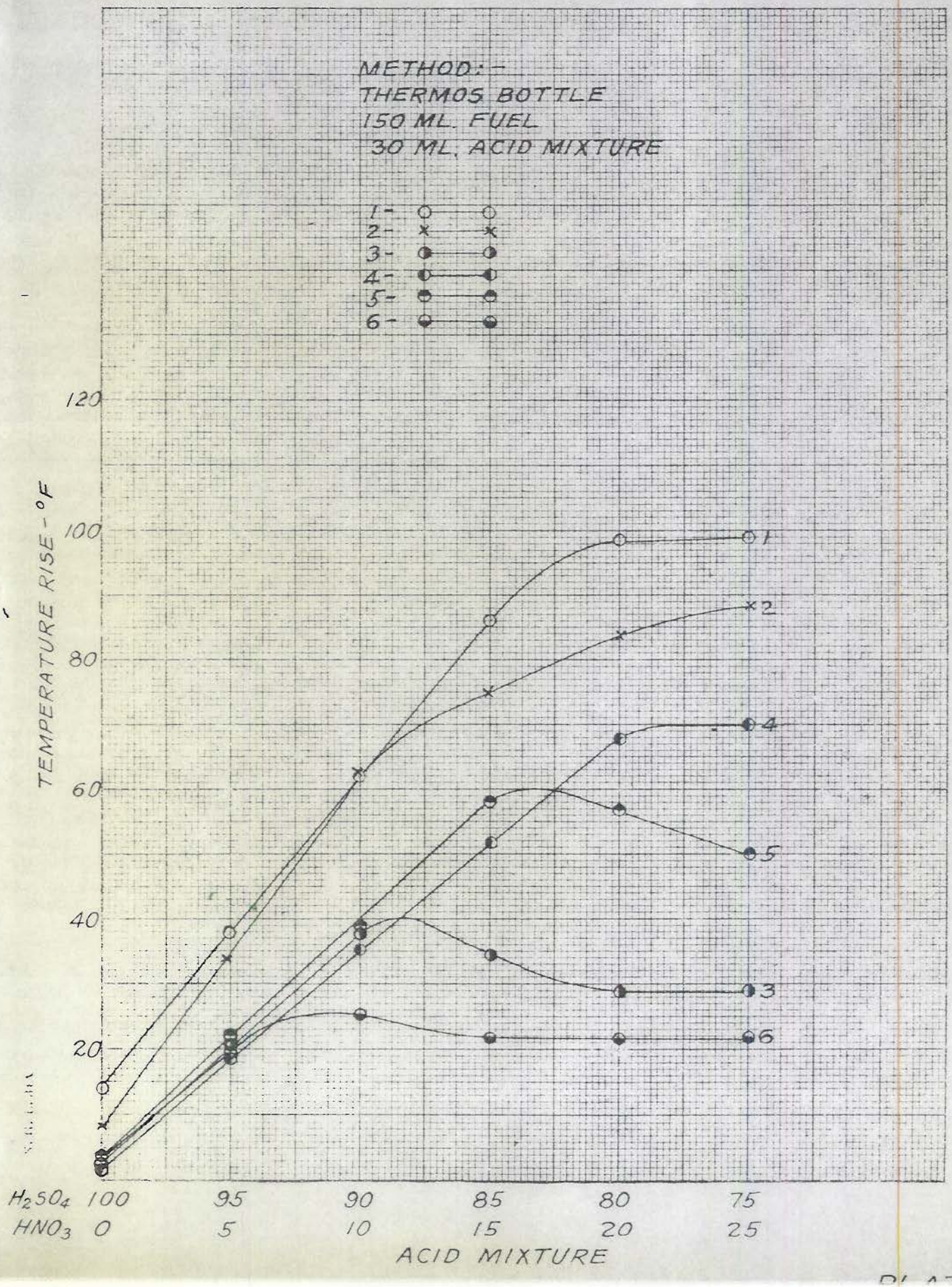
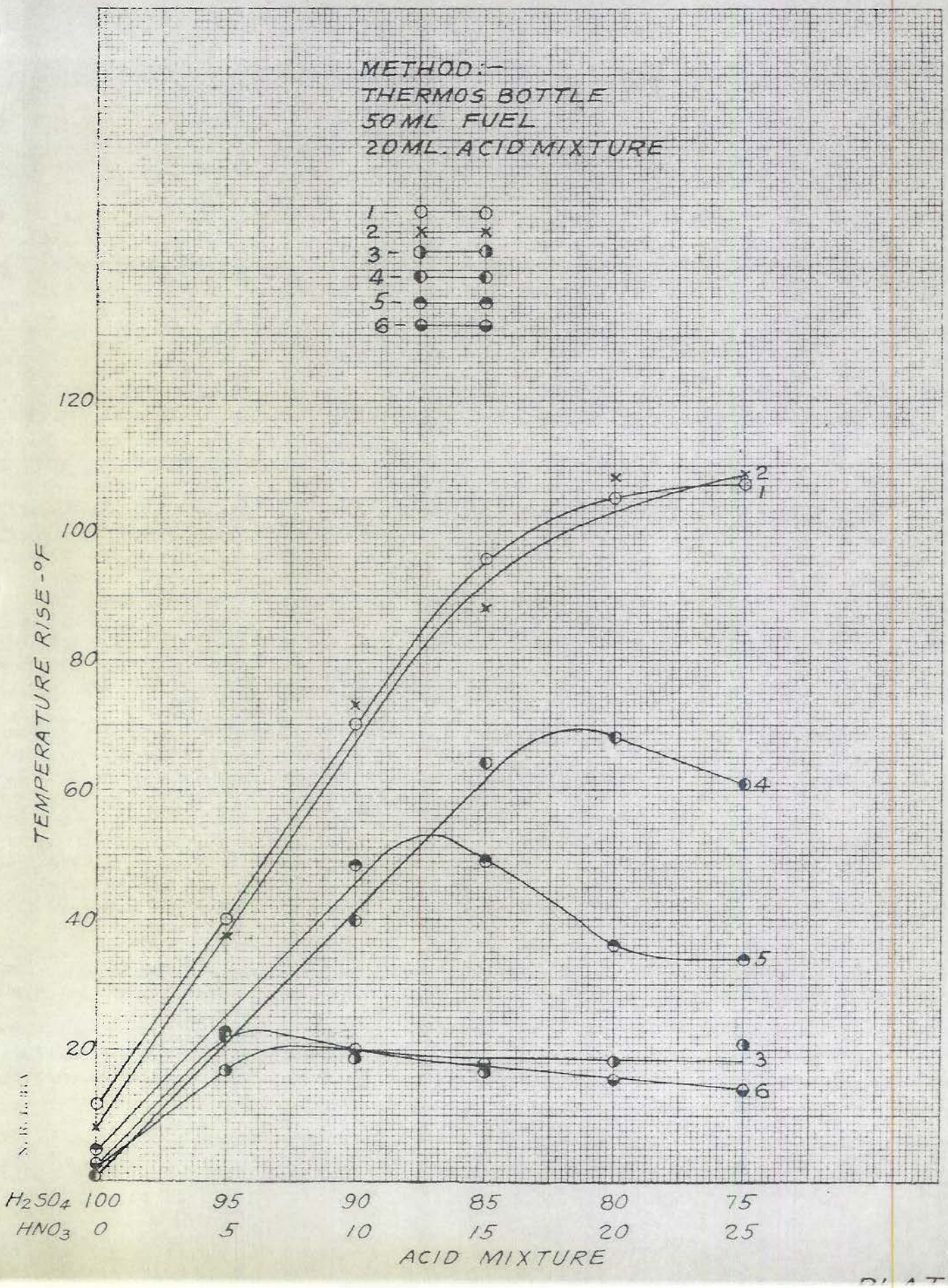


PLATE I


METHOD:-
THERMOS BOTTLE
50 ML FUEL
20 ML. ACID MIXTURE
1
2
3
4
5
6
120
100
80
60
40
20
TEMPERATURE RISE - °F
H_2SO_4 100 95 90 85 80 75
HNO_3 0 5 10 15 20 25
ACID MIXTURE

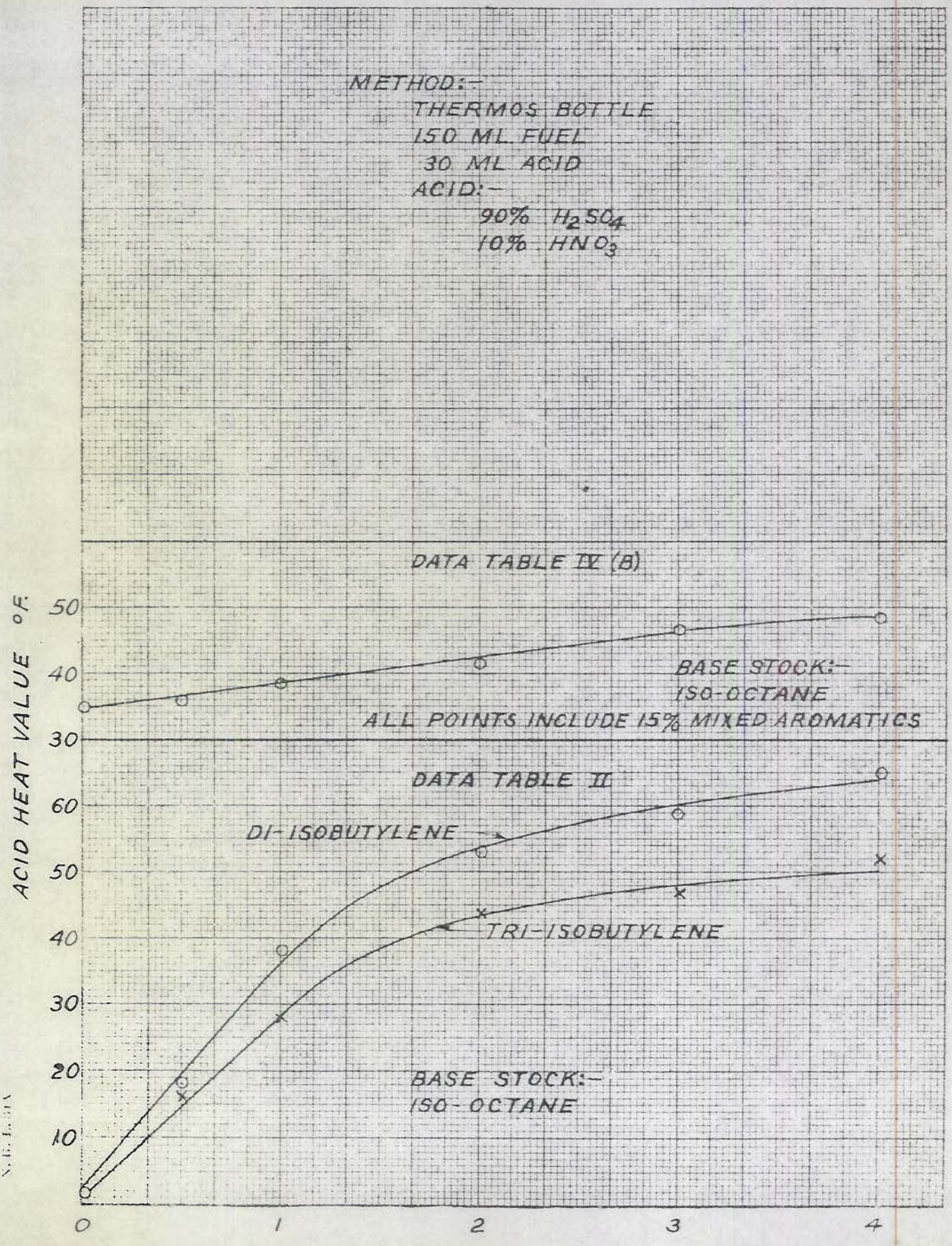

METHOD:-
THERMOS BOTTLE
150 ML. FUEL
30 ML. ACID
ACID:-
90% H_2SO_4
10% HNO_3
DATA TABLE IV (B)
BASE STOCK:-
ISO-OCTANE
ALL POINTS INCLUDE 15% MIXED AROMATICS
DATA TABLE II
DI-ISOBUTYLENE
TRI-ISOBUTYLENE
BASE STOCK:-
ISO-OCTANE
ACID HEAT VALUE °F.
50
40
30
60
50
40
30
20
10
0
1
2
3
4
% DI-ISOBUTYLENE OR TRI-ISOBUTYLENE

PLATE 3

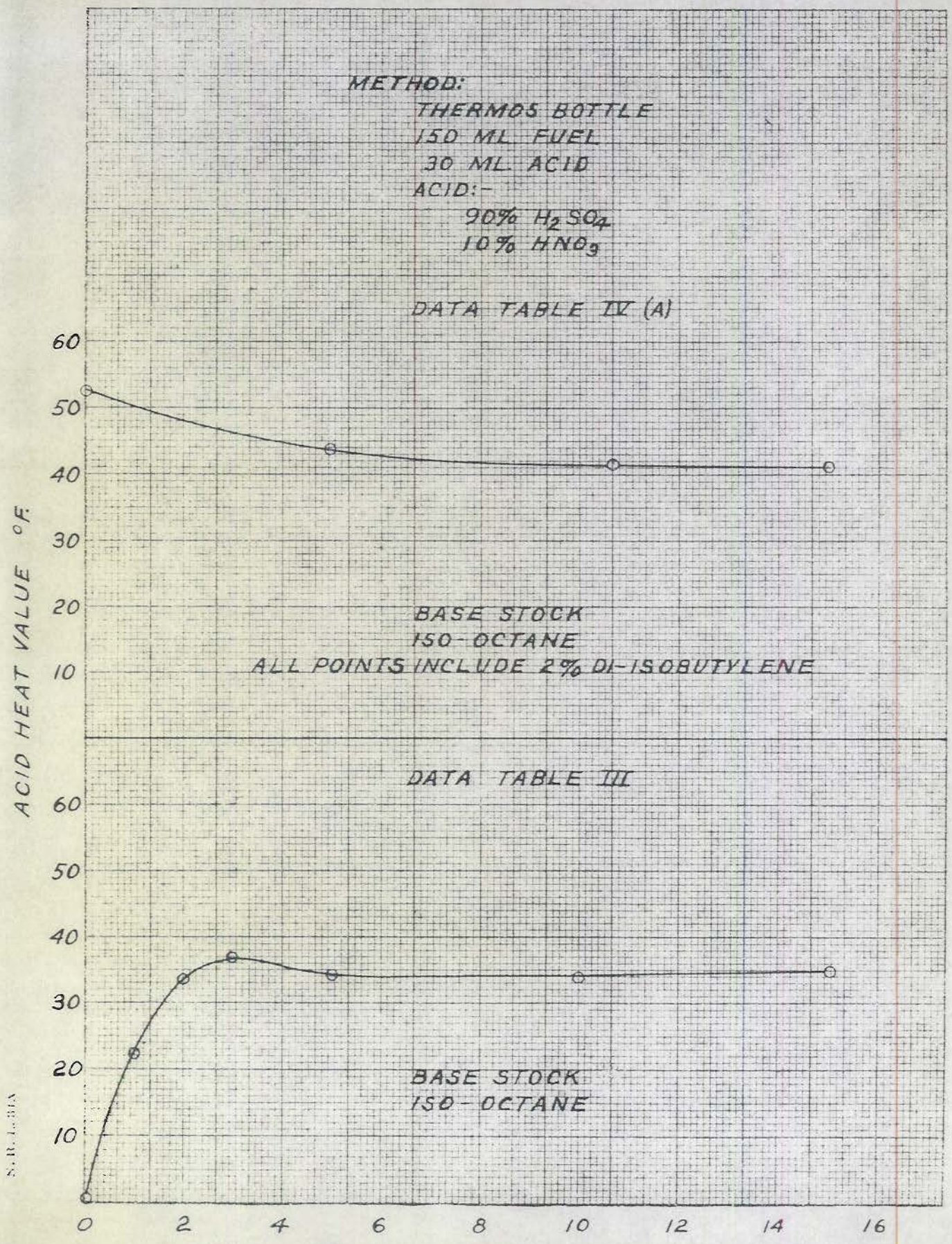

METHOD:
THERMOS BOTTLE
150 ML. FUEL
30 ML. ACID
ACID:-
90% H_2SO_4
10% HNO_3
DATA TABLE IV (A)
BASE STOCK
ISO-OCTANE
ALL POINTS INCLUDE 2% DI-ISOBUTYLENE
DATA TABLE III
BASE STOCK
ISO-OCTANE
ACID HEAT VALUE °F.
60
50
40
30
20
10
0
2
4
6
8
10
12
14
16
% MIXED AROMATICS

PLATE 4