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THE EFFECT OF ORGANIC SULFUR COMPOUNDS UPON THE INDUCTION PERIOD OF AVIATION GASOLINE

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- Report P-2625 -

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ABSTRACT

Small quantities of sulfur or organic sulfur compounds frequently are present in aviation gasoline. The effect of certain typical organic sulfur compounds on the ASTM induction period of aviation gasoline has been measured. It was found that the organic sulfur compounds examined had no adverse effect upon the induction period of leaded aviation gasoline.

INTRODUCTION

A. Authorization

1. This study has been carried out jointly under the authority of Bureau of Ships Project Order No. 396/46 and Bureau of Aeronautics Project Order No. 203/46. The investigation is part of a program of surveying conceivable influences which might deleteriously affect the storage stability of aviation gasoline in an effort to explain occasional anomalous decrease in the predicted storage life of fuels.

B. Statement of Problem

2. There are a wide variety of organic sulfur compounds which may be present in aviation gasoline, but the concentration of such substances is usually very low. It has been stated(1) that these sulfur compounds have an injurious effect upon the storage stability of the fuel. The purpose of this investigation is to demonstrate the role of individual organic sulfur compounds on the induction period of leaded aviation gasoline. It is realized that there is only a loose relationship between induction period and storage stability of aviation gasoline; however, estimation of the length of the induction period (or parallel relationship such as the measure of gum and precipitate formation in the fuel after oxidation under prescribed test conditions) is the only tool available for predicting in the laboratory the anticipated storage life of a given gasoline.

C. Known Facts Bearing on the Problem

3. The type and quantity of organic sulfur compounds present in aviation gasoline are dependent upon the production process and on the character of crude from which the gasoline is prepared. Many of the processes used for producing aviation gasoline components, such as sulfuric acid alkylation, give stocks which are virtually free from sulfur compounds. If the straight run gasoline (used for blending with other components) is distilled from selected crudes and properly treated to remove sulfur compounds, the finished aviation fuel should be very low in sulfur-bearing substances.

4. The following types of sulfur compounds have been found in fuels of the gasoline range: mercaptan, sulfide, disulfide, trisulfide, tetrasulfide, thiophene, tetrahydrothiophene and thiophenols. These are illustrated by type formula and a specific example in Table I. "R" is an alkyl group.

TABLE I

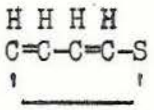
Type	Type Formula	Example
Mercaptan	R- S - H	Amyl mercaptan, $C_5H_{11}SH$
Sulfide	R - S -R	di-Amyl sulfide, $C_5H_{11}S$ C_5H_{11}
Thiophene		2-Methyl thiophene, CH_3 C_4H_3S

TABLE I (Cont'd.)

Type	Type Formula	Example
Tetrahydrothiophene	$\underline{CH_2CH_2CH_2CH_2S}$	2-Methyl tetrahydrothiophene, $CH_3C_4H_7S$
Disulfide	R-S - S-R	di-Amyldisulfide, C_5H_{11}-S-S-C_5H_{11}
Trisulfide	RSSS R	di-Ethyl trisulfide
Tetrasulfide	RSSSS R	di-Amylytetrasulfide, C_5H_{11}-SSSS-C_5H_{11}
Thiophenol (Aryl mercaptan)	C_6H_5SH	p-Thiocresol, CH_5 C_6H_4SH

All of these sulfur compounds except disulfide, trisulfides and tetrasulfide are naturally occurring in the gasoline. The disulfides and trisulfides are formed from mercaptans by oxidation during doctor sweetening and disulfides by copper sweetening.(2) The tetrasulfides may result from careless operation of doctor sweetening and are uncommon. The thiophene type is the product of high temperature treatment and is likewise seldom encountered in aviation gasoline. Tetrahydro-thiophene compounds are found in California straight run fuels. These compounds are simply cyclic sulfides and since they are not readily available, no substances of this type were examined in this study. It is expected that the behavior of the cyclic sulfides will be very similar to the straight chain type. The reaction of straight chain sulfides will be reported herein.

5. Sulfur compounds have been blamed for many of the difficulties encountered in gasoline storage and use. It is thought that haze and color formation in gasoline is partly attributable to sulfur containing substances.(3) Corrosion of engine parts by sulfurous and sulfuric acids resulting from combustion of sulfur compounds has been claimed but no conclusive correlation between sulfur content and corrosion activity at the concentration levels imposed by the restrictions of aviation gasoline specifications ever seems to have been worked out.(4) Of specific sulfur compounds the mercaptan type has a very offensive odor and impairs the lead response of blending stocks. Also a factor influencing lead response (rise in octane number as a function of added tetraethyl lead) is the quantity and identity of the sulfur compounds present in the fuel; in general, the higher the concentration of sulfur compounds the poorer the lead response with mercaptans and polysulfides being the worst offenders.(5)(2) For these reasons sulfur compounds are removed from aviation gasoline (insofar as is economically and practicably feasible) or are converted by chemical means to relatively innocuous substances.

6. Only one report is found in the literature treating the effect of sulfur compounds on the stability of gasoline. This is a study by Gruse and Stevens of the influence of sulfur compounds upon the induction period of lead-free di-isobutylene blends containing 0.025% sulfur, as various sulfur compounds.(6)

These authors found that mercaptan and polysulfides are deleterious to the induction period of this fuel while the sulfides and disulfides appear to be without consequence. The present investigation is conducted on highly leaded, olefin-free aviation gasoline; moreover, data in the above mentioned work does not permit construction of concentration versus induction time curves; therefore no direct comparison of the results of the present study to that of Gruse and Stevens appears possible.

D. Theoretical Considerations

7. There are no reports in the published literature concerning the effect of sulfur compounds on stability of leaded aviation gasoline.* On the basis of the known chemistry of sulfur compounds certain expectations may be evolved. The mercaptans are good reducing agents and on the basis of the work of Dennison(7), mercaptans may be expected to reduce the peroxides, and thus lengthen the induction period. Other sulfhydryl compounds such as thiophenol, thiocresols, etc., are expected to give similar results. As far as could be found, there is no basis for any predictions concerning the effects, good or bad, of any of the other sulfur compounds listed in Table I.

E. Narrative of Original Work Done at the Laboratory

(a) Preparation of Gasolines and Sulfur Compounds

8. One gasoline used in this study was prepared by mixing 5 parts each of isooctane, straight run gasoline (Shell mixed), straight run gasoline (Texas), and sulfuric acid alkylate; 2 parts single pass Houdry gasoline; and 3 parts of aromatic mixture consisting of 1:3:2:1 of benzene, toluene, xylene, cumene. This blend was leaded to 4.3 cc TEL/gallon with 1-T aviation fluid and mixed thoroughly. Analysis by the lamp sulfur method(8) and showed 0.0016% sulfur. The concentration of olefins in the finished blend was negligible, i.e., less than 1%. A portion of this study was carried out using instead of the blend above, a second gasoline identified as 33R (115/145) secured from the Naval Air Station, Patuxent, Maryland. Again, the sulfur content is low (0.001% or less) and olefins nil. This gasoline is hereinafter referred to as 33R while the blend described above is identified by the symbol "NRL".

9. The sulfur compounds used in this work were the best procurable from the Eastman Kodak Company. They include n-Amyl mercaptan ($C_5H_{11}SH$), iso-Amyl mercaptan ($C_5H_{11}SH$), di-isoAmyl Sulfide [$(C_5H_{11})_2S$], n-di-amyl Disulfide [(C_5H_{11}) S-S (C_5H_{11})], p-Thio cresol ($CH_3\ C_6H_4\ SH$), n-Propyl sulfone [$(CH_3\ CH_2CH_2)_2SO_2$], n-Amyl sulfite [$(C_5H_{11})_2\ SO_3$], and n-Amyl sulfone [$(C_5H_{11})_2SO_2$]. The two mercaptans were distilled before use and the disulfide was fractionated under vacuum. p-Thio cresol was purified by recrystallization. A small batch of di-isoamyl sulfoxide was prepared by method of Gozdar and Smiles.(9) All the sulfur compounds were weighed out into a known volume of xylene and the proper aliquot of this solution is

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Note: Private communications from certain industrial laboratories indicate that the influence of traces of sulphur dioxide, alkyl sulfates and sulfuric acid has been found negligible.

added to each sample of gasoline to give the desired concentration of sulfur. The inhibitor was added to the gasoline in the same manner; an aminophenol type inhibitor (UOP #4) was used throughout this work. The concentration of inhibitor was adjusted so that the length of the induction period was about ten hours. All subsequent induction periods using the particular sulfur compound were made with the same inhibitor content. In consequence, it is noted that the initial induction periods of the finished gasoline samples used in the several series of runs, as exhibited in plates I - VI, are not identical but vary somewhat with chance variations in the concentration of inhibitor added to adjust the initial induction period to approximately 10 hours.

(b) Measurement of Induction Period

10. After each sample of gasoline is made up to the desired concentration of sulfur compound and inhibitor, length of the induction period is measured. The end of the induction period is signified by the commencement of oxygen absorption by the sample and identified as a two pound pressure drop in one hour or less. The technique for making these measurements is described in reference (11); no iron catalyst was used. In general it has been found that the results from induction period measurements are reproducible to ±5% and nearly all of the results presented in this report gave this degree of accuracy. Each induction period value is the average of six determinations.

(c) Discussion of Results

11. It is noted from plates I and II that the two amyl mercaptans have a singular effect on the induction period of aviation gasoline. At low concentrations a small increase in concentration of mercaptan gives an increase in the induction period. Both the "NRL" blend and 33R fuels show this behavior. This increase in induction period is thought due to the reducing action of the mercaptans upon incipiently formed peroxides. Such destruction of peroxides would break the chain of reactions leading to gum formation and precipitation, and thus give a longer induction period.

12. As the concentration of mercaptan is increased, a value is reached above which the induction period declines. This decline is not to be expected on the basis of the above theory. It is not due to some catalytic activity of the oxidation products of the mercaptans as work upon possible oxidation products (discussed later in this report) shows. It has been shown that mercaptans have anti-oxidant action in lubricating oil and in rubber, and it is probable that the mercaptan is acting here as an inhibitor rather than as a reducing agent for the peroxides. Blake and Davis have shown(10) that there are inhibitors which show the same effect as the mercaptan shows, namely, that there is a concentration above which the inhibitory power of the anti-oxidant declines. If the mercaptan is an inhibitor, that fact would account for leveling off the concentration-induction time curve at the initial induction period of the mercaptan free gasoline. If the oxidation products of the mercaptans have a pro-oxidant activity, this curve should decline further rather than level out at about 10 hours induction period.

13. It was decided to study the effect of some of the possible oxidation products of the mercaptan upon the mercaptan containing gasoline. To do this di-isoamyl disulfide was added to the gasoline (33R) containing isoamyl mercaptan (0.003%S) at the point of optimum concentration for induction period improvement. (See plate I). The disulfide was added in quantities to give 0.03, 0.04 and 0.05% sulfur. The induction periods came out at 58, 54 and 40 hours respectively showing that the disulfide has a slight effect in neutralizing the influence of mercaptan on induction time, but not enough to account for the decline in activity of the mercaptan noted in paragraph 12 above. This same effect was observed for the sulfone and sulfoxide which were studied in the same manner. It is thus concluded that these possible oxidation products of the mercaptan are not responsible for the decline in inhibitory power which is observed with increase in mercaptan concentration.

14. From a practical point of view the effect of the high concentration of the mercaptans is not important because any mercaptan (in gasoline range) above the concentration of 0.003% sulfur is very noticeable by odor and gasoline containing such high mercaptan content would be rejected as being "sour". With this limitation it is concluded that the mercaptans, in the concentrations in which they occur in aviation gasoline, do not adversely affect the induction period of the leaded aviation gasoline.

15. The sulfides and disulfides are shown to have practically no effect upon the induction period of the gasoline. The data demonstrating this are presented in plate III and plate IV. Thiophene likewise does not influence the induction period of leaded aviation gasoline.

16. p-Thiocresol (plate V) has the same effect as the alkyl mercaptan; i.e., it lengthens the induction period in small concentrations; in this case, however, the effect remains constant rather than declining in the range of higher concentrations.

17. In an effort to discover if other possible oxidation products of mercaptans had any accelerating effect upon oxidation of leaded gasoline, n-propyl sulfone, n-amyl sulfite, n-amyl sulfone and iso amyl sulfoxide were examined by the above methods and, as is shown in plate VI, are found to play no role which results in change of the induction period.

18. In the operation of the doctor sweetening process, excess sulfur is sometimes left dissolved in the gasoline. To show what effect this sulfur might have on the induction period of gasoline, a known quantity of roll sulfur was dissolved in xylene and the proper aliquot of this solution is added to the gasoline to produce the desired concentration of sulfur in gasoline. Table II shows the results of the induction period measurements upon the sulfur containing gasoline.

TABLE II

Roll Sulfur in Aviation Gasoline

Sulfur Concentration	Induction Period (Hours)
None	11
0.010 grams/100 ml.	11
0.020 " " "	11
0.040 " " "	11
0.050 " " "	11

It is concluded from this data that elemental sulfur has no influence upon the induction period of the aviation gasoline.

CONCLUSIONS

19. It has been shown with a series of experiments upon different types of sulfur compounds that these sulfur compounds do not have any adverse influence upon the induction period of aviation gasoline in the concentrations in which the sulfur compounds occur in leaded aviation gasoline. Mercaptans in low concentrations appear to lengthen induction time, an effect which becomes less noticeable as concentration increases. However, reasons more cogent than induction period improvement, i.e., foul odor, corrosion of certain metals and lowered lead response, militate against the use of mercaptans for increasing the oxidation resistance of gasolines. The influence of a wide variety of other sulfur compounds and elemental sulfur is found to be entirely neutral.

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(4) Nash: Principles of Motor Fuel Preparation and Application -
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(7) Dennison - Ind. and Eng. Chem. 36, 477 (1944); 37, 1102, (1945)

(8) ASTM Manual (1943) P. 303 Method D90-41T

(9) Gozdar and Smiles, J. Chem. Soc. (London) 93, 1834 (1910)

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(Publishers: Reinhold Publishing Corp.)

(11) ASTM Manual (1943) P.255 Method D525-42T

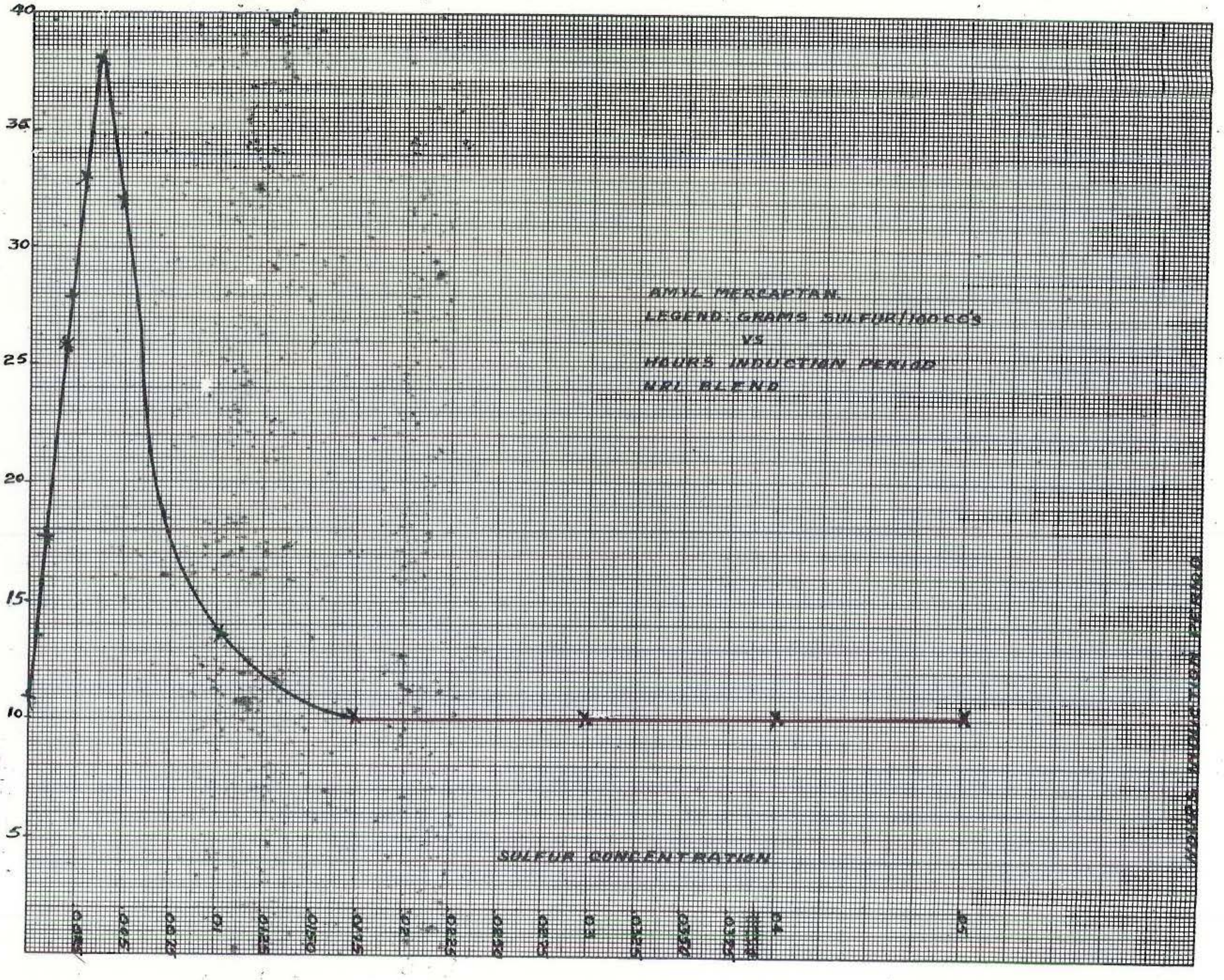

AMYL MERCAPTAN.
LEGEND: GRAMS SULFUR/100 CC's
VS
HOURS INDUCTION PERIOD
NRL BLEND
SULFUR CONCENTRATION
HOURS INDUCTION PERIOD
40
35
30
25
20
15
10
5
.0025
.005
.0075
.01
.0125
.0150
.0175
.02
.0225
.0250
.0275
.03
.0325
.0350
.0375
.04
.05

PLATE. I.

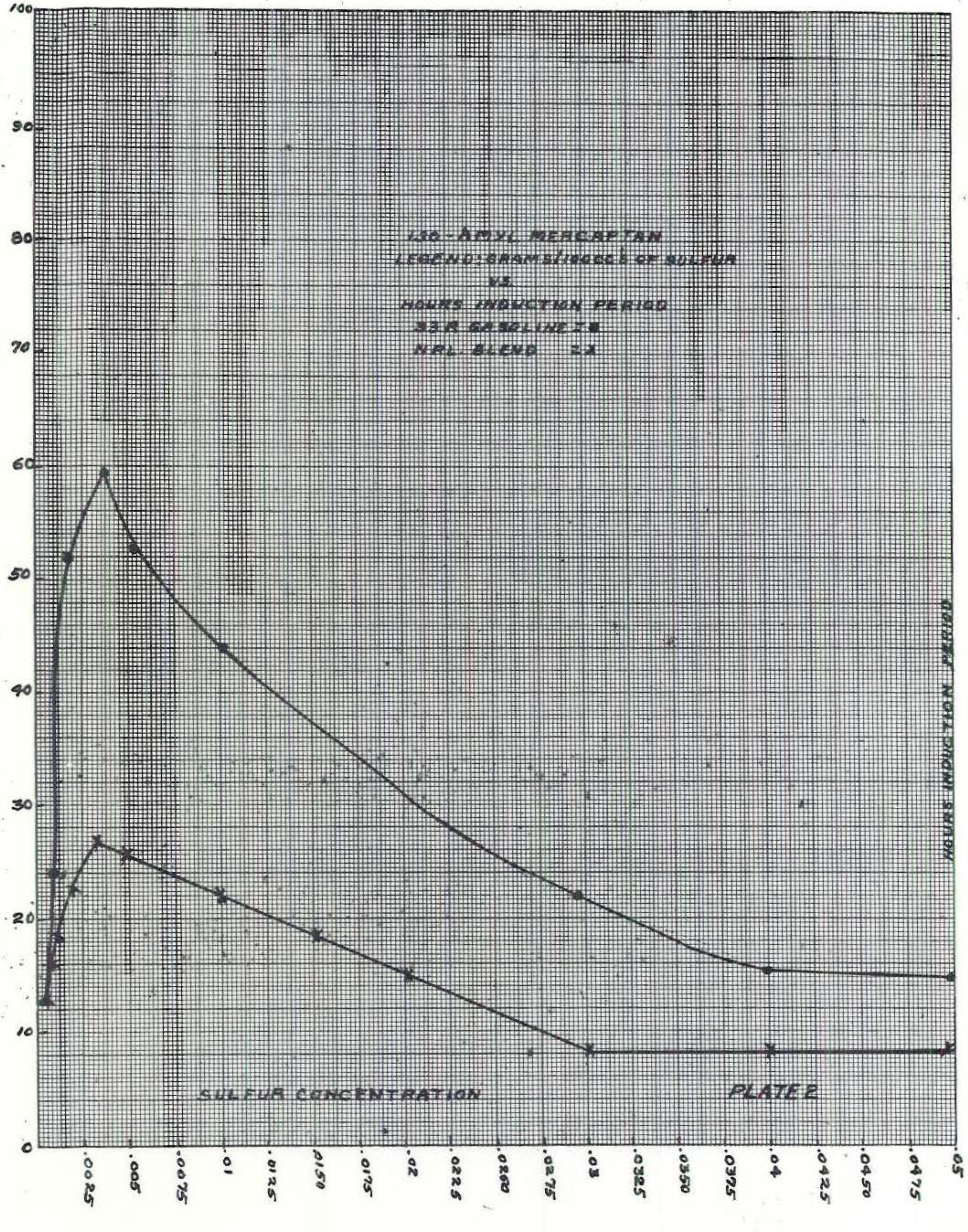
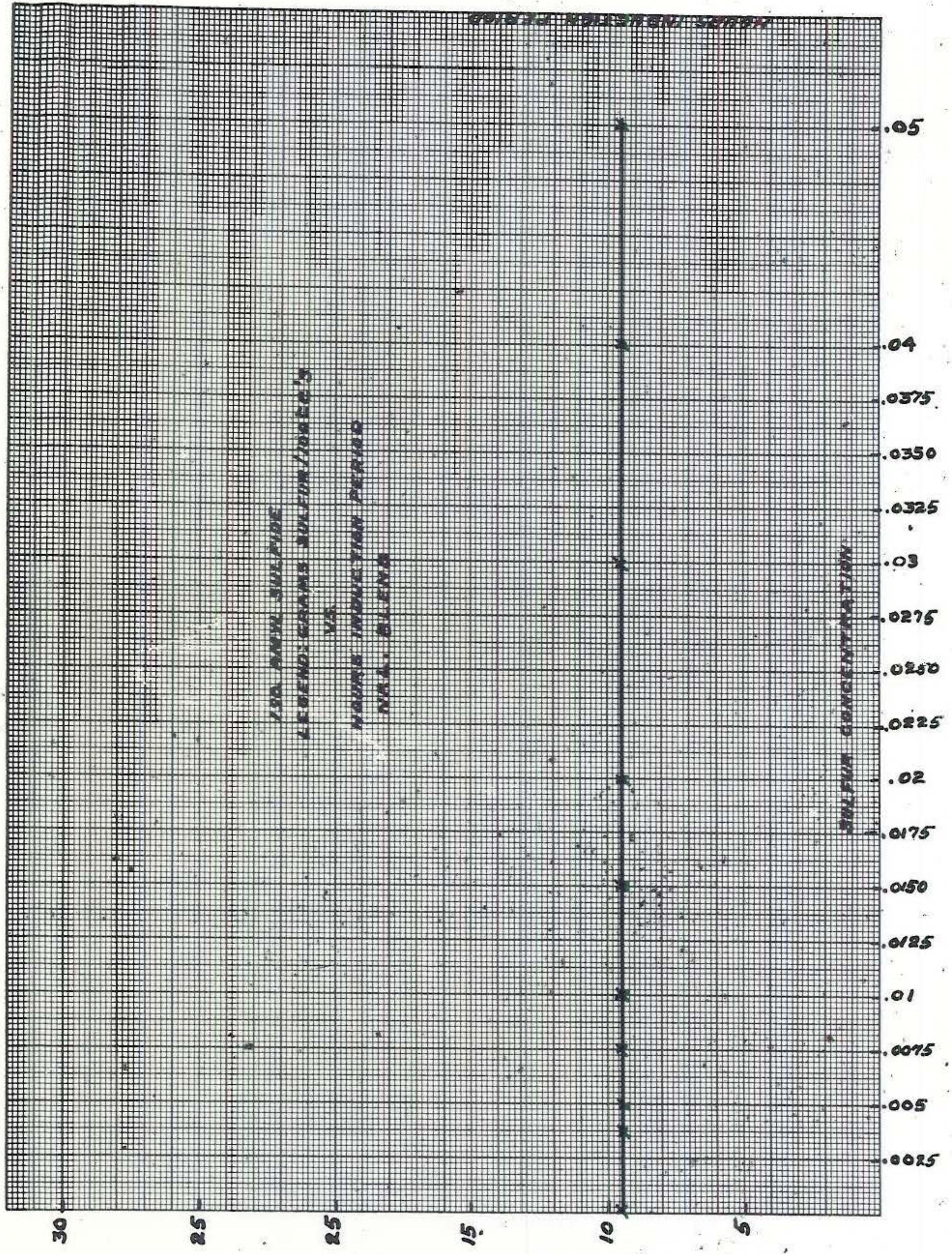

ISO - AMYL MERCAPTAN
LEGEND: GRAMS/100CC's OF SULFUR
VS.
HOURS INDUCTION PERIOD
33 R GASOLINE I B
NPL BLEND 2X
HOURS INDUCTION PERIOD
SULFUR CONCENTRATION
100
90
80
70
60
50
40
30
20
10
0
.0025
.005
.0075
.01
.0125
.0150
.0175
.02
.0225
.0250
.0275
.03
.0325
.0350
.0375
.04
.0425
.0450
.0475
.05

PLATE 2



HOURS INDUCTION PERIOD
ISO. AMYL SULFIDE
LEGEND: GRAMS SULFUR/100CC'S
VS.
HOURS INDUCTION PERIOD
N.R.L. BLEND
SULFUR CONCENTRATION
.05
.04
.0375
.0350
.0325
.03
.0275
.0250
.0225
.02
.0175
.0150
.0125
.01
.0075
.005
.0025
30
25
25
15
10
5

PLATE 3

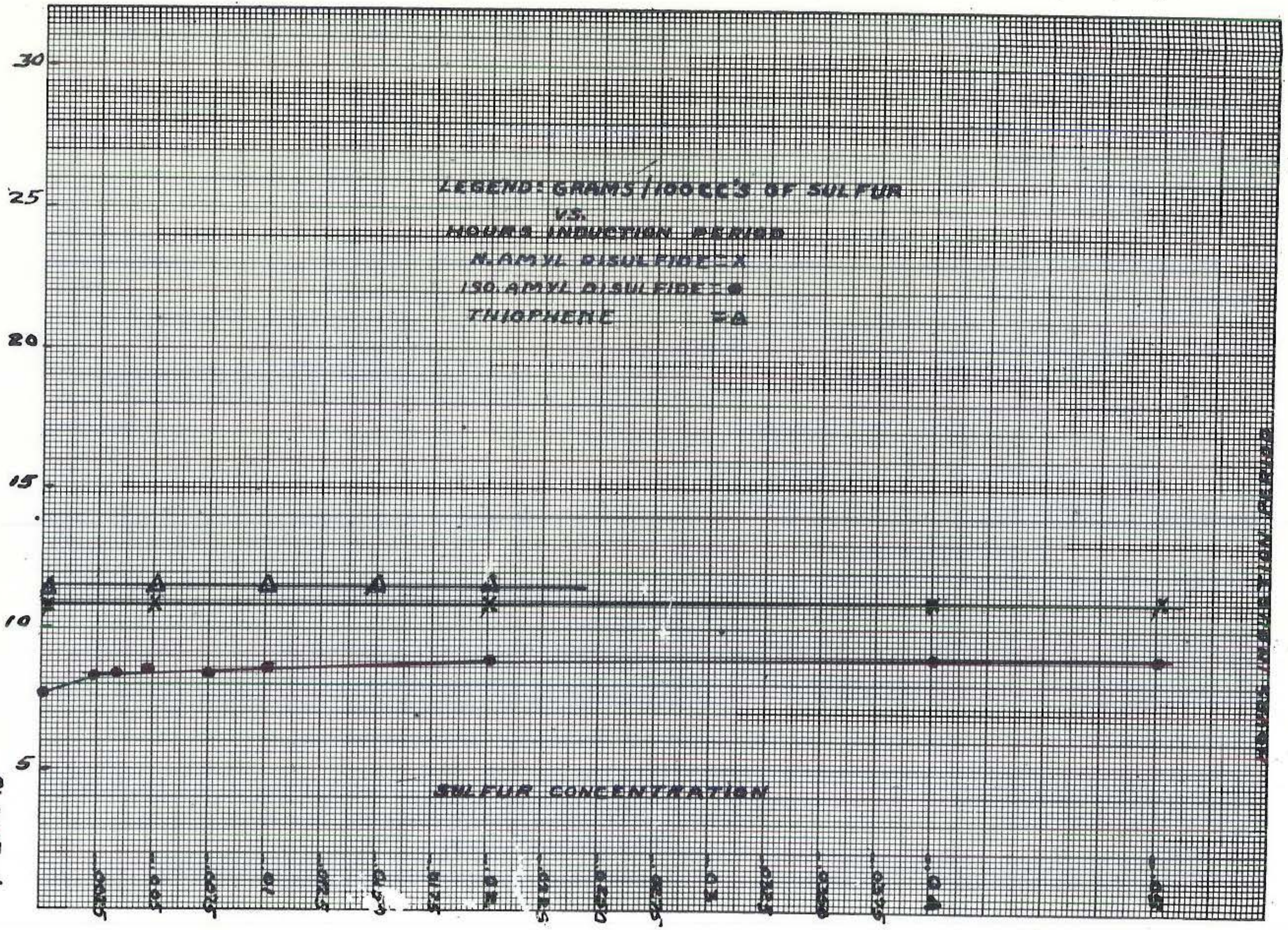

LEGEND: GRAMS/100CC'S OF SULFUR
VS.
HOURS INDUCTION PERIOD
N. AMYL DISULFIDE = X
ISO. AMYL DISULFIDE = ●
THIOPHENE = Δ
30
25
20
15
10
5
.0025
.005
.0075
.01
.0125
.015
.0175
.02
.0225
.0250
.0275
.03
.0325
.0350
.0375
.04
.05
SULFUR CONCENTRATION
HOURS INDUCTION PERIOD

PLATE 4

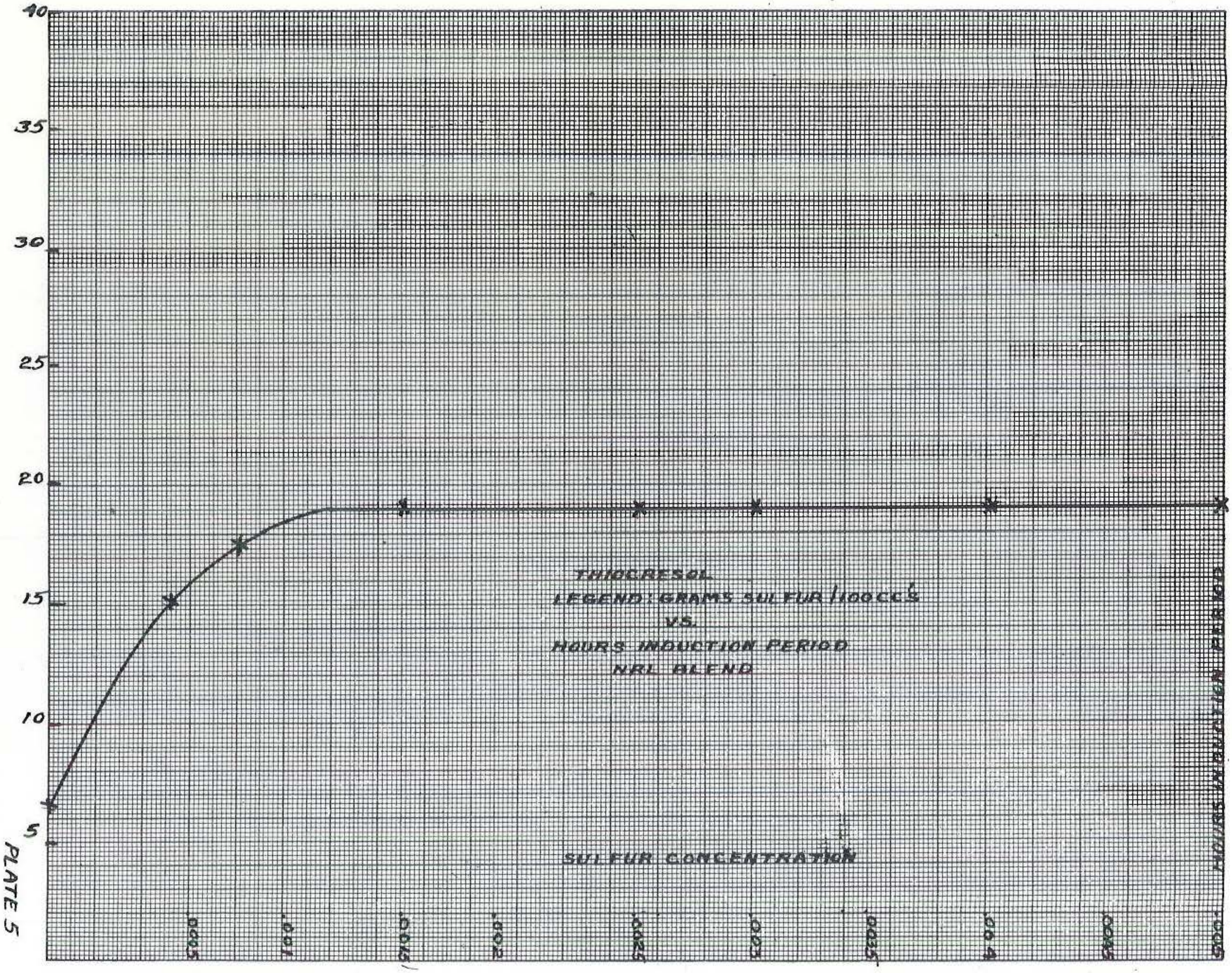

THIOCRESOL
LEGEND: GRAMS SULFUR / 100 CC'S
V.S.
HOURS INDUCTION PERIOD
NRL BLEND
SULFUR CONCENTRATION
HOURS INDUCTION PERIOD
40
35
30
25
20
15
10
5
.0005
.001
.0015
.002
.0025
.003
.0035
.004
.0045
.005

PLATE 5

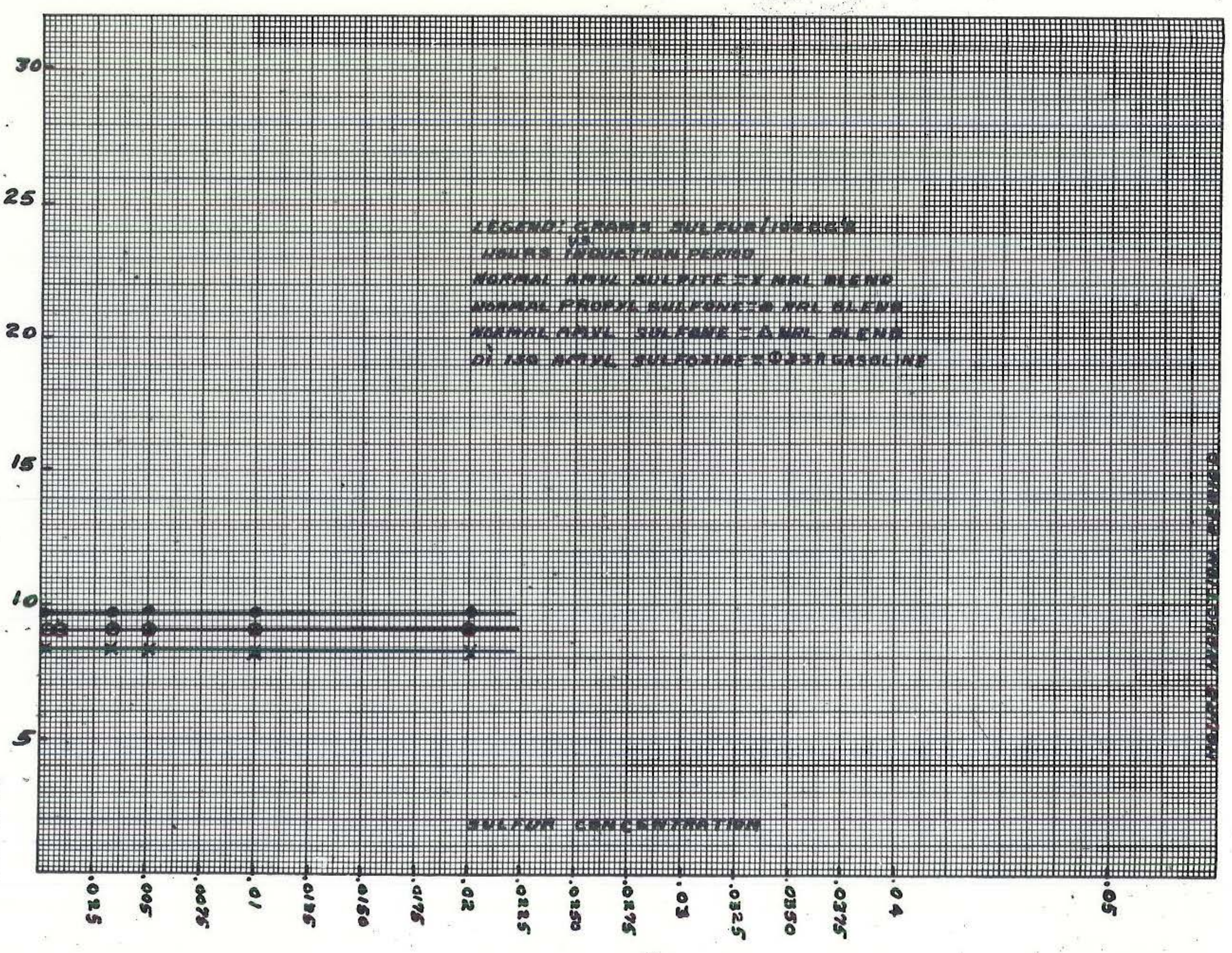

LEGEND: GRAMS SULFUR/100CC'S
VS.
HOURS INDUCTION PERIOD
NORMAL AMYL SULFITE = X NRL BLEND
NORMAL PROPYL SULFONE = ● NRL BLEND
NORMAL AMYL SULFONE = ▲ NRL BLEND
DI ISO AMYL SULFOXIDE = ⊕ 33R GASOLINE
30
25
20
15
10
5
.025
.005
.0075
.01
.0125
.0150
.0175
.02
.0225
.0250
.0275
.03
.0325
.0350
.0375
.04
.05
SULFUR CONCENTRATION
HOURS INDUCTION PERIOD

PLATE 6

DISTRIBUTION

BuAer	(5)
BuShips	(5)