FR-2344

August 1944 NRL Report #P-2344

NAVY DEPARTMENT

First Report of Progress on Development of Test Method for Estimating Solvent Power and Aromatic and Naphthenic Content of Thinners Used in Navy Aeronautical Finishes

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

Number of Pages: Text - 8 Tables - 7 Plates - 10

Authorization: BuAer ltr Aer-E-254-AHM/6-28, 61285 of 4/3/44, and BuAer Project Order 88/44.

Date of Tests: April 1944 to August 1944.

Prepared by: D. E. Neunherz
D. E. Neunherz, Lt.(jg), USNR.

Reviewed by: Dan Fore Jr.
Dan Fore, Jr., Chief, Fuels Section

P. Borgstrom, Superintendent, Chemistry Division

Approved by: A. H. Van Keuren, Rear Admiral, USN, Director

DISTR:
BuAer (10)
SONRD (2)
ONI (3)(for further transmittal to Alusna, London)
BCSO (2)
BAD (1)

ABSTRACT

Petroleum thinners of the AN-VV-N-96 Type I contain primarily three classes of hydrocarbons: aromatics, naphthenes, and paraffins. Data are presented on the specific gravity, refractive index, mixed aniline point and solvent power (as determined by the kauri butanol method) for mixtures of the aromatic hydrocarbon toluene with representative members of other hydrocarbon classes of the appropriate boiling range. From these data, in conjunction with the given specifications, it is possible to establish minimum requirements for the aromatic-free portion of the thinner. Two commercial thinners have been checked against these requirements. The estimation of the various hydrocarbon components in the thinner is facilitated by graphs.

TABLE OF CONTENTS

INTRODUCTION

A. Authorization

1. This investigation was conducted under Project Order 88/44, specifically authorized by Bureau of Aeronautics letter Aer-E-254-AMM/6-28, Serial No. 61285 of April 3, 1944, to the Naval Research Laboratory.

B. Statement of Problem

2. The problem, as stated in the BuAer letter above, is to develop "a test method for estimating the aromatic portion and naphthene fraction of the non-aromatic portion of solvents for Navy aeronautical finishing materials, particularly Spec. AN-VV-N-96 Type I and Spec. AN-T-8 thinners. The purpose of this investigation is to recommend specific requirements for inclusion in the specifications for the purpose of determining the solvent power of these products. Such a test method should insure an accuracy of ± 1% for the aromatic portion and pending further study of the solvency of naphthenes, an accuracy of ± 5% for the naphthenes in the non-aromatic portion. As a second phase of this project it is requested that NRL determine the solvency of naphthenes as compared with aromatics, particularly with regard to the reinforcing action of the naphthenes with increase in aromatic content, using any standard method for determining solvency such as the dilution ratio method."

C. Known Facts Bearing on the Problem

3. The existing specifications present certain limitations on the nature of the hydrocarbon components in the thinner. Unsaturated hydrocarbons, for example, could not be tolerated because of stability requirements. The aromatics are limited in number by boiling range considerations. The proportion of paraffin hydrocarbons is restricted by the aniline point specifications, etc. Having thus narrowed the field of the investigation, the second angle of attack is a survey of existing procedures for the estimation of the possible hydrocarbon components of paint thinners, and the devisement of some relationship between hydrocarbon type concentration and the solvent power of the finished thinner. In regard to the second phase of this study, numerous methods for determining solvent power of hydrocarbon, and procedures for estimating hydrocarbon types in mixtures exist. Some of those are described below.

(a) Aromatic hydrocarbons can be quantitatively removed from paraffins and naphthenes by reaction with sulfuric acid. Two or three volumes of 94-98% sulfuric acid remove substantially all of the aromatic hydrocarbons from gasoline, for example. A measure of the volume change occurring when a sample of mixed hydrocarbons is contacted with sulfuric acid containing phosphorous pentoxide is the basis for a method (ES-45) developed by the American Society for Testing Materials for the determinations of total olefins and aromatics.

(b) Silica gel and certain activated carbons selectively adsorb aromatics, and a method of aromatic analysis based on the refractive indices of the hydrocarbon before and after percolation through silica gel or carbon has been described in NRL Report No. P-2096.

(c) The relative proportions of paraffins and naphthenes in a mixture of these hydrocarbons have been estimated by many investigators on the basis of aniline point determinations. Paraffin hydrocarbons have high aniline points, aromatics low, and naphthenes intermediate.

(d) The densities and refractive indices of hydrocarbons have been correlated with their structure. One relationship is that of the refractivity intercept which is equal to the refractive index minus one-half of the density:

$$\text{Refractivity Intercept} = N_D^{20} - \frac{D_4^{20}}{2}$$

The following are the values of refractivity intercept for the hydrocarbon types under consideration:

Aromatics	= 1.0627
Paraffins	= 1.0461
Naphthenes	= 1.0400

(e) The solvent power of hydrocarbon has been determined in various ways (not always in mutual agreement) including measurement of resin solution viscosities, the dilution ratio method, and the kauri butanol method. Of these methods the last seemed to be most suitable for the purpose of the present investigation.

4. The kauri butanol value of a solvent is defined as the number of cubic centimeters of the solvent that must be added to 20 grams of the standard kauri solution at 77° F., to produce sufficient precipitation of the gum so that a printed sheet of paper (10-point print) will appear blurred and be illegible when viewed through the flask containing the solution.

5. Standardization of the kauri butanol method between various laboratories has been described by Baldeschwieler, Morgan, and Troeller in Ind. Eng. Chem. Anal. Ed. 7, 374 (1935), 9 540 (1937). The KB values of benzene and n-heptane are determined, and solvent powers of 100 and 25.4%, respectively, are assigned to these hydrocarbons. All other hydrocarbons have solvent powers in proportion to their KB values on this scale.

D. Theoretical Considerations

6. If the refractive indices, the densities, or the aniline points of two hydrocarbons are known, it is possible to predict with a good degree of accuracy what these properties will be for known ratios of the two hydrocarbons, since the properties involved are essentially proportional on a volume basis. It is apparent that these considerations can be extended to more complex mixtures of hydrocarbons. In the present investigation the physical requirements for the aromatic-free portion of the thinner are correlated with the percentage of aromatics in a thinner which just passes specifications.

7. In this work it has been assumed that the aromatic hydrocarbon involved is toluene. It is unlikely that much benzene can be present in the thinner, but ethylbenzene and para- and meta-xylene could distill over within the given boiling range specifications. At any rate densities, refractive indices, aniline points, and solvent powers of the various aromatics are substantially identical so that little error is introduced by the above assumption.

METHODS

8. The methods used in this study are described below:

(a) Preparation of Samples - The samples were ordinarily 100 ml. in size. The hydrocarbons were measured by means of a burette. Anhydrous sodium sulfate was used to dry the hydrocarbon mixtures. A mixture containing 60% toluene, for example, would be made up of 60 ml. of toluene and 40 ml. of other hydrocarbon. In general, C.P. hydrocarbons were used when available, or the best commercial products that could be obtained.

(b) Measurement of Specific Gravity - Specific gravity measurements were made by means of the Fisher-Davidson Gravitometer using toluene as the reference liquid. Two or three ml. of sample were all that was required.

(c) Measurement of Refractive Index - Refractive index measurements were made on a Bausch and Lomb precision refractometer. These measurements are of value in judging the purity of the various hydrocarbons.

(d) Determination of Aniline Point - The ASTM standard method D 611-43T was used. In determining mixed aniline points, 5 ml. of the unknown hydrocarbon were added to 5 ml. of 60° C. aniline point hydrocarbon plus 10 ml. of freshly distilled aniline.

(e) Determination of Distillation Range - The determination of the distillation characteristics of the materials followed ASTM Standard Method D 86-40.

(f) Determination of Solvent Power - The solvent power of the samples was estimated by the kauri butanol method, described in paragraphs 4 and 5 above. The standard kauri gum solution was prepared by refluxing 100 g. of kauri gum with 500 g. of n-butyl alcohol, cooling this solution, and finally filtering it after 4 days of standing. Approximately two gram samples of the kauri butanol standard were weighed into 25 ml. Erlenmeyer flasks. The hydrocarbon was titrated from a 10 ml. jacketed burette maintained at 25° C. (77° F.). Duplicate determinations were made on every sample. The KB values were calculated on the basis of 20 gram samples by simple proportion.

(g) Preparation of Thinners Meeting Minimum Specifications - Two commercial thinners, one Grade A, the other Grade B, were contacted at room temperature for one hour with concentrated sulfuric acid, in order to remove the aromatics. The ratio of acid to thinner was 2:1 by volume. Complete removal of aromatics was assured by percolating the acid-treated residue through silica gel until a minimum refractive index was obtained. The minimum grade B thinner was prepared by diluting the original thinner with aromatic-free residue prepared as above, in effect reducing the aromatic content of the original thinner. The minimum Grade A thinner was prepared in two ways: Method One consisted of adding toluene and n-heptane to the aromatic-free residue, and Method Two consisted in adding toluene and n-heptane to the original Grade A thinner. These minimum thinners barely met existing specifications in respect to aniline point and specific gravity.

DATA OBTAINED

9. Graphical Representation

(a) Plates 1, 2, 3, and 5 show the data on specific gravity, refractive index, mixed aniline point and solvent power of mixtures of toluene with hydrocarbons of various other classes. These data are summarized in Table II.

(b) Plate 4 is the standardization curve relating solvent power to kauri butanol value. This curve was obtained as explained in paragraph 5.

(c) Plate 6 shows the solvent power of two naphthene-paraffin mixtures. The data for these are given in Table III.

(d) Plate 7 shows the required specific gravity of the non-aromatic portion of AN-VV-N-96 Type I thinners for various proportions of toluene. This curve was derived on the basis of present specific gravity tolerances and the assumption of linearity of this property with concentration (Plate 1).

(c) Plate 8 gives a series of empirically derived curves which are of value in estimating the refractive index of the aromatic-free portion of a thinner whose aromatic content and refractive index are known. For example, a thinner with a refractive index of 1.4665 and an aromatic content of 60% would have a refractive index of about 1.4250 for the aromatic-free portion. These curves fit the data of Table II to within two or three in the third place after the decimal.

(f) Plate 9 shows the required aniline points of the aromatic-free portions of Grade A and Grade B thinners. These curves were derived from a consideration of the data shown in Plate 3 and in Tables II and IV.

(g) The curves on Plate 10 were derived from the curves shown on Plate 5 and data from Table II.

10. Data in Tabular Form - The column headings in the tables have the following meanings:

D_4^{20} - - - - specific gravity 20° C./4° C.

N_D^{20} - - - - refractive index at 20° C., with Sodium D line.

A.P. - - - - aniline point, °C.

M.A.P. - - - - mixed aniline point °C. (A.P. of equal volume of sample mixed with 60° A.P. hydrocarbon)

K.B. - - - - kauri butanol value

S.P. - - - - solvent power, %

(a) Table I is an estimate of the ranges in properties of the various classes of hydrocarbons to be found in the thinners under consideration. These values were selected from the literature.

(b) Tables II - VII are self-explanatory.

11. Probable Errors

(a) Aniline points - The observed data check with literature values within one or two degrees centigrade. In the present work no attempt was made to purify any of the hydrocarbons, nor was a correction made for the emergent stem of the thermometer.

(b) Specific gravity - A comparison of observed values with literature values for those hydrocarbons of reasonable purity indicates the data is reliable within ± 0.003 units. Greater accuracy could have been obtained by other methods, but for the present purposes this seems satisfactory.

(c) Refractive index - There was no need to use a refractometer any better than the ordinary Abbe type in this work. The precision instrument was available, however, and so it was used.

(d) Solvent power - The kauri butanol values in every case are the averages of at least two determinations. It is a little more difficult to secure good duplicates for highly aromatic solvents than for low aromatic solvents, but in any event this duplication was within about 1.5% and usually better than that.

DISCUSSION

12. The present preliminary investigation covers roughly the range of properties specified by AN-VV-N-96 Type I thinners. Much more data would be helpful, particularly on samples of commercially available thinners, but a start has been made. It is interesting to note that the two thinners examined in the current work were the prototypes from which the original Grade A and Grade B specifications were drawn.

13. It is apparent that the present investigation has leaned more towards the establishment of minimum specifications on the aromatic-free portion of thinners than to the development of test methods for hydrocarbon type analysis. Satisfactory methods already exist for aromatic analysis (i.e., the previously mentioned NRL Report No. P-2096). At any rate, from the data herein, the aromatic content of the thinners can be estima ted to within about 1% if the aniline points, refractive indices, or solvent powers of both the thinner and the aromatic-free portion are known. Somewhat less satisfactory is the determination of the relative proportions of naphthenes and paraffins in a mixture on the basis of data supplied herein. However, an examination of the solvent power or aniline point of such a mixture can form the basis for an estimate of the relative proportions of naphthenes and paraffins accurate enough for the purpose at hand.

14. The data in this report and the method of approach can be used at some future date, should it become desirable to alter the specifications. It will be unnecessary to repeat a large program of laboratory experimentation because new curves can be prepared if, for example, it is desired to change the mixed aniline point specification for Grade A thinner to 25° C. from 27° C.

15. It is believed that the data in this report may be of value to the manufacturers of petroleum thinners. With a knowledge of the stocks he has available, the manufacturer can blend his components more skillfully, using the relationships presented herewith. It is interesting to note that the aromatic-free portions of Grade A and Grade B thinners are practically identical as indicated by physical properties; the difference between the thinners lies in their aromatic content.

16. It is generally accepted that paraffins reduce and naphthenes enhance the solvency of aromatics beyond a straight additive value. The data presented in this report tend to confirm this, at least insofar as the depressing effects of paraffins are concerned. Possibly the inhancing power of naphthenes is somewhat masked by the method of reporting solvent power, which is postulated upon a linear relationship between mixtures of benzene and n-heptane.

17. The present investigation has not been concerned with certain other stipulations in the specifications such as odor, acidity, stability, copper corrosion, etc. There would seem to be nothing in the present work which would run afoul of these other considerations.

18. No detailed analysis of the data in this report has thus far been made on the basis of refractivity intercept, for example. It is possible that some interesting relationships could be developed by incorporating boiling point and molecular weight considerations.

19. An examination of the data in Tables V and VI is necessary for the development of requirements for solvent power which can be incorporated into specifications. It is proposed that these specifications for solvent power be worded as follows:

(a) The solvent power for Grade A thinner as measured by the kauri butanol method shall be not less than two-thirds of the solvent power of pure toluene, and the solvent power of the aromatic-free portion of this thinner shall be not less than one-third that of pure toluene.

(b) The solvent power for Grade B thinner as measured by the kauri butanol method shall be not less than one-half of the solvent power of pure toluene, and the solvent power of the aromatic-free portion of this thinner shall be not less than one-third that of pure toluene.

CONCLUSIONS

A. Facts Established

20. The required refractive indices, aniline points, specific gravities, and solvent powers of the aromatic-free portions of Grade A and of Grade B thinners have been established as a function of the aromatic contents of the thinners.

21. The principal difference between Grade A and Grade B thinners is the aromatic content.

B. Opinions

22. Additional work is needed to supplement the present data, particularly in the matter of naphthene-paraffin analysis and in evaluation of commercially available thinners.

RECOMMENDATIONS

23. A specification on the solvent power should be incorporated into AN-VV-N-96 Type I thinners. It is recommended that control of solvent power be obtained by including in the specification the following requirements:

(a) The solvent power for Grade A thinner as measured by the kauri butanol method shall be not less than two-thirds of the solvent power of pure toluene, and the solvent power of the aromatic-free portion of this thinner shall be not less than one-third that of pure toluene.

(b) The solvent power for Grade B thinner as measured by the kauri butanol method shall be not less than one-half of the solvent power of pure toluene and the solvent power of the aromatic-free portion of this thinner shall be not less than one-third that of pure toluene.

TABLE I

Properties of Various Hydrocarbons in the Boiling Range of Thinners

		B.P.-°C.	N_D^{20}	D_4^{20}	A.P.
Paraffins,	C-7	79-98	1.38-1.39	0.67-.70	66-78
	C-8	99-126	1.39-1.41	.69-.73	68-80
	C-9	122-151	1.40-1.42	.71-.75	66-83
Aromatics,	benzene	80	1.50	.88	<-30
	toluene	111	1.50	.87	-30
	xylenes	136-144	1.50	.86-.88	<-20 -30
Naphthenes,	C-7	75-103	1.39-1.42	.72-.77	40-50
	C-8	104-130	1.41-1.43	.74-.77	45

TABLE II

Properties of Toluene Mixtures with other Hydrocarbons

n-Heptane

% Toluene	D_4^{20}	N_D^{20}	K.B.	S.P.	M.A.P.
0	0.686	1.38740	26.64	25.4	64.5
20	.723	1.40822	37.9	33.0	53.8
40	.760	1.42952	53.9	43.7	42.4
60	.795	1.45125	74.5	57.5	29.8
80	.833	1.47331	98.9	73.7	16.1
100	.868	1.49573	129.95	95.0	1.0

Methylcyclohexane

0	0.772	1.42277	50.8	41.6	49.7
20	.787	1.43577	64.8	50.8	40.9
40	.809	1.45005	80.5	61.3	31.8
60	.830	1.46459	97.1	72.5	22.0
80	.852	1.47985	114.4	84.3	11.7
100	.868	1.49568	129.95	95.0	1.0

50:50 Methylcyclohexane-n-Heptane

0	0.731	1.40448	37.73	32.8	57.1
20	.757	1.42132	50.45	41.2	47.4
40	.784	1.43912	66.85	52.1	37.1
60	.812	1.45732	86.25	65.2	25.7
80	.841	1.47599	108.25	80.1	13.5
100	.868	1.49534	131.0	95.3	1.0

Di-Iso Butylene

0	0.720	1.40993	36.5	32.0	52.2
20	.750	1.42627	49.25	40.3	42.7
40	.781	1.44326	65.3	51.2	32.9
60	.808	1.46065	84.4	64.0	22.6
80	.839	1.47780	105.65	78.2	11.7
100	.868	1.49534	131.0	95.3	1.0

Cyclohexane

0	0.779	1.42599	59.2	47.2	43.9
20	.793	1.43801	73.9	57.0	35.9
40	.810	1.45119	88.8	67.0	27.5
60	.829	1.46517	102.7	76.3	19.1
80	.847	1.48010	118.8	87.0	9.5
100	.868	1.49583	131.4	95.5	1.0

(Table II Continued)

% Toluene	D_4^{20}	N_D^{20}	K.B.	S.P.	M.A.P.
		Cyclohexene			
0	0.809	1.44431	85.6	65.0	21.7
20	.819	1.45414	97.0	72.5	17.5
40	.831	1.46427	107.0	79.0	13.4
60	.843	1.47466	114.8	84.5	9.1
80	.855	1.48513	123.2	90.0	5.0
100	.868	1.49583	132.9	97.0	1.0
		Xylene			
0	0.864	1.49603	125.2	91.3	4.2
20	.866	1.49598	125.2	91.3	3.3
40	.866	1.49588	125.7	91.6	3.1
60	.867	1.49583	126.1	92.1	2.2
80	.867	1.49583	125.8	91.9	1.7
100	.868	1.49583	133.5	97.0	1.0
		Iso-octane			
0	0.694	1.39080	25.67	24.5	69.6
20	.730	1.41087	37.55	32.5	57.4
40	.764	1.43152	54.55	44.0	45.5
60	.800	1.45261	76.65	59.0	31.7
80	.835	1.47377	103.7	77.0	17.5
100	.868	1.49534	131.0	95.3	1.0

TABLE III

Properties of Paraffin-Naphthene Mixtures

Cyclohexane-Iso-octane

% Naphthene	D_4^{20}	N_D^{20}	K.B.	S.P.	M.A.P.
0	0.694	1.39080	25.7	24.5	69.6
20	.714	1.39791	31.5	28.5	64.4
40	.729	1.40490	37.3	32.3	59.1
60	.745	1.41193	44.5	37.2	54.0
80	.764	1.41900	51.4	42.0	48.9
100	.779	1.42599	59.2	47.2	43.9

n-Heptane-Methylcyclohexane

0	0.690	1.38843	26.6	25.4	64.0
20	.707	1.39515	31.3	28.3	61.0
40	.723	1.40205	35.6	31.3	58.2
60	.740	1.40892	40.4	34.5	55.3
80	.757	1.41580	45.7	38.0	52.4
100	.772	1.42277	50.8	41.6	49.7

TABLE IV

Aniline Points of Thinner Hydrocarbons

Hydrocarbon	Aniline Points	
	obs.	literature
iso-octane	79.0	80.4
n-heptane	68.7	70.6
Grade A min.-arom.free residue	58.7	-
Grade B-arom.free residue	54.35	-
50:50 methylcyclohexane-n-heptane	54.3	-
Grade A-arom.free residue	53.85	-
di-isobutylene	42.9	-
methylcyclohexane	39.1	40.3
cyclohexane	29.5	30.4
cyclohexene	<-29	<-20
toluene	<-41	<-30

TABLE V

Variation of Thinner Properties with Aromatic Content

	D_4^{20}	N_D^{20}	K.B.	S.P.	M.A.P.
Grade A*	0.824	1.46628	91.9	69.0	22.6
Grade A arom. free residue	.749	1.41311	39.5	34.0	56.7
Grade A arom. free residue + 60% toluene	.817	1.46092	87.1	66.0	26.0
Grade A arom. free residue + 67.5% toluene	.826	1.46729	94.7	70.8	21.35
Grade A arom. free residue + 75% toluene	.834	1.47372	101.9	75.9	16.9
Grade B*	0.790	1.44232	66.9	52.2	37.9
Grade B arom. free residue	.744	1.41205	39.3	33.7	57.0
Grade B arom. free residue + 38% toluene	.790	1.44171	65.8	51.8	38.0
Grade B arom. free residue + 42% toluene	.794	1.44492	69.35	54.0	36.0
Grade A arom. free residue + 38% toluene	.791	1.44287	66.7	52.1	37.9

*As available commercially.

TABLE VI

Properties of Minimum Specification Thinners

	D_4^{20}	N_D^{20}	K.B.	S.P.	M.A.P.
Grade A min.[ab]	.810	1.45770	83.3	63.3	27.0
Grade A min.[ac]	.810	1.45835	82.4	62.5	27.0
Grade A min.[cd]	.810	1.45765	80.8	61.5	27.0
Grade A min.[e] arom.free res.	.726	1.40448	35.0	31.0	59.35
Grade B min.[f]	.786	1.43896	63.6	50.1	40.0
Grade B min. arom.free res.	.744	1.41205	39.3	33.7	57.0

a. 60.5% aromatics, 14.5% n-heptane, 25.0% arom.-free residue.

b. made from arom.-free residue + toluene + n-heptane.

c. made from Grade A + toluene + n-heptane.

d. 59.3% aromatics.

e. 36.7% n-heptane, 63.3% arom.-free residue.

f. 35.0% aromatics, 65.0% arom.-free residue.

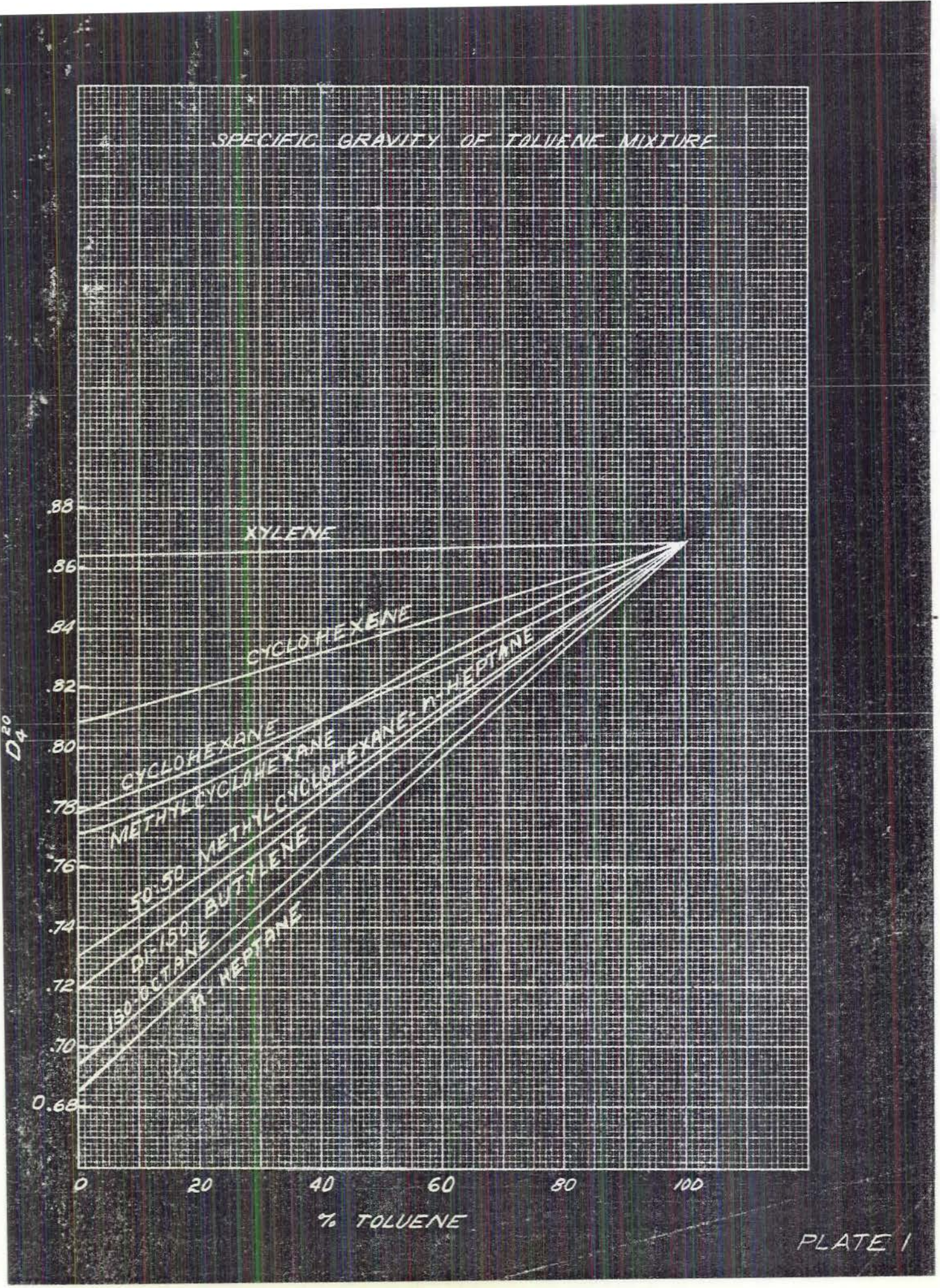
TABLE VII

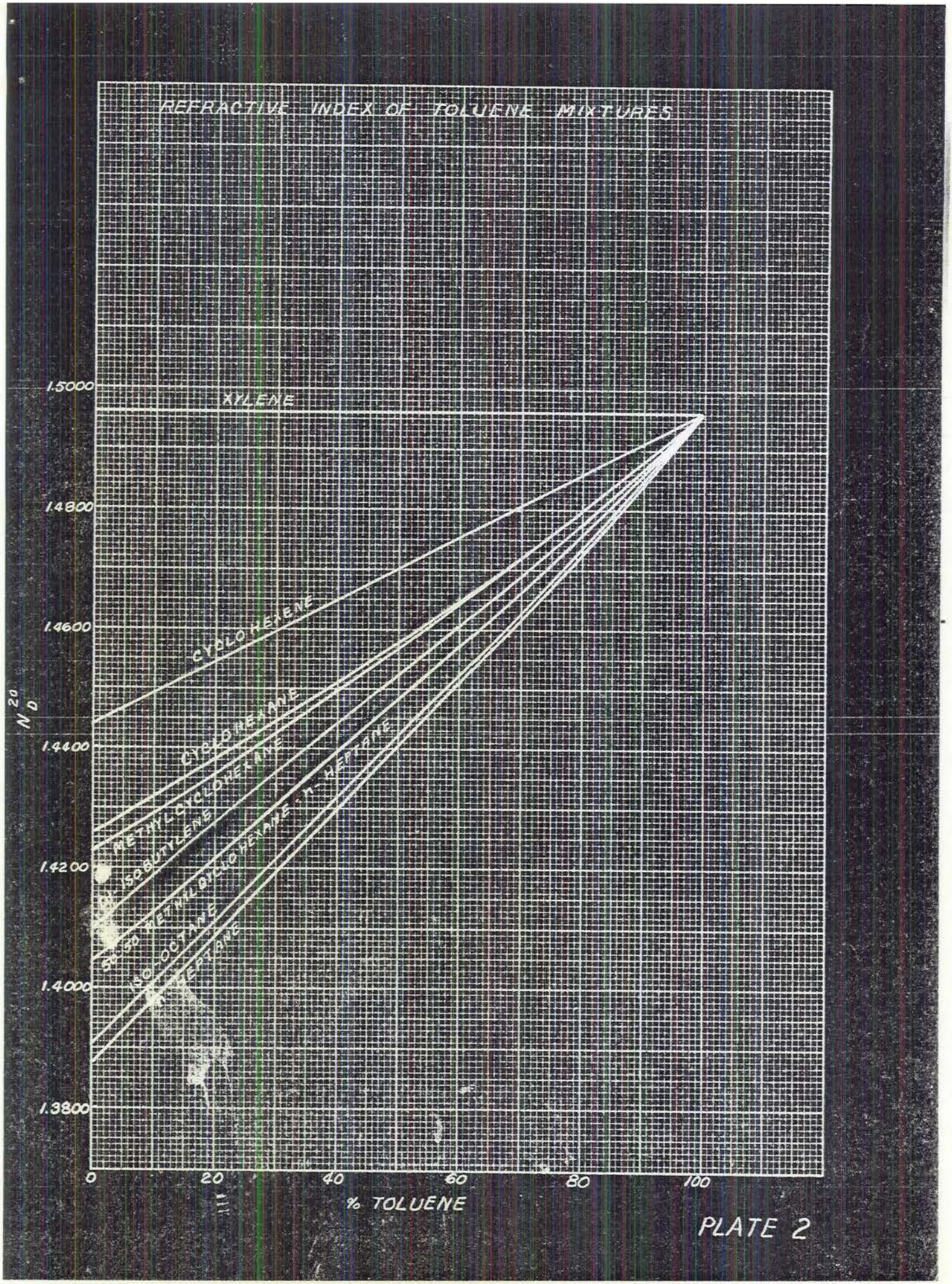
Distillation Ranges of Thinners

Temperature - °C.

	Grade A		Grade B	
	As rec'd.	min.*	As rec'd.	min.*
IBP	99.0	98.0	95.0	96.8
10%	108.4	106.0	102.8	102.5
20	110.5	107.5	104.2	104.0
30	112.6	108.7	105.8	105.8
40	114.7	110.1	107.5	107.6
50	116.3	112.2	109.6	109.3
60	118.9	114.3	111.7	111.5
70	121.6	117.2	114.2	114.0
80	125.0	121.0	117.6	117.3
90	130.5	127.8	123.0	122.5
95	135.0	133.0	128.3	128.0
E.P.	138.5	137.0	135.0	134.0
recovery	99.0	98.7	98.9	98.9
residue	0.9	1.0	0.8	0.8
loss	0.1	0.3	0.3	0.3

*Just passes specifications on sp.g., and mixed aniline point.


SPECIFIC GRAVITY OF TOLUENE MIXTURE
.88
.86
.84
.82
.80
.78
.76
.74
.72
.70
0.68
D_4^{20}
XYLENE
CYCLOHEXENE
CYCLOHEXANE
METHYLCYCLOHEXANE
50-50 METHYLCYCLOHEXANE-N. HEPTANE
DIISO BUTYLENE
ISO-OCTANE
N. HEPTANE
0
20
40
60
80
100
% TOLUENE
PLATE I


REFRACTIVE INDEX OF TOLUENE MIXTURES
XYLENE
CYCLOHEXENE
CYCLOHEXANE
METHYLCYCLOHEXANE
ISOBUTYLENE
2,2,4-TRIMETHYLPENTANE
n-HEPTANE
1.5000
1.4800
1.4600
1.4400
1.4200
1.4000
1.3800
N_D^{20}
0
20
40
60
80
100
% TOLUENE
PLATE 2

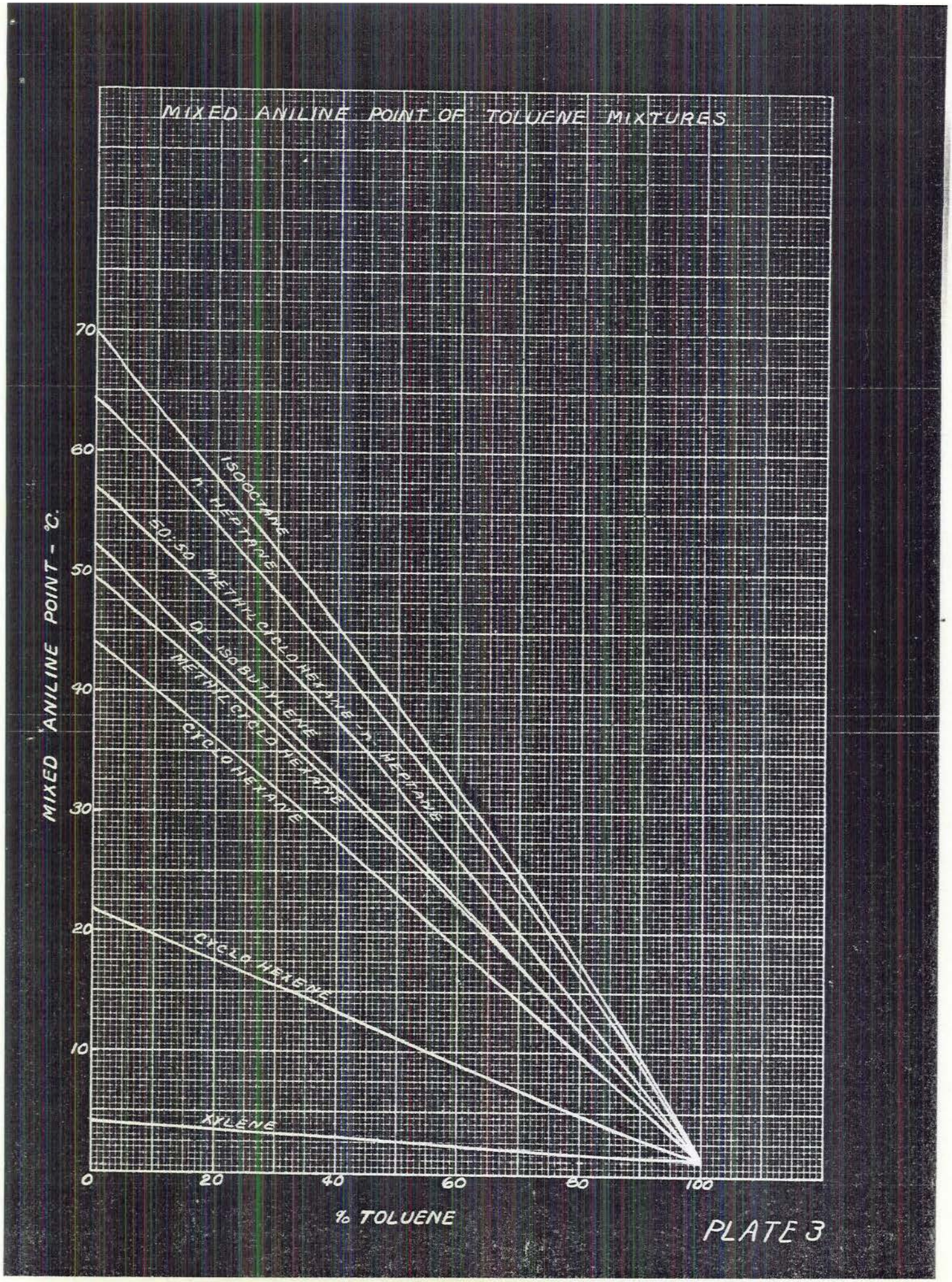

MIXED ANILINE POINT OF TOLUENE MIXTURES
MIXED ANILINE POINT - °C.
70
60
50
40
30
20
10
0
20
40
60
80
100
% TOLUENE
ISOOCTANE
N. HEPTANE
60-50
METHYL CYCLOHEXANE
DI ISOBUTYLENE
METHYL CYCLO PENTANE
CYCLOHEXANE
N. HEXANE
CYCLO HEXENE
XYLENE

PLATE 3

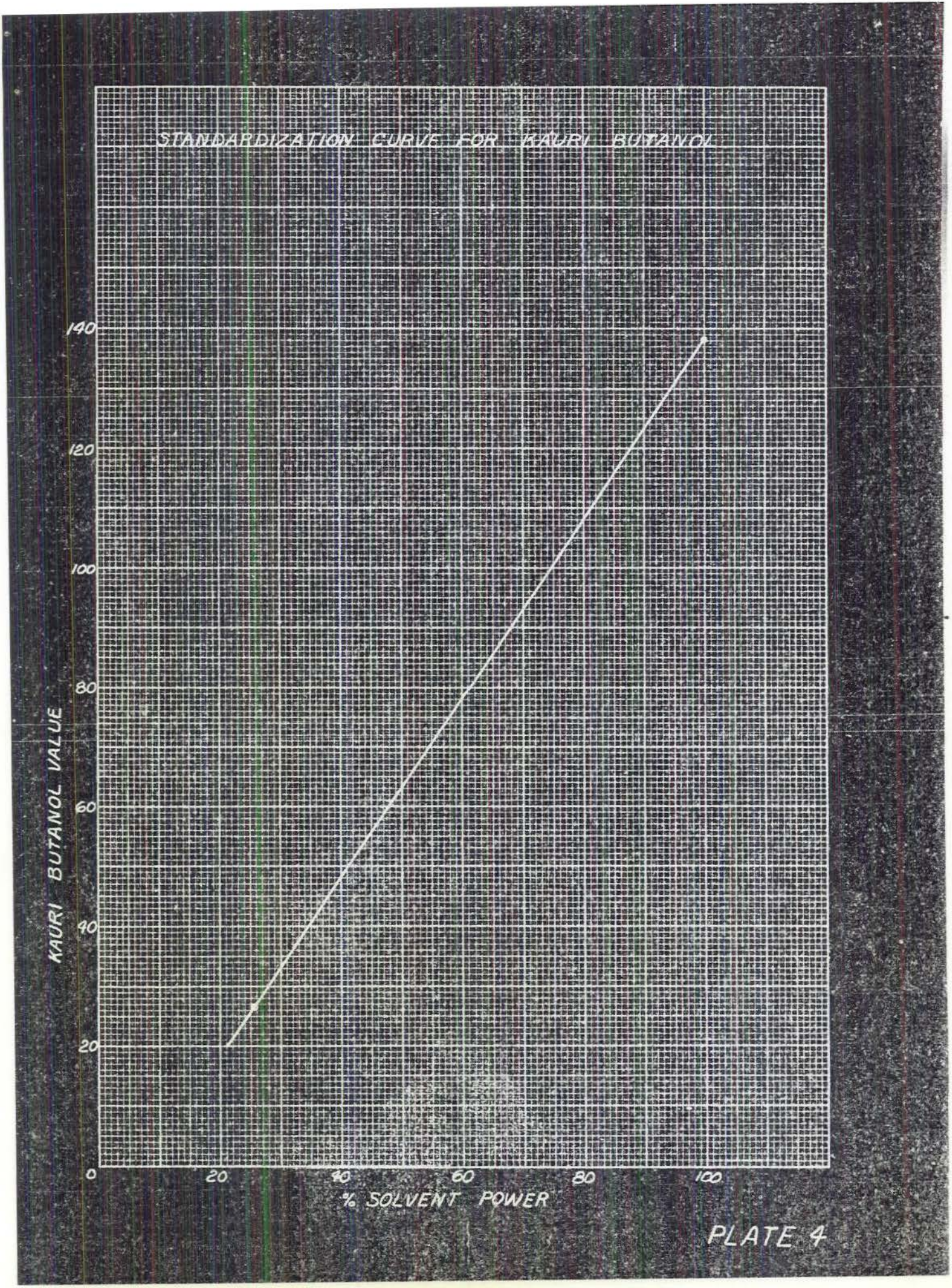
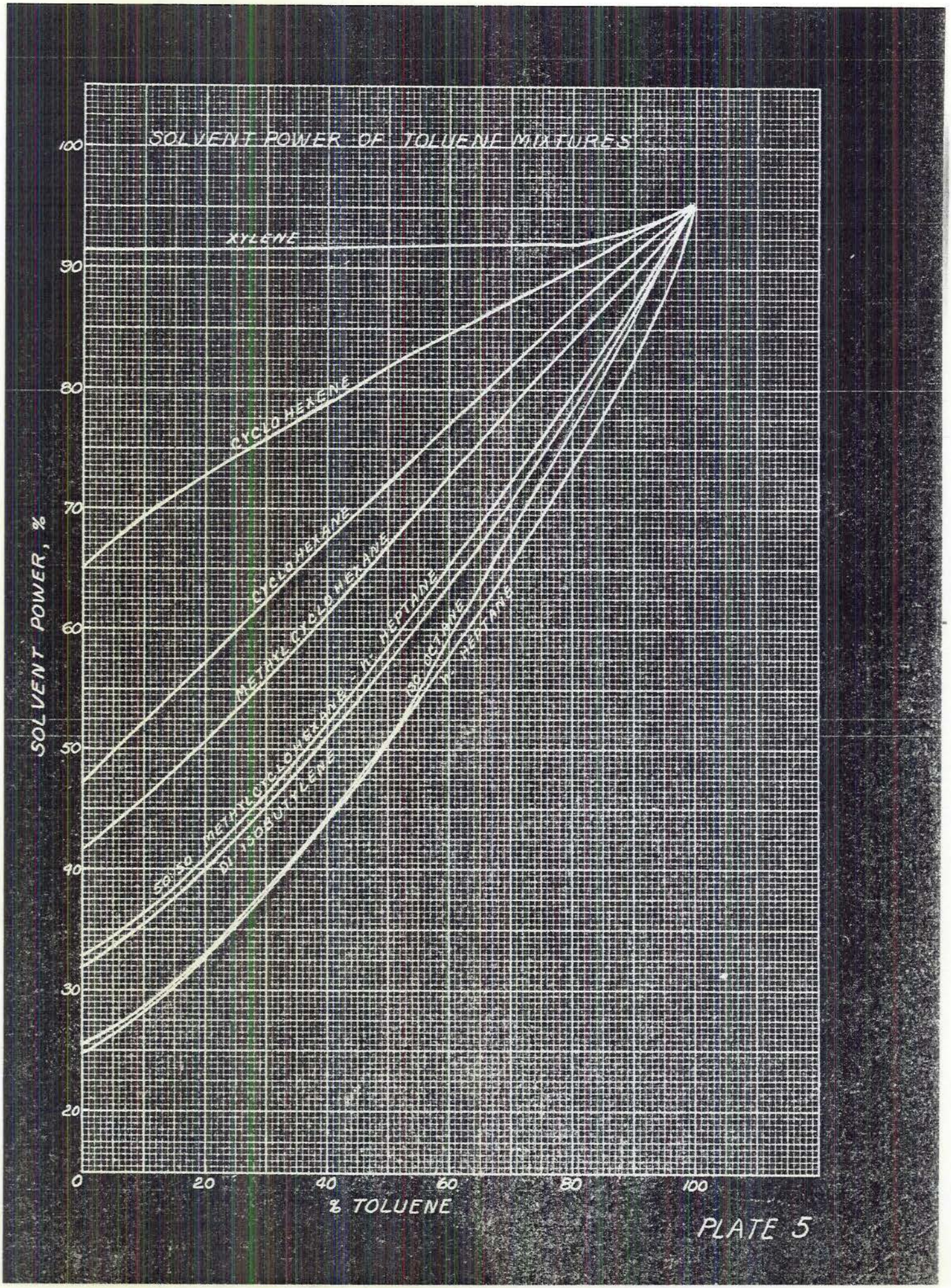

STANDARDIZATION CURVE FOR KAURI BUTANOL
KAURI BUTANOL VALUE
0
20
40
60
80
100
120
140
20
40
60
80
100
% SOLVENT POWER

PLATE 4


SOLVENT POWER OF TOLUENE MIXTURES
SOLVENT POWER, %
% TOLUENE
XYLENE
CYCLOHEXANE
METHYL CYCLOHEXANE
SOLVO
METHYLCYCLOHEXANE-DIISOBUTYLENE
n-HEPTANE
SO. SOLVANE
n-HEXANE
0
20
40
60
80
100
PLATE 5

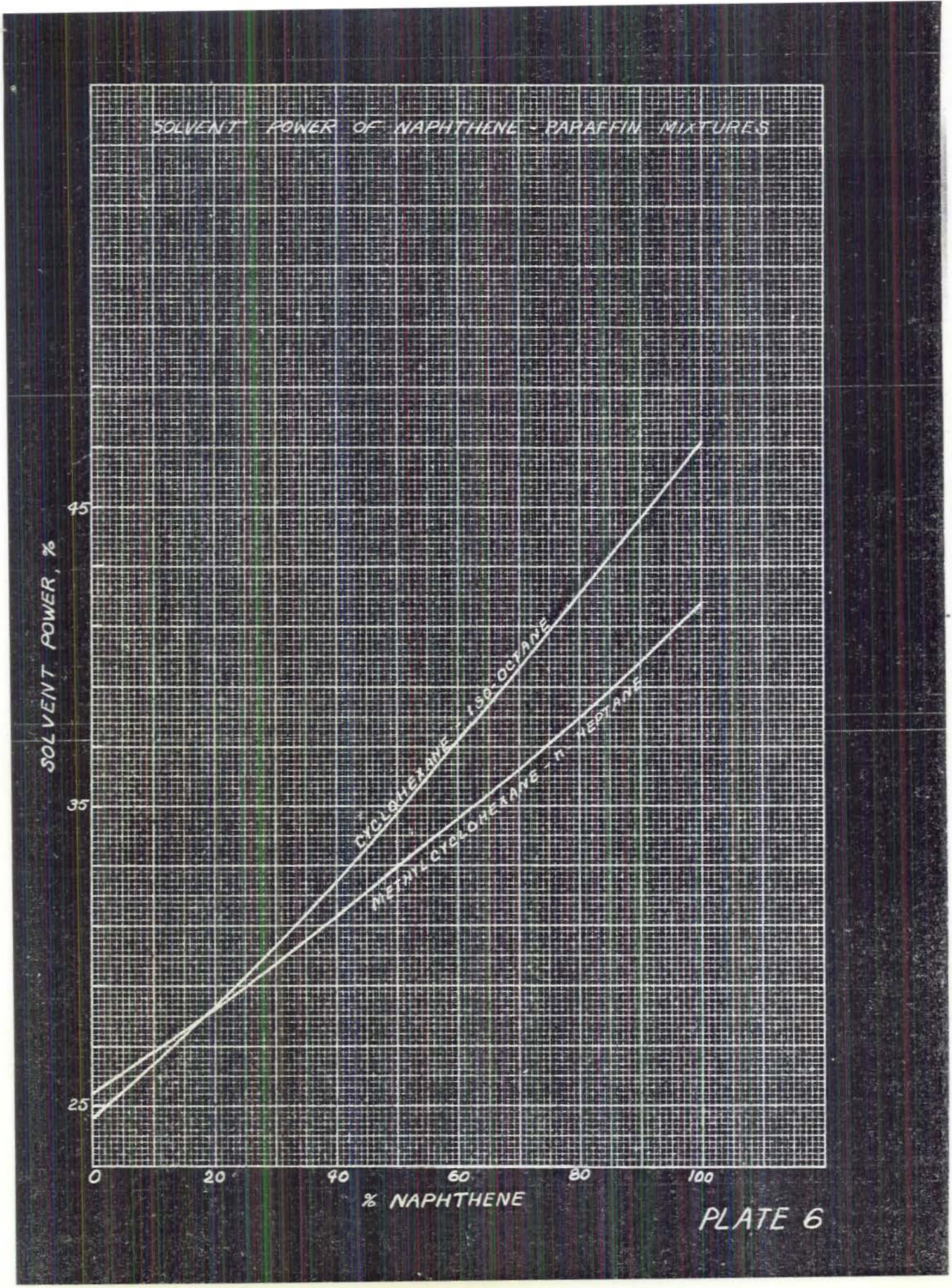

SOLVENT POWER OF NAPHTHENE - PARAFFIN MIXTURES
SOLVENT POWER, %
45
35
25
0
20
40
60
80
100
% NAPHTHENE
CYCLOHEXANE - ISO OCTANE
METHYL CYCLOHEXANE - N. HEPTANE

PLATE 6

REQUIRED SPECIFIC GRAVITY OF NON-AROMATIC PORTION OF AN-VV-N-96 TYPE I THINNERS

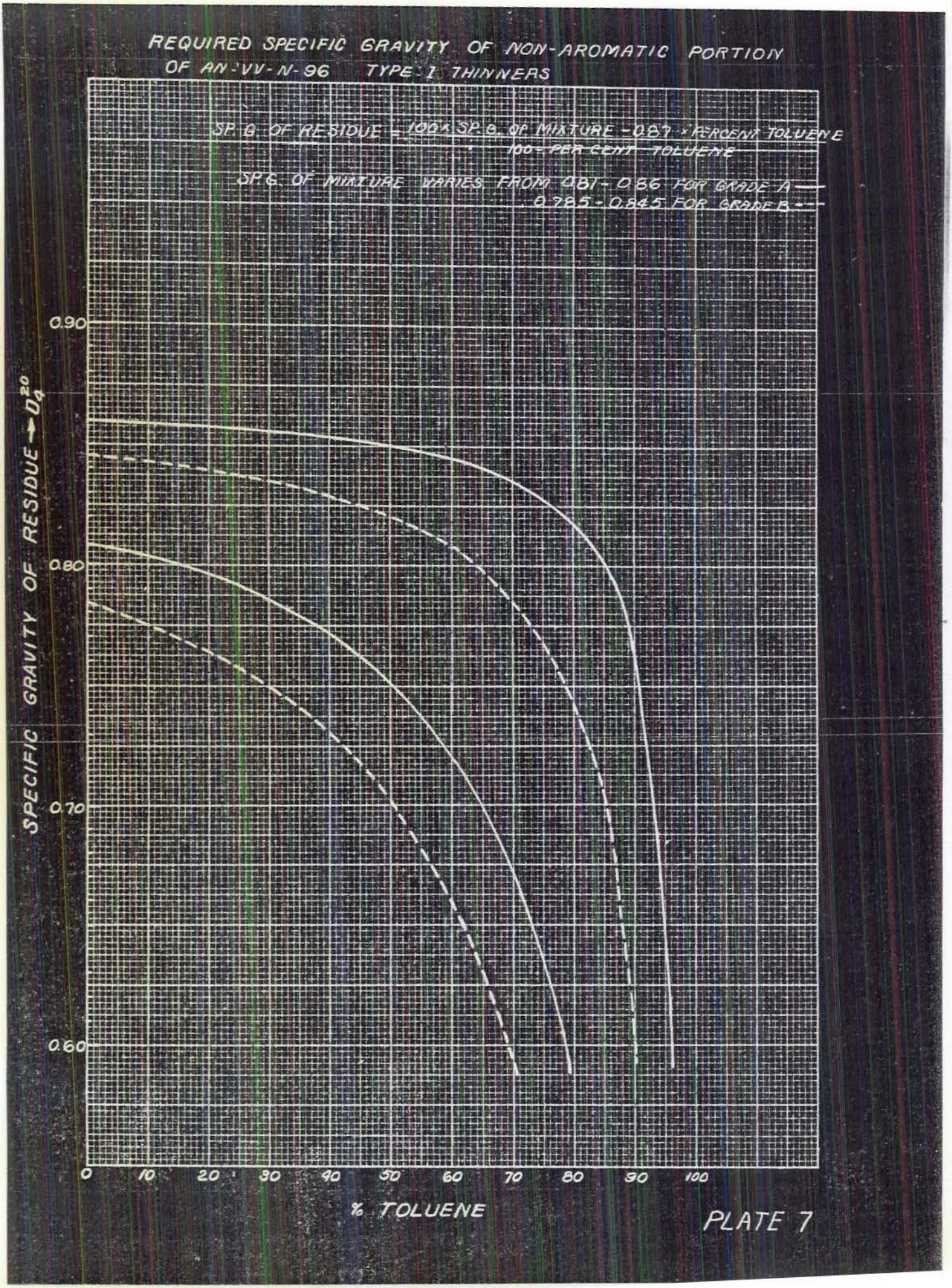


PLATE 7

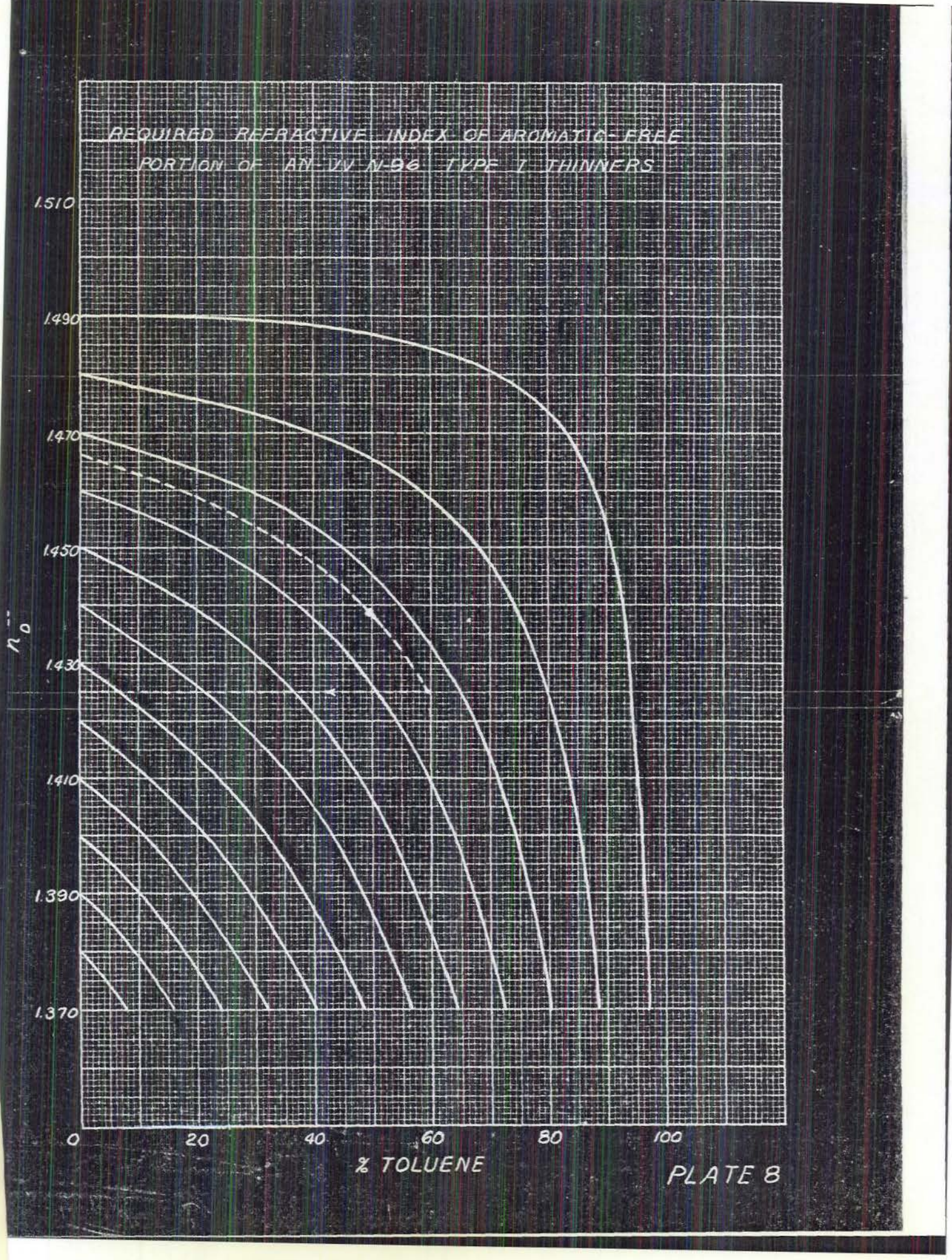

REQUIRED REFRACTIVE INDEX OF AROMATIC-FREE PORTION OF AN-VV-N-96 TYPE I THINNERS
1.510
1.490
1.470
1.450
1.430
1.410
1.390
1.370
n_D
0
20
40
60
80
100
% TOLUENE

PLATE 8

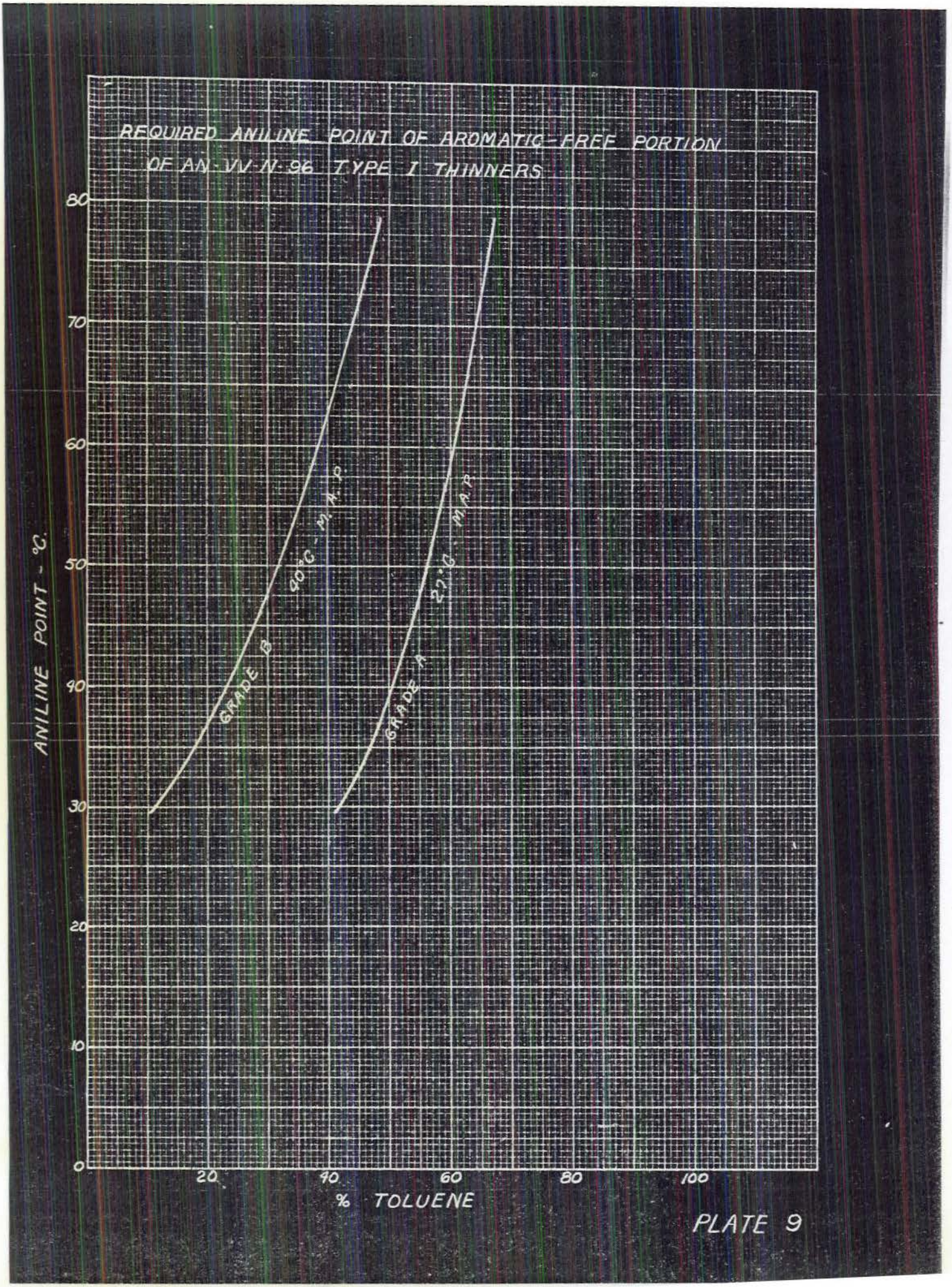
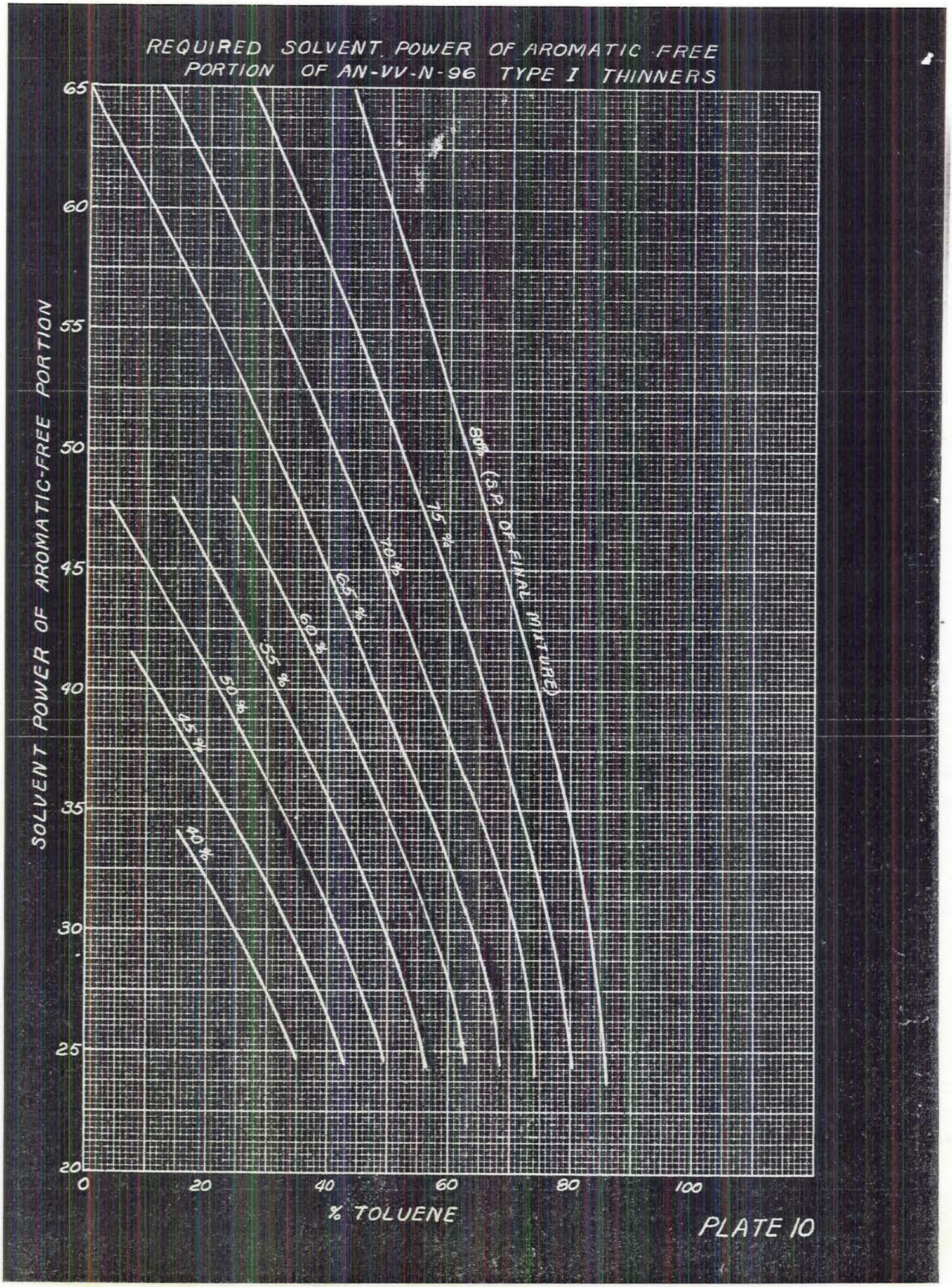

REQUIRED ANILINE POINT OF AROMATIC-FREE PORTION
OF AN-VV-N-96 TYPE I THINNERS
ANILINE POINT - °C.
0
10
20
30
40
50
60
70
80
20
40
60
80
100
% TOLUENE
GRADE B 40°C - M.A.P.
GRADE A 27°C - M.A.P.

PLATE 9


REQUIRED SOLVENT POWER OF AROMATIC FREE PORTION OF AN-VV-N-96 TYPE I THINNERS
SOLVENT POWER OF AROMATIC-FREE PORTION
65
60
55
50
45
40
35
30
25
20
0
20
40
60
80
100
% TOLUENE
80° (B.P. OF FINAL MIXTURE)
75 %
70 %
65 %
60 %
55 %
50 %
45 %
40 %
PLATE 10

C O P Y

AN-VV-N-96
August 27, 1941

ARMY-NAVY AERONAUTICAL SPECIFICATION
NAPHTHA; PETROLEUM; AROMATIC

This specification was approved on the above date by joint action of the War and Navy Departments, for use in the procurement of aeronautical supplies and shall become effective not later than February 27, 1942. It may be put into effect, however, at any earlier date after promulgation.

A. APPLICABLE SPECIFICATIONS

A-1. The following specifications of the issue in effect on date of invitation for bids shall form a part of this specification:

A-1a. AN Aeronautical Specification.-

AN-TT-C-516 Coatings, Protective, Organic (for Aircraft); General Specifications (Methods for Sampling and Testing)

B. GRADE AND TYPES

B-1. Grade.- This specification covers one grade of aromatic petroleum naphtha only.

B-2. Types.- The naphtha shall be furnished in the following types by boiling point as specified:

Type I 88-140°C. (190-285°F.) Boiling Range
Type II 135-191°C. (275-375°F.) Boiling Range
Type III 171-218°C. (340-425°F.) Boiling Range

C. MATERIAL AND WORKMANSHIP

C-1. Material.- Shall be of the aromatic petroleum diluent type, obtained by extraction of petroleum distillates with selective solvents without the admixture of other compounds.

C-2. Workmanship.- Shall conform to the best commercial practice covering this class of material.

C O P Y

AN-VV-N-96 -2
(August, 1941)

D. GENERAL REQUIREMENTS

D-1. Appearance.- Shall be clear and free from separated water, sediment, and suspended matter when examined by transmitted light.

D-2. Odor.- Shall be sweet, slightly aromatic, and not noticeable after drying from filter paper.

D-3. Acidity.-

D-3a. Material.- Not more than 0.03 mg of potassium hydroxide shall be required to neutralize the acidity of 1 g of the naphtha.

D-3b. Residue.- After distillation the material shall contain no free mineral acid.

D-4. Non-volatile.- Shall not exceed 0.2 g per 100 ml.

D-5. Stability.- The naphtha shall show no appreciable change in appearance, color, odor, or acidity after being subjected to the Stability test outlined in section F.

E. DETAIL REQUIREMENTS

E-1. The color, Specific Gravity, Flash Point, Distillation, and Mixed Aniline Point shall be as shown in Table I.

E-2. Copper Corrosion.- The material shall show no more than a very slight discoloration after being subjected to the test outlined in AN-TT-C-516 for three hours at the temperature shown in Table I.

F. METHODS OF SAMPLING, INSPECTION, AND TESTS

F-1. General.- Sampling, inspection, tests, and test reports shall be in accordance with applicable methods of Specification AN-TT-C-516 except that tests for Stability, Distillation, and Mixed Aniline Point shall be conducted as specified herein.

F-2. Test Methods.-

F-2a. Stability.-

Apparatus.- Shall consist of a 225 ml, approximate, glass container (an eight-ounce oil bottle is suggested), a suitable metal bomb to hold the glass at the required pressures, and a water or steam bath.

TABLE I

Physical Requirements

	TYPE I	TYPE II	TYPE III
Color, Saybolt (min.)	25	21	18
Specific Gravity at 20°/20°C.(68°/68°F.)	.785-.845	.825-.865	.855-.885
Flash Point (min.)	-	27°C.(80°F.)	50°C.(122°F.)
Distillation.-			
Initial Point (min.)	88°C.(190°F.)	135°C.(275°F.)	171°C.(340°F.)
50 Percent between	100-116°C (212-240°F.)	146-157°C.) (295-315°F.)	182-200°C. (360-392°F.)
End Point (max.)	141°C.(285°F.)	191°C.(375°F.)	218°C.(425°F.)
Mixed Aniline Point (max.)	40°C.(104°F.)	28°C.(82°F.)	34°C.(93°F.)
Copper Corrosion	50°C.(122°F.)	100°C.(212°F.)	100°C.(212°F.)

Procedure.- Place approximately 200 ml of the naphtha in the glass container and place in the metal bomb (at room temperature); cover the glass container with a loose cap of glass or oxygen resistant composition (do not plug the neck), and close the bomb. Charge with oxygen to 95 to 100 pounds per square inch pressure and release the charge (to the air). Repeat the charging and release operation. Charge with oxygen a third time to 98 to 100 pounds per square inch pressure and test for leaks. If no leaks are shown, place the assembly in a steam or water bath at 98 to 100°C. (208 to 212°F.) for four hours, plus or minus five minutes. At the completion of the four hours oxidation cool the assembly in cold water, release the pressure, remove the sample and examine for appearance, color, odor, and acidity, as required under Stability (section D).

F-2b. Distillation.- The procedure shall conform to the requirements of Specification AN-TT-C-516, except that the End Point shall be recorded as the temperature at which the bottom of the flask becomes dry.

COPY

F-2c. Mixed Aniline Point.- Pipette into a six-inch test tube 10 ml of anhydrous aniline, 5 ml of the naphtha under test, and 5 ml of any naphtha - regardless of its boiling range - which has an aniline point of 60°C.(140°F.). (The aniline point of the 60°C. naphtha is taken as the critical solution temperature of 5 ml of aniline and 5 ml of naphtha.) Take the critical solution temperature in degrees Centigrade by warming or cooling with ice or running water. Temperature should be checked three or four times to the nearest 0.2°C.(0.36°F.). Guard against contamination with water during the test.

G. PACKING, PACKING, AND MARKING FOR SHIPMENT

G-1. Packaging, packing, and marking shall be in accordance with applicable methods of Specification AN-TT-C-516.

H. REQUIREMENTS APPLICABLE TO INDIVIDUAL DEPARTMENTS

H-1. There are no requirements applicable to the individual Departments.

I. NOTES

I-1. The aromatic petroleum naphtha covered by this specification is intended for use in the manufacture of organic protective coatings and cleaning compounds used on aircraft.

I-2. This specification supersedes the current issues of U. S. Army Specification No. 14101 and Navy Aeronautical Specification RM-106 for Army and Navy aeronautical use.

I-3. Ordering Data.- The material shall be purchased by volume, the unit being a U. S. gallon at 20°C.(68°F.). The volume shall be determined by dividing the net weight, in pounds, by weight per gallon. Determine the specific gravity in accordance with Specification AN-TT-C-516 and multiply by 8.33 to give the weight in pounds per U. S. Gallon.

I-4. Specifications.- When requesting specifications, refer to both title and number.

I-4a. Copies of this specification and other Army-Navy Aeronautical Specifications may be obtained upon application to either the Materiel Division, Air Corps, Wright Field, Dayton, Ohio, or to the Bureau of Aeronautics, Navy Department, Washongton, D. C. Naval activities should make application to the Manager, Naval Aircraft Factory, U. S. Navy Yard, Philadelphia, Pa.

C O P Y

AN-VV-N-96 -5
(August, 1941)

NOTICE: When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

C O P Y

AN-VV-N-96
AMENDMENT-2
September 28, 1942
Superseding
Amendment-1
January 29, 1942

ARMY-NAVY AERONAUTICAL SPECIFICATION
NAPHTHA; PETROLEUM; AROMATIC

This amendment, approved on the above date by joint action of the War and Navy Departments, forms a part of and should be attached to AN Aeronautical Specification AN-VV-N-96, dated August 27, 1941. It shall become effective immediately upon issue.

Paragraph A-1a: Add "AN-R-T-541 Toluene".

Section B: Rewrite as follows:

"B. TYPES AND GRADES.

B-1. Types.-Aromatic, petroleum naphtha shall be furnished in the following types by boiling point as specified:

Type I	88 - 140°C.	(190-285°F.)Boiling Range
Type II	129.4- 191°C.	(265-375°F.)Boiling Range
Type III	171 - 281°C.	(340-425°F.)Boiling Range

B-2. Grades.-The naphtha shall be furnished in Grades A and B as specified as follows for Type I, and in one grade only for Types II and III:

Grade A High Aromaticity
Grade B Low Aromaticity"

Paragraph C-1: Add the following phrase to the end of the paragraph:

"except that the Grade A, Type I, Naphtha may be a blend containing toluene conforming to Specification AN-R-T-541."

C O P Y

AN-VV-N-96 -2
Amendment -2

TABLE I: Change the column for Type I and II to read as follows:

TABLE I
Physical Requirements

	TYPE I		TYPE II
	Grade A	Grade B	
Color, Saybolt (min.)	25	25	21
Specific Gravity at 20°/20°C.(68°/68°F.)	.810-.860	.785-.845	.825-.865
Flash Point (min.)			27°C.(80°F.)
Distillation.-			
Initial Point (min.)	88°C.(190°F.)	88°C.(190°F.)	129.4°C. (265°F.)
50 Percent between	100-116°C. (212-240°F.)	100-116°C. (212-240°F.)	143.3-157°C. (290-315°F.)
End Point (max.)	141°C. (285°F.)	141°C. (285°F.)	191°C. (375°F.)
Mixed Aniline Point (max.)	27°C. (80.6°F.)	40°C. (104°F.)	28°C.(82°F.)
Copper Corrosion	50°C. (122°F.)	50°C. (122°F.)	100°C. (212°F.)

PATENT NOTICS: The following paragraph has been added to the end of this specification:

NOTICE: When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.