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THE LOW-TEMPERATURE SOLUBILITY OF 24 AROMATIC AMINES IN AVIATION GASOLINE

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

MEMORANDUM REPORT

for the

Army Air Forces, Air Technical Service Command

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INTRODUCTION

A general investigation on the suitability of aromatic amines as antiknock additives in aviation gasolines is being conducted at the Cleveland laboratory of the NACA at the request of the Army Air Forces, Air Technical Service Command. The present report is the second in a series dealing with the low-temperature solubility of aromatic amines in aviation gasolines. The first paper in the series (reference 1) reports tests and results for 15 aromatic amines. The antiknock effectiveness of 2-percent blends of various amines in AN-F-28, Amendment-2, fuel (grade 130) is reported in references 2 to 4. Reference 5 presents tests and data on the suitability of amine blends for overwater storage.

The purpose of the present report is to present the low-temperature solubility in gasoline of 24 aromatic amines. The solubilities of the amines at -60° C, the standard freezing specification for current Army-Navy aviation fuels, was a particular objective of the tests. Solubilities were determined at temperatures as low as -65° C and in concentrations as high as 10 percent by weight. These conditions are more severe than those specified by the Army and the Navy and therefore permit a critical evaluation of the suitability of aromatic amines as fuel additives on the basis of solubility alone.

Because gasoline composition affects the solubility of the amines, the amine solubilities were determined in an aromatic-free gasoline, a gasoline of known aromatic content, and a typical AN-F-28 fuel. The investigation was conducted between March and September 1944.

GASOLINE AND AMINE SPECIFICATIONS

The fuels used for the present investigation are the same as those used in reference 1; their compositions are as follows:

1. Grade 65 base stock from which aromatic hydrocarbons were successively extracted with 10-percent fuming sulfuric acid and silica gel

2. The extracted grade 65 base stock to which was added 15 percent by volume of an aromatic-hydrocarbon mixture of five parts xylene, two parts cumene, and one part toluene

3. Different batches of AN-F-28, Amendment-2, fuel (grade 130) containing 12 to 20 percent aromatics

The physical properties of the amines tested are given in table I.

APPARATUS AND PROCEDURE

The cloud-point apparatus is illustrated in figure 1 and the apparatus for obtaining saturated samples is shown in figure 2; they are both described in reference 1.

The incipient-separation temperature, or cloud point, was determined whenever possible with blends of known amine content. In cases where supercooling made the cloud-point method unreliable, saturated gasoline samples were withdrawn from the mixtures of gasoline and amine and were subsequently analyzed by one of the two methods described in reference 1.

RESULTS AND DISCUSSION

Figures 3 to 5 present the solubilities of the amines in each of the three test fuels. Any amine concentration lying above the dashed line at -60° C failed to meet current Army-Navy freezing specifications.

No data for amines more soluble than 10 percent by weight at -60° C were obtained or plotted in the figures. Those amines include:

o-Isopropylaniline
p-Isopropylaniline
N-Isopropyl-*p*-isopropylaniline
Cumidines from synthetic cumene
Cumidines from refinery cumene

N-Methylcumidines
N-Methyl-p-tert-butylaniline
N-Methyl-2,4-xylidine
N-Methylxylidines
2,4-Diethylaniline
2-Methyl-5-isopropylaniline
N,N-Dimethyl-2-methyl-5-isopropylaniline
N,N-Dimethyl-2,4,6-trimethylaniline
Pseudocumidine (tech.)

Because p-phenylenediamine and N-methyl-p-phenylenediamine were less than 0.5 percent by weight soluble in the test gasolines at room temperature, no additional solubility data were taken for these compounds. The N,N'-dimethyl-p-phenylenediamine was soluble to the extent of 1 to 2 percent by weight at room temperature but was too unstable to permit accurate measurement of solubility by the method employed. N,N-Diethyl-p-phenylenediamine was tested only in the aromatic-free gasoline.

As has been previously observed (reference 1), the composition of the test gasolines has a marked effect on the solubility of the amines. At any temperature, the amines were approximately twice as soluble in the aromatic gasoline and in AN-F-28 fuel, which contains 12 to 20 percent aromatics, as in the aromatic-free gasoline.

A summary of the solubilities of the aromatic amines at -60° C, determined by interpolating or extrapolating the experimental data, is presented in table II. The data for commercial xylidines, obtained from reference 6, are included for comparison.

The solubility of an aromatic amine in the aromatic-free gasoline at -60° C may be taken as an indication of the maximum concentration in which the amine may be added to current aviation fuels solely on the basis of solubility. The aromatic hydrocarbons present in most of the current aviation fuels would provide a margin of safety in preventing separation of the amine at -60° C.

CONCLUSIONS

The following amines meet present Army-Navy freezing specifications when blended with aviation gasoline in concentrations up to 2 percent by weight:

o-Isopropylaniline
p-Isopropylaniline
N-Isopropyl-p-isopropylaniline
Cumidines from synthetic cumene

Cumidines from refinery cumene
N-Methylcumidines
p-tert-Butylaniline
N-Methyl-p-tert-butylaniline
2,6-Xylidine
N-Methyl-2,4-xylidine
N-Methylxylidines
2,4-Diethylaniline
2-Methyl-5-isopropylaniline
N,N-Dimethyl-2-methyl-5-isopropylaniline
2,4,6-Trimethylaniline
N,N-Dimethyl-2,46-trimethylaniline
Pseudocumidine (tech.)

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics
Cleveland, Ohio, November 17, 1944.

REFERENCES

1. Olson, Walter T., and Kelly, Richard L.: The Low-Temperature Solubility of Aniline, the Toluidines, and Some of Their N-Alkyl Derivatives in Aviation Gasoline. NACA Memo. rep., June 5, 1944.

2. Branstetter, J. Robert: Knock-Limited Performance of Blends of AN-F-28 Fuel Containing 2 Percent Aromatic Amines - I. NACA Memo. rep., April 17, 1944.

3. Alquist, Henry E., and Tower, Leonard K.: Knock-Limited Performance of Blends of AN-F-28 Fuel Containing 2 Percent Aromatic Amines - II. NACA Memo rep., June 26, 1944.

4. Alquist, Henry E., and Tower, Leonard K.: Knock-Limited Performance of Blends of AN-F-28 Fuel Containing 2 Percent Aromatic Amines - III. NACA Memo rep., Aug. 23, 1944.

5. Olson, Walter T., Tischler, Adelbert O., and Goodman, Irving A.: Gasoline-Water Distribution Coefficients of 27 Aromatic Amines. NACA Memo. rep., Aug. 3, 1944.

6. Olson, Walter T.: The Low-Temperature Solubility of Technical Xylidines in Aviation Gasoline. NACA Memo. rep., June 4, 1943.

TABLE I - PHYSICAL PROPERTIES OF AROMATIC AMINES

Amine	Boiling range at 760 mm Hg except where noted (°C)	Index of refraction n_D^{20}	Density (grams/ml)
o-Isopropylaniline	219-220	1.5484	0.9643
p-Isopropylaniline	225.5-226.5	1.5432	.9514
N-Isopropyl-p-isopropylaniline	246-247	1.5209	.9075
Cumidines from synthetic cumene	225-226	1.5448	.9536
Cumidines from refinery cumene	220-241	1.5434	.9531
N-Methylcumidines	237.5-241.5	1.5390	.9366
p-tert-Butylaniline	96.5-98 at 5-6 mm	1.5388	.9446
N-Methyl-p-tert-butylaniline	245.5-249.5	1.5348	.9305
2,6-Xylidine	216-217	1.5616	.9768
N-Methyl-2,4-xylidine	221-222	1.5542	.9582
N-Methylxylidines (from bromo-xylenes)	220-227	1.5540	.9586
2,4-Diethylaniline	241-242	1.5433	.9511
2-Methyl-5-isopropylaniline	240-242	1.5408	.9436
N,N-Dimethyl-2-methyl-5-isopropylaniline	84 at 5 mm	1.5124	.9028
2,4,6-Trimethylaniline	110 at 15 mm	1.5502	.9615
N,N-Dimethyl-2,4,6-trimethylaniline	213.5	1.5116	.9066
Pseudocumidine (tech.)	225-241	1.5568	.9720
2-Methoxyaniline	224-225	1.5750	1.0931
Diphenylamine	M.P.[1] = 52.9-53.6	------	------
p-Phenylenediamine	M.P.[1] = 140.0-142.0	------	------
N-Methyl-p-phenylenediamine	121 at 5 mm	1.621	------
N,N-Dimethyl-p-phenylenediamine	108-111 at 4-5 mm	------	------
N,N-Diethyl-p-phenylenediamine	117 at 2.5 mm	------	------
N,N'-Dimethyl-p-phenylenediamine	117 at 1 mm	------	------

[1]Melting point (M.P.) measured for this solid instead of boiling range.

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TABLE II - SOLUBILITY OF AROMATIC AMINES AT - 60° C

The following amines had solubilities less than 0.5 percent by weight at -60° C and therefore are unsatisfactory as fuel additives on the basis of solubility:

2-Methyloxyaniline
Diphenylamine
p-Phenylenediamine
N-Methyl-p-phenylenediamine
N,N-Dimethyl-p-phenylenediamine
N,N-Diethyl-p-phenylenediamine
N,N'-Dimethyl-p-phenylenediamine

Amine	Solubility in aviation fuels (percentage by weight)		
	Aromatic-free grade 65	Aromatic-free grade 65 plus 15 percent by volume aromatics[1]	AN-F-28
o-Isopropylaniline	>10	>10	>10
p-Isopropylaniline	>10	>10	>10
N-Isopropyl-p-isopropylaniline	>10	>10	>10
Cumidines from synthetic cumene	>10	>10	>10
Cumidines from refinery cumene	>10	>10	>10
N-Methylcumidines	>10	>10	>10
p-tert-Butylaniline	2.8	4.6	6.1
N-Methyl-p-tert-butylaniline	>10	>10	>10
2,6-Xylidine	4.6	11.1	9.1
N-Methyl-2,4-xylidine	>10	>10	>10
N-Methylxylidines (from bromo-xylenes)	>10	>10	>10
2,4-Diethylaniline	>10	>10	>10
2-Methyl-5-isopropylaniline	>10	>10	>10
N,N-Dimethyl-2-methyl-5-isopropylaniline	>10	>10	>10
2,4,6-Trimethylaniline	3.6	6.1	6.8
N,N-Dimethyl-2,4,6-trimethylaniline	>10	>10	>10
Pseudocumidine (tech.)	>10	>10	>10
XYLIDINES[2] (commercial)	3.7	>10	>10

[1]Aromatic mixture consisted of five parts xylene, two parts cumene, and one part toluene.

[2]Data from reference 6.

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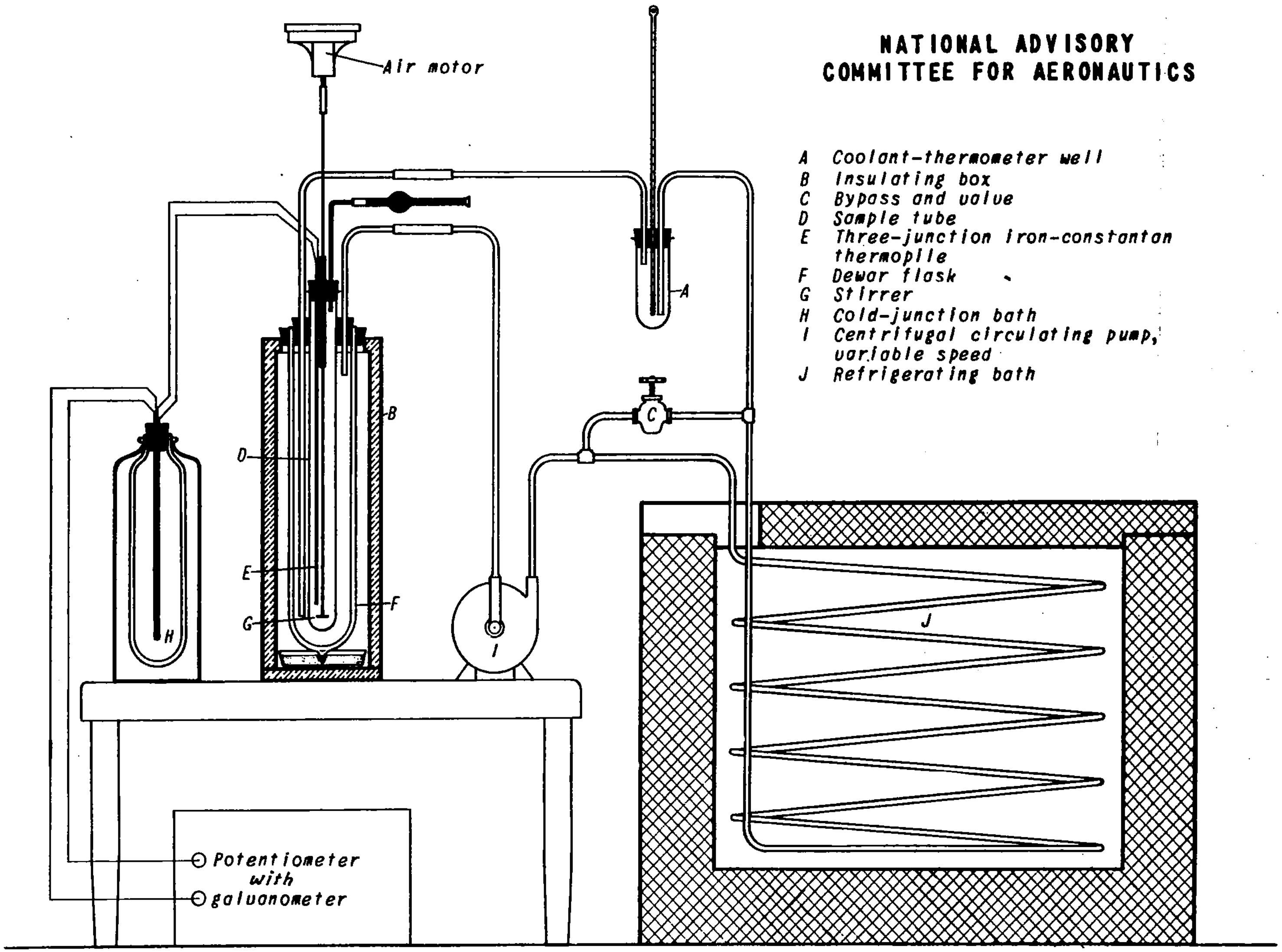

Figure 1. - Cloud-point apparatus.

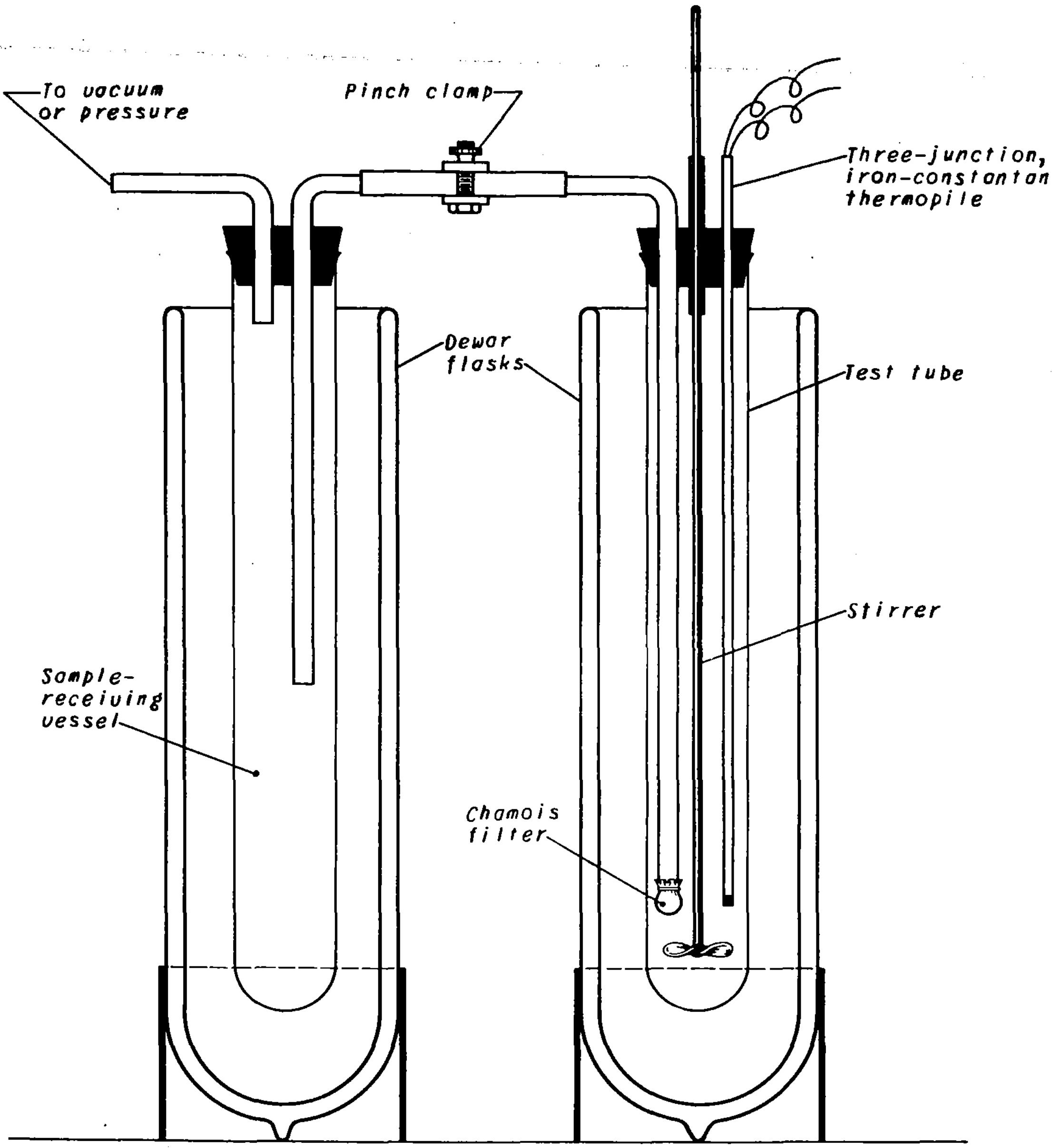

Figure 2. - Apparatus for obtaining saturated samples.

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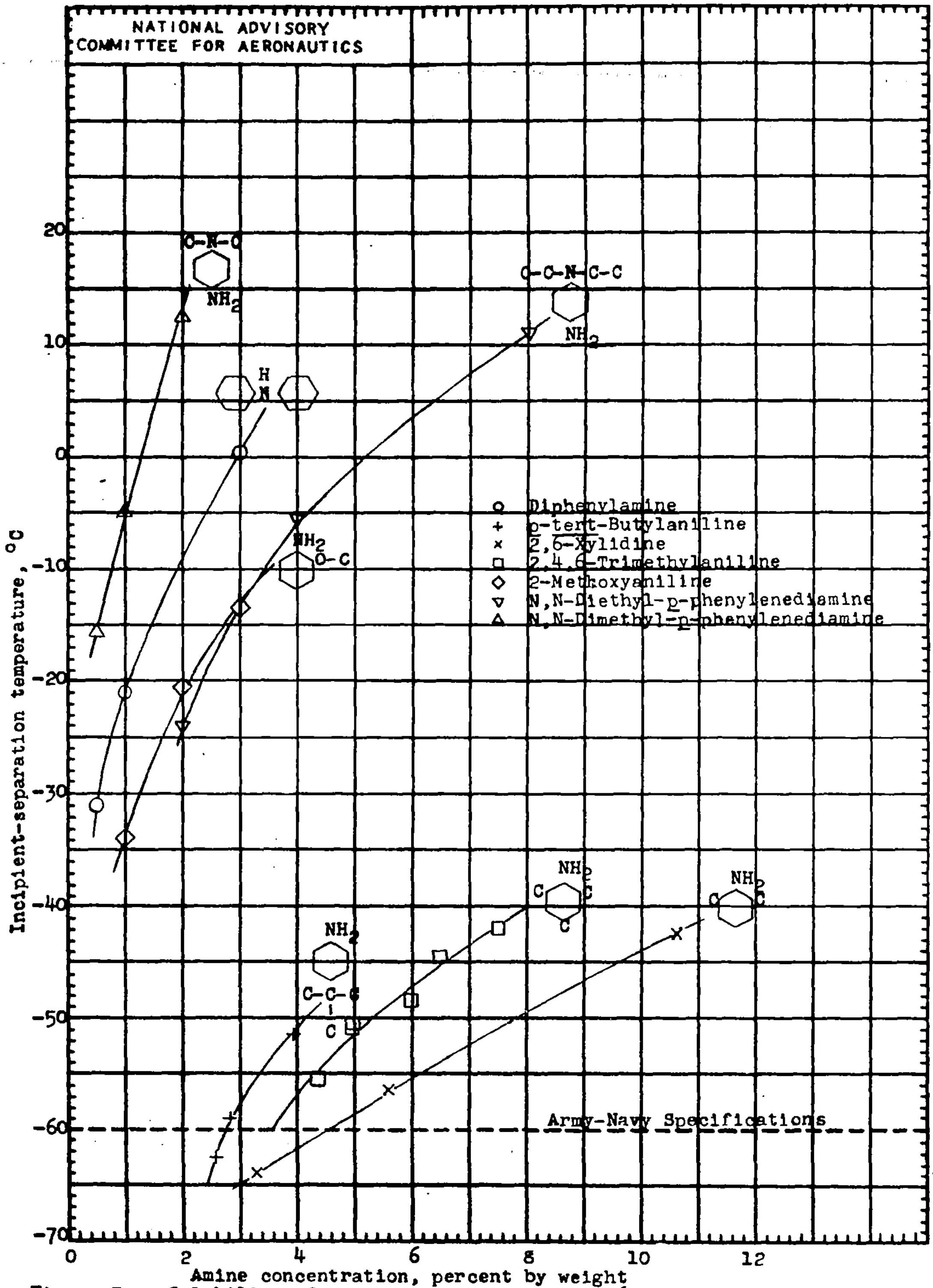

Figure 3. - Solubility of aromatic amines in grade 65 base stock with the aromatic hydrocarbons extracted.

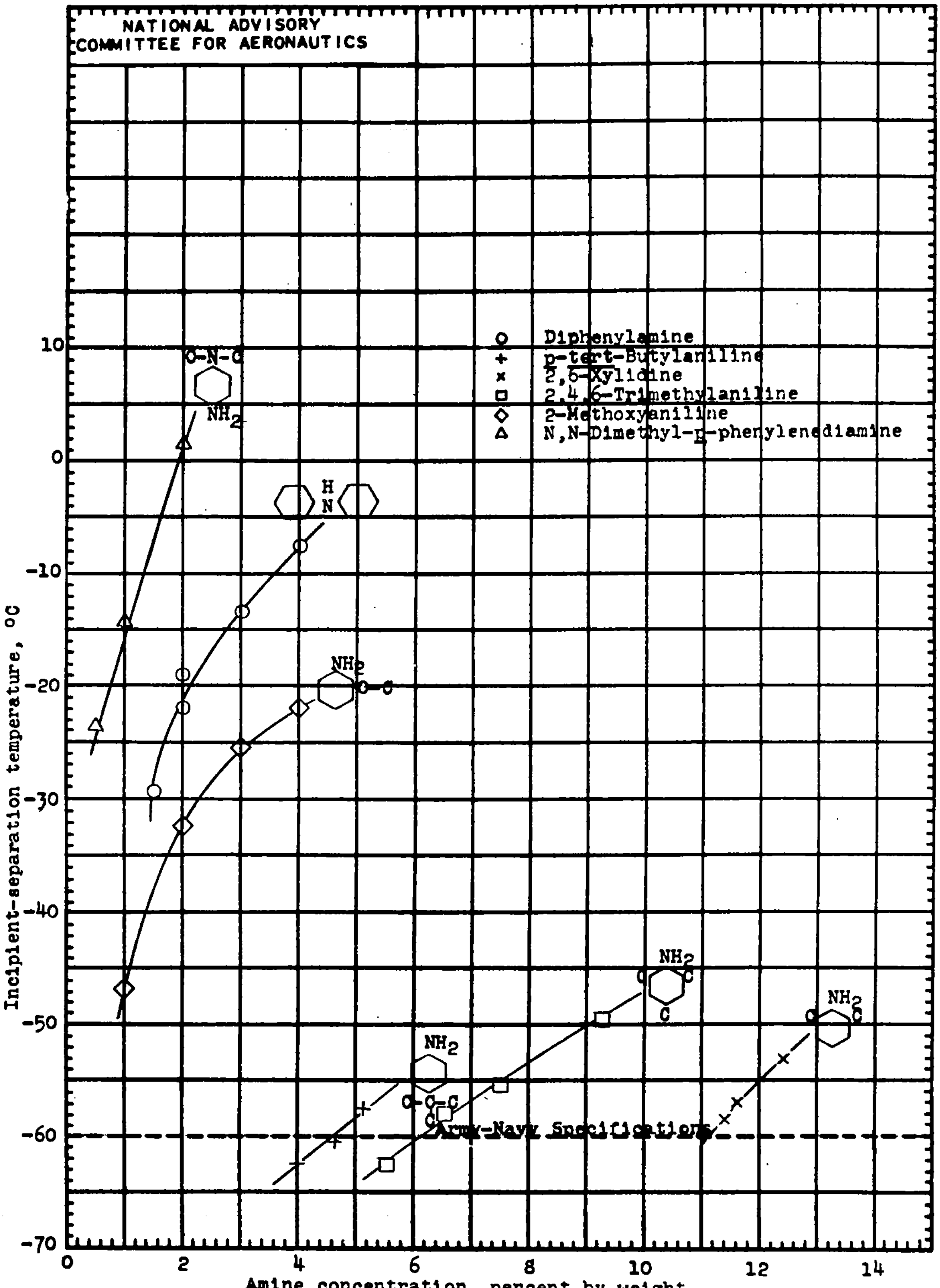

Figure 4. - Solubility of aromatic amines in a blend of 85 percent extracted grade 65 base stock and 15 percent by volume of an aromatic mixture consisting of 15 parts xylene, 2 parts cumene, and 1 part toluene.

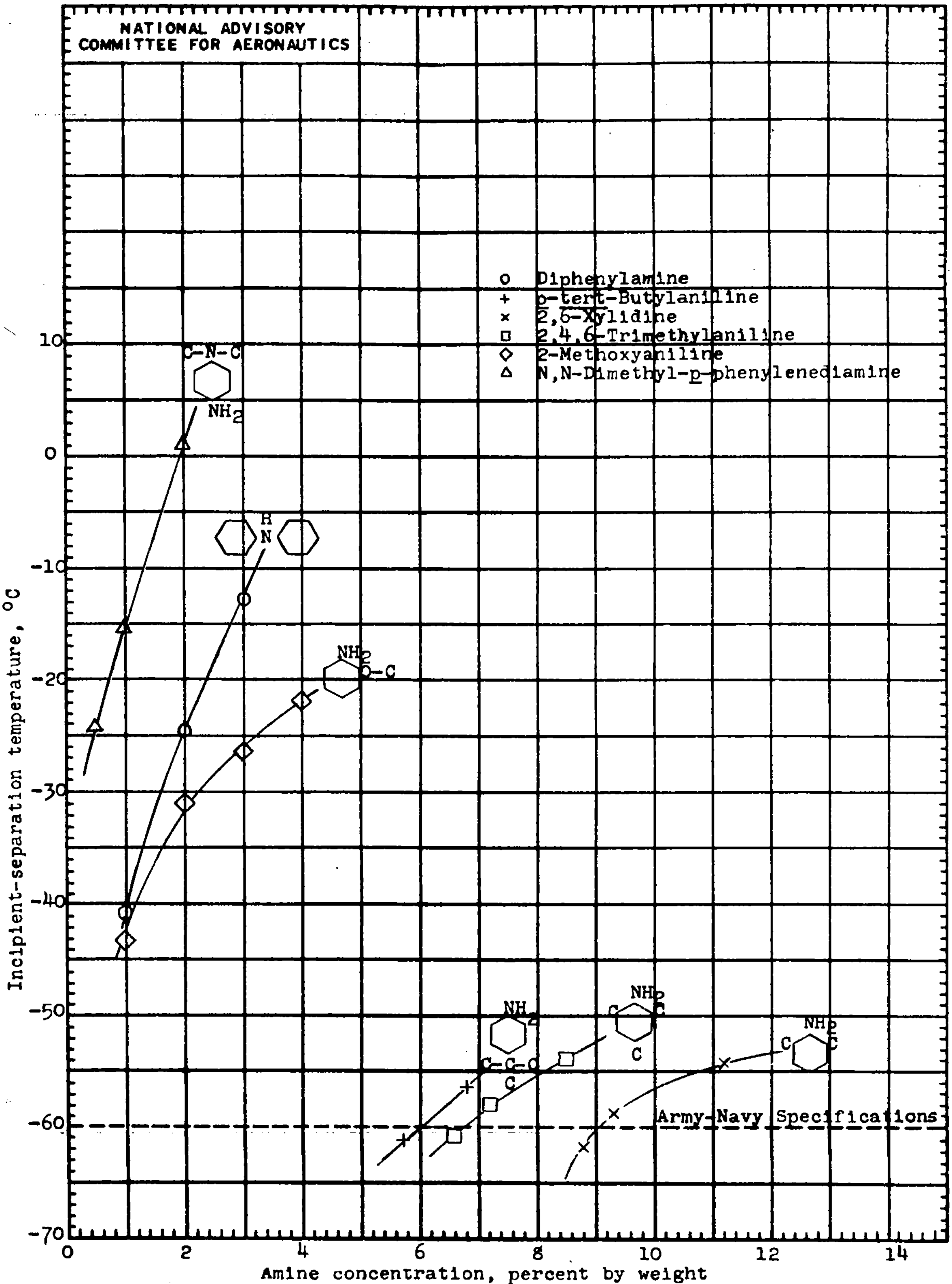

Figure 5. - Solubility of aromatic amines in grade 130 gasoline.