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THE LOW-TEMPERATURE SOLUBILITY OF 42 AROMATIC AMINES IN AVIATION GASOLINE

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NACA

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

MEMORANDUM REPORT

for the

Air Technical Service Command, Army Air Forces

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INTRODUCTION

At the request of the Air Technical Service Command, Army Air Forces, a general investigation of the suitability of aromatic amines as antiknock additives for aviation gasoline has been conducted at the NACA Cleveland laboratory between April 1943 and April 1945. The program included the determinations of antiknock effectiveness (references 1 to 6), of suitability for overwater storage (reference 7), and of the solubility in gasoline at low temperatures (references 8 and 9) for aviation gasolines containing aromatic amines.

The present paper is the third and final report on the solubilities of amines in aviation gasoline at low temperatures, such as would be encountered in cold-weather operation or in flight, and summarizes the data reported in the first two papers (references 8 and 9); solubilities of seven additional amines, N-methyl-o-toluidine, N-methyl-toluidines from chlorotoluenes, o-ethylaniline, N-methyl-p-ethylaniline, N-methylethylaniline (mixed isomers from chloroethylbenzenes), N-methyl-p-isopropylaniline, and N-methyldiphenylamine, are included herein. Solubilities of the 42 amines were measured at temperatures as low as -65° C, 5° below the usual Army-Navy freezing specification of -60° C, and at concentrations as high as 10 percent by weight, well above the 1- to 3-percent range in which amines have been used in gasoline. Determination of solubility at -60° C was a particular objective in obtaining the data. Because gasoline composition affects the solubility of the amines, solubilities were determined in an aromatic-free gasoline, a gasoline of known aromatic content, and a typical AN-F-28 fuel.

GASOLINE AND AMINE SPECIFICATIONS

The base fuels used for the present investigation are the same as those used in references 8 and 9 and have the following compositions:

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

2. 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 typical current aviation gasoline, AN-F-28, Amendment-2, fuel containing 12 to 20 percent aromatic hydrocarbons by volume

The physical properties determined at the Cleveland laboratory for the amines are given in table I. The amines reported herein for the first time are N-methyl-o-toluidine, N-methyl-toluidines from chlorotoluenes, o-ethylaniline, N-methyl-p-ethylaniline, N-methyl-ethylaniline (mixed isomers from chloroethylbenzenes), N-methyl-p-isopropylaniline, and N-methyl-diphenylamine.

APPARATUS AND PROCEDURE

The apparatus used is shown in figure 1. A gasoline-sample tube 30 by 2.5 centimeters was provided with a vent and drying tube, an air-motor-driven glass stirrer rotating in a bushing, and a three-junction iron-constantan thermopile. The gasoline-sample tube was held in place with a rubber stopper in a 25 by 7 centimeter clear glass Dewar flask through which acetone as a coolant was circulated by a centrifugal pump. The acetone was cooled by circulating it through approximately 35 feet of copper tubing coiled in a dry-ice kerosene bath. The coolant temperature was regulated by means of a valve line bypassing the refrigeration bath. A thermometer in a well in the coolant line permitted visual observation of the coolant temperature. The Dewar flash containing the sample tube was supported in a tight-fitting insulated box provided with windows. A small quantity of phosphorous pentoxide was placed in the bottom of the insulated box as a drying agent to prevent fogging of the glass Dewar flask by condensed water. The three-junction iron-constantan thermopile was used to measure the gasoline temperature with distilled-water ice as the standard reference temperature. The thermopile was calibrated against a platinum resistance thermometer, which had been calibrated by the National Bureau of Standards.

The samples were prepared by weighing a quantity of the aromatic amine on an analytical balance and then adding gasoline to the amine until the resulting solution had a specified amine content.

The gasoline solution was transferred to the sample tube. The glass stirrer was started and the solution was slowly cooled until the amine separated from the gasoline and formed a cloud; this temperature was recorded. The solution was then slowly warmed until the amine went into solution and the cloud disappeared. These two temperatures were averaged to give the incipient-separation temperature or "cloud point." Cloud points were reproducible among samples to within ±1.5° C.

Data for N-butylaniline, p-toluidine, p-tert-butylaniline and 2, 4, 6-trimethylaniline are not included in this report because their solubilities were determined by the saturation method (reference 8) and the accuracy of the previously reported results is doubtful. At constant temperature a sample of gasoline saturated with amine is drawn through a filter tube into a cooled receiving vessel by low pressure. The amine has a tendency to so clog the chamois filter that at low pressure some of the gasoline is transferred by vaporization to the receiver. Inasmuch as the amine is not transferred with the vaporized gasoline, the results by the saturation method tend to be low.

RESULTS AND DISCUSSION

The solubilities of the amines in the aromatic-free gasoline, in the gasoline of 15 percent aromatic content, and in the AN-F-28 fuel are presented in figures 2, 3, and 4, respectively. The amines that were soluble to at least 10 percent by weight at -60° C in each of the gasolines are:

N-Ethylaniline
N-Propylaniline
N-Isopropylaniline
N-tert-Butylaniline
N,N-Diethylaniline

N-Methyl-p-toluidine
N-Methyl-o-toluidine
N-Methyltoluidines (from chlorotoluenes)
N-Ethyl-p-toluidine
N-Isopropyl-p-toluidine
N-Methyl-p-ethylaniline
N-Methylethylaniline, mixed isomers (from chloroethylbenzenes)
o-Isopropylaniline
p-Isopropylaniline
N-Methyl-p-isopropylaniline
N-Isopropyl-p-isopropylaniline
Cumidines (from synthetic cumenes)
Cumidines (from refinery cumenes)
N-Methylcumidines (from bromocumenes)
N-Methyl-p-tert-butylaniline
N-Methyl-2,4-xylidine
N-Methylxylidines (from bromoxylenes)
2,4-Diethylaniline
2-Methyl-5-isopropylaniline
N,N-Dimethyl-2-methyl-5-isopropylaniline
N,N-Dimethyl-2,4,6-trimethylaniline
Pseudocumidine (technical)

At room temperature N-methyl-p-phenylenediamine and p-phenylenediamine were less than 0.5 percent by weight soluble in the test gasolines; no additional solubility data were taken for these compounds. At room temperature N,N'-dimethyl-p-phenylenediamine was soluble to the extent of 1 to 2 percent by weight 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.

The composition of the gasoline influenced the amine solubilities to a large extent. The addition of 15 percent aromatics to the aromatic-free gasoline approximately doubled or tripled the amine solubility. Solubilities in the AN-F-28 fuel were of the same magnitude as in the gasoline containing 15 percent aromatics. Representative samples of AN-F-28 fuel contained 12 to 20 percent by volume of aromatics.

A summary of the solubilities of the amines at -60° C in the different test gasolines is presented in table II. The results were obtained by interpolating or extrapolating the experimental data. The data for commercial xylidines obtained from reference 10 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 on the basis of solubility alone. The aromatic hydrocarbons present in most of the current aviation fuels would provide a margin of safety in preventing this concentration of amine from separating 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:

N-Methylaniline
N-Ethylaniline
N-Propylaniline
N-Isopropylaniline
N-tert-Butylaniline
N,N-Dimethylaniline
N,N-Diethylaniline
N-Methyl-p-toluidine
N-Methyl-o-toluidine
N-Methyltoluidines (from chlorotoluenes)
N-Ethyl-p-toluidine
N-Isopropyl-p-toluidine
N-Methyl-p-ethylaniline
N-Methylethylaniline, mixed isomers (from chloroethylbenzenes)
o-Isopropylaniline
p-Isopropylaniline
N-Methyl-p-isopropylaniline
N-Isopropyl-p-isopropylaniline
Cumidines (from synthetic cumenes)
Cumidines (from refinery cumenes)
N-Methyl-p-tert-butylaniline
Xylidines (commercial)
N-Methyl-2,4-xylidine
N-Methylxylidines (from bromoxylenes)
2,4-Diethylaniline
2-Methyl-5-isopropylaniline
N,N-Dimethyl-2-methyl-5-isopropylaniline
N,N-Dimethyl-2,4,6-trimethylaniline
Pseudocumidine (technical)
N-Methyldiphenylamine

Adding an alkyl group to the nitrogen of the amine had a greater solubilizing effect than adding the same alkyl group to the aromatic ring. For example, N-methylaniline is more soluble than any of the toluidines and N-ethylaniline is more soluble than o-ethylaniline.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, November 9, 1945.

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TABLE I - PHYSICAL PROPERTIES OF AROMATIC AMINES

Amine	Boiling range[a] (°C)	Index of refraction n_D^{20}	Density (grams/ml)
Aniline	184-184.5	1.5853	1.0220
N-Methylaniline	195-196	1.5704	.9860
N-Ethylaniline	203-204	1.5538	.9607
N-Propylaniline	220.5-223.5	1.5425	.9448
N-Isopropylaniline	206.5-209	1.5404	.9374
N-tert-Butylaniline	95 at 16 mm	1.5270	.9244
N,N-Dimethylaniline	192.5-193.5	1.5580	.9564
N,N-Diethylaniline	215-217	1.5418	.9347
o-Toluidine	198.5-201.5	1.5718	.9989
m-Toluidine	202.5-203.5	1.5674	.9893
N-Methyl-p-toluidine	209-211	1.5570	.9610
N-Methyl-o-toluidine	206.5-207.5	1.5646	.9763
N-Methyltoluidines (from chlorotoluenes)	208.5-215.0	1.5600	.9668
N-Ethyl-p-toluidine	217-220	1.5439	.9441
N-Isopropyl-p-toluidine	222-223	1.5319	.9238
o-Ethylaniline	211	1.5602	.9810
N-Methyl-p-ethylaniline	227.5	1.5485	.9485
N-Methylethylaniline, mixed isomers (from chloroethylbenzenes)	222.5-230.5	1.5493	.9503
o-Isopropylaniline	219-220	1.5484	.9643
p-Isopropylaniline	225.5-226.5	1.5432	.9514
N-Methyl-p-isopropylaniline	240	1.5390	.9347
N-Isopropyl-p-isopropylaniline	246-247	1.5209	.9075
Cumidines (from synthetic cumenes)	225-226	1.5448	.9536
Cumidines (from refinery cumenes)	220-241	1.5434	.9531
N-Methylcumidines (from bromocumenes)	237.5-241.5	1.5390	.9366
N-Methyl-p-tert-butylaniline	245.5-249.5	1.5348	.9305
2-Methoxyaniline	224-225	1.5750	1.0931
Xylidines (commercial)	216-219.5	1.5601	.9771
2,6-Xylidine	216-217	1.5616	.9768
N-Methyl-2,4-xylidine	221-222	1.5542	.9582
N-Methylxylidines (from bromoxylenes)	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
N,N-Dimethyl-2,4,6-trimethylaniline	213.5	1.5116	.9066
Pseudocumidine (technical)	225-241	1.5568	.9720
Diphenylamine	[b]52.9-53.6	----------	-------
p-Phenylenediamine	[b]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	----------	-------
N-Methyldiphenylamine	295-296	1.6224	1.0527

[a]Boiling range at 760 mm Hg except where noted.

[b]Melting point measured for this solid rather than boiling range.

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TABLE II - SOLUBILITY OF AROMATIC AMINES

IN THREE AVIATION FUELS AT -60° C

[Percentages by weight]

Amine	Aromatic-free grade 65	Aromatic-free grade 65 plus 15 percent by volume aromatics[a]	AN-F-28
Aniline	<0.5	0.5	-------
N-Methylaniline	3.6	12(-62° C)	>10
N-Ethylaniline	>10	>10	>10
N-Propylaniline	>10	>10	>10
N-Isopropylaniline	>10	>10	>10
N-*tert*-Butylaniline	>10	>10	>10
N,N-Dimethylaniline	4.7	9.8	8.3
N,N-Diethylaniline	>10	>10	>10
o-Toluidine	1.3	4.2	4.4
m-Toluidine	<0.5	2.6	3.6
N-Methyl-*p*-toluidine	>10	>10	>10
N-Methyl-*o*-toluidine	>10	>10	>10
N-Methyltoluidines (from chlorotoluenes)	>10	>10	>10
N-Ethyl-*p*-toluidine	>10	>10	>10
N-Isopropyl-*p*-toluidine	>10	>10	>10
o-Ethylaniline	0.9	>10	>10
N-Methyl-*p*-ethylaniline	>10	>10	>10
N-Methylethylaniline, mixed isomers (from chloroethylbenzenes)	>10	>10	>10
o-Isopropylaniline	>10	>10	>10
p-Isopropylaniline	>10	>10	>10
N-Methyl-*p*-isopropylaniline	>10	>10	>10
N-Isopropyl-*p*-isopropylaniline	>10	>10	>10
Cumidines (from synthetic cumenes)	>10	>10	>10
Cumidines (from refinery cumenes)	>10	>10	>10
N-Methylcumidines (from bromocumenes)	>10	>10	>10
N-Methyl-*p*-*tert*-butylaniline	>10	>10	>10
2-Methoxyaniline	<0.5	<0.5	<0.5
Xylidines (commercial) reference 10	3.7	>10	>10
2,6-Xylidine	4.6	11.1	9.1
N-Methyl-2,4-xylidine	>10	>10	>10
N-Methylxylidines (from bromoxylenes)	>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
N,N-Dimethyl-2,4,6-trimethylaniline	>10	>10	>10
Pseudocumidine (technical)	>10	>10	>10
Diphenylamine	<0.5	-------------	<0.5
p-Phenylenediamine	[b]<0.5	[b]<0.5	[b]<0.5
N-Methyl-*p*-phenylenediamine	[b]<0.5	[b]<0.5	[b]<0.5
N,N-Dimethyl-*p*-phenylenediamine	<0.5	<0.5	<0.5
N,N-Diethyl-*p*-phenylenediamine	<0.5	-------------	-------
N,N'-Dimethyl-*p*-phenylenediamine	<0.5	-------------	-------
N-Methyldiphenylamine	3.3	>10	>10

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

[b]Solubility at room temperature.

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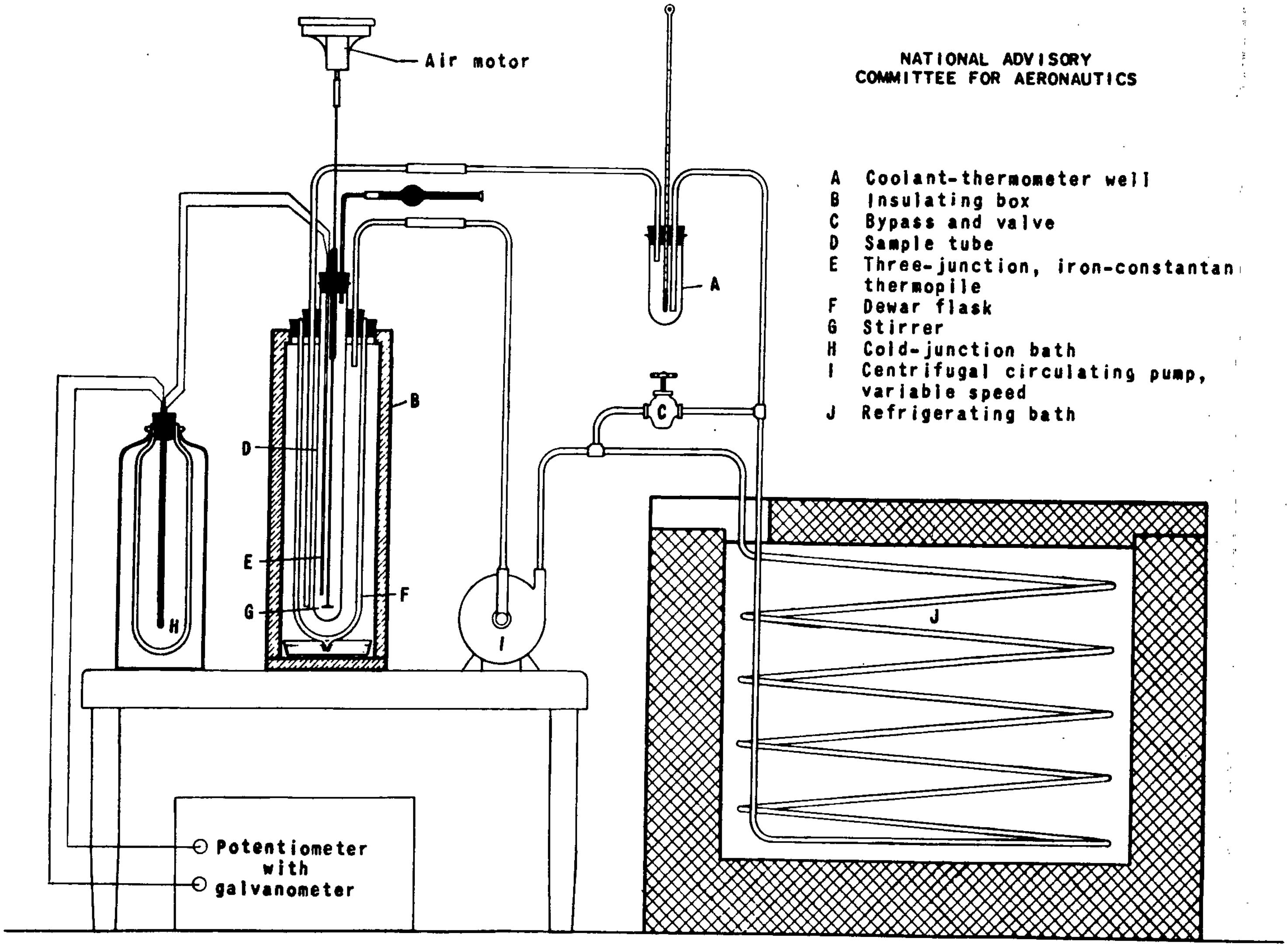

Figure 1. - Apparatus for the determination of cloud point.

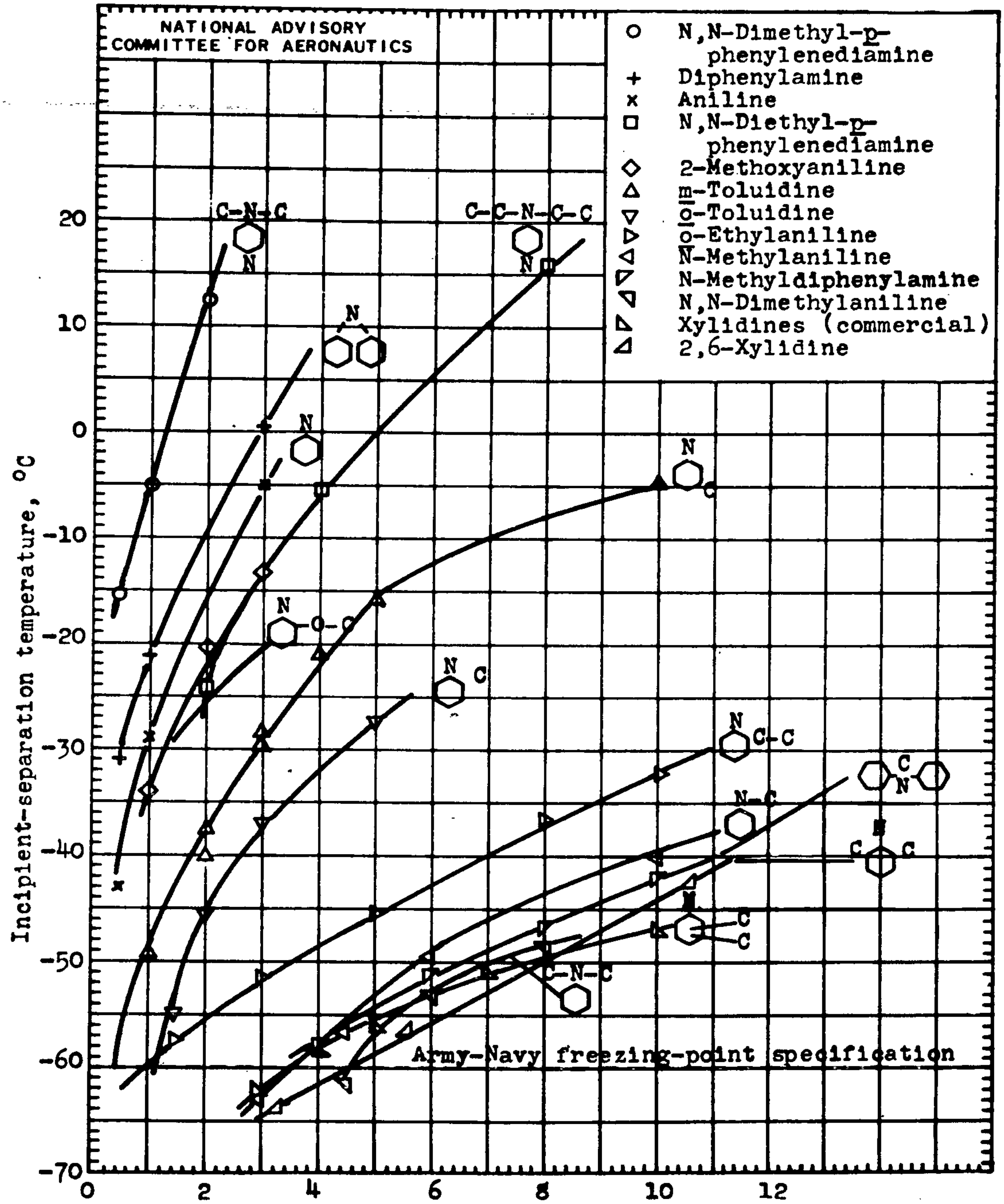

Figure 2. - Solubility of aromatic amines in grade 65 base stock with the aromatic hydrocarbons extracted.

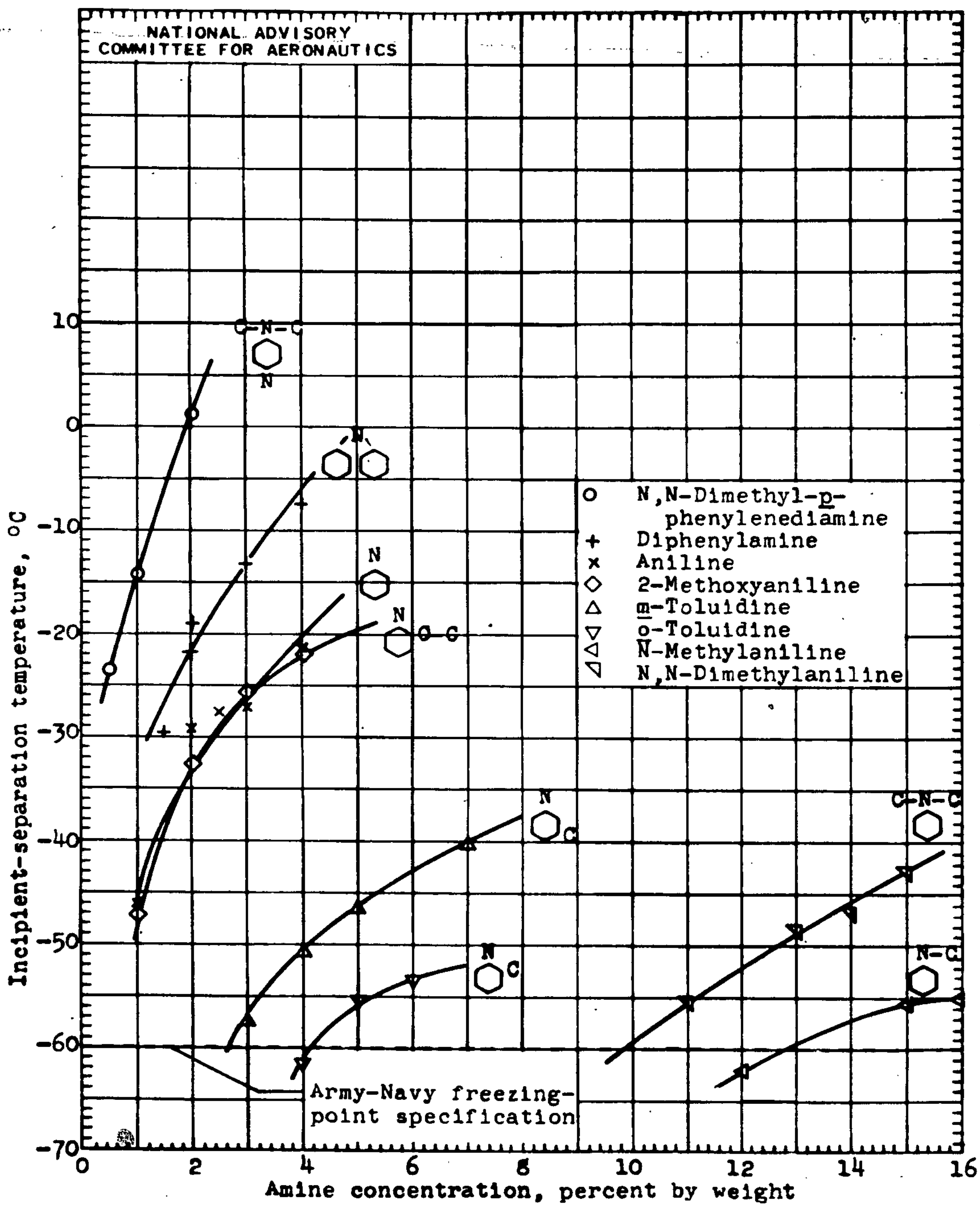

Figure 3. - Solubility of aromatic amines in blend of 85 percent extracted grade 65 base stock and 15 percent by volume of aromatic mixture consisting of 15 parts xylene, 2 parts cumene, and 1 part toluene.

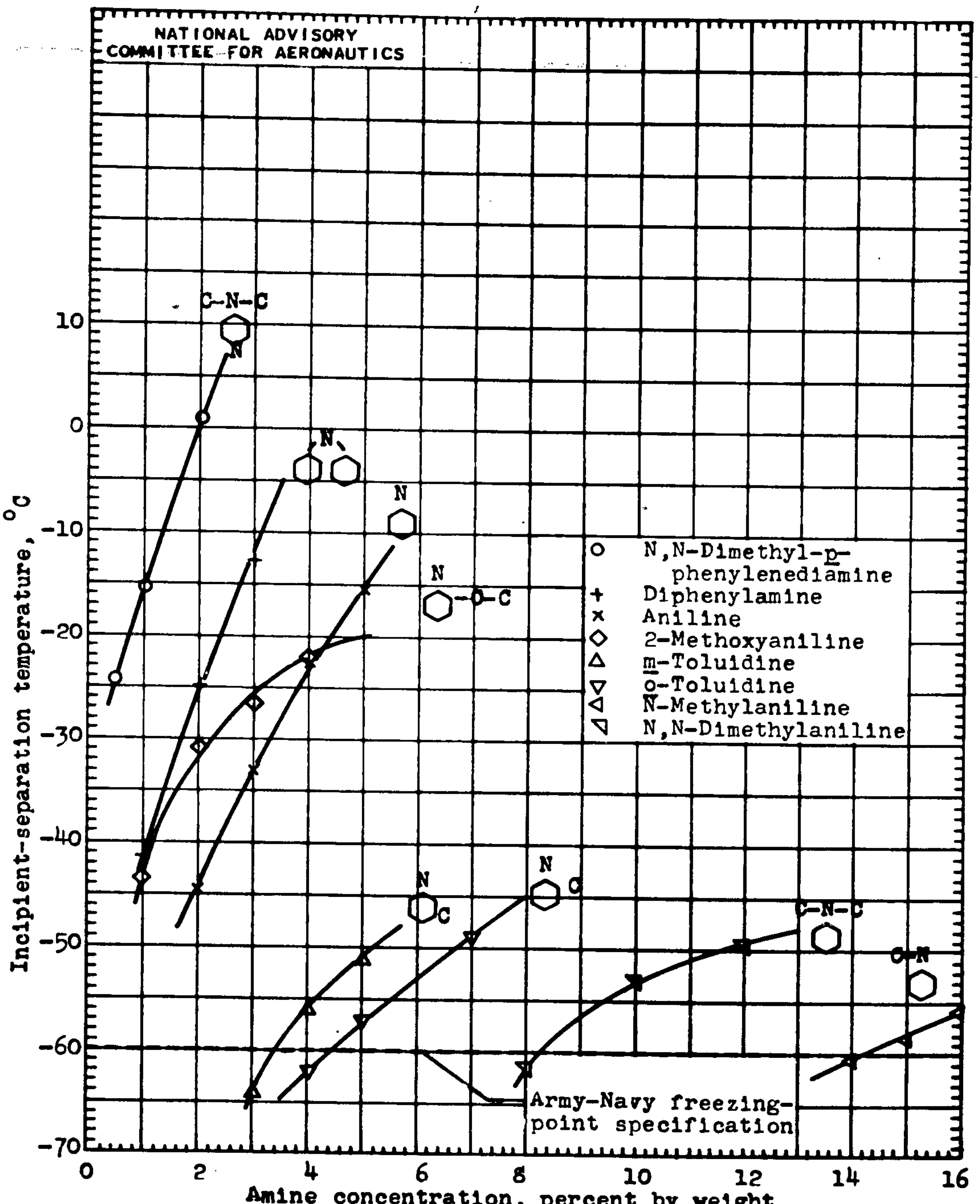

Figure 4. - Solubility of aromatic amines in AN-F-28, Amendment-2, fuel.