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RESEARCH MEMORANDUM

KNOCK-LIMITED POWER OUTPUTS FROM A CFR ENGINE USING INTERNAL COOLANTS

III - FOUR ALKYL AMINES, THREE ALKANOLAMINES SIX AMIDES, AND EIGHT HETEROCYCLIC COMPOUNDS

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON

February 3, 1947

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SUMMARY

Investigations were conducted to determine the antiknock effectiveness of various additive-water solutions used as internal coolants in conjunction with AN-F-28, Amendment-2, fuel in a modified CFR engine. Each internal-coolant solution was injected at a coolant-fuel ratio of 0.50 and contained 70-percent water and 30-percent by weight of each of the following compounds:

Alkyl amines
- Isopropylamine
- Isobutylamine
- *tert*-Butylamine
- Monoamylamine

Alkanolamines
- Ethanolamine
- Diethanolamine
- 2-Amino-2-methyl-1-propanol

Amides
- Formamide
- N-Ethylformamide
- N-Ethylacetamide
- N-Ethylpropionamide
- N,N-Dimethylformamide
- N,N-Diethylacetamide

Heterocyclic compounds
- 2,2-Dimethylethylenimine
- Morpholine
- Pyridine
- 2-Methylpyridine
- 3-Methylpyridine
- 4-Methylpyridine
- 2,6-Dimethylpyridine
- 2-Vinylpyridine

Results of investigations are also presented for AN-F-28, Amendment-2, fuel run with no internal coolant and with water alone as the internal coolant at coolant-fuel ratios of 0.35 and 0.50. Three of the alkyl amines, the six amides, and six of the heterocyclic compounds raised the knock limit of the base fuel more than an equivalent amount of water at most of the fuel-air ratios investigated. Ethanolamine and 2-amino-2-methyl-1-propanol raised the knock limit more than an equivalent amount of water at fuel-air ratios greater than 0.093. The 21 compounds investigated were less effective in raising the knock limit than monomethylamine, dimethylamine, and ethylenediamine, which were previously investigated.

INTRODUCTION

An investigation of the antiknock effectiveness of various additive-water solutions when used as internal coolants has been conducted at the NACA Cleveland laboratory. Nine compounds have been previously run in a CFR engine and the results are presented in references 1 to 3. Of the nine compounds, monomethylamine, dimethylamine, and ethylenediamine permitted the greatest increases in knock-limited power. From considerations of the physical properties, however, the use of these compounds as internal coolants would be restricted. For example, monomethylamine and dimethylamine are gaseous at room temperature and have limited solubilities in water. Ethylenediamine, as well as monomethylamine and dimethylamine, is corrosive in contact with copper.

In an effort to find a good antiknock-coolant additive with more desirable physical properties than those of the nine compounds previously investigated, water solutions of four alkyl amines, three alkanolamines, six amides, and eight heterocyclic compounds were investigated and the results are presented.

INTERNAL COOLANTS AND BASE FUEL

Each additive-water solution contained 30-percent additive by weight. Boiling points and solubilities of the pure additives are presented in the following table:

Additive	Physical properties			
	Boiling point (°C)	Solubility (a)		
		Water	Alcohol	Ether
Alkyl amines				
Isopropylamine	34	∞	∞	∞
Isobutylamine	68	∞	∞	∞
tert-Butylamine	46	∞	∞	∞
Monoamylamine (mixed isomers)	84-110	vs	-------	-----
Alkanolamines				
Ethanolamine	172	∞	∞	vss
Diethanolamine	268	∞	∞	ss
2-Amino-2-methyl-1-propanol	165	∞	-------	-----
Amides				
Formamide	211	∞	∞	ss
N-Ethylformamide	198	∞	∞	∞
N-Ethylacetamide	205	∞	∞	-----
N-Ethylpropionamide[b]	-------	-------	-------	-----
N,N-Dimethylformamide	155	s	s	s
N,N-Diethylacetamide	187	s	s	s
Heterocyclic compounds				
2,2-Dimethylethylenimine	71	-------	-------	-----
Morpholine	128	∞	s	s
Pyridine	115	∞	∞	∞
2-Methylpyridine	128	vs	∞	∞
3-Methylpyridine	144	∞	∞	∞
4-Methylpyridine	143	∞	∞	∞
2,6-Dimethylpyridine	143	{∞ cold, s hot}	s	s
2-Vinylpyridine	159	vss	vs	vs

[a]The following abbreviations are used to indicate the solubilities of the additives: ∞, infinitely soluble; vs, very soluble; s, soluble; ss, slightly soluble; vss, very slightly soluble.

[b]No data are available for this compound.

In addition to runs made with additive-water solutions as internal coolants, runs were also made with water alone as the internal coolant.

The additive-water solutions were prepared at this laboratory from commercial-grade compounds and distilled water. The 2,2-dimethylethylenimine and the *tert*-butylamine compounds were not available commercially and were prepared at this laboratory. The correct concentration of 2,6-dimethylpyridine could be maintained only at temperatures of 20° C or less. This solution was kept in an ice bath while being run.

The merits of the internal-coolant solutions were determined by the effect of the coolant on the knock-limited performance of AN-F-28, Amendment-2, fuel. A single batch of this fuel was used in this present investigation and in the investigations reported in references 2 and 3.

In order to avoid confusion, the following definitions are used:

(1) Fuel: AN-F-28, Amendment-2, used as base fuel

(2) Water-fuel ratio: weight ratio of water containing no additive to AN-F-28, Amendment-2, fuel

(3) Additive-water ratio: weight ratio of pure additive to water

(4) Internal coolant: either pure water or additive-water solution

APPARATUS AND PROCEDURE

The engine, auxiliary equipment, and procedure of investigating the internal coolants were the same as described in reference 3. The additive-water solutions were run at a coolant-fuel ratio of 0.50. Water alone was run at coolant-fuel ratios of 0.35 and 0.50 by weight.

The following engine conditions were maintained constant throughout the program:

Engine speed, rpm	2500
Compression ratio	7.0
Spark advance, deg B.T.C.	30
Inlet-air temperature, °F	250
Jacket temperature, °F	250

PRESENTATION AND DISCUSSION OF RESULTS

Knock-limited indicated mean effective pressures and indicated specific fuel consumptions plotted against fuel-air ratio for fuel with and without water as an internal coolant are presented in figure 1. Similar data for fuel with internal-coolant solutions containing 70-percent water by weight and 30-percent of each of the 21 additives are presented in figures 2 to 4.

The following table indicates the reproducibility of the data by giving ratios of arithmetical-mean deviation to average knock-limited indicated mean effective pressure (expressed as percentage) as determined from the runs of fuel alone and with water as an internal coolant:

Water-fuel ratio	Number of runs	Ratio of arithmetical-mean deviation to knock-limited imep (percent)					
		Fuel-air ratio					
		0.05	0.06	0.07	0.08	0.09	0.10
0	4	3.4	3.3	2.8	3.8	2.0	2.7
0.50	2	--------	5.5	1.0	.8	2.0	1.8

The values in this table were determined from runs made at intervals throughout the program and indicate that a good degree of reproducibility was obtained. The reproducibility of the knock-limited performance when using internal-coolant additives, however, was not checked because of limited supplies.

The results obtained in this investigation are presented in table I in terms of the ratios of the knock-limited indicated mean effective pressures obtained when using coolant additives to those obtained when using water alone at two different water-fuel ratios. The upper and lower values were determined by the following ratios:

upper value,

$$\frac{\text{knock-limited imep of } 0.50\ (0.30 \text{ additive} + 0.70 \text{ water}) + 0.50 \text{ fuel}}{\text{knock-limited imep of } 0.35 \text{ water} + 0.65 \text{ fuel}}$$

lower value,

$$\frac{\text{knock-limited imep of } 0.50\ (0.30 \text{ additive} + 0.70 \text{ water}) + 0.50 \text{ fuel}}{\text{knock-limited imep of } 0.50 \text{ water} + 0.50 \text{ fuel}}$$

An upper value above 1.00 indicates that the addition of the additive raised the knock limit. This improvement in knock-limited performance can be attributed to the effect of the additive as an antiknock agent and to the improvement in cooling resulting from the addition of more internal coolant per pound of fuel. A lower value above 1.00 indicates that the additive raised the knock limit a greater amount than an equivalent amount of water. As before, this improvement may result from the antiknock quality of the additive as well as the cooling properties. From this discussion, an upper value above 1.00 together with a lower value below 1.00 therefore denotes that the additive raised the knock limit but not as much as an equivalent amount of water.

Monoamylamine, diethanolamine, 2,2-dimethylethylenimine, and morpholine were less effective than water as internal coolants for all values of fuel-air ratio. Ethanolamine and 2-amino-2-methyl-1-propanol were more effective than water as internal coolants at fuel-air ratios greater than 0.093 but were less effective than water at lower fuel-air ratios. The alkyl amines (with the exception of monoamylamine), the amides, and the heterocyclic compounds (with the exception of 2,2-dimethylethylenimine and morpholine) were more effective than water as internal coolants for most values of fuel-air ratio.

The bar graph (fig. 5) compares at fuel-air ratios of 0.06, 0.08, and 0.10 the effectiveness of the internal-coolant additives run during this investigation with that of six internal coolants previously reported in reference 3. The values used in the graph are ratios of the knock-limited indicated mean effective pressure permitted with an additive-water solution as the internal coolant to that permitted with water alone as the internal coolant at a coolant-fuel ratio of 0.50. Monomethylamine, dimethylamine, and ethylenediamine are more effective as internal-coolant additives than any of the other 24 compounds.

SUMMARY OF RESULTS

The results of investigations of water solutions of four alkyl amines, three alkanolamines, six amides, and eight heterocyclic compounds as internal-coolant additives in a CFR engine may be summarized as follows:

1. Three alkyl amines, the six amides, and six heterocyclic compounds were more effective than water as internal coolants for most values of fuel-air ratio.

2. Monoamylamine, diethanolamine, 2,2-dimethylethylenimine, and morpholine were less effective than water as internal coolants for all values of fuel-air ratio. Ethanolamine and 2-amino-2-methyl-1-propanol raised the knock limit at fuel-air ratios greater than 0.093.

3. The 21 compounds investigated were less effective in raising the knock limit than monomethylamine, dimethylamine, and ethylenediamine, which were previously investigated.

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National Advisory Committee for Aeronautics,
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REFERENCES

1. Bellman, Donald R., and Evvard, John C.: Knock-Limited Performance of Several Internal Coolants. NACA ACR No. 4B08, 1944. (Classification changed from "Confidential" to "Restricted", April 1946.)

2. Bellman, Donald R., Moeckel, W. E., and Evvard, John C.: Knock-Limited Power Outputs from a CFR Engine Using Internal Coolants. I - Monomethylamine and Dimethylamine. NACA ARR No. E4L21, 1944.

3. Bellman, Donald R., Moeckel, W. E., and Evvard, John C.: Knock-Limited Power Outputs from a CFR Engine Using Internal Coolants. II - Six Aliphatic Amines. NACA ACR No. E5H31, 1945. (Classification changed from "Confidential" to "Restricted", April 1946.)

TABLE I - SUMMARY OF ANTIKNOCK EFFECTIVENESS OF VARIOUS

COMPOUNDS AS INTERNAL-COOLANT ADDITIVES

[CFR engine; AN-F-28, Amendment-2, fuel; engine speed, 2500 rpm; compression ratio, 7.0; spark advance, 30° B.T.C.; inlet-air temperature, 250° F; jacket temperature, 250° F. For each additive there are two rows of values. The upper value is the ratio

$$\frac{\text{knock-limited imep of 0.50 (0.30 additive + 0.70 water) + 0.50 fuel}}{\text{knock-limited imep of 0.35 water + 0.65 fuel}}$$

The lower value is the ratio

$$\frac{\text{knock-limited imep of 0.50 (0.30 additive + 0.70 water) + 0.50 fuel}}{\text{knock-limited imep of 0.50 water + 0.50 fuel}}$$]

Additive	Fuel-air ratio[a]					
	0.05	0.06	0.07	0.08	0.09	1.10
Alkyl amines						
Isopropylamine	1.01	1.14	1.30	1.14	1.12	1.01
	.97	1.00	1.10	1.07	.98	.99
Isobutylamine	1.17	1.23	1.39	1.28	1.32	1.09
	1.12	1.08	1.18	1.20	1.15	1.07
tert-Butylamine	1.05	1.16	1.37	1.21	1.21	1.02
	1.00	1.02	1.17	1.14	1.07	1.00
Monoamylamine (mixed isomers)	.84	.96	1.09	1.04	1.02	.92
	.80	.84	.93	.97	.90	.90
Alkanolamines						
Ethanolamine	0.77	0.86	1.13	1.04	1.09	1.25
	.74	.76	.96	.98	.96	1.23
Diethanolamine	.69	----	----	.62	.77	.73
	.66	----	----	.58	.67	.72
2-Amino-2-methyl-1-propanol	.77	.86	.96	.97	1.08	1.04
	.74	.76	.81	.91	.95	1.02

[a]The compounds were not considered as fuels and the heats of combustion were neglected in computing the fuel-air ratios.

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TABLE I - SUMMARY OF ANTIKNOCK EFFECTIVENESS OF VARIOUS

COMPOUNDS AS INTERNAL-COOLANT ADDITIVES - Continued

Additive	Fuel-air ratio[a]					
	0.05	0.06	0.07	0.08	0.09	0.10
Amides						
Formamide	1.04	1.04	1.30	1.19	1.27	1.13
	.99	.92	1.11	1.11	1.12	1.10
N-Ethylformamide	1.07	1.19	1.33	1.28	1.24	1.07
	1.02	1.05	1.13	1.21	1.09	1.05
N-Ethylacetamide	.99	1.18	1.26	1.20	1.22	1.04
	.95	1.04	1.08	1.12	1.07	1.02
N-Ethylpropionamide	1.03	1.22	1.38	1.23	1.28	1.09
	.99	1.08	1.17	1.16	1.12	1.06
N,N-Dimethylformamide	.93	1.11	1.26	1.13	1.12	.96
	.89	.98	1.07	1.06	.99	.94
N,N-Diethylacetamide	.93	1.10	1.28	1.18	1.10	.96
	.89	.97	1.09	1.11	.96	.94
Heterocyclic compounds						
2,2-Dimethylethylenimine	0.82	0.91	1.09	0.99	1.03	0.97
	.79	.80	.93	.93	.91	.95
Morpholine	.79	.88	1.06	1.01	.98	.89
	.76	.77	.90	.95	.85	.87
Pyridine	.98	1.16	1.38	1.27	1.25	1.03
	.94	1.02	1.17	1.19	1.10	1.01
2-Methylpyridine	.96	1.12	1.37	1.30	1.25	1.06
	.92	.99	1.16	1.22	1.10	1.03
3-Methylpyridine	.93	1.12	1.32	1.19	1.26	1.05
	.89	.99	1.12	1.12	1.10	1.03
4-Methylpyridine	.96	1.12	1.38	1.32	1.27	1.06
	.92	.98	1.18	1.24	1.12	1.03
2,6-Dimethylpyridine	.90	1.13	1.37	1.25	1.28	1.05
	.86	.99	1.16	1.17	1.13	1.03
2-Vinylpyridine	1.09	1.24	1.31	1.24	1.22	1.07
	1.05	1.09	1.12	1.16	1.07	1.04

[a]The compounds were not considered as fuels and the heats of combustion were neglected in computing the fuel-air ratios.

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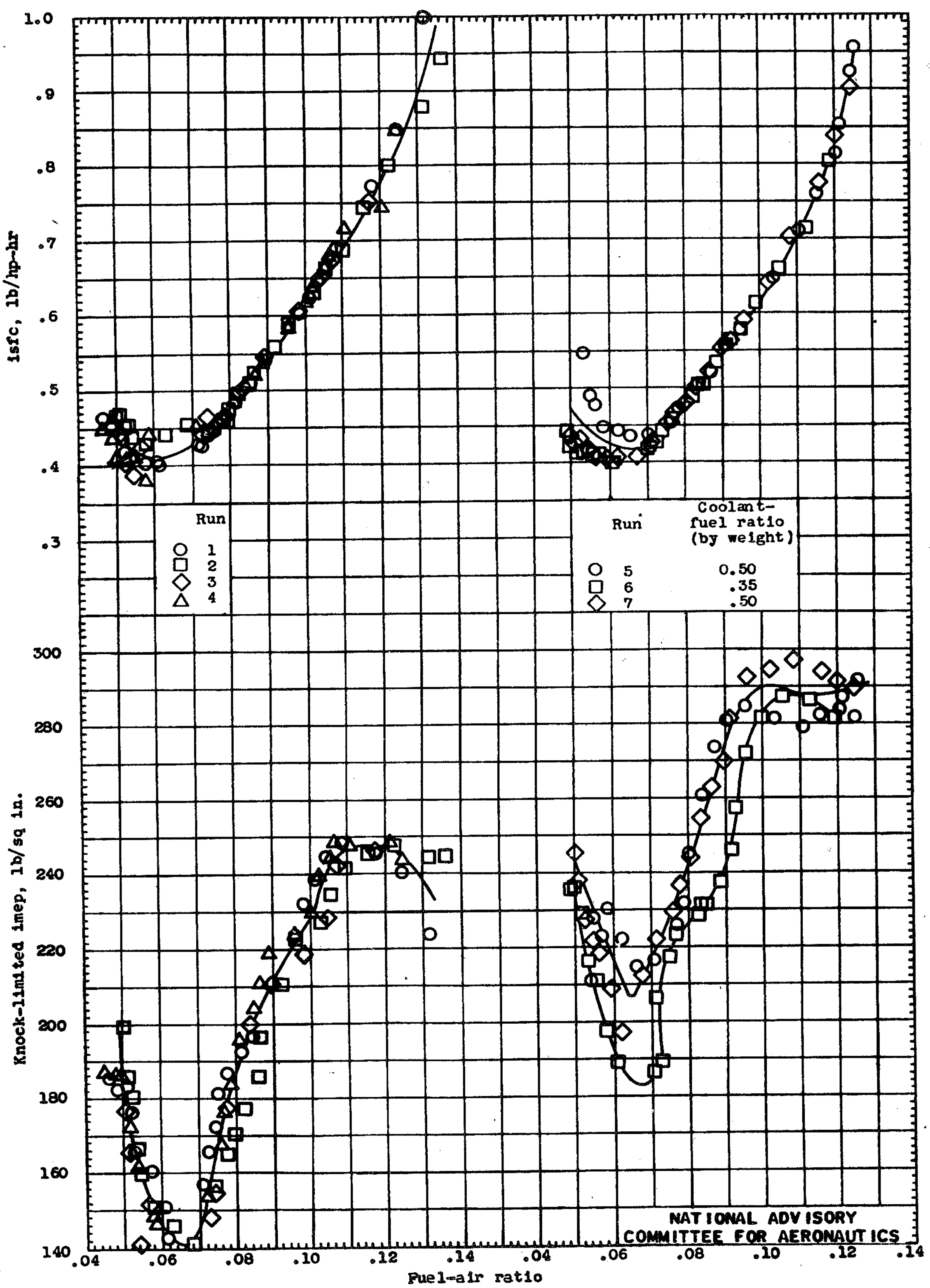
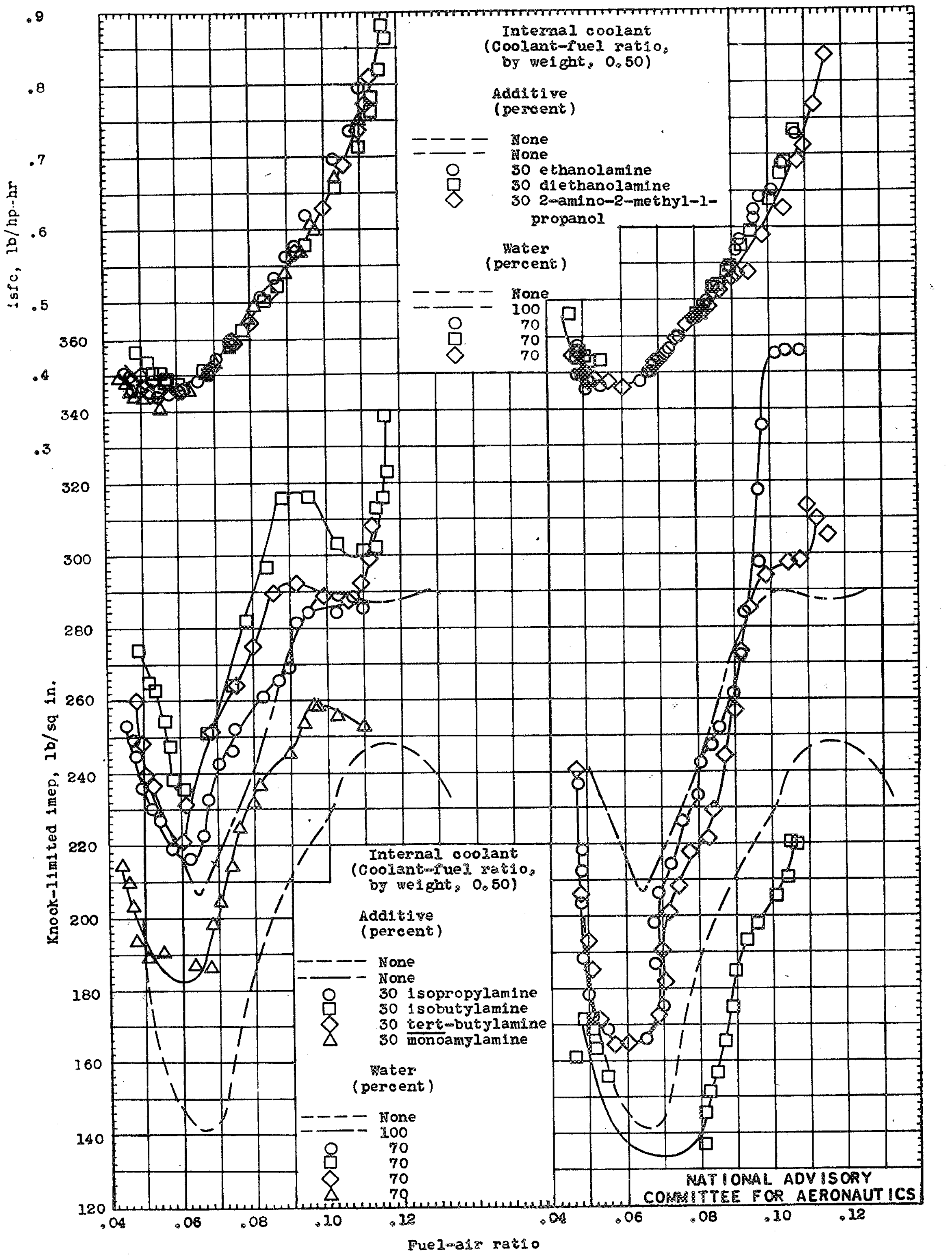


(a) No internal coolant. (b) Internal coolant, water.

Figure 1. - Effect of water as internal coolant on knock-limited performance of AN-F-28, Amendment-2, fuel. CFR engine; engine speed, 2500 rpm; compression ratio, 7.0; spark advance, 30° B.T.C.; inlet-air temperature, 250° F; jacket temperature, 250° F.



(a) Internal-coolant additives, alkyl amines. (b) Internal-coolant additives, alkanolamines.

Figure 2. - Effect of various alkyl amines and alkanolamines as internal-coolant additives on knock-limited performance of AN-F-28, Amendment-2, fuel. CFR engine; engine speed, 2500 rpm; compression ratio, 7.0; spark advance, 30° B.T.C.; inlet-air temperature, 250° F; jacket temperature, 250° F.

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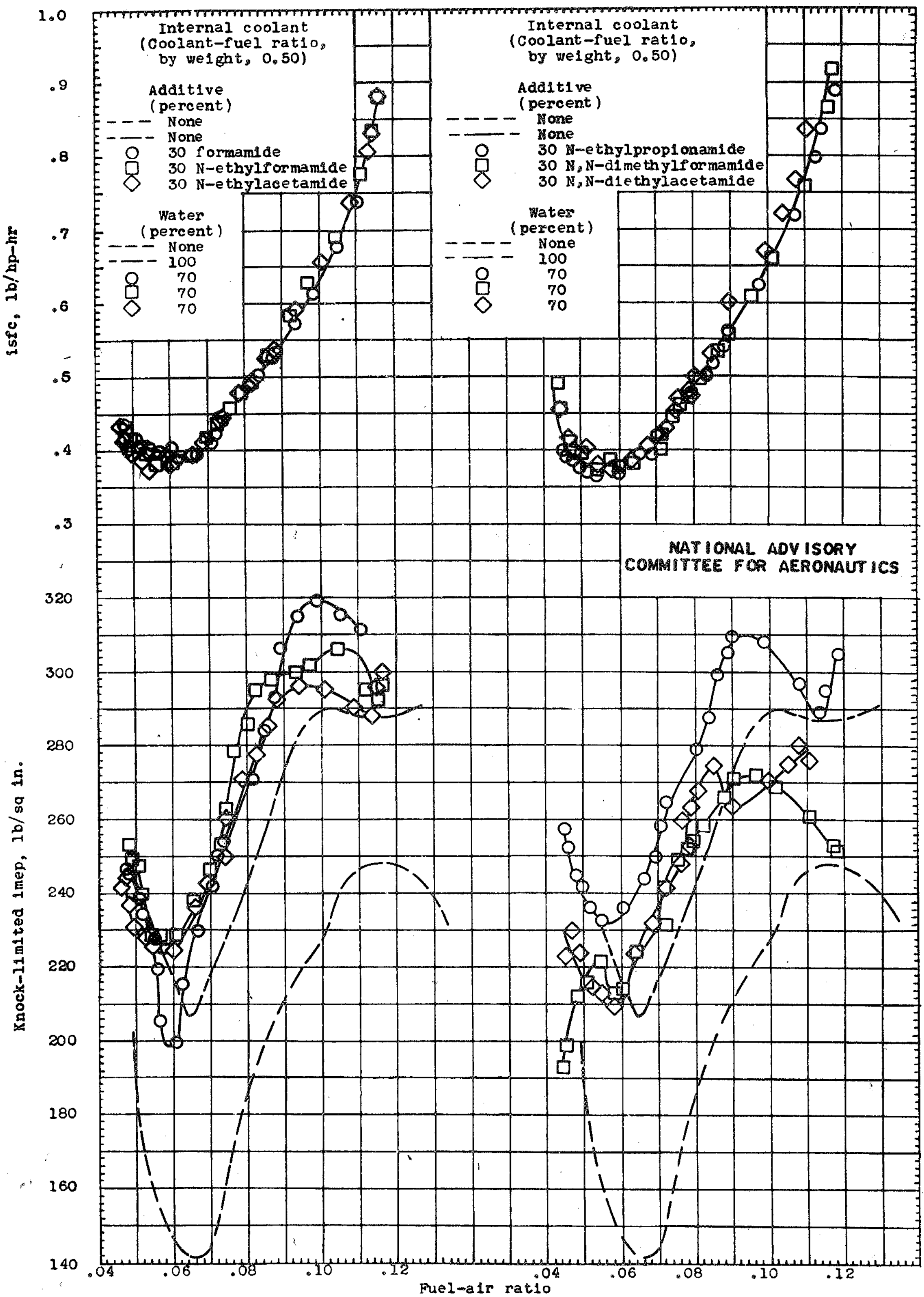


Figure 3. - Effect of various amides as internal-coolant additives on knock-limited performance of AN-F-28, Amendment-2, fuel. CFR engine; engine speed, 2500 rpm; compression ratio, 7.0; spark advance, 30° B.T.C.; inlet-air temperature, 250° F; jacket temperature, 250° F.

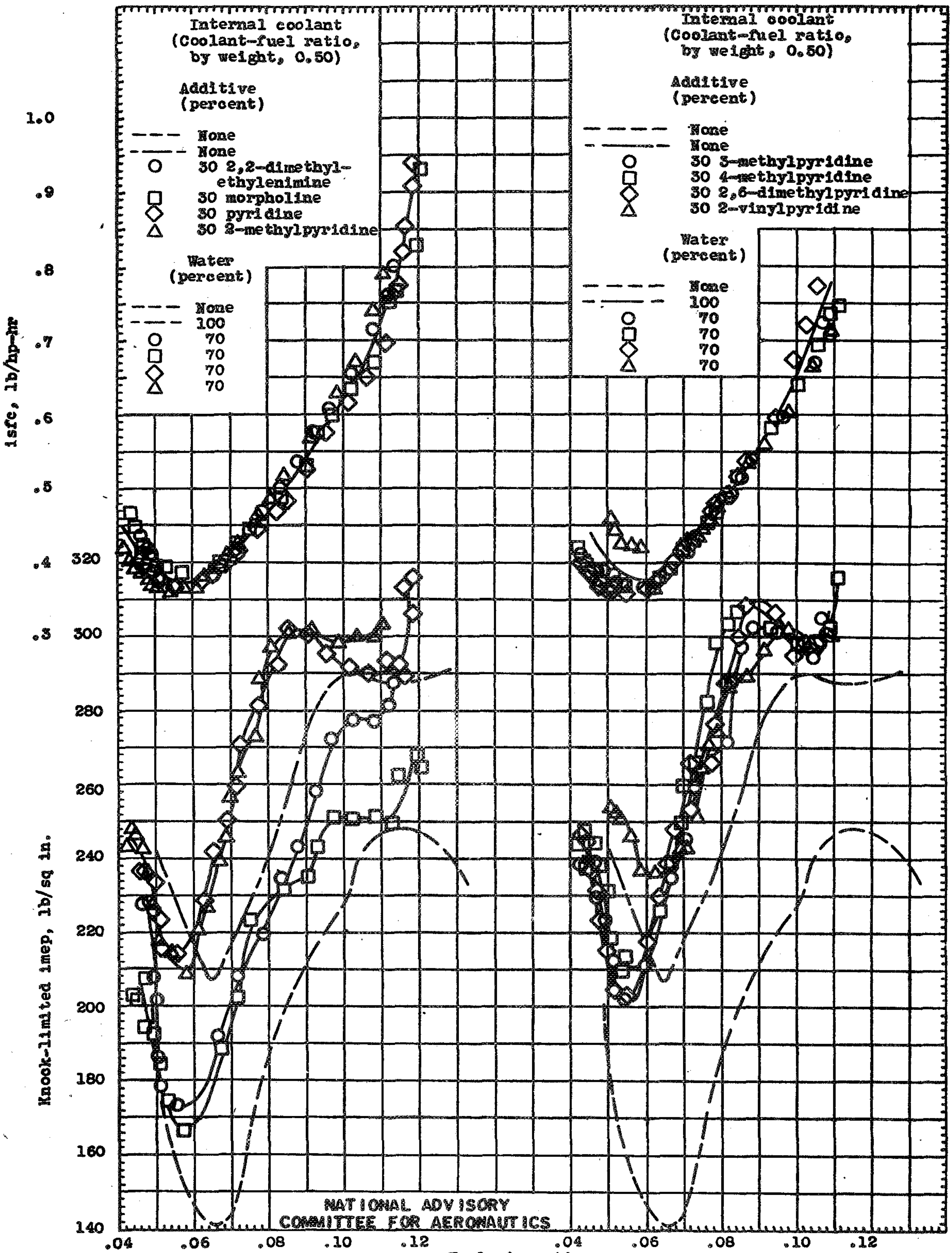
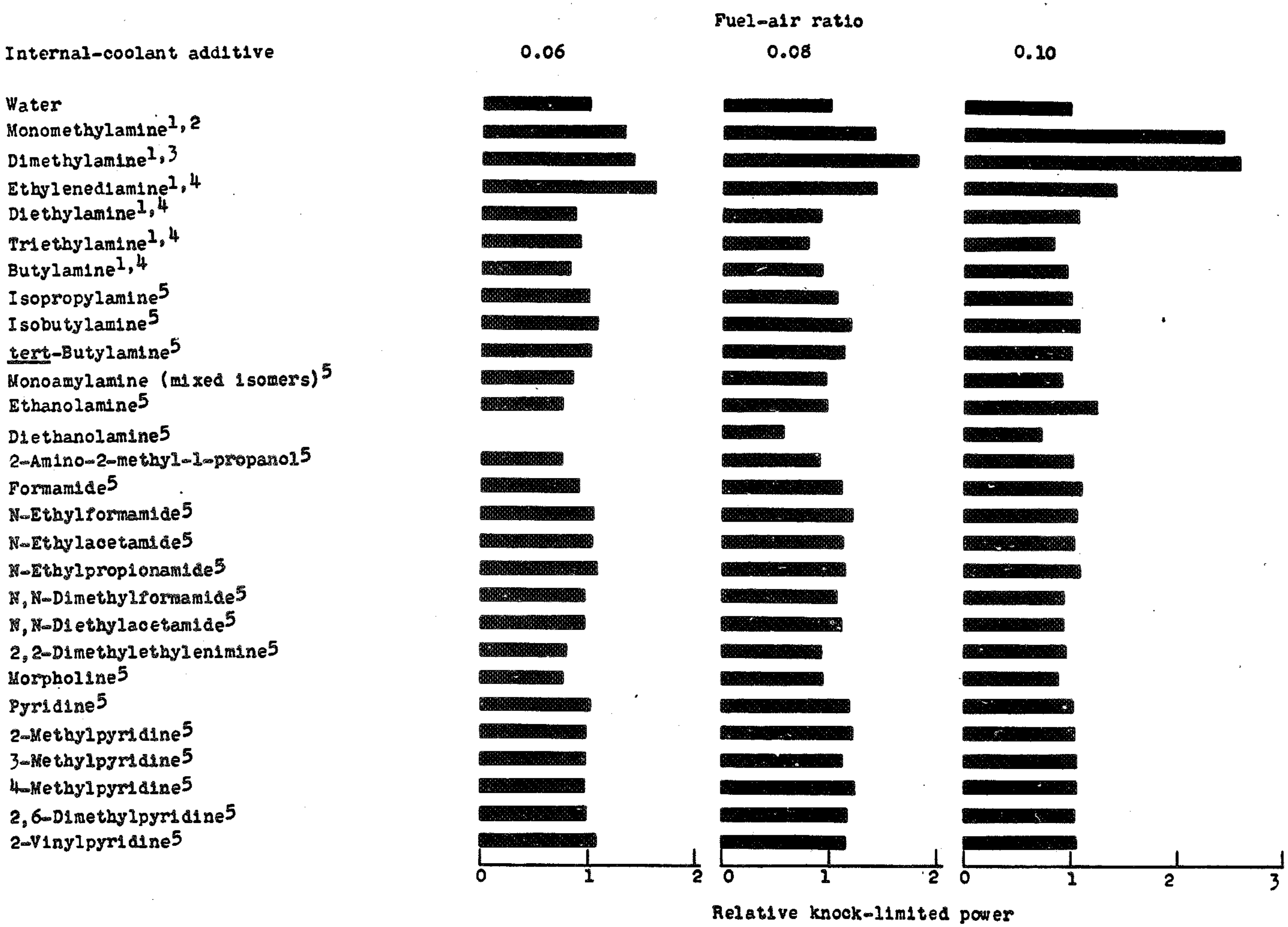


Figure 4. - Effect of various heterocyclic compounds as internal-coolant additives on knock-limited performance of AN-F-28, Amendment-2, fuel. CFR engine; engine speed, 2500 rpm; compression ratio, 7.0; spark advance, 30° B.T.C.; inlet-air temperature, 250° F; jacket temperature, 250° F.



[1]Data obtained from reference 3.
[2]32-percent by weight additive in water.
[3]26-percent by weight additive in water.
[4]25-percent by weight additive in water.
[5]30-percent by weight additive in water.

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Figure 5. - Relative knock-limited powers permitted by various internal-coolant additives at coolant-fuel ratio of 0.50. Values in graph are ratios of knock-limited indicated mean effective pressure permitted with additive-water solution as internal coolant to that permitted with water alone as internal coolant.