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EFFECTS OF VARIOUS ADDITIVES ON PHYSICAL PROPERTIES AND PERFORMANCE OF MONOMETHYLHYDRAZINE

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ABSTRACT

The freezing and boiling points of 0-40% mixtures of various nitrogen compounds and water in monomethylhydrazine (MMH) were determined experimentally. The additives for these mixtures were selected on the basis of chemical similarity to MMH, mixture thermal stability, probability of contamination occurrence, cryoscopic and ebullioscopic effects, and anticipated effects on propellant performance.

Theoretical specific impulses were calculated as a function of additive concentration using nominal values of the Saturn S-IVB Vehicle Auxiliary Propulsion System as a basis.

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RESEARCH AND DEVELOPMENT OPERATIONS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

TECHNICAL MEMORANDUM X-53356

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SUMMARY

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The freezing and boiling points of 0-40% mixtures of various nitrogen compounds and water in monomethylhydrazine (MMH) were determined experimentally. The additives for these mixtures were selected on the basis of chemical similarity to MMH, mixture thermal stability, probability of contamination occurrence, cryoscopic and ebullioscopic effects, and anticipated effects on propellant performance.

Theoretical specific impulses were calculated as a function of additive concentration using nominal values of the Saturn S-IVB Vehicle Auxiliary Propulsion System motor as a basis.

Based on the results of these studies, N,N-dimethylformamide and water appear to be the most suitable additive for increasing the liquid range of MMH without degrading its performance.

Author

INTRODUCTION

The Attitude Control System of the Saturn S-IVB Stage is located close to the liquid oxygen tank which causes cooling of the propellants with corresponding increases in viscosity during standby. Conversely, during and immediately after engine operation, heat transfer through propellant lines and associated hardware causes heating of the propellants with corresponding increases in vapor pressure.

Theoretically, additions of any of a wide range of solutes to one or both propellants would increase the boiling points and decrease the freezing points, thereby increasing the liquid ranges and alleviating the problems associated with heating and cooling of the propellant.

This report describes an investigation to determine experimentally the effects of various additives on the viscosity and liquid range of MMH and an analytical investigation of the effects of these additives on the performance characteristics of this propellant.

ADDITIVE SELECTION CRITERIA

The additives that are selected should provide maximum decreases in the freezing point and maximum increases in the boiling point of MMH; they should be chemically compatible with the propellant and the associated hardware and should not affect adversely the propellant performance. To provide maximum changes in freezing and boiling points, the additives should be of low molecular weight. To provide maximum chemical compatibility and minimum performance degradation, the additives should be chemically similar to MMH.

Based upon these criteria, the following compounds were selected for testing:

a. Urea
b. Acetamide
c. 1-methyl-1-phenylhydrazine
d. N,N-dimethylformamide
e. Formamide

Tests also were made using water as an additive since it may be present as an impurity in MMH.

EXPERIMENTAL AND ANALYTICAL

The freezing points and boiling points of MMH additive solutions were determined in the conventional manner by the use of a Beckman Molecular Weight Determination Apparatus and a Cottrell Boiling Point Apparatus, respectively.

Heats of combustion were determined for the pure compounds by the Parr Bomb adiabatic calorimetric method (ref. 1). These data then were used to calculate heats of formation using the conservation of mass and energy correlations (Hess's Law of Constant Heat Summation (ref. 2)).

Freezing and boiling points of the soluble mixtures are given in Table I. Note that formamide is insoluble in MMH. Heats of combustion and formation are given in Table II.

Theoretical performance data were determined using the NASA-Lewis Research Center Computer Program (ref. 3 and 4) with an IBM 7094 computer for N_2O_4/MMH with and without the various additives under the nominal operating conditions for the S-IVB Auxiliary Propulsion System engine, i.e., 100 psig chamber pressure and an expansion ratio of 31. A plot of the Isp versus propellant mixture ratio (O/F) for pure MMH and N_2O_4 is shown in FIG 1. Effects of the additives on Isp values for an O/F ratio of 1.2 are graphically presented in FIG 2 through FIG 7. Since the effects of the various additives on performance characteristics were substantially linear, gain or loss values showing the effects of one percent additions of the various additives on Isp for the N_2O_4/MMH additive propellant combination were estimated as follows: Urea - 0.4, acetamide - 3.8, 1-methyl-1-phenylhydrazine - 0.5, N,N-dimethylformamide - 0.2, formamide - 1.6, water - 0.2.

DISCUSSION AND CONCLUSIONS

Data for the physical property measurements indicate that N,N-dimethylformamide (DMF) and water are the most effective additives in increasing the boiling point and decreasing the freezing point. Neither imposes an appreciable penalty on rocket performance in the concentration ranges of interest. Thus, five percent DMF or water added to MMH will increase the density approximately one percent, decrease the freezing point 18 degrees, and increase the boiling point approximately 2 degrees. The corresponding changes in specific impulse are approximately plus one second for DMF and minus one second for water. Of the two, DMF is considered preferable since water is more likely to cause corrosion. Also, DMF forms a dipole-dipole complex, which increases the high-temperature stability characteristics of MMH.

However, before either can be recommended as an additive for MMH, additional studies are needed to determine the following:

a. Corrosion effects of water on system hardware

b. Absolute viscosity of MMH-DMF and MMH-water mixtures

c. Effects of DMF and water on ignition time delay of MMH/N_2O_4.

REFERENCES

1. Oxygen Bomb Calorimetry and Oxygen Bomb Combustion Methods. Parr Manual No. 120, Parr Instruments Company, Moline, Illinois, 1948.

2. Glasstone, Samuel: Textbook of Physical Chemistry. D. Van Nostrand, Inc., 1946, pp. 203-207.

3. Gordon, Sanford; and Zeleznik, Frank J.: Computation of Chemical Equilibrium Composition, Rocket Performance and Chapman-Jouguet Detonations. NASA TN D-1454, October 1962.

4. Gordon, Sanford; and Zeleznik, Frank J.: Computation of Chemical Equilibrium Composition, Rocket Performance and Chapman-Jouguet Detonations - Supplement I. NASA TN D-1737, October 1963.

TABLE I

PHYSICAL PROPERTIES OF MONOMETHYLHYDRAZINE SOLUTIONS

Additive	Composition wt., % MMH	Additive	Density @ 26.5±1.5°C g/cc	Freezing Point °C	Boiling Point °C
Urea	100	0	0.869	-52	88
	95	5	0.890	-56	90
	90	10	0.910	-60	91
	80	20	0.950	below -70*	96
	70	30	0.991	below -70*	102
	60	40	1.031	below -70*	107
Acetamide	100	0	0.869	-52	88
	95	5	0.878	-56	90
	90	10	0.887	-56	91
	80	20	0.907	below -70*	91
	70	30	0.926	below -70*	96
	60	40	0.946	below -70*	107
1-methyl-1-phenyl-hydrazine	100	0	0.869	-52	88
	95	5	0.878	-55	90
	90	10	0.887	-58	91
	80	20	0.901	below -70*	93
	70	30	0.915	below -70*	95
	60	40	0.929	below -70*	106
N,N-dimethyl-formamide	100	0	0.869	-52	88
	95	5	0.875	below -70*	91
	90	10	0.880	below -70*	93
	80	20	0.885	below -70*	94
	70	30	0.890	below -70*	96
	60	40	0.895	below -70*	97
Water	100	0	0.869	-52	88
	95	5	0.884	below -70*	90
	90	10	0.899	below -70*	92
	80	20	0.921	below -70*	96
	70	30	0.943	below -70*	100
	60	40	0.965	below -70*	104

* Becomes highly viscous (≥1000 poises).

TABLE II

THERMAL PROPERTIES

Compound	$H_{combustion}$ (Cal/mole)	$H_{formation}$ (Cal/mole)
Nitrogen Tetroxide	0	-6,800
Monomethylhydrazine	-14,340	12,700
Urea	-151,500	-79,540
Acetamide	-282,600	-436,800
1-methyl-1-phenylhydrazine	-15,250	32,950
N,N-dimethylformamide	-201,613	38,000
Formamide	-134,900	-190,620
Water	0	-68,380

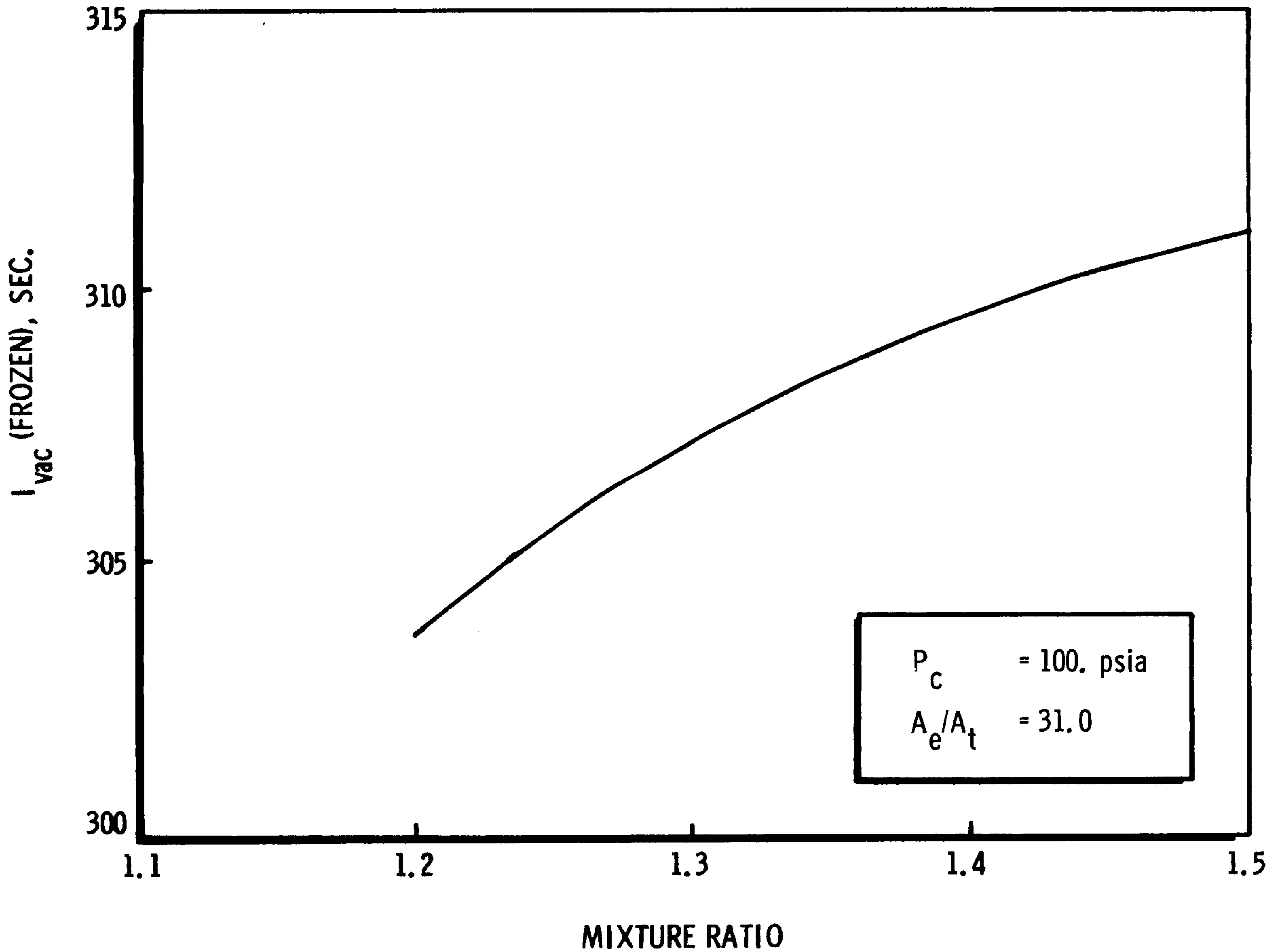

FIGURE 1. EFFECT OF VARIATIONS IN MIXTURE RATIO ON SPECIFIC IMPULSE

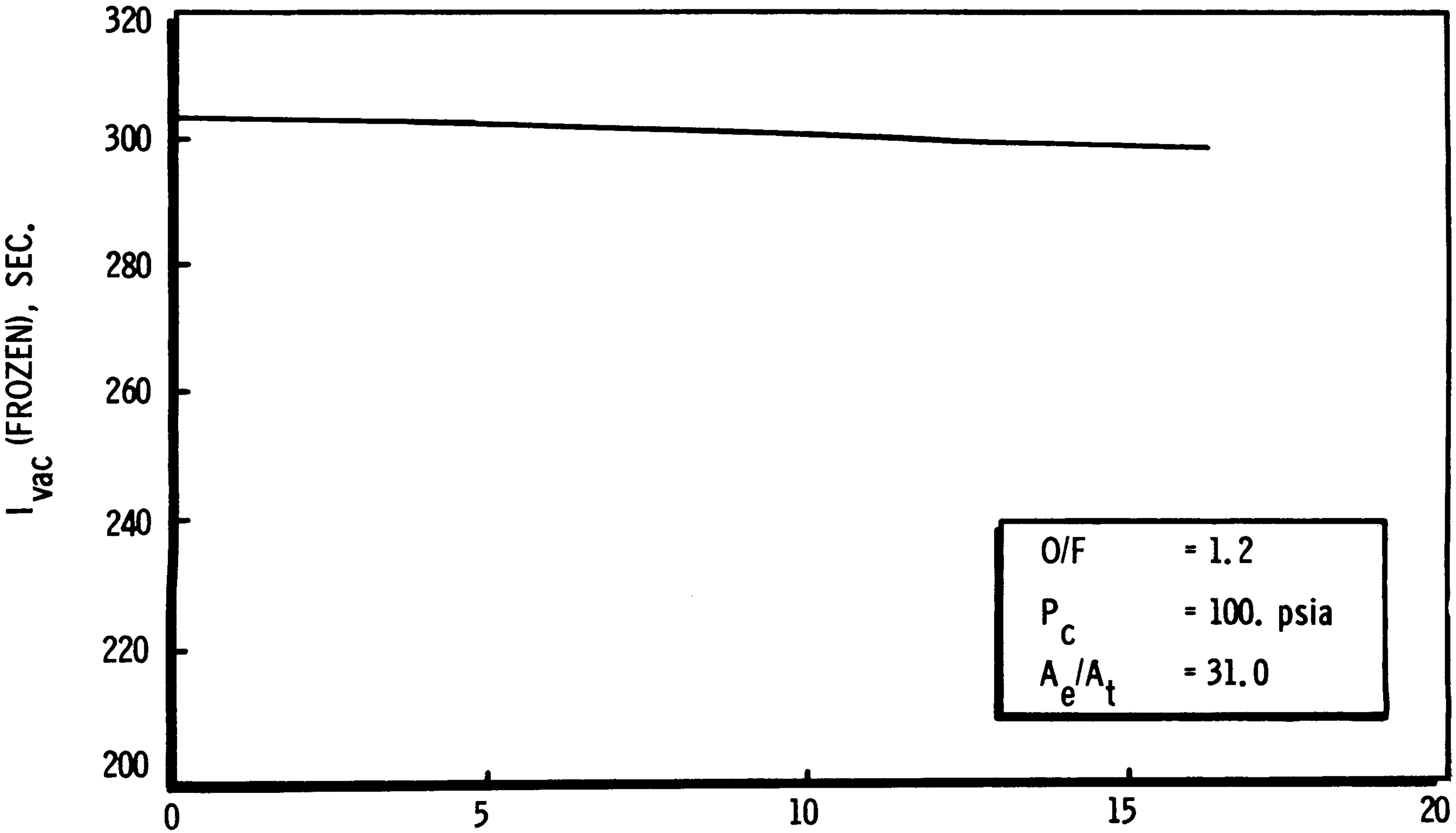

FIGURE 2. EFFECT OF ADDITION OF UREA ON SPECIFIC IMPULSE

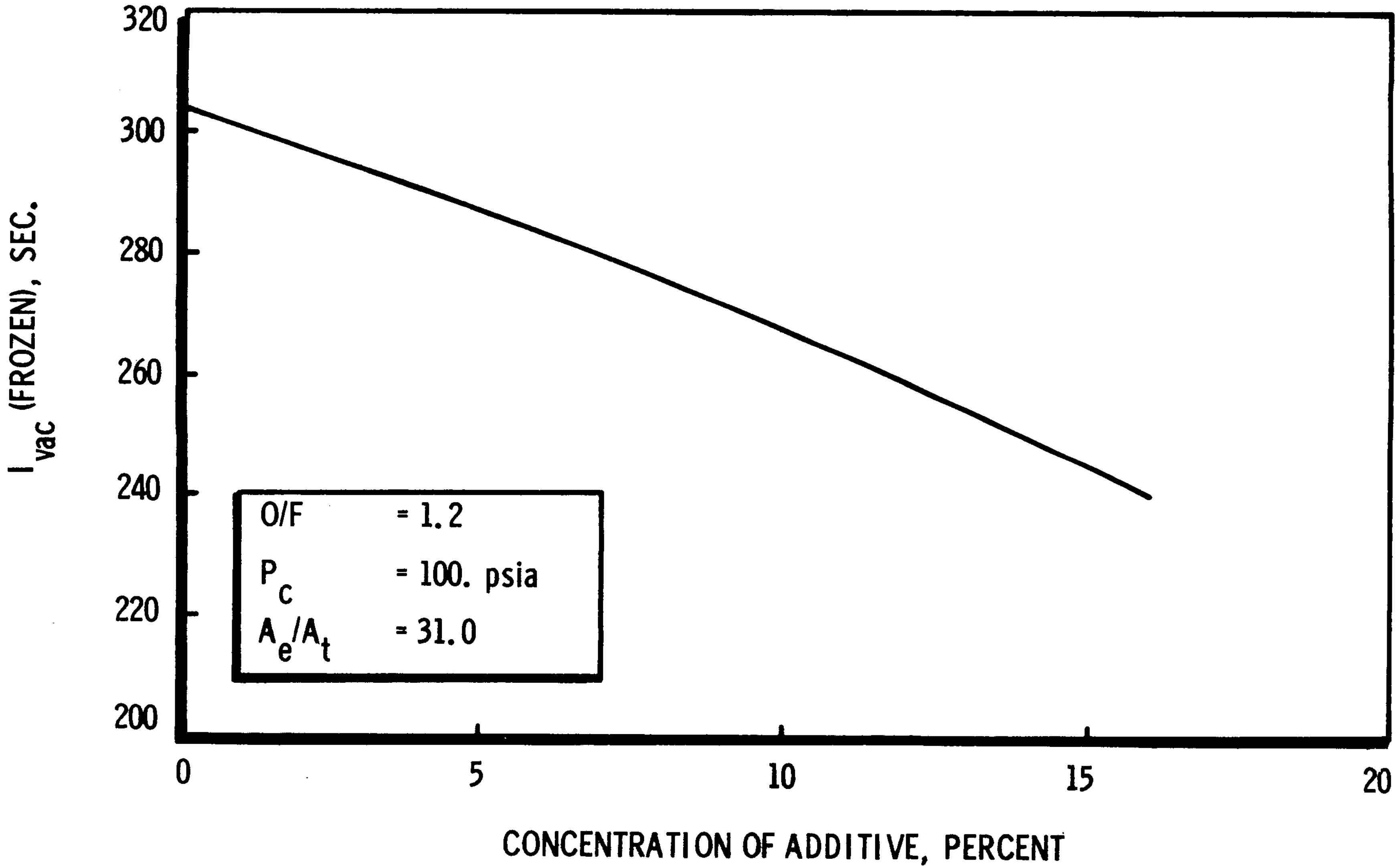

FIGURE 3. EFFECT OF ADDITION OF ACETAMIDE ON SPECIFIC IMPULSE

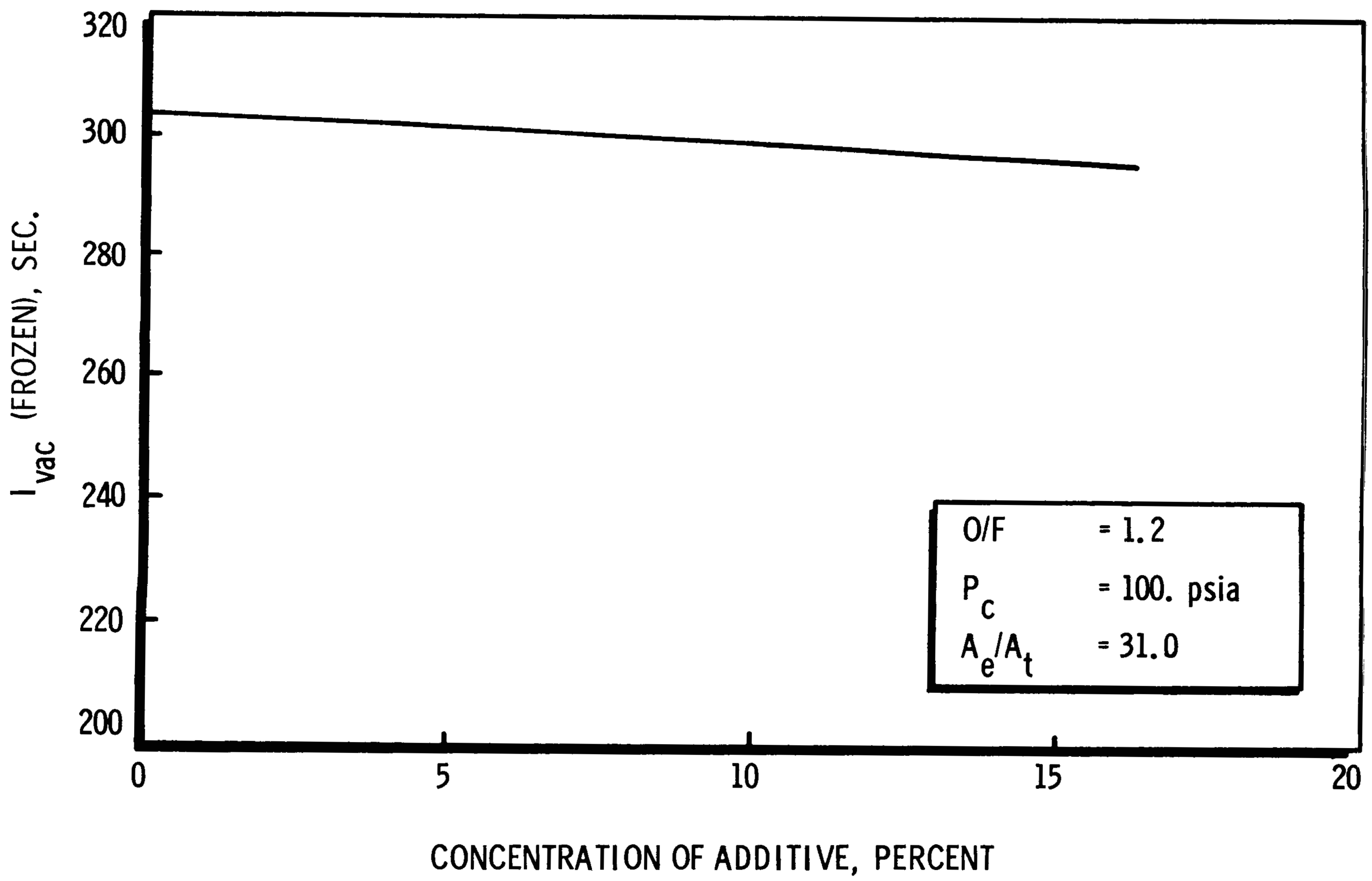

FIGURE 4. EFFECT OF ADDITION OF 1-METHYL-1-PHENYLHYDRAZINE ON SPECIFIC IMPULSE

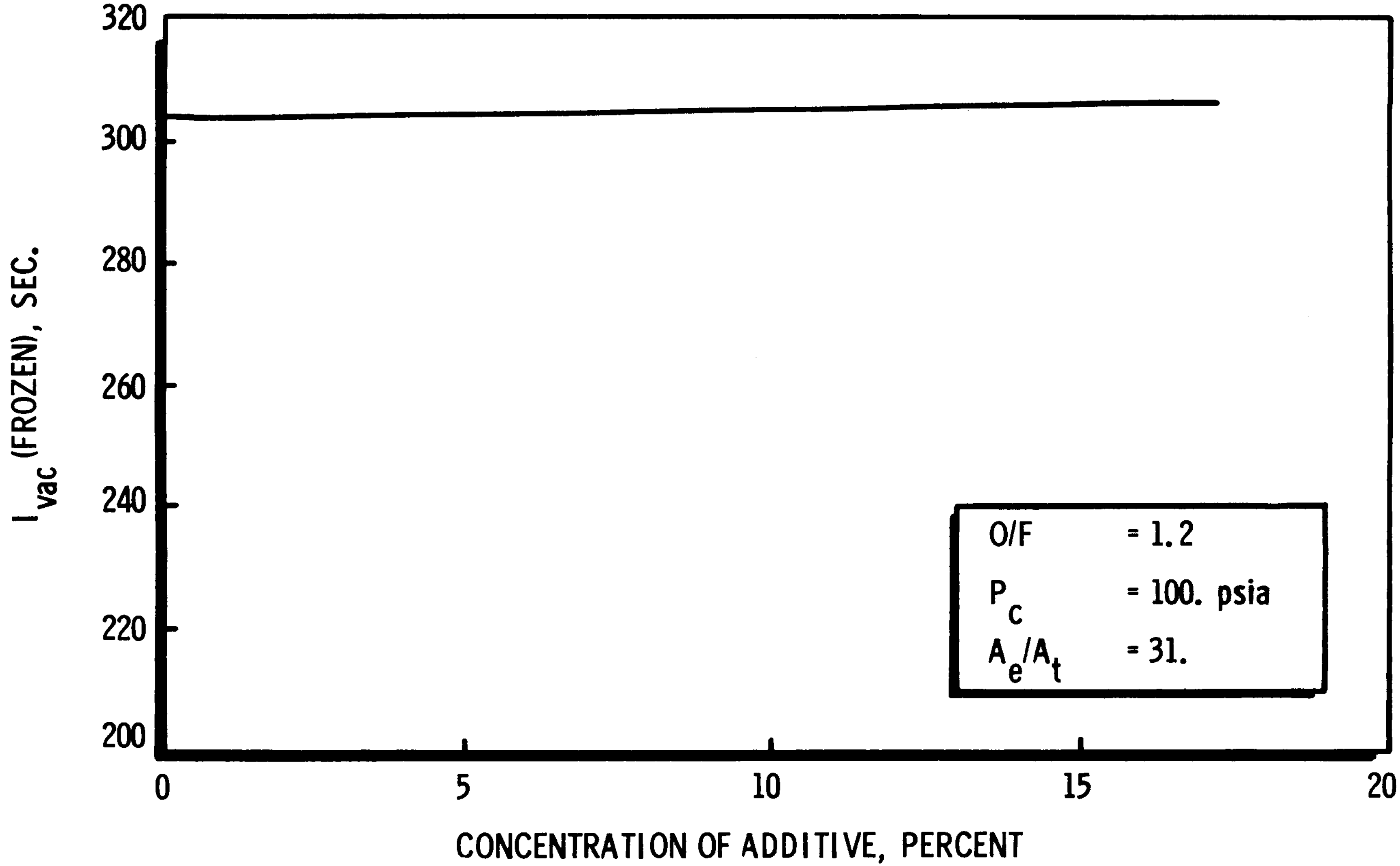

FIGURE 5. EFFECT OF ADDITION OF N, N-DIMETHYLFORMAMIDE ON SPECIFIC IMPULSE

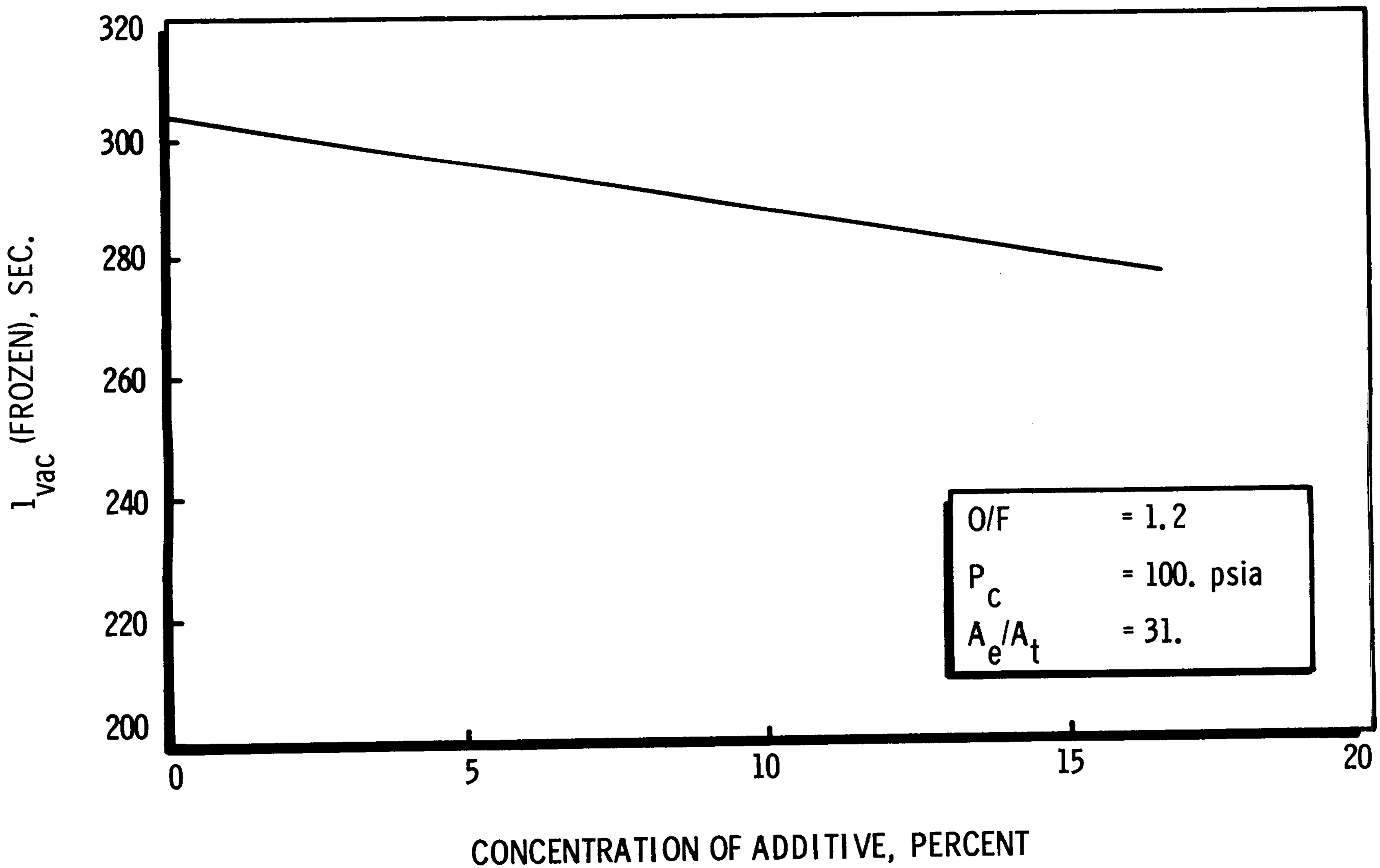

FIGURE 6. EFFECT OF ADDITION OF FORMAMIDE ON SPECIFIC IMPULSE

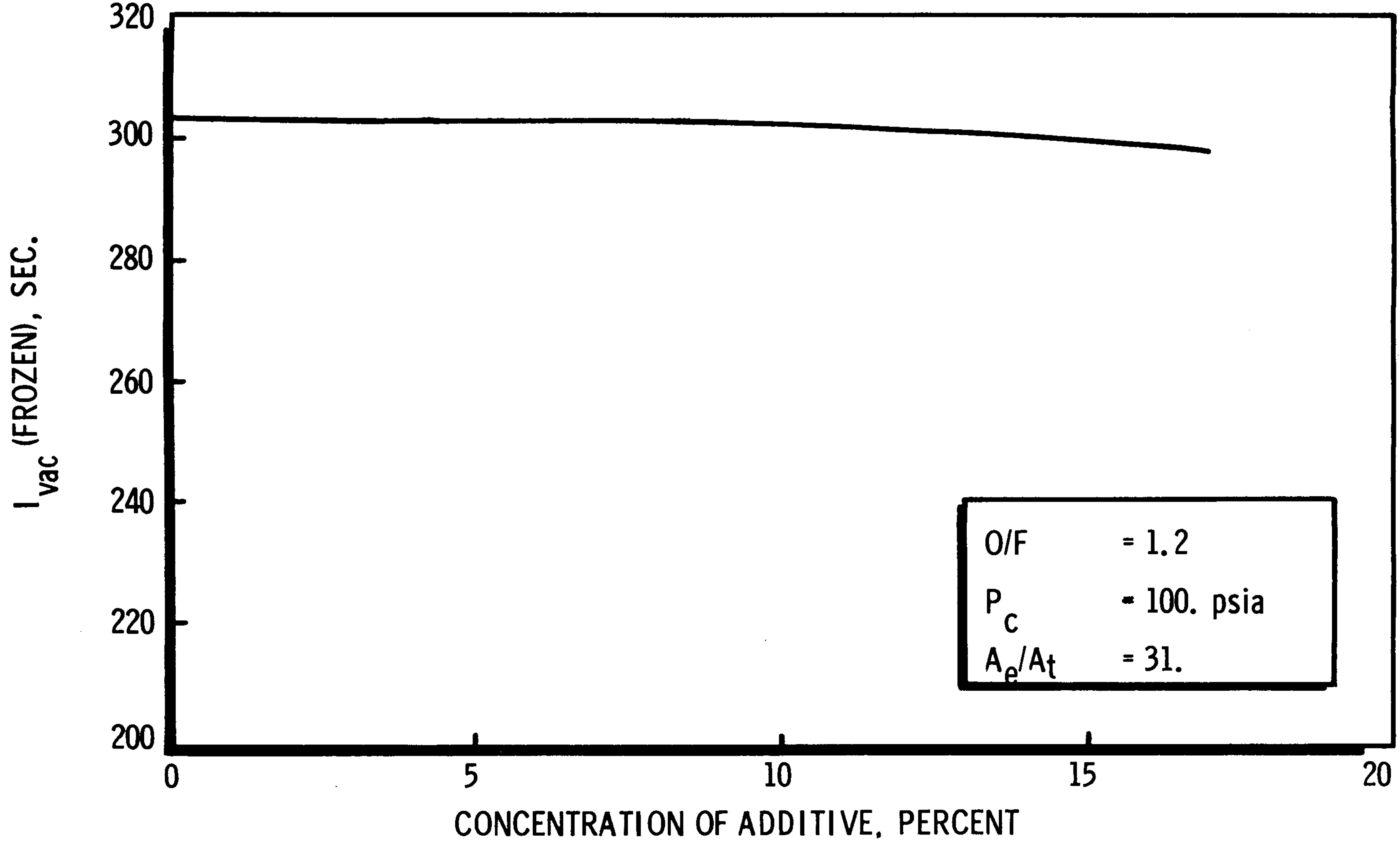

FIGURE 7. EFFECT OF ADDITION OF WATER ON SPECIFIC IMPULSE

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This document has also been reviewed and approved for technical accuracy.

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