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PREDICTED PERFORMANCE OF ENERGETIC PLASTICIZER FORMULATIONS.(U)
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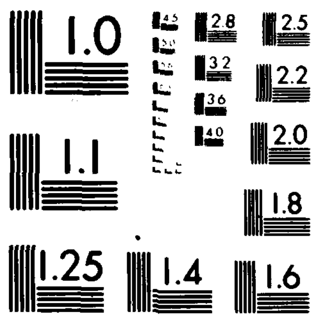

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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT 80-0015

JUNE 1980

PREDICTED PERFORMANCE OF ENERGETIC PLASTICIZER FORMULATIONS

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PROJECT 2303

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

FJSRL-TR-80-0015

This document was prepared by the Energetic Materials Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit Number 2303-F3-01, Energetic Materials Research. Dr. Melvin L. Druelinger was the Project Scientist in charge of the work.

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FJSRL-TR-80-0015

PREDICTED PERFORMANCE OF ENERGETIC

PLASTICIZER FORMULATIONS

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TECHNICAL REPORT FJSRL-TR-80-0015

JUNE 1980

Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: (14) FJSRL-TR-80-0015 ✓	2. GOVT ACCESSION NO.: ADA087658
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): (6) Predicted Performance of Energetic Plasticizer Formulations	5. TYPE OF REPORT & PERIOD COVERED: (9) Technical rept.
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): (10) Larry P. Davis, Robert A. Hildreth, Melvin L. Druelinger	8. CONTRACT OR GRANT NUMBER(s): (17) F3
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Frank J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, CO 80840	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: (16) 61102F/2303/F3-01
11. CONTROLLING OFFICE NAME AND ADDRESS: Frank J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, CO 80840	12. REPORT DATE: (11) June 1980
	13. NUMBER OF PAGES:
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (12) 19	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

energetic plasticizers
energetic polymers
heats of formation
specific impulse
bis-fluorodinitroethyl alkyl ethers
dinitropropylvinylether polymer
MNDO calculations

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Calculations of heats of formation (MNDO) and specific impulse for a series of bis-fluorodinitroethyl alkyl ethers have been made. This series also included oxygen and sulfur hetero atoms, N-H, $N-NO_2$ and $CFNO_2$ substituents. These calculations reveal a trend toward decreasing Isp values as the hydrocarbon chain increases. The results suggest that ideal target molecules for synthetic efforts are the smaller members of this family of compounds, and that such compounds → over

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could be of value in applications as energetic plasticizers in propellant/munition formulations. The results also indicate that these compounds are promising in view of their increased performance compared to formulations using non-energetic plasticizers.

LIST OF FIGURES

LIST OF TABLES

PREFACE

This document, FJSRL-TR-80-0015, summarizes computer calculations (MNDO) of heats of formations and resultant specific impulse data on formulations including energetic plasticizers. This work was done under Work Unit 2303-F3-01 and was not previously published by the authors.

TABLE OF CONTENTS

I. INTRODUCTION

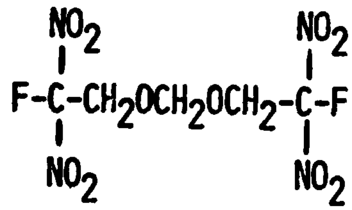
Composite energetic materials (explosives and propellants) in use today are composed of approximately 80-85% energetic materials and 15-20% low energy materials. These low energy materials are generally comprised of 10-15% plasticizer and other additives. In order to improve the energy content of such composites, work is being done to increase the energy content of the low energy materials fraction.

Recent work at the Seiler Laboratory and Los Alamos Scientific Laboratory (LASL) resulted in the development of a new class of polynitroethylvinylether polymers[1]. Dinitropropylvinylether polymer (DNPVEP), shown in Figure 1, was found to have excellent thermal (DTA = 220°C, exo.), physical and chemical properties. The incorporation of such energetic binder (polymer) ingredients into solid propellant and explosive formulations is an excellent concept for increasing the energy output during the combustion and detonation processes. Subsequent work on DNPVEP revealed a critical lack of available plasticizers that would plasticize this energetic binder[2]. Two energetic plasticizers available, FEFO (Figure 1) and nitroglycerin (NG), suffer from thermal stability and sensitivity problems for applications at the higher operating temperatures projected for future systems. Thus, synthesis of a new class of energetic plasticizers was initiated at this laboratory.

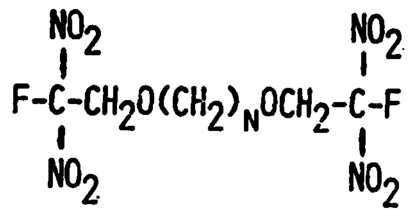
This new class of energetic plasticizers was modeled after the structural features present in the energetic binder DNPVEP. These bis-fluorodinitroethyl alkyl ethers (FEME, Figure 1) have very similar chemical functionalities to the DNPVEP including ether linkages and polynitroethyl side chains. During the synthesis of examples of this class[3], we decided to investigate

FIGURE 1. FORMULATION INGREDIENTS

- **ENERGETIC PLASTICIZERS**



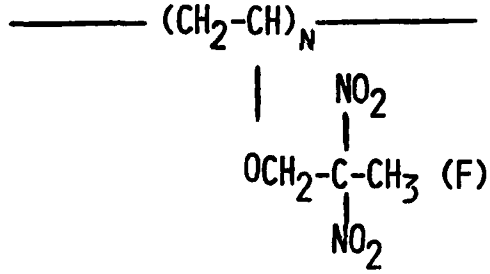
FEFO (ACETAL)



N = 2-6,8

FEME (ETHER)

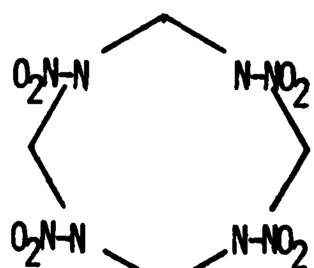
- **ENERGETIC BINDER**



N = VERY LARGE

DNPVEP (ETHER)

- **FUEL**



HMX

FIGURE 1 (CONTINUED). FORMULATION INGREDIENTS

- AMMONIUM PERCHLORATE (AP)

$$NH_4ClO_4$$

- NITROGLYCERIN (NG)

$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

- DIOCTYL ADIPATE

$$C_8H_{17}O_2C(CH_2)_4CO_2C_8H_{17}$$

- HYDROXY TERMINATED POLYBUTADIENE (HTPB)

$$HO(CH_2\text{-}CH\text{=}CH\text{-}CH_2)_N OH$$

- POLYETHYLENE GLYCOL 4000 (PEG 4000)

$$HO\text{-}(CH_2CH_2O)_N H$$

calculated energy content improvements in formulations utilizing the energetic plasticizers compared to formulations using non-energetic plasticizers. In addition to the carbon chain examples, various potential energetic plasticizers, heteroatoms and nitro substituents were investigated.

II. CALCULATIONAL PROCEDURES

Experimental heats of formation are not available for the FEME series of plasticizers, so the MNDO molecular orbital computer program developed by M. J. S. Dewar at the University of Texas[4] was used to calculate heats of formation for the various plasticizers. The calculation was performed with complete geometry optimization of the molecule. Previous calculations with MNDO have shown that for molecules of this size, the calculated heat of formation is usually too high. However, actual trends among the various plasticizers should be reproduced well by the calculated heats of formation.

The heat of formation is used along with the density and chemical composition as input to the performance program ISP[5]. This program calculates an equilibrium isentropic expansion from the rocket motor chamber to any arbitrary exit pressure. The Isp's calculated in this report were those for the expansion to sea level, 14.696 psia. Compositions of the propellant with and without the energetic plasticizers were used as input in order to make performance comparisons. These compositions were varied to achieve maximum Isp, but were kept within reasonable bounds for a standard aluminized solid propellant[6]. Densities of the energetic plasticizers were assumed to be the same as that of FEFO, 1.595g/cc.

III. RESULTS

Table I gives the calculated heats of formation for the various plasticizers. Included for comparison is a second theoretical value for FEFO apparently based on a group-addivity calculation[6]. The group additivity scheme will probably produce a heat of formation lower than the true one since it does not take into account destabilizing steric interference which will be present among the nitro groups. Thus the true heat of formation probably lies between the MNDO result and the group additivity result.

Because of uncertainty in the heat of formation, a sensitivity study was performed in order to calculate its effect on the predicted performance. Table II, which gives the calculated performances of the various plasticizer compositions based on derivatives of FEME-3, shows that there is a difference of about 2.5 sec in the Isp between the two different heats of formation for FEME-3. One heat of formation is the MNDO-calculated number, and the other is the group additivity estimated one for FEFO. (The two extra methylene groups make little difference in the heat of formation.) Thus the best value for Isp probably lies between the two given in the table.

Figure 2 shows the trend in predicted performance as the number of methylene groups in the plasticizer increases. Note that there is a slow decrease of about 0.2 sec/methylene group. These calculations are based on the group additivity calculated heats of formation and may, therefore, be somewhat pessimistic. It is obvious, however, that the predicted performances for the energetic plasticizer formulations are several seconds higher than the standard non-energetic formulation and approach the performance given by using nitroglycerin as a plasticizer (See Table III for these compositions).

Table III gives the compositions used to achieve the best Isp's shown in the previous table and Figure 2. Recall that these compositions were kept within reasonable bounds for an aluminized solid propellant. The compositions which give the best Isp are identical for all of the FEME-3 derivatives, and vary in a regular fashion as the number of methylene groups increase. Note the large differences in composition between the standard propellant composition and the energetic plasticizer combinations.

IV. CONCLUSIONS

The Isp calculations indicate that these energetic plasticizers have promise as useful additives to propellant and explosive formulations. The results reveal a trend toward decreasing Isp values as the hydrocarbon chain increases. The improvement in calculated Isp values (4-6 seconds) over non-energetic plasticizer formulations are high enough that these energetic plasticizers should warrant serious consideration for future applications. In addition, if an energetic binder were included in the formulations used in these calculations the total improvement in specific impulse would probably be on the order of 6-8 seconds.

It is important to note that these calculations were not totally optimized for formulation composition, but were based on reasonable estimates. Also, it should be noted that the ISP program assumes ideal combustion and expansion, and, thus non-ideal combustion or expansion could change the results somewhat.

However, these results are deinitely encouraging and the Isp technique should be used as a guide for the synthesis of other potential energetic plasticizers. To verify these calculated improvements, experimental work on actual formulations and measured performance should be done.

TABLE I

CALCULATED HEATS OF FORMATION

(Kcal/mol)

COMPOUND	ΔHf
$FC(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2F$ FEFO (FEME-1)	-89.0, - 178.8[1]
$FC(NO_2)_2CH_2OCH_2CH_2OCH_2(NO_2)_2F$ FEME-2	-94.7
$FC(NO_2)_2CH_2OCH_2CH_2CH_2OCH_2C(NO_2)_2F$ FEME-3	-99.0
$FC(NO_2)_2CH_2OCH_2OCH_2OCH_2C(NO_2)_2F$ FEME-3-O	-127.7
$FC(NO_2)_2CH_2OCH_2SCH_2OCH_2C(NO_2)_2F$ FEME-3-S	-85.6
$FC(NO_2)_2CH_2OCH_2NHCH_2OCH_2C(NO_2)_2F$ FEME-3-NH	-83.5
$FC(NO_2)_2CH_2OCH_2N(NO_2)CH_2OC(NO_2)_2F$ FEME-3-NNO_2	-54.3
$FC(NO_2)_2CH_2OCH_2CF(NO_2)CH_2OCH_2C(NO_2)_2F$ FEME-3-$CFNO_2$	-118.1

[1] Based on group additivity value.

TABLE II

CALCULATED PERFORMANCE FOR VARIOUS COMPOSITIONS[1]

Composition	Maximum Sea Level Isp(sec)[2]
Standard	267.7
Nitroglycerine Plasticizer	274.0
FEME-3	271.1 (Group additivity ΔH_f°)
FEME-3	273.6
FEME-3-O	273.6
FEME-3-S	272.0
FEME-3-NH	274.1
FEME-3-NNO_2	274.9
FEME-3-$CFNO_2$	273.9

[1] See Table III for compositions

[2] Unless specified, based on MNDO heat of formation

Figure 2 Calculated Specific Impulse as a Function of FEME Number

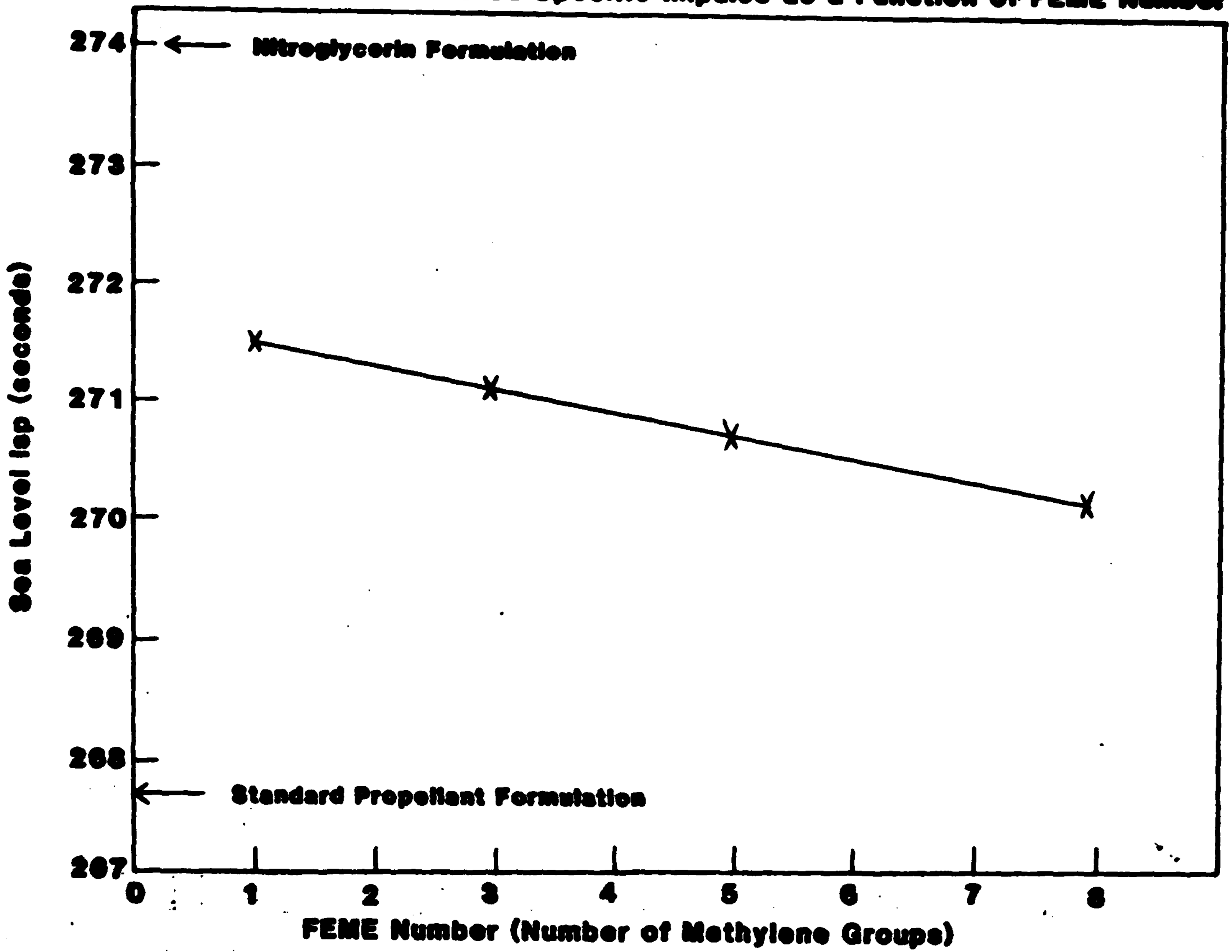


TABLE III

COMPOSITIONS OF MAXIMUM PERFORMANCE

Formulation	Weight Fraction				
	HMX	AP	Al	Binder[1]	Plasticizer[2]
Standard (DOA Plasticizer)	.27	.43	.22	.065(HTPB)	.015(DOA)
Nitroglycerin Plasticizer	.61	.01	.20	.04	.14(Nitroglycerin)
FEPO[3]	.59	.03	.18	.05	.15
FEME-3[3]	.54	.08	.18	.05	.15
FEME-3	.60	.04	.16	.05	.15
FEME-5[3]	.49	.13	.18	.05	.15
FEME-8[3]	.43	.19	.18	.05	.15
FEME-3-O	.60	.04	.16	.05	.15
FEME-3-S	.60	.04	.16	.05	.15
FEME-3-NH	.60	.04	.16	.05	.15
FEME-3-NNO_2	.60	.04	.16	.05	.15
FEME-3-$CFNO_2$	.60	.04	.16	.05	.15

[1] Unless specified, binder is PEG4000

[2] Unless specified, plasticizer is FEME plasticizer

[3] Composition for group additivity ΔH_f°

ACKNOWLEDGEMENTS

We would like to acknowledge Mr. Robert Hall of AFRPL for providing us with a copy of their ISP program and Capt Fred Myers of AFRPL for providing guidance on propellant compositions and for helpful discussions. We would also like to acknowledge Mrs. Betty Darcy for typing this manuscript.

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