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AFRPL-TR-66-329

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DESENSITIZATION OF AVAILABLE HIGH-ENERGY NF COMPOUNDS (U)

FINAL REPORT
DECEMBER 1966

Prepared For

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards, California

By

J. A. Brown, J. F. Coburn, Jr., M. Collins
Esso Research and Engineering Company
Linden, New Jersey

Contract No. AF 04(611)-9969 (U)
Esso Report No. ED-8

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J. F. COBURN, Jr.
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December 1966

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Linden, New Jersey

CONFIDENTIAL

FOREWORD

(U) This report describes research aimed at the desensitization, via empirical approaches, of available high-energy NF compounds, and is the Final Report of this investigation. The research was carried out for the Air Force under Contract No. AF 04(611)-9969(U); the Project Engineers were 1st Lt. Thomas J. Gilding and Mr. J. L. Trout of the Air Force Flight Test Center, Edwards Air Force Base, California. Research was initiated 1 July 1964, and this report covers the period 1 July 1964 - 15 November 1966.

(U) The following technical personnel carried out the research:

Dr. J. A. Brown (Project Leader)
Dr. J. F. Coburn, Jr. (Chemist)
Dr. M. Collins (Chemical Engineer)

Other technical personnel contributed briefly for particular problems. The project was under the general supervision of Dr. J. R. Lovett, Director, and Dr. W. G. May, Senior Research Associate.

(U) This technical report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

UNCLASSIFIED ABSTRACT

(U) A literature survey covering 54 NF and PFG compounds of widely varying structure types, an extensive empirical desensitization program on selected model PFG compounds, and a limited fundamental investigation of explosion phenomena have indicated that high-energy NF compounds are inherently ultra-sensitive and cannot be made insensitive except at an unacceptable sacrifice of energy. It appears to be futile to search for insensitive high-energy structures or dramatically effective desensitization techniques. Improvements can be made by both these approaches, but they are an order of magnitude smaller than what is needed.

(U) Nevertheless, it appears that high-impulse propellants based on PFG compounds can be made with no greater impact sensitivity than conventional double-base composites. There is, however, no reason to expect that card-gap sensitivity can be similarly improved.

(U) An improved thermal sensitivity test has been developed which yields activation energies and frequency factors from actual exploding condensed phase samples. The experimental procedure is an improvement of the Picatinny Arsenal Autoignition Test, and the data are unfolded by the treatments of Zinn and Mader and Frank-Kamenetskii. Calculated values for minimum explosion temperature are in good agreement with measured ones, calculated $T_{250\mu\ sec}$ values agree with those determined by the Wenograd test, and activation energies for PETN and nitroglycerin agree well with those given in the literature.

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1. INTRODUCTION

(C) Perfluoroguanidine (PFG) chemistry has produced many high-energy tris-NF_2 solid and liquid compounds for use as advanced oxidizers in high-energy formulations. However, their extreme impact and friction sensitivities have hindered their evaluation as solid propellant ingredients and raised questions as to their potential utility.

(C) Preliminary evidence had indicated that NF compounds could be desensitized to some degree, and there was preliminary evidence that certain chemical structures were considerably less sensitive than others. Consequently, this program was initiated to investigate the following working questions:

- Just how sensitive are NF compounds?
- What are the least sensitive structures?
- How much can NF compounds be desensitized?
- Will the desensitization work in propellants?

These questions have been attacked by a literature survey, by empirical sensitivity and desensitization studies on compounds and formulations, and by limited fundamental studies on explosion phenomena.

2. SUMMARY

(U) This report is a summary and an integrated review of all the work done on this contract over the past two years, along with the conclusions drawn therefrom. Data published in earlier reports are reviewed in summary form only, but work heretofore unpublished is treated in detail. Appendix 4 is an annotated bibliography of the earlier reports.

(C) A literature survey of fifty-four different NF compounds, both $-OCX_3$* and $-CNF_2$, along with a number of $-ONO_2$ compounds for orientation, has shown that explosive compounds in general are more sensitive the higher their heat of explosion. OCX_3 compounds are all ultra-sensitive regardless of their heat of explosion. The few apparent exceptions to this rule all appear to be explainable as artifacts of abnormal physical states, as for example, very fine powders. The data hold out no hope for insensitive, high-energy, NF structures.

(C) Empirical desensitization studies have shown that desensitization up to an order of magnitude can be obtained in most cases - usually at an energy cost which makes the advantage problematical. However, two orders of magnitude are needed to equal the sensitivity of conventional "handleable" explosives. There are five general desensitization techniques: coating, dilution, pulverization, thickening and inhibition; but there are more exceptions than rules. Each compound is a new case and needs to be examined individually. Enough energetic compounds and enough desensitization techniques have been screened to make it unlikely that further work would produce dramatically better results.

(C) Propellants in the 285-290 Isp range and no more impact-sensitive than conventional double-base composites can probably be formulated from NF compounds by utilizing the desensitizing techniques of dilution and inhibition and by avoiding hard particles such as boron. Friction sensitivity can probably be controlled as well. Sensitivity to high-order shock (card-gap) has not been studied; however, other work has given no reason to expect that it can be similarly improved.

(U) An improved thermal sensitivity test has been developed which yields activation energies and frequency factors from actual exploding condensed phase samples. The experimental procedure is an improvement of the Picatinny Arsenal Autoignition Test, and the data are unfolded by the treatments of Zinn and Mader and Frank-Kamenetskii. Calculated values for minimum explosion temperature are in good agreement with measured ones, calculated $T_{250\mu\ sec}$ values agree with those determined by the Wenograd test, and activation energies for PETN and nitroglycerin agree well with those given in the literature.

---

* PFG-alcohol adducts. $X = NF_2$.

(C) Thermal sensitivity data on high-energy OCX_3 compounds indicate that their activation energies are essentially "normal" ones, with no particularly weak bonds or structural instabilities evident. Frequency factors, and consequently calculated decomposition rates, are high; and there is, of course, a very high heat release upon decomposition. This suggests that it is probably futile to search for novel and insensitive high-energy CNF_2 compounds.* CNF_2 compounds' great sensitivity seems to be due solely - and inevitably - to their high energy content. Small differences can be effected by structural changes, but not large ones.

(C) High-energy CNF_2 compounds are inherently sensitive and cannot be made insensitive. It may be possible to live with them by accepting and adjusting to their sensitivity (this will have to be judged by the users); but there seems to be no way to overcome their sensitivity.

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* $-ONF_2$ compounds have been reported to be surprisingly insensitive. They have not been examined by us.

3. SENSITIVITY AND DESENSITIZATION OF NF MATERIALS

(U) This section presents an overview of the past two years' desensitization studies on NF oxidizers and NF propellant formulations and presents summary data. More detailed data have been published in the foregoing Quarterly Progress Reports of this series and are not repeated here; a bibliography of these QPR's, with DDC accession numbers, is given in Appendix 4.

(U) Due to the scarcity and cost of NF materials, this investigation has necessarily been limited to small-scale laboratory tests such as impact, friction, and spark. The larger scale tests, such as card-gap, which may well be more meaningful in finished ordnance items, have had to be omitted.

(C) The desensitization studies and sensitivity comparisons have been instructive, but it is not yet sufficiently clear just what laboratory sensitivity tests really mean in terms of field hazards; and we are not yet able to say, for example, that a given E_{50} is acceptable whereas a lower one is not. It probably depends a great deal on the configuration of the ordnance used in the field. For example, one laboratory micromotor loaded with 10 grams of a propellant having the formulation:

32% FA-PETRIN
4% HPVA
3.5% Boron
59.5% FA-TNENE

Calc. Isp = 286 sec.

and a sensitivity of

E_{50} (PA) 5.5 Kg-cm.
E_{50} (B-12) 15 Kg-cm.
Friction H4

was recently dropped 60 feet onto a concrete pad without harm. Apparently the motor shell protected the propellant from the impact. It may yet turn out that the most practical "desensitization" technique is insulation of the propellant from external stimuli.

3.1. SURVEY - SENSITIVITY OF NF COMPOUNDS

(U) It has long been accepted that NF compounds are extremely sensitive to accidental initiation and so are very dangerous to handle; but not many systematic, quantitative data have been published. Such research reports as have appeared have generally been limited to a relatively few compounds each and/or have mostly concerned themselves with very light materials such as Delta, R, or IBA which demanded special testers not comparable to those of other laboratories. We have been

privileged to examine an advance copy of a comprehensive literature survey made by Stanford Research Institute.* This survey contains data on nearly 400 NF compounds gleaned from nearly 1000 research reports. Most of the data are highly qualitative, e.g., "explodes with friction"; and very few of the numerical data are comparable to other numerical data.

(U) By far the most extensive compilation with directly comparable data appears to be the files of our own laboratory, which contain systematic sensitivity data on fifty-four different NF compounds** - all on the same tester - along with a number of conventional nitro compounds for orientation. Consequently, we have performed a "literature survey" in our own files. We know of no comparable published compilation elsewhere. These sensitivity data are analyzed and interpreted below; detailed data tables are given in Appendix 1.

3.1.1. Impact Sensitivity Correlates with Energy Content

(U) It has been known for many years that there is a gener l correlation between the impact sensitivity and the heat of explosion of energetic compositions. The following figure, taken from an earlier survey*** illustrates his relationship for a variety of compositions.

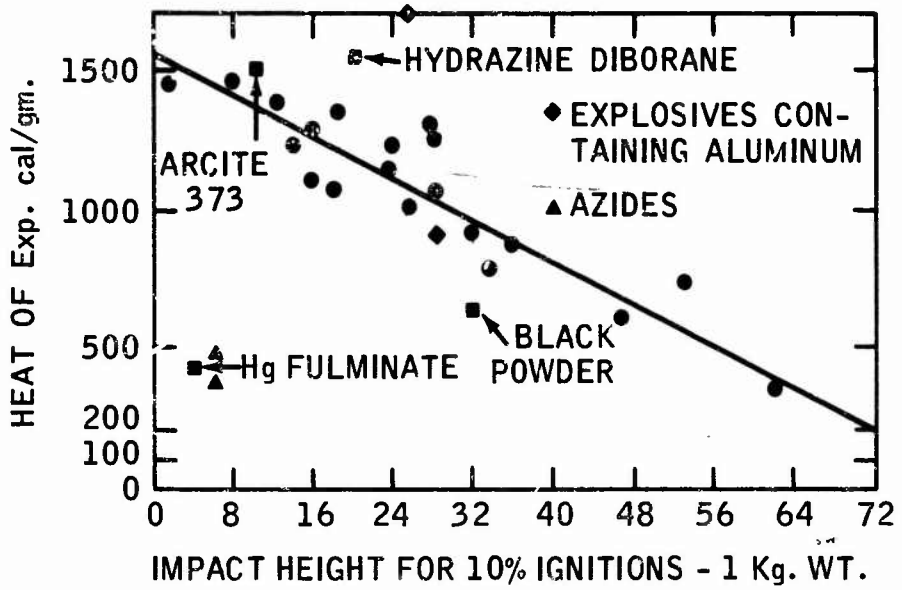
---

* M. E. Hill and R. A. Bell, Stanford Research Institute, Contract AF 04(611)-11547, "Compilation of Data on Sensitivity of NF Compounds - A Handbook (U)" Confidential Report, to issue approximately February 1967.

** Synthesized and characterized at Esso Research under Contract DA-01-021-AMC-11735(Z).

*** Esso Research and Engineering Co., "Quarterly Progress Report on Research on Advanced Propellants (U)" Dec. 11, 1959-March 10, 1960, Contract DA-30-069-ORD-2487. Data largely from Picatinny Arsenal Technical Report 1740, Rev. 1, "Properties of Explosives of Military Interest."

IMPACT SENSITIVITY VS. HEAT OF EXPLOSION

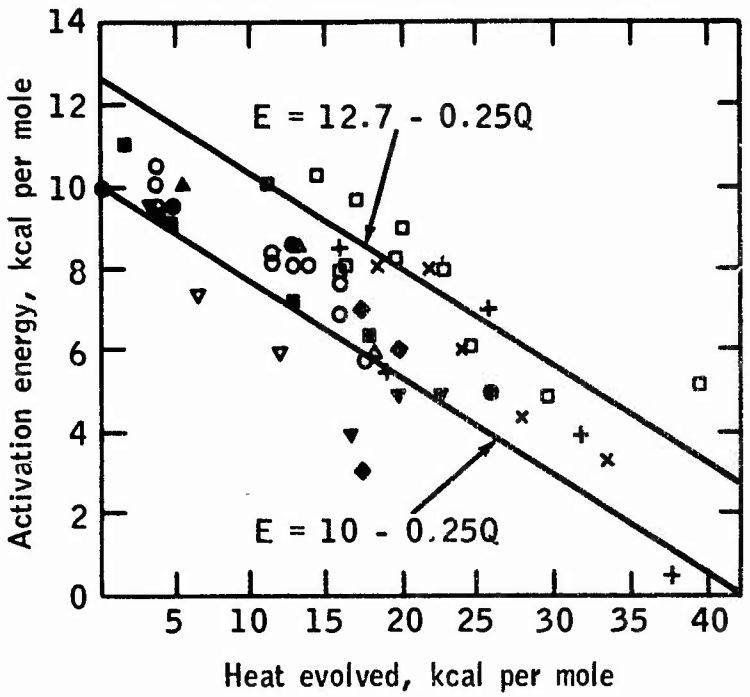


Clearly, most of these compositions do correlate, with a few exceptions which will be discussed below.

(U) This correlation is very reminescent of Semenov's correlation between heat of reaction for a wide varicty of exothermic reactions and the reactions' activation energy.*

* N. N. Semenov "Some Problems in Chemical Kinetics and Reactivity," Chap. 1, Princeton Univ. Press, 1958 (Translated by M. Boudart from Semenov's Russian text of 1954).

ACTIVATION ENERGY VS. HEAT OF RFACTION



● H + RH ⟶ H_2 + R
○ CH_3 + RH ⟶ CH_4 + R
■ D + RH ⟶ HD + R
\+ OH + RH ⟶ H_2O + R
△ H + RCHO ⟶ H_2 + RCO
× H + RCl ⟶ HCl + R
▼ CH_3 + RCl ⟶ CH_3Cl + R
◆ H + RBr ⟶ HBr + R
▲ CH_3 + RBr ⟶ CH_3Br + R
□ Na + RCl ⟶ NaCl + R

Semenov's examples were not explosions; but explosions are exothermic reactions, and it seems intuitively obvious that impact sensitivity should be a function of activation energy (among other factors).

(U) Returning to the plot of impact sensitivity versus heat of explosion, a few substances, such as azides and mercury fulminate, are more sensitive than the correlation would predict, implying a more labile structure than usual. Heterogeneous materials, such as aluminized propellants, are less sensitive than the correlation would predict, presumably due to the effective segregation of fuel and oxidizer and the consequent much higher activation energy needed; but there appear to be no homogeneous materials significantly less sensitive than the correlation would predict. Hydrazine diborane, $H_3B \cdot H_2NNH_2 \cdot BH_3$, appears to be such a material, but it is felt that its apparent insensitivity is an artifact of its very fine state of division (it is an extremely fine powder). As discussed below, finely-divided solids appear less sensitive on the Picatinny Arsenal impact tester then do the same solids in massive form.

(U) Kamlet* has shown that an even better correlation exists between impact sensitivity and "oxidant balance" for nitro explosives, but the general conclusions are the same: high energy means high sensitivity. We have preferred to use Q, the calculated heat of detonation, for our correlating parameter, because of its involvement in our determination of activation energies and frequency factors for thermal explosions (cf Section 4, below), and because one can readily see its participation in a servo loop whereby one exploding molecule initiates one or more others.

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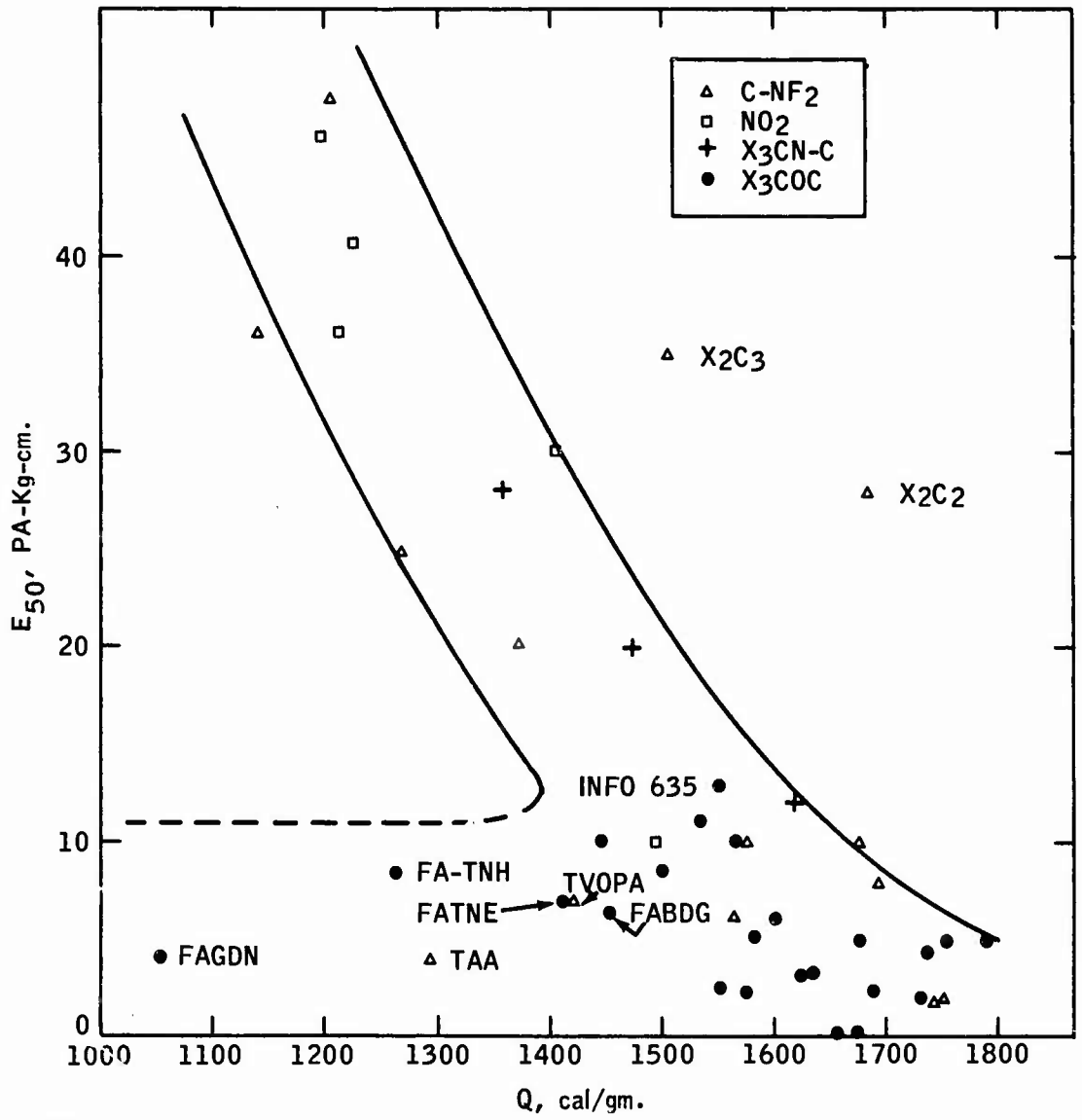
* M. J. Kamlet, "A Correlation of Impact Sensitivities of Explosives with Oxidant Balances (U)," NAVORD 6126, 28 September 1958.

(C) The following figure is a plot of impact sensitivity versus Q for all NF compounds for which we have reliable data.*

IMPACT SENSITIVITY VS. ENERGY FOR NF COMPOUNDS



* A few of the raw data have been rejected as incorrect due to the extreme fluffiness of the solid samples, but everything else is shown. The original data, including the rejected ones, are given in Appendix .

It is clear from the figure that the correlation holds, and that almost all compounds from conventional NO_2 to exotic OCX_3 lie within one band, the "Main Sequence," sloping upward to the left.* Low-energy OCX_3 compounds, however, apparently fall well below the Main Sequence, suggesting that OCX_3 compounds really fall on a horizontal sequence which intersects the Main Sequence in the region where most of the OCX_3 compounds of interest happen to fall. This is discussed in more detail in the following section.

(C) It is felt that the main reason for the width of the band is data scatter due to variations in the physical properties of the samples. It is well established that finely-divided solids appear less sensitive than the same solids in massive form:

	E_{50}, PA, Kg-cm.	
	Fine	Massive
Poly-FA-BDE	22	10
FA-TNENE	35	2.3
FA-PO	10	2.5
BDM	43	19

It follows that all solids really should be compared at the same fineness level and that scatter in fineness will result in scatter in E_{50}. Similarly, it is well established that liquids are desensitized somewhat by thickening (cf. FA-BDN thickened by polymer addition, Section 3.2.4.); and it follows that all liquids really should be compared at the same viscosity. Scatter in viscosity will result in scatter in E_{50}. These points are additionally illustrated by comparing the sensitivities of monomers versus their polymers:

	E_{50}, PA, Kg-cm.	
	Monomer	Polymer
TAA	4	48 (solid)
TAMA	6	36 (solid)
FA-BDE	3.5	10 (solid)
FA-G	1	2.5 (liquid)

The thicker materials are invariably less sensitive. Moreover, the observed effects of fineness and viscosity are comparable to the data scatter observed. An attempt has been made to minimize scatter due to physical properties in this analysis by always taking the lowest E_{50} where two or more results were obtained on the same compound.

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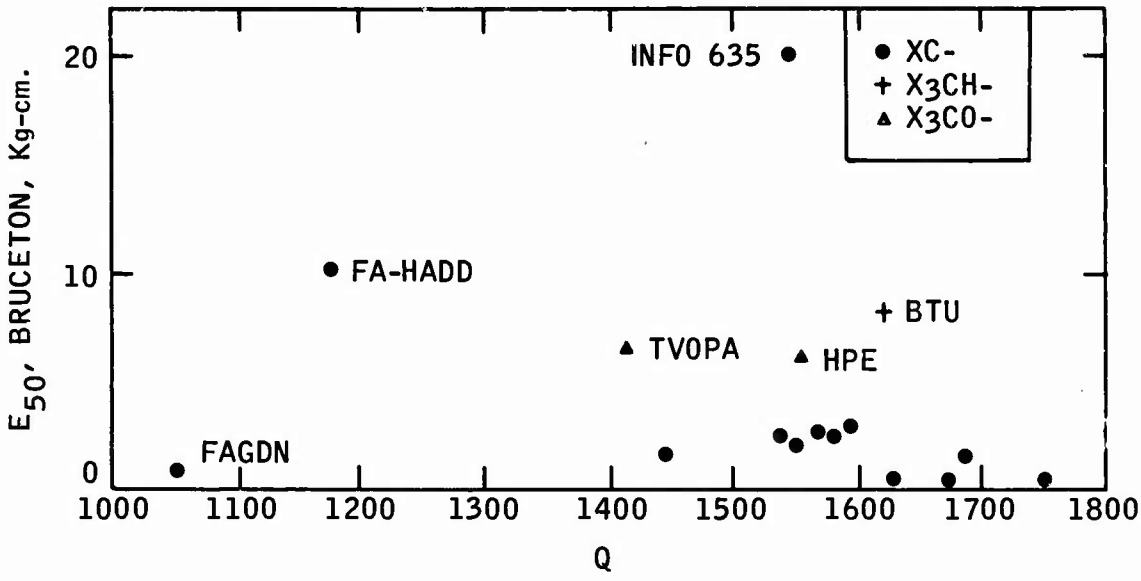
* The few apparent exceptions may or may not be valid, as discussed in Section 3.1.3., below.

3.1.2. All -OCX_3 Compounds
Are Ultra-Sensitive

(C) The great majority of OCX_3 compounds studied fall on the Main Sequence, above 1400 cal/gm heat of explosion and below 10 Kg.-cm. E_{50}. The few OCX_3 compounds of lesser energy, however, also fall below 10 Kg-cm., implying that the energetics of the OCX_3 group itself is of more importance than the energetics of the molecule as a whole. In other words, OCX_3 compounds seem to have a sequence of their own - a horizontal one. This is seen even more vividly in the following figure which plots Bruceton E_{50} versus Q for such compounds as have been tested on the Bruceton machine. There is no discernable trend of E_{50} with heat of explosion.

IMPACT SENSITIVITY VS. ENERGY FOR NF COMPOUNDS



(C) Moreover, if one plots Picatinny Arsenal E_{50} versus Q for different chemical classes of OCX_3 compounds, one finds no distinctions among OCX_3-substituted alkanes, ethers and alcohols, nitro compounds, and nitrate esters. All classes lie within the scatter band, and none even tend to cluster near one edge of the band. It is probable that differences would appear if the impact tests were run with much greater precision*, but it is clear that the differences would be so small as to be of no practical significance.

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* The thermal sensitivity data of Section 5.1. indicate that there are indeed sensitivity differences due to chemical structure, but that they are quite small compared to the resolution of the normal impact sensitivity test.

3.1.3. NCX_3 and CX Compounds Appear to Lie on the Main Sequence

(C) Three NCX_3 compounds, BPBTC, BTBU, and BTU, were included in this survey and were found to fall on the Main Sequence rather than on the horizontal sequence of OCX_3 compounds. Only two examples are well up on the Main Sequence, and these are both powdered solids, which makes the data suspect. Nevertheless, all three compounds fall so well on the sequence that there seems to be no justification for rejecting the data. In this light, NCX_3 compounds still appear to offer hope of at least "normal" sensitivity, whereas OCX_3 compounds do not.

(C) CX compounds, too, are distributed along the Main Sequence except for TAA monomer whose great sensitivity can perhaps be explained away on the basis of the reactivity of its unsaturation; poly-TAA is far up on the Main Sequence, where it belongs energy-wise. The saturated CX compounds are all on the Main Sequence or even above it. Lesser confidence should perhaps be placed in the data for bis(NF_2)propane and bis(NF_2)ethane, which fall well above the Main Sequence; these data are the oldest in the survey and were obtained long before the bulk of the data were. If these can be discounted, the saturated CX compounds all lie on the Main Sequence.

3.1.4. The Data Hold Out No Hope for Insensitive, Energetic Molecules

(C) Taken as a whole, the above data hold out no prospects for any molecular structure of dramatically lower sensitivity than "normal." Sensitivity increases monotonically with energy. There are structures with greater sensitivity than "normal," but effectively none with lesser sensitivity. To place any great credance in the X_2C_3 and X_2C_2 data is to grasp at straws. Insensitive NF_2 compounds can certainly be made, but they will be low-energy; and conventional compounds of comparable energy are far easier to obtain. Sensitivity increases monotonically with energy, and there are no examples of even doubtful validity of insensitive compounds of 1800 cal/gram or more. The one avenue to high energy and low sensitivity still apparent is to segregate the fuel and the oxidizer moieties in separate molecules or even separate crystals, as in the metallized composite propellants.

(C) Minor improvements in sensitivity can be made by tinkering with physical properties, which presumably alters the efficiency of conversion of mechanical energy inputs into hot-spots; but these improvements are small compared to the disparity between OCX_3 compounds and conventional explosive and propellant materials. Such desensitization is the subject of the next two sections.

3.2. DESENSITIZATION OF NF COMPOUNDS

(C) A number of model, ultrasensitive NF compounds have been studied for their sensitivity and their susceptibility to desensitization via additives and physical treatments such as coating, thickening, and blending into propellant formulations. Compounds studied include:

poly-FA-BDE	$(F_2N)_3COCH_2CH(-O-)_nCHCH_2OC(NF_2)_3$	solid (polymer)
INFO-635	$(F_2N)_3COCH_2CH_2NH_2 \cdot HClO_4$	solid (ionic crystal)
FA-TNENE	$(F_2N)_3COCH_2CH_2N(NO_2)CH_2C(NO_2)_3$	solid (organic crystal)
FA-BDN	$(F_2N)_3COCH_2CH(ONO_2)CH(ONO_2)CH_2OC(NF_2)_3$	liquid (PFG adduct)
HPE	$F_2NCH_2CH(NF_2)CH(NF_2)OCH(NF_2)CH(NF_2)CH_2NF_2$	liquid (N_2F_4 adduct)
FA-G	$CH_2(O)CH-CH_2OC(NF_2)_3$	liquid (PFG adduct)

(C) Significant desensitization, up to an order of magnitude, has been obtained in most of the systems studied, and some regular relationships have been uncovered; however, dramatic desensitization has not been obtained, and there are no visible prospects for desensitizing high-energy NF compounds to the level of neat nitroglycerin.

(C) The successful desensitization techniques found can be organized into five categories:

- Coatings
- Dilution
- Pulverization
- Thickening
- Inhibition

Most of these have precedents in published work on conventional explosives. For example, HMX has long been desensitized by wax coating, and nitroglycerin is shipped as a dilute solution. There are few, if any, really clear examples of inhibition; but it has at least been hinted at. These five categories are each discussed and illustrated below.

3.2.1. Coatings

(C) Coating would appear to be a general treatment for insulating a material from external stimuli, but it has limited effectiveness in desensitization. Coating is very effective against spark sensitivity, where this exists. For example, poly-FA-BDE, a very spark-sensitive material, is completely desensitized to spark by wetting down with virtually any liquid. However, most of these coatings are not effective against friction or impact.

SENSITIVITY OF WETTED POLY-FA-BDE

Wetting Liquid	Spark to explode, Joules, (Enough liquid to wet)	Friction, Grit (at 25% liquid)	E_{50}, Kg-cm, P.A. (at 25% liquid)
(None)	< 0.016	4	22
CH_2Cl_2	> 1.8	--	--
FC-75 Halocarbon	> 1.8	5.5	21
Ethanol	> 1.8	5.5	18
Water	> 1.8	5.5	23
Benzene	> 1.8	6	7
CH_3CN	> 1.8	5.5	30.5
Acetone	> 1.8	5.5	24
(propellant matrix)	> 1.8	5.5	6 (typical)

A few liquid coatings do desensitize poly-FA-BDE dramatically against friction; but it takes 25 wt.% to do it. Twenty wt.% is ineffective, and none of the liquids exhibit significant impact desensitization even at 25 wt.%.

SENSITIVITY OF WETTED POLY-FA-BDE

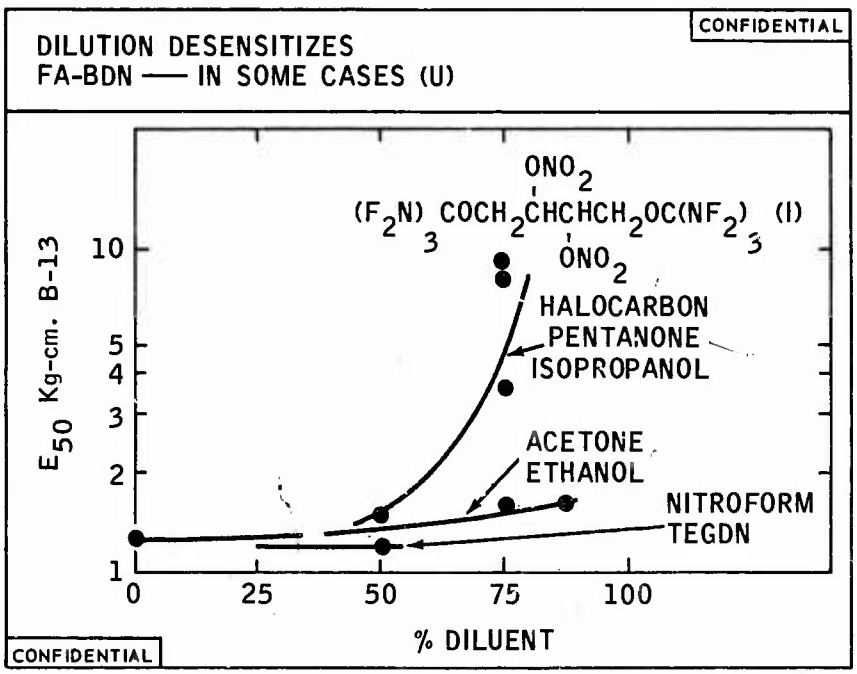
Wetting liquid 25 wt.%	Friction, Grit	E_{50}, Kg-cm. P.A.
(None)	4	22
TEGDN	> 9	20.5
Tributyrin	> 9	20.5
Halocarbon Oil 11-21	> 9	23
HMPA	> 9	23

·stings of wax or polymers on poly-FA-BDE behave similarly. Twenty-five per cent or more gives good spark protection but little or no impact or f .ction desensitization. Similar findings apply to coatings and coverings on other solids such as INFO-635 and FA-TNENE.

3.2.2. Dilution

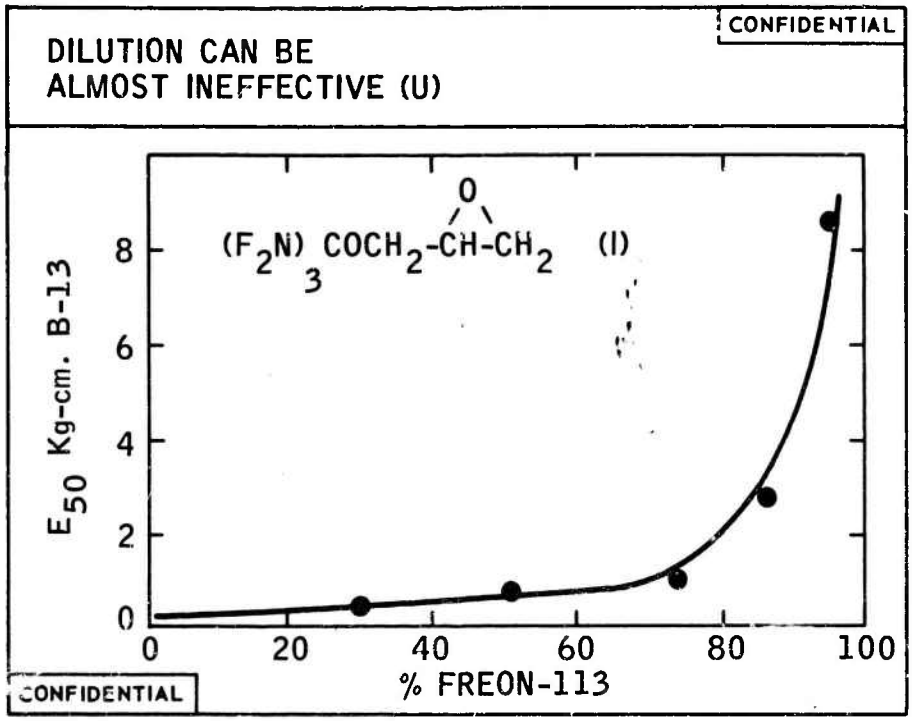
(U) Dilution has long been used for desensitizing explosives. Nitroglycerin, for example, is shipped as a 10% solution in alcohol or acetone; and NF materials themselves are commonly shipped as dilute solutions. However, dilution is not always effective, and every case should be confirmed experimentally.

(C) Dilution studies on FA-BDN indicate that some diluents desensitize it, some sensitize it, and some have little effect.



The halocarbon/pentanone/isopropanol curve represents the greatest desensitization obtained by solvent addition, and is designated "simple dilution" to distinguish it from thickening and inhibition effects, discussed below. It is striking that 75% or more diluent is needed for any really effective desensitization. Some diluents - admittedly energetic ones - actually sensitize FA-BDN; and, surprisingly, acetone and ethanol - the first ones to be considered from nitroglycerin experience - are almost completely ineffective. One must choose a desensitizing diluent carefully.

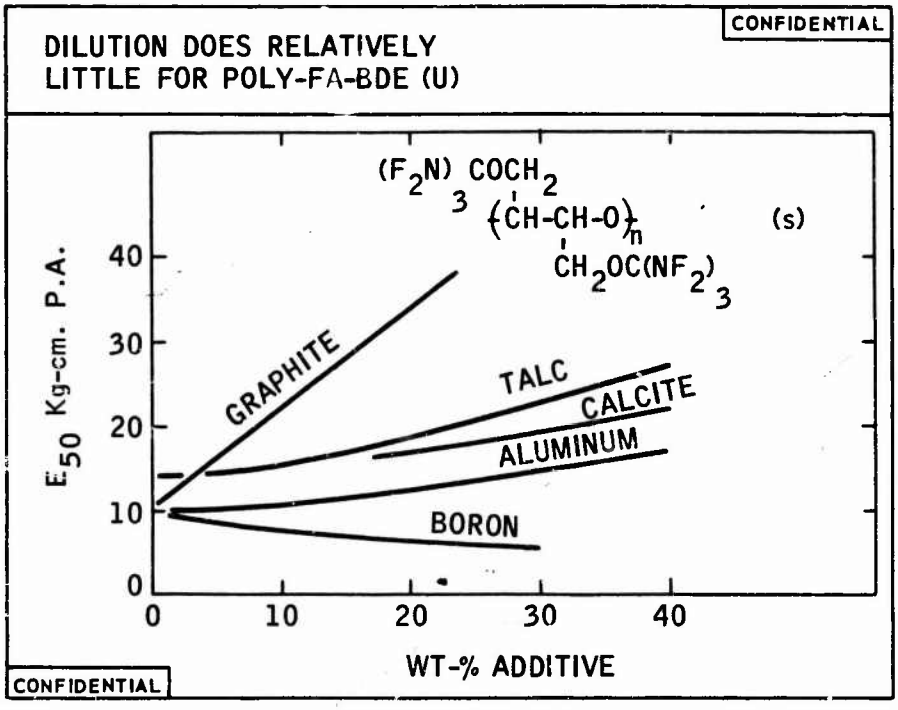
(C) Non-desensitization by dilution is illustrated even more vividly by the case of liquid FA-G in Freon 113:



This NF compound is not desensitized to a really safe level even at 95% diluent! The "solutions" were crystal clear to the eye and did not separate on standing; but they did show a strong Tyndall beam, indicating that they were not molecular dispersions. Solutions of FA-G in CH_2Cl_2 did not show a Tyndall beam and were normally desensitized. It is postulated that the acetone and ethanol "solutions" of FA-BDN may also have been colloidal dispersions rather than true solutions.

(C) These data would seem to imply that there is little hope for good impact desensitization via coatings. The FA-G was certainly dispersed to colloidal size, and the individual micro-droplets were certainly well separated by the inert continuous phase; yet the dispersions were virtually as sensitive as the pure FA-G.

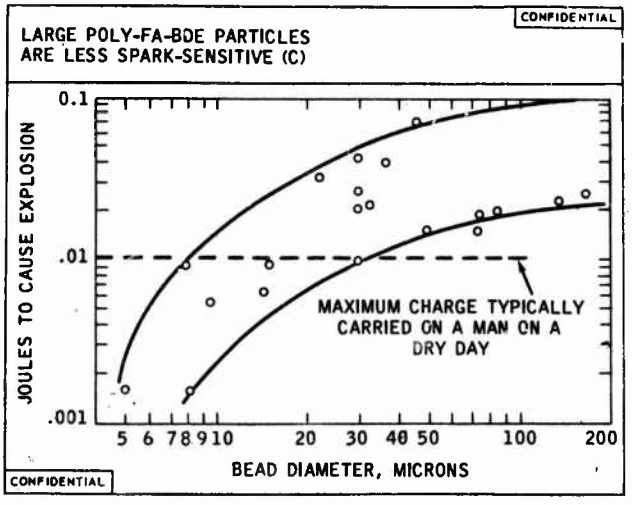
(C) A similar phenomenon is observed in the "dilution" of powdered solids by admixture of other powders. Poly-FA-BDE is either sensitized or desensitized by adding other solids, depending upon the hardness of the additive.



The soft materials, graphite and talc, are moderately effective desensitizers, while crystalline boron, with a Mohs hardness of 9, is a sensitizer. Similar results have been obtained on other solids, and details are given in the foregoing reports (cf. Appendix 4).

3.2.3. Pulverization

Control of particle size often affects at least the apparent sensitivity of solids. This is particularly true of spark sensitivity and is illustrated below:



(C) Impact sensitivity, too, appears to be a function of particle size, at least when measured in the Picatinny Arsenal tester, with higher bulk density appearing more sensitive.

Sample	E_{50}, Kg-cm. P.A.
Poly-FA-BDE	
1-5μ powder	22
0.1 mm flakes	11
FA-TNENE	
Fine powder	35
1/2" xtals	6.5
Cast button	2.3

This effect has been noted on almost every solid tested in this laboratory, the only exceptions being waxy, low-melting solids which could not be obtained in really fluffy form for comparison. However, this effect appears to be an artifact of the Picatinny Arsenal machine. The following table presents Bruceton impact data on samples of poly-FA-BDE, FA-TNENE, and INFO-635 as loose powders and as wafers compacted by compression at 20,000 psi.

	E_{50}, Kg-Cm, Bruceton 12	
Sample	Loose	Compacted
poly-FA-BDE	2.6	3.2
FA-TNENE	1.4	2.3
INFO-635	25.0	25.0

(C) The empirical validity of desensitization by pulverization is an open question. The lesser impact sensitivity of fine powders is probably reflected in better handling safety--so long as one does not run into increased spark sensitivity--but blends of these solids with liquids, as in a propellant formulation, seem to behave more like the dense form than the fluffy form (cf. Section 3.3.). Moreover, extensive comparisons with related liquid compounds and other solid compounds (cf. Section 3.1.) indicate that the dense form gives more meaningful results in structural and energy comparisons.

3.2.4. Thickening

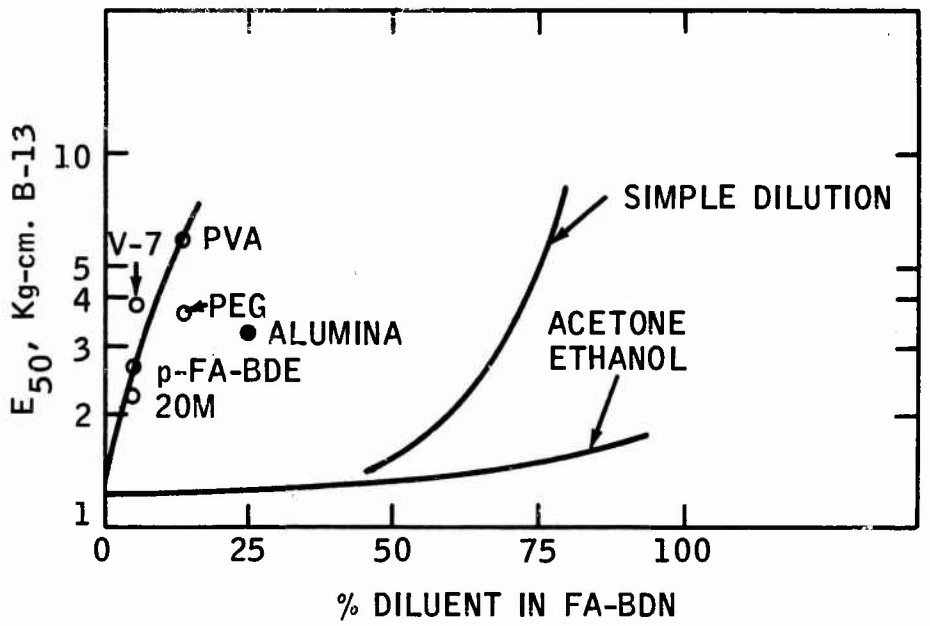
(C) Thickening and gelation can desensitize liquids towards impact. The following table presents some representative data on FA-BDN thickened with various additives.

THICKENING DESENSITIZATION OF FA-BDN

Additive	E_{50}, Kg-Cm, B-13 0%	5%	15%	25%
15% PVA	0.6		5.6	
5% Gelva V-7 Resin	0.6	3.8		
5% Carbowax 20M	0.6	2.2		
15% Polyethylene Glycol 3000	0.6		3.6	
5% Poly-FA-BDE	0.6	2.6		
25% Colloidal Alumina	0.6			3.2

Thickening can be much more effective than simple dilution, as shown on the following plot, which compares the above data to the dilution data presented earlier. Nearly an order of magnitude desensitization can be obtained with 15% additive. One of the most interesting thickener-desensitizers is poly-FA-BDE, since it is energetic itself. It is discussed further under propellant desensitization, Section 3.2.

THICKENING IS MORE EFFECTIVE THAN DILUTION (U)



(C) The additives shown are the best found. Many other thickeners were much less effective, and a few--notably colloidal silica--were actual sensitizers. The effect is highly specific; the effective additives were less effective when tested in another NF liquid, HPE; and none of these materials was effective in desensitizing FA-BDN towards friction.

3.2.5. Inhibition

(C) Inhibitors--defined as additives which desensitize without appreciable alteration of obvious physical properties such as viscosity--in some cases show appreciable impact desensitization and sometimes dramatic friction desensitization. The impact desensitization is comparable to that via thickening. In addition, tributyrin, DMP, Triton X-100, and diphenylpicrylhydrazil desensitize the very friction sensitive FA-BDN to completely off-scale in the Esso friction tester.

Additive	E_{50}, Kg-Cm, B-13	Friction, Grit
(None)	0.6	0-4
15% Triacetin	2.2	5.5
15% Tributyrin	2.0	> 9
10% Dimethylphthalate	2.0	> 9
15% Triton X-100	2.5	> 9
15% Ethyl Centralite	4.0	5.5
15% Diphenylpicrylhydrazil	1.0	> 9

Again, the effect is highly specific. The same additives were much less effective in desensitizing HPE towards impact, although most of them were effective in desensitizing it towards friction. No effective chemical additives were found for the solids poly-FA-BDE, UNFO-635, or FA-TNENE.

3.2.6. Summary

(C) The foregoing data lead to three general conclusions:

- Significant desensitization can be obtained in most cases, up to an order of magnitude, usually--but not always--at an energy cost which makes the advantage problematical. Moreover, two orders of magnitude are needed in order to equal the sensitivity of conventional "handleable" explosives.

- There are five general desensitization techniques, but there are more exceptions than rules. Each compound is a new case and needs to be examined individually for desensitization effectiveness, even for shipping safety.

- Further breakthroughs are unlikely. Enough energetic compounds and enough desensitizing techniques have been screened to make it unlikely that further work will produce dramatically better results. However, application of what we have to propellant systems is in order, and this is discussed in the next section.

3.3. SENSITIVITY OF NF PROPELLANTS

(C) Propellant formulations have been studied briefly, both as practical examples of desensitization techniques such as coating, dilution, and gelation; and to establish whether marked sensitivity differences are to be expected as one result of composition differences. The data indicate that NF propellants in the 280-285 Isp range can very probably be formulated with no greater impact sensitivity than conventional double-base composites by applying the lessons learned in the foregoing section.

3.3.1. Simple Correlations Fail to Predict Formulation Sensitivity

(C) The most straight-forward criterion for predicting formulation sensitivity would appear to be the sensitivity of the most sensitive ingredient, but this approach has not been successful. Of 50 formulations studied, 22 are more sensitive than the most sensitive ingredient, 24 are less sensitive and only 4 are correctly predicted. The standard deviation of the predicted from the measured impact sensitivity is 3.8 kg.-cm. The magnitude of the standard deviation is so great as to render any prediction meaningless (90% of the formulation E_{50}'s are from 2.5 to 10.5 kg.-cm).

(C) Other simple correlations also fail to predict formulation sensitivity. The sensitivity does not appear to be proportional to Isp nor is it in line with increasing $-NF_2$ content.

REPRESENTATIVE FORMULATION SENSITIVITY DATA

Formulation No.**	Impact E_{50}, kg.-cm., P.A.	Isp	NF_2 Content
306-135-1	4	287.9	44.00%
10-29-1	4	288.4	46.45
D-A-1	4.6	290.2	40.27
65-3-8-1	5.5	284.6	33.46
5-25-1	5.5	286.2	33.50
65-3-8-2	5-6	283.1	42.24
D-A-2	5.8	290.0	56.07
306-125-3-2	7	287.4	54.62
306-136-1	7	290.2	39.69
306-117-2	7.2	294.7	50.47
306-135-2	9	289.3	54.81

* At Esso Research, under Contract DA-01-021-AMC-11735(Z), for the Department of the Army, Army Missile Command (Redstone Arsenal). These data have been reported to the Army in various DA-01-021-AMC-11735(Z) reports in connection with the evaluation of the individual propellant formulations. The critique reported herein was performed under contract AF 04(611)-9969.

** Compositions are given in Appendix 2.

The postulated desensitization techniques of dilution, thickening, and encapsulation have had no apparent effect. Instead of being desensitized, 44% of the formulations tested are actually more sensitive than the most sensitive ingredient.

(C) The lack of any sensitivity trend with either Isp or NF_2 content, however, is encouraging, because it means that the highest energy formulations are not necessarily the most sensitive ones.

3.3.2. The Plasticizer-Oxidizer Pair Is One Key to Sensitivity

(C) The sensitivity of plastisols appears to be more dependent upon the plasticizer concentration than upon the plasticizer sensitivity. A 50/50 mixture of poly-FA-BDE and FA-TNE fused to a smooth, slightly tacky plastisol which was more sensitive than either poly-FA-BDE or FA-TNE alone; but when plastisol glasses or waxes were formed from poly-FA-BDE and FA-BDN, the sensitivity was proportional to the plasticizer content.

SENSITIVITY OF POLY-FA-BDE PLASTISOLS

Sample	% Plasticizer	Impact Sensitivity P.A. E_{50}, kg.-cm.
poly-FA-BDE	0	11-22
50/50 poly FA-BDE/FA-TNE	50	4
FA-TNE	100	7
90/10 poly FA-BDE/FA-BDN	10	9.5
50/50 poly FA-BDE/FA-BDN	50	7.5
FA-BDN	100	4

If the plastisol is part of a formulation, the same phenomenon is observed, that is, the impact sensitivity is proportional to the plasticizer content.

SENSITIVITY OF PLASTISOLS IN FORMULATIONS*

Plasticizers	Impact Sensitivity P.A. E_{50}, kg.-cm. Oxidizer	
	poly-FA-BDE	FA-TNENE
32.4% DEGDN	5.5	4
59.4% DEGDN	3.5	4
32.4% TVOPA	7.5	5.3
59.4% TVOPA	2.5	4
32.4% FA-PETRIN	7	5.5
59.4% FA-PETRIN	3.5	5
34.2% FA-PEDIN	10	7
59.4% FA-PEDIN	6.5	4

* 32.4% plasticizer, 60.50% oxidizer, 3.60% HPVA/PAPI, 3.5% boron
59.4% plasticizer, 30.50% oxidizer, 6.60% HPVA/PAPI, 3.5% boron

(C) Although the sensitivity of plastisols or formulations appears dependent upon the plasticizer concentration, it is independent of the plasticizer sensitivity in the systems studied.

PLASTICIZER SENSITIVITY

Plasticizer	Impact Sensitivity, E_{50}, kg.-cm. poly-FA-BDE Formulation	FATNENE Formulation	Plasticizer Only
DEGDN	5.5	4	10.4
TVOPA (34.4%)	7.5	5.3	6.5
FA-PETRIN (34.4%)	7	5.5	5.5
FA-PEDIN (34.4%)	10	7	5.5

(U) It is clear from the foregoing data that propellant sensitivity is not a simple function of any one compositional parameter. Consequently, some simpler, model systems have been studied; and these are discussed below.

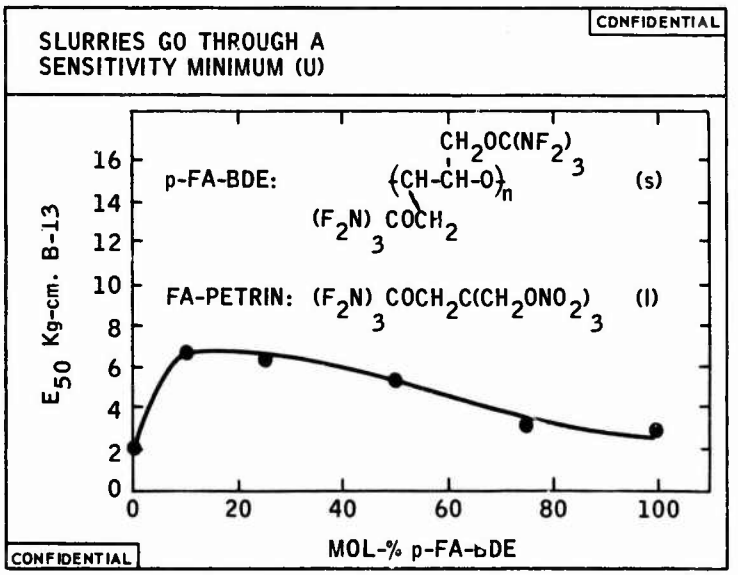
3.3.3. Binary Oxidizer-Plasticizer Mixtures go Through a Minimum in Impact Sensitivity (Maximum in Drop Height)

(C) As the first step upward in complexity in the study of formulation sensitivity, the effect of plasticizer concentration in simple binary plasticizer-oxidizer mixtures has been evaluated for a series of cases of interest. Impact data for the Bruceton test are shown in the table below.

IMPACT SENSITIVITY OF OXIDIZER-PLASTICIZER MIXTURES

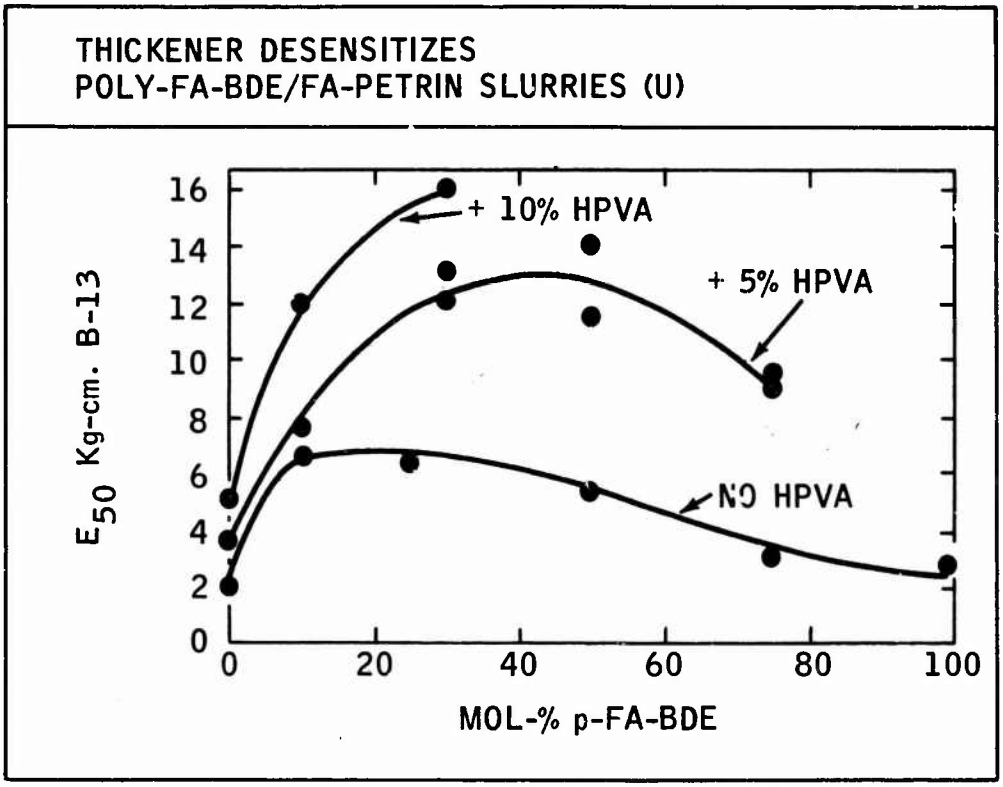
	E_{50}, kg-cm, Bruceton-13				
Mol.% Oxidizer	P-FA-BDE FA-BDN	P-FA-BDE FA-PETRIN	P-FA-BDE TVOPA	FA-TNENE FA-PETRIN	FA-TNENE TVOPA
0	0.7	2.0	5.2	2.0	5.2
5	---	---	6.2	---	---
10	1.2	6.7	---	4.4	---
25	3.8	6.3	8.3	3.7	5.0
50	5.5	5.2	7.2	4.0	5.7
75	2.8	3.4	5.4	3.9	3.9
90	---	---	1.9	---	---
100	2.1	2.1	2.1	2.1	1.7

In general, the plasticizer-oxidizer mixtures are less sensitive than the individual ingredients and a maximum (minimum sensitivity) occurs in the concentration-drop height curve between 10% and 40% solids. The typical case of P-FA-BDE/FA-PETRIN is presented below as a plot. The other cases are all similar.



3.3.4. Impact Sensitivity of Oxidizer-Plasticizer Mixtures is Reduced by Addition of a Binder

(C) The addition of a binder polymer, HPVA, to the above slurries results in a further desensitization at all ratios, and greater amounts of polymer produce greater desensitization. The following curve is for HPVA/p-FA-BDE/FA-PETRIN; similar curves were obtained for each of the other systems of Section 3.3.3.



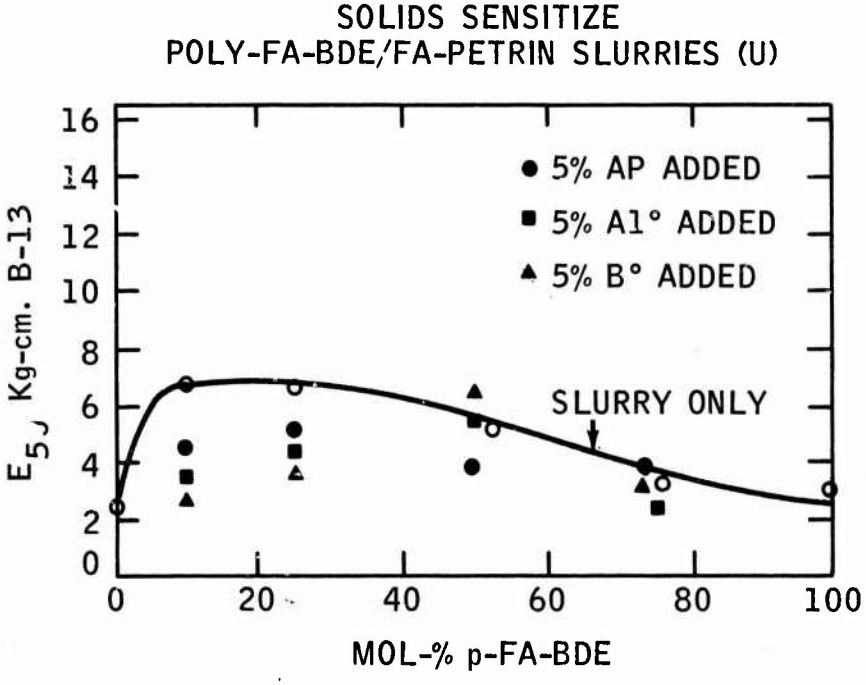
(C) It is interesting that these curves all appear to go through a maximum somewhere in the mid-range. This may be strictly a mechanical effect: the system goes from a thin slurry at the left side of the chart to a dry, crumbly paste at the right, and is a rather smooth, creamy paste in the mid-range. The mid-range is, of course, the range of interest in practical propellant compositions.

(C) The addition of binder produces a marked change in the physical state of the mixture, yielding a gel-like structure. The cushioning effect of the "gel" may be responsible for the desensitization. The binder was not cross-linked or cured in any way; it was dissolved in the plasticizer before blending in the solid oxidizer.

(C) In a brief study, the effect of 10% and 20% binder, both crosslinked and uncrosslinked, on the E_{50} of FA-PETRIN was investigated. At 10% binder, there was no significant difference between crosslinked and uncrosslinked. At 20%, both systems gave completely indeterminate results, with patternless, muffled fires interspersed with misses all the way from 38 to 80 cm drop height. Perhaps the most significant observation of all was the muffled nature of the explosions. They were difficult to distinguish from the crash of the falling weight, in vivid contrast to the usual ear-splitting reports of PFG adducts. Moreover, there was almost always a considerable amount of unconsumed material left on the impact tool after a positive test. Evidently, the desensitized mixtures tended towards low-order burning with subsequent quenching. Such behavior would be a different aspect of desensitization from those noted previously and would be of considerable future interest.

3.3.5. The Addition of Solids Sensitizes Propellant Mixtures

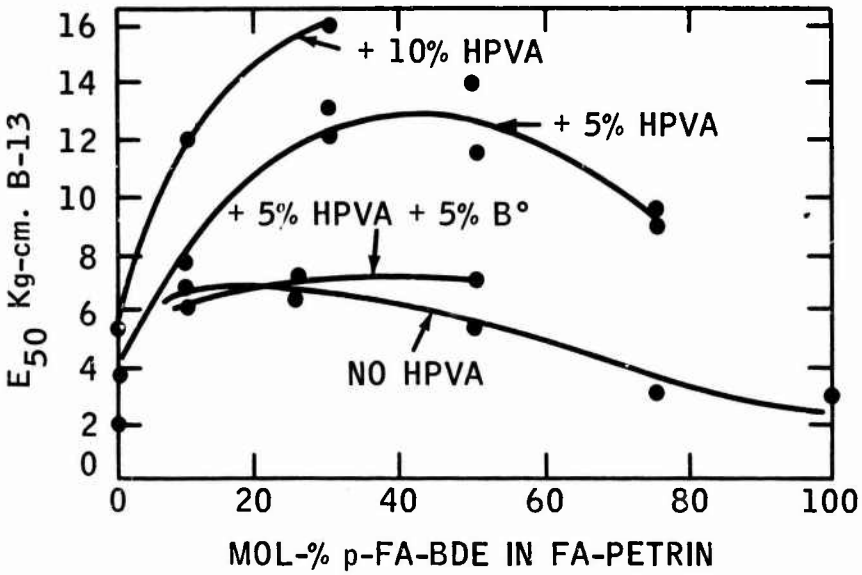
(C) The addition of AP, aluminum, or boron to the oxidizer/plasticizer slurries of Section 3.3.3. results in sensitization in most cases. The case of P-FA-BDE/FA-PETRIN is presented below:



The other cases are all similar. The added solids sensitize in most mixtures, and it makes little or no difference which solid is added.

(C) If both HPVA and boron be added, the solid seems to sensitize about as much as the polymer desensitizes; and the sensitized-desensitized mixtures has nearly the same E_{50} as the simple binary slurry. The following figure is for the P-FA-BDE/FA-PETRIN case.

BORON RE-SENSITIZES
DESENSITIZED SLURRIES (U)



This would seem to mean that the optimum design from a sensitivity standpoint would be to omit the metal fuel, which contributes only an impulse point or so anyway in most cases, and to use as much binder as is tolerable from an energy standpoint. It would also seem worthwhile to try to substitute the relatively soft HMX for AP in systems which use AP.

(C) It would further seem worthwhile to add one or more of the non-thickener "inhibitor" additives from Section 3.2.5. to the thickened, metal-less propellant formulations in hopes of gaining additional desensitization via the inhibition route. Triton X-100 and ethyl centralite suggest themselves.

3.3.6. Summary

(C) The NF propellant sensitivity work leads to three general conclusions:

- Additives and thickening desensitize somewhat. Improvement by a factor of 3 or 4 can readily be obtained, and at least some of the thickeners are themselves energetic.

- Hard solids sensitize. Therefore, the exclusion of hard solids such as boron is in order, and all-organic formulations may be best.

- We can do better than we have by careful attention to the sensitization/desensitization lessons learned herein. It seems reasonable to expect that high-energy NF formulations can be made which are no more impact-sensitive than conventional double-base composite formulations.

4. ACTIVATION ENERGIES FROM CONDENSED-PHASE THERMAL EXPLOSIONS

(U) This section gives details on an improved thermal sensitivity test based on refinements to the conventional autoignition test. The data are unfolded by the nonsteady-state treatments of Zinn and Mader and Frank-Kamenetskii to yield activation energies, frequency factors, reaction rates and critical explosion temperatures for exploding, condensed-phase samples.

4.1. NEED FOR AN IMPROVED THERMAL SENSITIVITY TEST

(U) Thermal sensitivity data, giving effective activation energies and frequency factors for the explosion process, offer the most direct and least complicated measure of the effects and mechanisms of varying chemical structures and desensitizing treatments.

4.1.1. Better Sensitivity Data Are Needed for Structure-vs.-Sensitivity Studies

(U) The study of the effect of chemical structure on sensitivity requires more selective sensitivity tests than are now available. Impact tests, for example, have been shown by many workers to be very dependent on the physical characteristics of the sample: fine powders appear less sensitive than the same material in coarse form, and explosive liquids appear less sensitive when thickened with a small amount of soluble gellant. Consequently, if a structure change under study results in a change in viscosity or crystal form, the physical desensitization obtained can very well obscure the chemical one. Friction tests are doubtless subject to similar reservations. What is needed is a nonmechanical sensitivity test which is not disturbed by purely physical changes.

(U) In principle, thermal sensitivity should be the most basic measurement of all, since explosion is a chemical process the energetics of which are thermal in nature. Appropriate plots of explosion delay times versus initiating temperatures can yield effective activation energies and frequency factors for the explosion processes actually occurring in realistic samples. These parameters in turn give direct insights into the mechanisms which are occurring and possible ways to interfere with them. For example, a change in activation energy upon addition of an additive could imply complex formation; and a change in frequency factor would imply dilution or chain breaking. The magnitude of the frequency factor also has implications as to the length of the reaction chains involved and therefore as to the amount of an inhibitor which might be required.

(U) Conceptually, one can picture a typical explosion event as a two-step process. In the first step, some mechanical stimulus does work on the sample to give a hot-spot. The hot-spot then grows through thermochemical mechanisms to a runaway reaction, or explosion.

Conventional sensitivity tests give dsta about the overall process but not about the individual steps. If, however, one could add insight into the second step via thermal sensitivity testing, one would then be in a position to infer the energetics and perhsps the mechsnisms of the first step. Knowledge of the first step would place one in s position to drsw conclusions as to methods and prospects for interrupting the process, i.e., desensitizing the material.

(U) In addition to applications in empirical desensitization, good kinetic parsmeters on condensed phsse reactions would also provide a much-needed bridge between empirical investigations and more basic investigations on the energetics of high-energy compounds.

4.1.2. Existing Thermal Sensitivity Tests Are Not Satisfactory for Ultrasensitive Materials

(U) A number of thermal sensitivity tests have been devised and used in the past. These have been quite useful for "conventional" explosives; but they fsil to give useful dats for ultrasensitive materials where the ignition delsys of interest are short; i.e., comparable to the heating time of the ssmple contsiners. The Picatinny Arsenal sutoignition test, for example, requires times on the order of four seconds to raise the sample to within 10 degrees of the nominal bath temperatures. The Wenograd test responds in m croseconds, but there is still considerable question as to just how much of the observed delay is chemicsl resction time and how much is container heating time. The Wenograd test also indicates liquid NF compounds to be generslly less sensitive than nitroglycerin, which is at wide vsrisnce with common observstion.

4.2. APPROACH TO AN IMPROVED THERMAL SENSITIVITY TEST

(U) Rsther than develop a new test, the chosen approach has been to modify an established "Slow" test to obtain relisble explosion delay times down to 100 milliseconds, at accurstely known temperatures. In addition, an improved mathematical model hss been developed to unfold the data more meaningfully.

(U) Thermsl initistion phenomena may be divided for convenience into three regions: sdisbstic, autoignition, and isothermal. The adiabatic region comprises those initistions which occur in microseconds, within which time heat flow within the sample is negligibly small. This is the time range during which stimuli sre commonly felt to be effective in mechanical sensitivity tests such ss the impsct test. The autoignition region comprises initistions which require times on the order of one to ten seconds. In this region, resction times csn be measured and kinetic parameters obtained from reslistic condensed phase explosions. Heat flow is apprecisble and must be described sccurstely if mesningful kinetic parameters are to be obtsined from the experimental dsts. The isothermal region comprises slow decompositions over periods of hours st invsrient temperstures. No explosion occurs. Isothermal decomposition hss been widely used to determine bond strengths, sctivation energies, etc.; but, of course, does

not represent realistic temperatures and rates for explosion processes. The autoignition region has been chosen for our thermal sensitivity work because it is fast enough to be a realistic explosion and slow enough to permit reasonable measurements of time and temperature.

4.2.1. Minor Modifications Improve the Response Time of the Picatinny Autoignition Test

(U) The Picatinny Arsenal Explosion Temperature Test*, or some version of it, has been widely used to rank the thermal sensitivity of conventional propellants and explosives. In this test, a sample contained in an empty No. 8 blasting cap shell is plunged into a molten Wood's metal bath held at a known temperature, and the time to explosion is observed. The logarithm of the delay time plotted against the reciprocal of the absolute temperature gives an approximately straight line, and the temperature corresponding to a five-second delay is read off the plot. The more "sensitive" the sample, the lower the temperature of the five-second point, and vice-versa.

(U) The test fails on ultrasensitive materials, however. These materials react in times that are short compared to the time required simply to heat the metal container, and the "five-second" temperatures obtained are little more than critical bath temperatures for explosion to occur or not to occur. In addition, the apparent reaction rates show a surprisingly low temperature dependency. Calculations of thermal flow through a metal shell indicate that the temperatures inside and outside a 1 mm thick shell may differ by as much as 40°C at the time of explosion.

(U) Much better response times can be obtained simply by thinning down the bottoms of the sample tubes to 0.08 mm thickness and by polishing the tubes to remove surface oxides immediately before use. Under these conditions, the sample temperature approximates the bath temperature to within 4°C after 100 milliseconds (with the bath at 350°C); and the observed reaction rates show a more nearly conventional temperature dependence.

4.3. EXPERIMENTAL PROCEDURE AND DATA REDUCTION

(U) This section details the experimental and mathematical techniques used.

4.3.1. An Autoignition Experiment is Performed

(U) The experimental procedure used is an elaboration of the Autoignition Test specified in PATR 1401 and similar to the one used by Henkin and McGill**. A 60 to 80 mg sample is weighed accurately into a copper No. 8 blasting cap shell which has been freshly polished and whose bottom has been accurately ground down to a thickness of 0.08 mm, and the sample is

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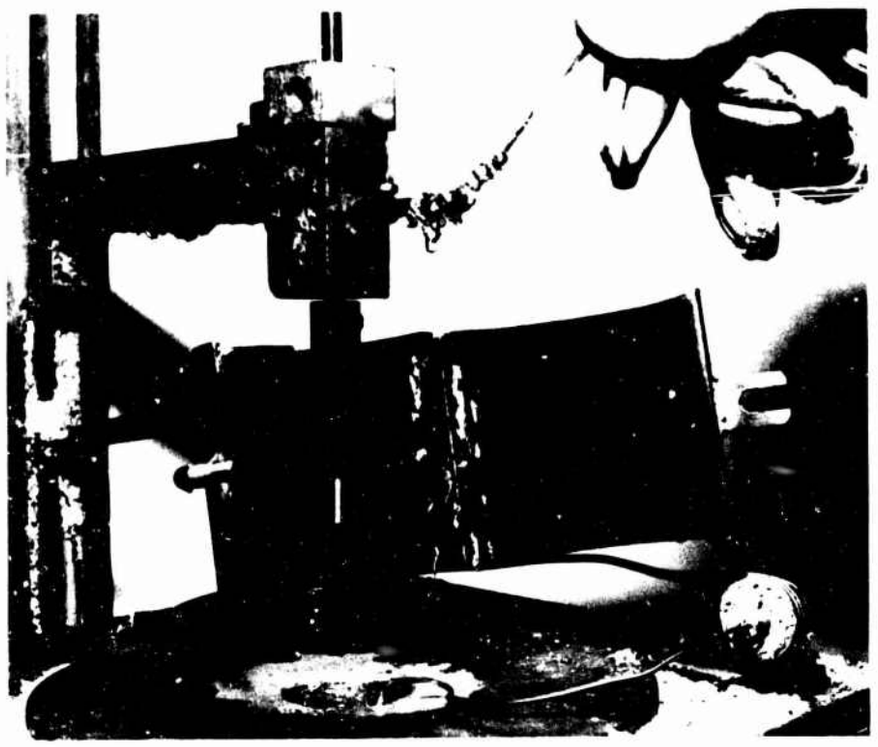
* Picatinny Arsenal Technical Report 1401.

** Henkin, H. and McGill, R., Ind. Eng. Chem., 44, 1391 (1952).

carefully spread around on the bottom to give an even slab configuration. Solid samples are pressed into a dense, even slab in the bottom of the shell by a 6000 psi hydraulic press, and the thickness of the slab is measured before the testing. Both liquid and solid samples are then sealed in by pressing a one-inch long Teflon plug above the sample. The loaded sample is then clipped into a plunger which drops it into a molten Wood's metal bath. Electrical contact between the bath and the sample shell starts an electronic timer as the sample enters the bath and a microphone stops the timer when the sample explodes. Explosion delay times are determined versus temperature for a range of temperatures selected to give delays ranging from 0.1 to about 10 seconds. Approximately ten samples are run.

(U) The following photograph shows the plunging apparatus. In this view, the splash shield is opened to show the sample shell (which is empty). In an experiment, the shield would be closed and the hand would be grasping the far end of a much longer lanyard.



(U) The following photograph shows a cut-away view of the sample shell before and after bottom thinning. The thinness and flatness of the heat transfer area are evident. The side walls are so much thicker than the bottom that essentially all the heat flow is considered to be through the bottom.

4.3.2. The Data Are Unfolded by a Modified Zinn-Mader Treatment

(U) The Zinn-Mader nonsteady-state mathematical treatment has been adopted as the model for the decomposition*. In this model, the surface of the explosive is instantaneously raised to a final temperature and the heat of reaction is both lost through the surface and conducted into the explosive. Over the temperature range used in our experiment, thermal run-away occurs well within the sample mass. Surface catalysis should therefore have no effect on the overall process. The data show that there is indeed very little, if any, catalytic effect from copper sample tubes.

(U) The explosion delay time is expressed as a function of activation energy, surface temperature, minimum temperature for explosion, and the physical properties of the sample:

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* Zinn, J., and Mader, C. L., J. Applied Physics, 31, 303 (1960).

$$t_{exp} = \frac{a^2}{\alpha} f\left(\frac{E}{T_m} - \frac{E}{T_i}\right)$$

where:

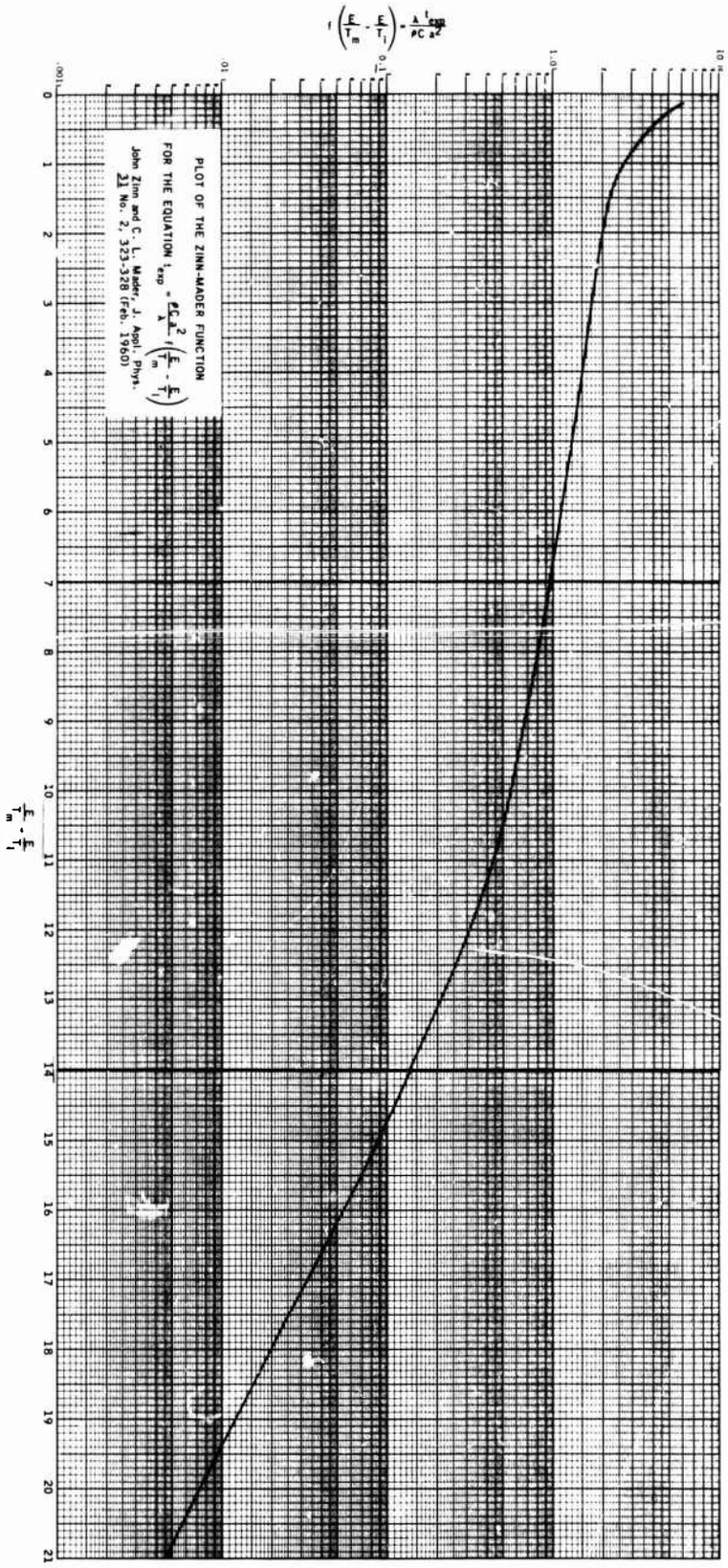
α = thermal diffusivity = $\frac{\lambda}{\rho C}$ (λ = thermal conductivity,) (ρ = density) (C = specific heat))

t_{exp} = time to explosion
a = sample thickness
E = activation energy
T_m = minimum temperature for explosion
T_i = surface temperature

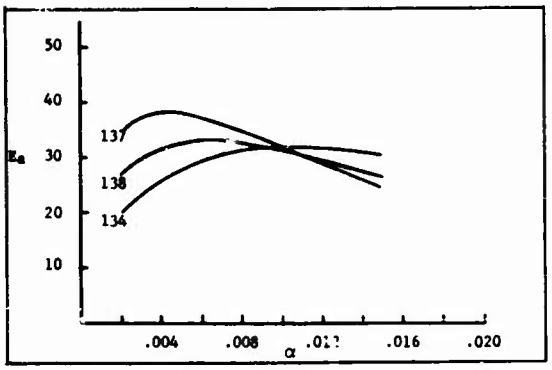
(U) Approximately ten experiments are run, at a range of temperatures empirically chosen to give explosion delay times ranging from approximately a tenth of a second to several seconds. t_{exp} is then plotted versus the corresponding T_i in order to determine T_m. The time/temperature curve rises rapidly at the lower temperatures and T_m is determined by extrapolation. T_m is fairly sharp and, once estimated, can readily be confirmed experimentally. With t_{exp}, T_i and T_m in hand, one then assumes a reasonable value of α (see below) and solves the Zinn-Mader equation for E. The actual Zinn-Mader function is a complex one, given by the following figure, and is solved graphically rather than analytically. The figure is taken from Zinn and Mader's paper and has been rederived and confirmed in detail by us from the basic Frank-Kamenetskii and Semenov equations. The figure as printed here is accurate enough to use in calculations.

(U) The constant α ($= \lambda/\rho C$) is, in general, not known for experimental materials, but it can be determined from the same experiments which determine E. If one has data from two (or more) thermal runs with the same explosive, the only unknown terms in the Zinn-Mader equation are the activation energy and α, and it is possible to solve for the α required to give the same activation energy for the two runs by treating the data sets as simultaneous equations. Briefly, one runs the thermal sensitivity test twice, using different sample thicknesses. Each set of data gives a curve of activation energy versus α, and the curves must intersect at those unique values of activation energy and α which satisfy both equations.

(U) Graphical solution is the easiest and most straight-forward approach to simultaneous solution of two or more complex relationships. Each thermal sensitivity run is plotted as activation energy versus α and the intersection or closest approach is found. An example is shown below for PETN (overleaf).


PLOT OF THE ZINN-MADER FUNCTION
FOR THE EQUATION $t_{exp} = \frac{\rho C_p a^2}{\lambda} f\left(\frac{E}{T_m} - \frac{E}{T_i}\right)$
John Zinn and C. L. Mader, J. Appl. Phys. 31 No. 2, 323-328 (Feb. 1960)
$f\left(\frac{E}{T_m} - \frac{E}{T_i}\right) = \frac{\lambda t_{exp}}{\rho C_p a^2}$
$\frac{E}{T_m} - \frac{E}{T_i}$

ACTIVATION ENERGY VS. THERMAL DIFFUSIVITY FOR PETN



Values derived from these intersections lead to the following results:

THERMAL SENSITIVITY OF PETN

Run	α	Ea
134	0.010	31.546
137	0.010	31.899
138	0.010	30.978

(U) The standard deviation in the activation energy at $\alpha = 0.010$ is 0.5 kcal/mole. The average value of Ea, 31.5 kcal/mole, is in excellent agreement with Cook's* value of 31.7 kcal/mole, derived by extrapolation of isothermal decomposition data to zero per cent decomposition with an assumed entropy of activation. It is also in good agreement with his range of 31.0 - 32.3 kcal/mole for breaking a nitrate bond, obtained in the same manner from studies of PETN, NG, RDX, and Tetryl.

(U) With Ea and T_m now known, Z, the frequency factor or collision number, is determined from the Frank-Kamenetskii equation**:

$$T_m = \frac{E}{2.303\ R \log\ (\rho a^2 QZE / \lambda R T_m^2 \delta)}$$

Q = heat of reaction, cal/gram
Z = collision number
δ = geometry factor (0.88 for slabs)

To obtain a value for ρ/λ, a value for the heat capacity must be estimated; however, an error by more than a factor of two is unlikely, and such an error would produce only an equal (maximum of 2X) error in the frequency factor. Moreover, this error would only have an effect on the calculated isothermal decomposition rate since in all adiabatic or autoignition processes, the frequency factor is coupled with the heat capacity and any error is cancelled.

* "The Science of High Explosives," M. A. Cook, Reinhold, New York, 1958, p. 178.

** Frank-Kamenetskii, "Diffusion and Heat Exchange in Chemical Kinetics," Princeton University Press, Princeton, New Jersey.

(U) Putting all the above together, then, one obtains the following values for PETN:

THERMAL SENSITIVITY OF PETN

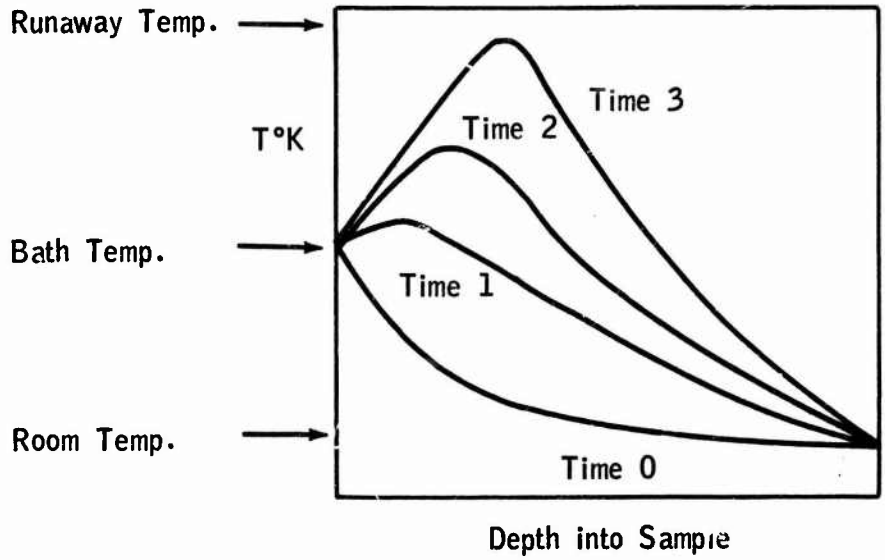
Run	α	Ea	Z
134	0.010	31.546	4.25×10^{10}
137	0.010	31.899	2.10×10^{10}
138	0.010	30.978	3.98×10^{10}

(U) As further illustration, a sample calculation of kinetic parameters from experimental data for nitroglycerin is given in Appendix 3.

4.3.3. Catalysis by the Copper Sample Tube Is Not Significant

(U) One would expect on the basis of theory that the metal of the sample holder would not have any catalytic effect on the explosion reaction. In the autoignition experiment, the surface of the explosive is raised to some subexplosion temperature; and the material begins to evolve heat. This heats the next layer to a higher temperature; but the surface itself, in thermal contact with the massive heat sink of the bath, does not rise in temperature. Thus, a thermal gradient is set up with the maximum temperature inside the sample. The gradient grows and steepens as the reaction proceeds, until finally thermal runaway (explosion) occurs deep inside the sample, completely removed from contact with the metal sample holder.

THERMAL GRADIENTS VS. DEPTH

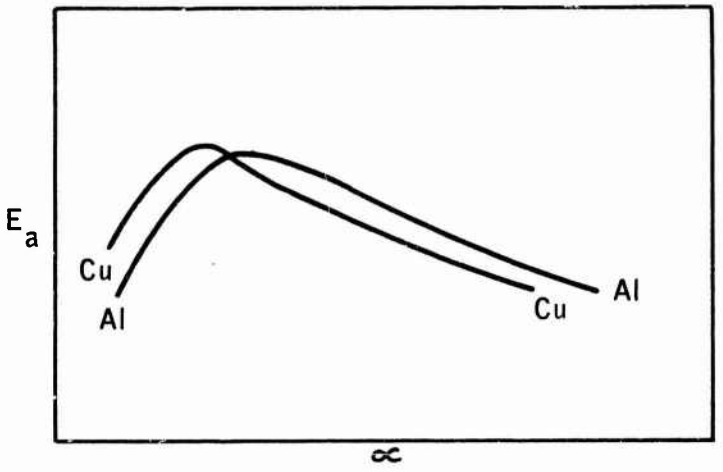


(U) The noncatalysis in copper has been confirmed experimentally by comparing the results from a sample run both in copper tubes and in aluminum tubes. The sample used was FA-PEDIN, chosen because it contains all the functional groups of interest and, in addition, is a liquid, presumably the worst case. Aluminum No. 8 blasting cap shells were prepared in the same manner as the standard copper shells. The bottoms were turned down to a thickness of 2 mil, and the shell was cleaned and polished prior to loading the sample. Because aluminum is softer than copper, it was necessary to shorten the Teflon plug used to seal the sample. Instead of the standard one inch long plug, a 2/3 inch Teflon plug was used in the aluminum holder. With samples of normal size, results from copper and aluminum tubes were virtually indistinguishable.

ACTIVATION ENERGY VS. THERMAL DIFFUSIVITY

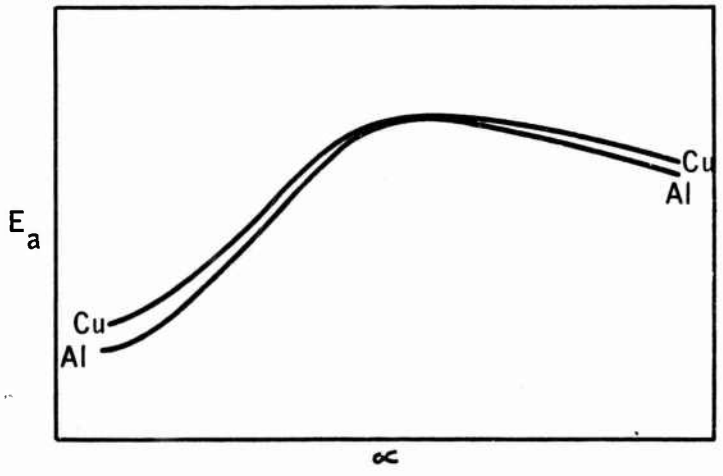
Sample thickness

Cu 0.058 cm.
Al 0.056 cm.



Sample thickness

Cu 0.082 cm.
Al 0.090 cm.

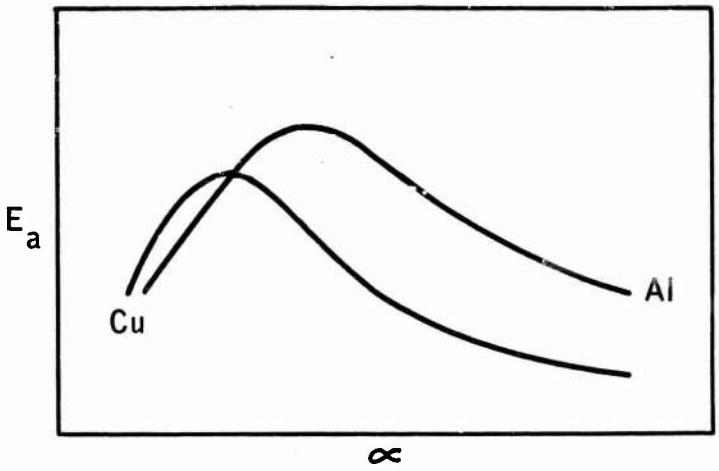


The slope and height of the two sets of curves are almost identical with the major difference being a shift of the aluminum curve to higher alpha values. This can readily be explained by the lesser confinement in the aluminum tube and the consequent greater volatilization of the sample. When smaller samples were used, the effect was more pronounced, as would be expected if volatization is a factor.

ACTIVATION ENERGY VS. THERMAL DIFFUSIVITY

Sample thickness

Cu 0.042 cm.
Al 0.048 cm.



The overall results from the aluminum tube series are well within experimental error of those from the copper tube work.

ALUMINUM VS. COPPER SAMPLE HOLDERS

Holder	Activation Energy	α
Copper	41.0 ± 3.1	0.005
Aluminum	44.8 ± 1.8	0.008

Whether surface catalysis is present or not, its effect on the kinetic parameters obtained from the thermal sensitivity test is negligible.

(U) It is felt that this immunity to catalysis is a result of the experimental arrangement which leads to thermal runaway inside the sample, out of contact with any metal surface. Other investigators, with other arrangements, have reported so much catalytic effect in their work that they had no confidence at all in their data.*

* A. Amster, 4th Sensitivity Seminar, Linden, New Jersey, 7-8 June 1966.

4.4. ACTIVATION ENERGIES AND FREQUENCY FACTORS

(U) This section presents all the kinetic data on pure compounds from the new thermal sensitivity test in tabular form for convenient reference. The data are analyzed and interpreted in Section 4.5.

(C) THERMAL SENSITIVITY DATA SUMMARY

Name	Compound	E_a, kcal/mol	Standard Deviation	Z, sec.$^{-1}$
NG	Nitroglycerin	36.6	---	4.8×10^{13}
PETN	Pentaerythritol tetranitrate	31.5	0.5	3.30×10^{10}
β-HMX	Cyclotetramethylene tetranitramine	30.7	1.7	1.10×10^{9}
TETRYL	Trinitrophenylmethylnitramine	26.2	1.4	1.79×10^{8}
FA-BDE	$(F_2N)_3COCH_2\overset{O}{\overset{/\backslash}{C}}HCHCH_2OC(NF_2)_3$	31.9	4.8	1.25×10^{11}
FA-BDG	$[CH(OH)CH_2OC(NF_2)_3]_2$	34.5	1.2	3.35×10^{11}
FA-BDN	$[CH(ONO_2)CH_2OC(NF_2)_3]_2$	40.9	6.7	3.09×10^{14}
poly-FA-BDE	$(F_2N)_3COCH_2CH\text{-}CHCH_2OC(NF_2)_3$ (O)$_n$	34.6	2.7	2.4×10^{11}
FA-PETRIN	$(O_2NOCH_2)_3CCH_2OC(NF_2)_3$	43.7	7.9	7.58×10^{15}
FA-PEDIN	$(O_2NOCH_2)_2C[CH_2OC(NF_2)_3]_2$	41.0	3.1	6.75×10^{14}
FA-PEMON	$O_2NOCH_2C[CH_2OC(NF_2)_3]_3$	37.2	0.6	3.05×10^{13}
FA-TNENE	$(NO_2)_3CCH_2N(NO_2)CH_2CH_2OC(NF_2)_3$	34.8	2.3	3.45×10^{12}
HPE	$F_2NCH_2CH(NF_2)CH(NF_2)OCH(NF_2)CHNF_2CH_2NF_2$	36.8	1.3	1.49×10^{11}

(C) Adiabatic reaction times calculated from these data correlate well with values obtained from the Wenograd test. One can calculate the initial temperature required to give thermal runaway in 250μ sec., and these temperatures are for the most part within experimental error of those actually measured by Rosen and Wenograd at NOL.

250μ sec. Explosion Temperatures

Compound	Esso	NOL
HPE	575 ± 33	544 ± 26
PETN	484 ± 26	430 ± 50
FA-BDG	475 ± 16	437 ± 12
FA-BDN	416 ± 41	394 ± 20
FA-PEDIN	395 ± 16	400 ± 16
FA-PETRIN	393 ± 37	353 ± 14

The agreement between our calculated values of $T_{250\mu}$ sec. and the values actually measured elsewhere would seem to indicate that the kinetic parameters derived from the thermal sensitivity test are indeed the correct ones.

5. SENSITIVITY STUDIES VIA THERMAL TESTING

(U) A number of insights can be drawn from consideration of the available thermal sensitivity data. Since the data are limited, all conclusions must be considered somewhat tentative; nevertheless they do rationalize the observed phenomena.

5.1. CHEMICAL STRUCTURE VERSUS THERMAL SENSITIVITY

(C) Analysis of the thermal sensitivities of several systematic series of PFG adducts indicates that, within a series, the effects of structure upon sensitivity are real but small; the effects of total energy content (Q) and physical properties are larger. Moreover, the activation energies and frequency factors of these PFG adducts at least are quite in line with those of conventional explosives.

5.1.1. Several Systematic Series Have Been Explored

(C) The FA-BDE series was chosen as exemplary of the effect of other molecular substituents on the basic $-OCX_3$ group.

FA-BDE	$X_3COCH_2\underset{\diagdown O \diagup}{CH}\text{-}CHCH_2OCX_3$	liquid
FA-BDG	$X_3COCH_2\overset{OH}{\overset{\vert}{C}}H\text{-}\overset{OH}{\overset{\vert}{C}}HCH_2OCX_3$	solid
FA-BDN	$X_3COCH_2\overset{ONO_2}{\overset{\vert}{C}}H\text{——}\overset{ONO_2}{\overset{\vert}{C}}HCH_2OCX_3$	liquid
poly-FA-BDE	$X_3COCH_2\overset{OR}{\overset{\vert}{C}}H\text{-}\overset{OR}{\overset{\vert}{C}}HCH_2OCX_3$	solid

($X = NF_2$, R = FA-BDE unit)

(C) The FA-PETN series represents the stepwise change from a conventional explosive, PETN, to a high-energy NF compound, FA-PE, while maintaining the same functional groups, OCX_3 and ONO_2. Each member of the series from PETN to FA-PE has one less ONO_2 group and one more OCX_3.

PETN	$(O_2NOCH_2)_4C$	solid
FA-PETRIN	$(O_2NOCH_2)_3COH_2OCX_3$	liquid
FA-PEDIN	$(O_2NOCH_2)_2C(CH_2OCX_3)_2$	liquid
FA-PEMON	$O_2NOCH_2C(CH_2OCX_3)_3$	liquid
FA-PE	$C(CH_2OCX_3)_4$	solid

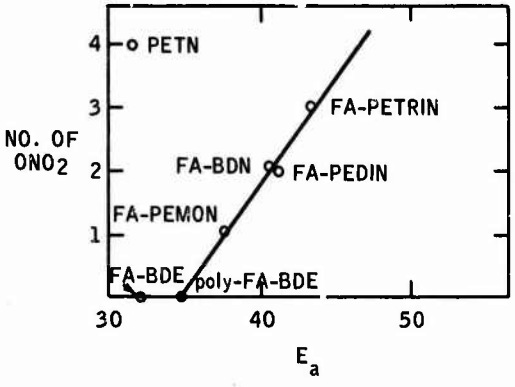
(FA-PE itself was unavailable, but the other four compounds were studied.)

(C) FA-TNENE, $X_3COCH_2CH_2\overset{\overset{NO_2}{|}}{N}CH_2C(NO_2)_3$, was included as an example of an -OCX /nitramine; and HPE, $CH_2(\overset{\overset{NF_2}{|}}{C}H)_2O(\overset{\overset{NF_2}{|}}{C}H)_2CH_2$, was included as an example of an NF_2, but non-PFG compound. In addition, tetryl and β-HMX were included as examples of non-PFG nitro and nitramine explosives.

5.1.2. In OCX_3 Compounds, the Number of ONO_2 Groups Correlates with Decomposition Kinetics

(C) A striking linear relationship exists between the number of nitrate groups and the activation energy for the FA-PETN and the FA-BDE series.

ACTIVATION ENERGY VS. NUMBER OF NITRATE GROUPS



(C) PETN itself and FA-BDE monomer fall off the line. FA-BDE monomer, of course, contains the extraneous, very reactive epoxide ring, which might be expected to dominate the decomposition. The discontinuity at PETN is significant, and it would suggest that the activation energy is associated with OCX_3 as influenced by ONO_2 rather than with ONO_2 as influenced by OCX_3.

5.1.3. The Data Suggest That All Thermal Explosions Go Through the Same Rate-controlling Step

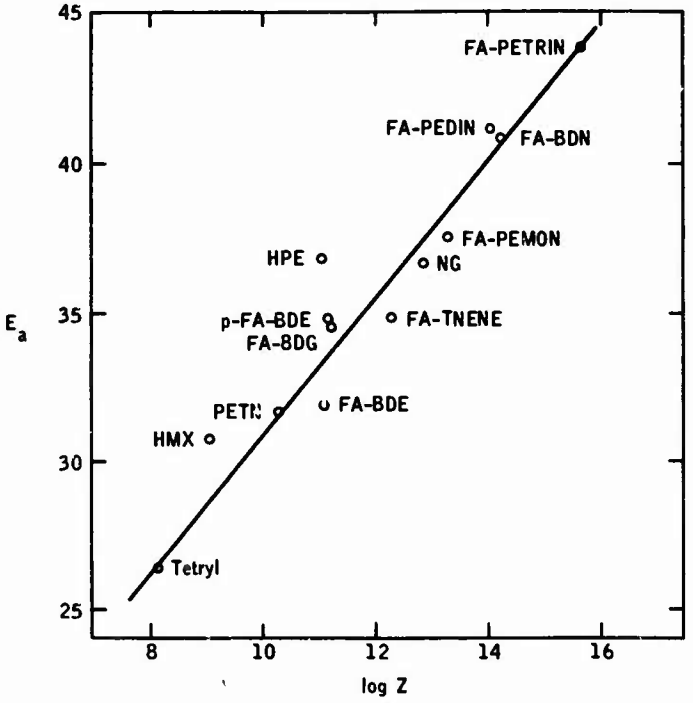
(C) It is striking that the two di-OCX_3/di-ONO_2 compounds, FA-BDN and FA-PEDIN, have virtually identical decomposition kinetics, even though they are derived from diverse parent systems.

Compound	Structure	E_a	Z
FA-BDN	$O_2NOCH-CH_2OCX_3$ $O_2NOCH-CH_2OCX_3$	40.9	3.09×10^{14}
FA-PEDIN	$O_2NOCH-CHOCX_3$ C $O_2NOCH-CHOCX_3$	41.0	6.65×10^{14}

This emphasizes that the observed kinetics are for the overall initiation process and not simply for breaking the first bond. If the influence of ONO_2 on OCX_3 were strictly electromeric, there should be a significant difference between 2-carbon and 3-carbon separations. In the midst of the explosion process, on the other hand, molecular integrity is lost; and neighboring fragments no longer know which molecule they came from.

(C) An even more striking relationship is seen if one plots the activation energies of all the compounds studied versus the corresponding frequency factors. One obtains a straight line which embraces both the OCX_3 compounds and the conventional explosives.

ACTIVATION ENERGY VS. FREQUENCY FACTOR FOR ALL MATERIALS STUDIED



Leffler* has pointed out that data for related reactions often fall into such a linear relationship and has shown that when they do, it suggests that they may be reacting by the same mechanism, or at least through a very similar rate-controlling step. (Leffler has also pointed out that such linear plots can be spurious. The frequency factor is partially a function of the activation energy; and consequently, random experimental errors will also result in a linear plot. But linear plots arising from random errors have a large scatter and the total range of the variables is comparable to the experimental uncertainty. Our data appear to be better than that, but the reservation should be noted.)

(U) IF all these reactions are indeed going by the same mechanism, it follows that the rate-controlling step cannot be the conventional well-defined breaking of some particular chemical bond, since there is no one energetic group which all these compounds share. Moreover, if the rate-controlling step is not weakest bond scission, it follows that structural changes, in the usual chemical sense, would not be expected to have any major effect on explosion sensitivity. This appears to be the case; such sensitivity differences as we find are quite small, whereas the reactivity differences commonly found in conventional kinetic studies are often many orders of magnitude. This is not to say that there are no sensitivity differences due to structure - there are - but they are small and it is reasonable that they should be small.

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* J. E. Leffler, J. Org. Chem., 20, 1202 (1955).

5.1.4. Within a Series, Thermal Sensitivity Data Correlate with Impact Sensitivities

(C) The calculated isothermal decomposition rates (the Arrhenius function of the activation energy and frequency factor) agree well with handling experience and with other measures of sensitivity. The following table ranks the FA-BDE series in order of increasing observed handling hazard and compares the thermal kinetic parameters.

THERMAL SENSITIVITY OF FA-BDE COMPOUNDS

Compound	E_a, kcal/mol	Z, $sec.^{-1}$	k, $sec.^{-1}$ at 540°K	at 640°K	at 740°K
poly-FA-BDE	34.6	2.46×10^{11}	2.45×10^{-3}	0.377	14.9
FA-BDG	34.5	3.35×10^{11}	3.66×10^{-3}	0.556	21.7
FA-BDN	40.9	3.09×10^{14}	8.68×10^{-3}	3.35	258
FA-BDE	31.9	1.25×10^{11}	15.4×10^{-3}	1.60	47.5

In general, all the k's line up in the same order, especially k_{540}, with some confusion between FA-BDN and FA-BDE. Indeed, these two are hard to distinguish in handling, both being ultra-sensitive; but FA-BDE seems somewhat the touchier, particularly in friction sensitivity.

(C) Much the same thing is seen in the FA-PETN series:

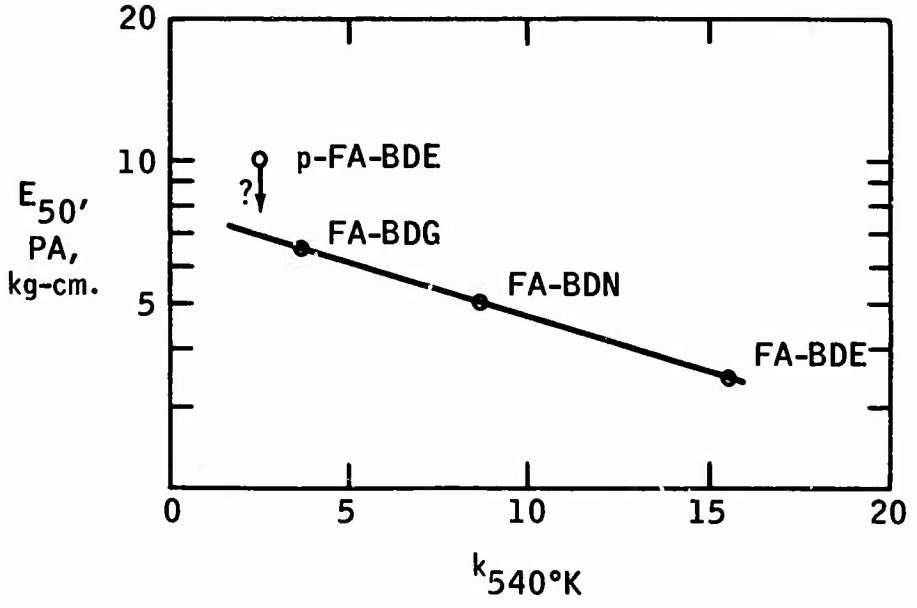
THERMAL SENSITIVITY OF FA-PETN COMPOUNDS

Compound	E_a, kcal/mol	Z, $sec.^{-1}$	k, $sec.^{-1}$ at 540°K	at 640°K	at 740°K
PETN	31.5	3.30×10^{10}	5.92×10^{-3}	0.579	16.5
FA-PETRIN	43.7	7.58×10^{15}	15.0×10^{-3}	8.77	915
FA-PEDIN	41.0	6.75×10^{14}	17.3×10^{-3}	6.76	528
FA-PEMON	37.2	3.05×10^{13}	26.9×10^{-3}	6.06	315

Again the k's line up in about the same way, with some confusion at higher temperatures; and the k_{540} agrees well with handling experience.

(C) Within classes, at least, k_{540} correlates with impact sensitivity. The following plot compares the measured Picatinny Arsenal E_{50} with the calculated k_{540} for the FA-BDE series:

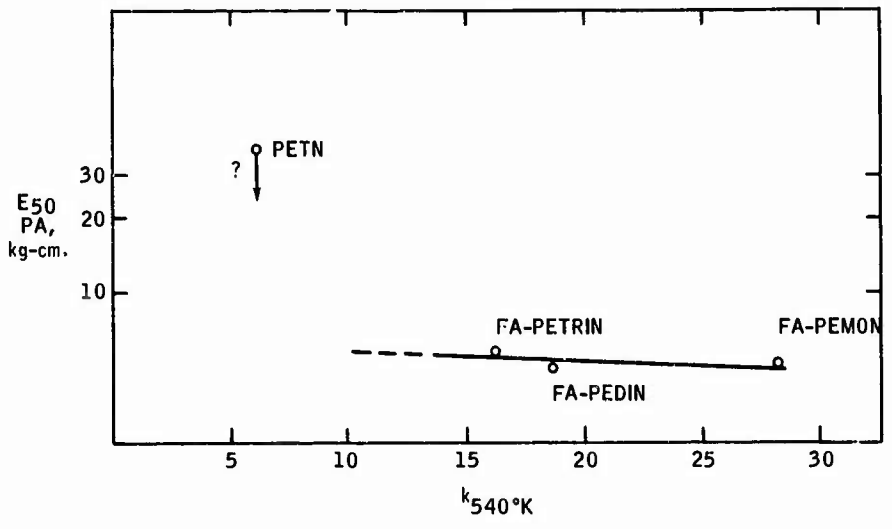
SENSITIVITY OF FA-BDE COMPOUNDS



Poly-FA-BDE falls above the plot; however, it will be recalled (cf. Sections 3.1. and 3.2.) that poly-FA-BDE is a powdery solid and has a variable E_{50} depending upon its bulk density. The 10 kg.-cm. E_{50} was obtained on a relatively dense sample; but the density was not 100%, and a fully compacted sample could easily be 3 kg.-cm. more sensitive.

(C) k_{540} for the FA-PETN series gives a similar diagram when plotted versus impact sensitivity.

SENSITIVITY OF FA-PETN COMPOUNDS



Again, the granular PETN falls above the plot. In this case, there is perhaps little reason to expect it to correlate with the others, since it contains no OCX_3 at all and is therefore really foreign to the group.

(C) It is striking that k_{640} and k_{740} do not correlate with E_{50}, as k_{540} does, but give scatter diagrams, even though the higher temperatures are more in the range of those found most meaningful at NOL in the Wenograd test. This may mean that the critical hot-spot temperature for OCX_3 compounds is lower than the critical temperature for conventional explosives. Another ramification of the Leffler plot (5.1.3. above) is that the slope of the line is that temperature at which all the reactions proceed at the same rate. This "isokinetic temperature" in our case is approximately 495°K (222°C), a surprisingly low value. A low value for OCX_3 compounds, however, would be entirely consistent with adiabatic thermal explosion theory where the evolved heat is fed back into the system via a formal servoloop, and also with the observed greater impact and friction sensitivity of OCX_3 compounds. It is also consistent with the observed poorer thermal storage stability of OCX_3 compounds and their lower DTA exotherms. The point is not completely clear, however; PETN also falls on the isokinetic Leffler plot.

(C) The correlations between impact sensitivity and thermal reaction rates would seem to imply that, in these cases, the observed sensitivity differences, such as they are, are indeed due to the chemical step and not to the mechanical step. There is no variation left to attribute to differences in mechanical properties. One cannot say that the sensitivity differences are due to differences in molecular structure. The E_a and Z obtained are those for the overall initiation process and are not necessarily those for the breaking of the chemical bond. They are undoubtedly functions of the bond energies but the numbers are also functions of the heat of explosion, the heat capacity, the density, and the thermal stability.

(C) Again, it should be emphasized that the sensitivity differences due to structure are small; the effects of heat release and physical properties are overwhelmingly larger.

5.1.5. Decomposition Rates Rank Nitrates Faster than Nitramines Faster than Nitros

(U) Arrhenius data from the open literature for a number of conventional explosives give calculated decomposition rates which rank nitrate decomposition faster than nitramine decomposition faster than nitro decomposition.

ISOTHERMAL DECOMPOSITION RATES

Compound	Class	k_{640} °K	Reference
NG	Nitrate	6840×10^5	Robertson
PETN	Nitrate	5647×10^5	Robertson
EDNA	Nitramine	243×10^5	Finkelstein
tetryl	Nitramine	194×10^5	Finkelstein
RDX	Nitramine	191×10^5	Finkelstein
β-HMX	Nitramine	50.8×10^5	Johnson
CH_3NO_2	Nitro	1.88×10^5	Cottrell
TNT	Nitro	0.54×10^5	Robertson

The same ordering is found in our autoignition thermal sensitivity data on three of these same explosives.

DECOMPOSITION DATA

Compound	Class	Ea, kcal/mol	Z, sec.$^{-1}$	k_{540} °F	k_{640} °F
PETN	Nitrate	33.3	1.10×10^{11}	3.78×10^{-3}	0.482
tetryl	Nitramine	26.2	1.79×10^{8}	2.74×10^{-3}	0.134
β-HMX	Nitramine	30.7	1.10×10^{9}	0.46×10^{-3}	0.0395

Since considerably different experimental conditions were used, the actual numbers obtained by the above investigators should not be compared directly with ours; but the ordering is certainly the same.

(C) The same ordering, Nitrate> nitramine, is found when PFG compounds are included.

ISOTHERMAL DECOMPOSITION RATES

Compound	Class	k_{640} °K
FA-PETRIN	PFG-Nitrate	8.77
FA-PEDIN	PFG-Nitrate	6.76
FA-PEMON	PFG-Nitrate	6.06
FA-TNENE	PFG-Nitramine	4.52
PETN	Nitrate	0.482
β-HMX	Nitramine	0.0395

With so few compounds studied, the comparison is far from rigorous; however, the weight of the empirical evidence also suggests that PFG-nitramines are somewhat better from a sensitivity standpoint.

5.1.6. HPE Provides a Comparison Between Tris and Non-Tris NF_2 Compounds

(C) HPE is an NF_2, but non-PFG, liquid tested in order to evaluate the C-NF_2 bond uncomplicated by possible effects of the O-CX_3 bond. Its activation energy was "normal," only marginally higher than that of the other saturated NF_2-only compounds. Its frequency factor was marginally lower, making its calculated isothermal decomposition rate also marginally lower.

THERMAL SENSITIVITY OF HPE

Compound	Ea, kcal/mol	Z, $sec.^{-1}$	$k_{540°K}$
HPE	36.8	1.49×10^{11}	0.191×10^{-3} $Sec.^{-1}$
FA-BDG	34.5	3.35×10^{11}	3.36×10^{-3}
Poly-FA-BDE	34.6	2.46×10^{11}	2.45×10^{-3}

Again, this would seem to indicate that the chemical bonds in NF_2 and OCX_3 compounds are essentially "normal," and that OCX_3 compounds are not particularly unstable from a structural standpoint.

5.1.7. The Data Hold Out No Hope For Insensitive OCX_3 Structures

(C) Taken as a whole, the foregoing data indicate that the activation energies of NF_2 and OCX_3 compounds are essentially normal ones, with no particularly weak bonds or structural instabilities evident. (It is true that autoignition activation energies are those of the explosion process and have not been shown to be equivalent to those of bond-breaking; but they obviously can be no higher than permitted by the intrinsic bond strengths.) Moreover, such structural or neighboring-group effects as are seen appear to be "averaged" effects rather than positionally-controlled inductive or resonance effects. More detailed studies of more model compounds are needed to support these conclusions rigorously, but the weight of the evidence points in this direction.

(C) This suggests that it is probably futile to search for novel and insensitive high-energy NF_2 compounds. NF_2 compounds' great sensitivity seems to be due solely - and inevitably - to their high energy content. Small differences can be effected by structural changes, but not large ones. As shown in Section 3, small improvements can be made by tinkering with physical properties, but again not large ones. High-energy NF_2 compounds are inherently sensitive and cannot be made insensitive. It may be possible to live with them by accepting and adjusting to their sensitivity, but there seems to be no way to overcome their sensitivity.

(C) This is not to say that radically different structures (ONF_2 compounds ?) may not be radically less sensitive; but it means that such a finding would be quite surprising, and suggests that investigators would do well to make very sure that all test conditions are comparable before claiming insensitive, high-energy compounds.

5.2. STUDIES OF DESENSITIZATION MECHANISMS

(U) This section reports a very preliminary study on selected desensitization mechanisms. It was a very brief study, at the very end of the program, and it raised more questions then it answered; but it illustrates how one might apply the thermal sensitivity test to mechanism problems.

5.2.1. Three Contrasting Cases Have Been Studied

(C) Four systems were studied, representing three different cases and two base compounds.

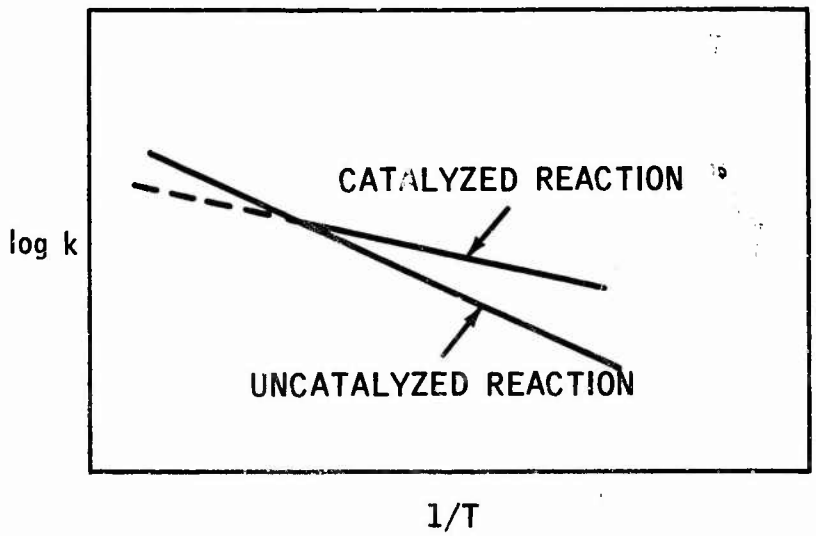
System	Case
FA-BDN/HPVA	Thickener, desensitized
FA-BDN/Silica	Thickener, sensitized
FA-BDN/Tributyrin	Non-thickener, desensitized
FA-PETRIN/HPVA	Thickener, desensitized

THERMAL AND IMPACT SENSITIVITY DATA

Sample	E_{50}, kg-cm	E_a, kcal/mol	Standard Deviation	Z, sec.$^{-1}$	k_{540}, x 10^3	k_{640}	k_{740}
FA-BDN	0.6	40.9	6.7	3.09×10^{14}	8.68	3.35	258
FA-BDN + 1% Silica	<0.6	33.0	1.5	9.87×10^{11}	43.6	5.33	(178)
FA-BDN + 2% Silica	<0.6	29.2	4.2	3.83×10^{11}	58.4	4.10	(91.2)
FA-BDN + 11% HPVA	3.2	35.9	3.5	3.12×10^{13}	92.5	17.2	781
FA-BDN + 20% TBN	3	27.4	1.0	6.61×10^{9}	53.9	(2.91)	(53.6)
FA-PETRIN	3	43.7	7.9	7.58×10^{15}	15	8.77	915
FA-PETRIN + 10% HPVA	6	34.5	1.5	1.02×10^{13}	111	16.9	(661)
FA-PETRIN + 20% HPVA	9	25.4	0.2	1.98×10^{9}	104	(4.25)	(62.5)

The rates for the desensitized mixtures are in all cases faster than the rates for the untreated materials, when examined within the experimental temperature range. Calculated values above the experimental temperature range are not to be taken very seriously. They would be correct only if there were no favorable change in mechanism available at the higher temperature. But there is a more favorable path - the uncatalyzed reaction.

CHOICE OF REACTION PATHS

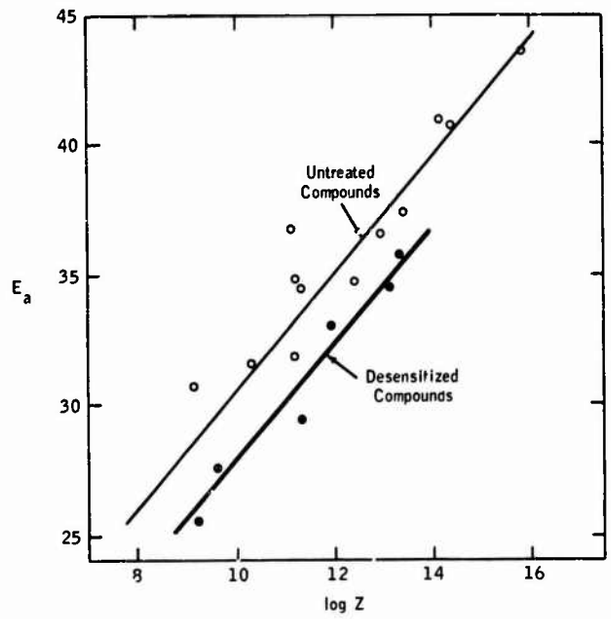


All kinetic texts point out that this is a very common situation when one has concurrent reactions differently influenced by temperature.*

* For example, see: C. N. Hinshelwood, "The Kinetics of Chemical Change," Clarenden Press, Oxford, 1940, p. 45.

(C) A plot of activation energy versus log Z for these desensitized systems gives a straight line, just as does a plot of the untreated compounds' data, but the line is displaced slightly.

ACTIVATION ENERGY VS. FREQUENCY FACTOR FOR DESENSITIZED MATERIALS



According to Leffler's analysis, this implies that the desensitization has altered the mechanism in some consistent way; but the smallness of the displacement and the similarity of the slopes indicate that it hasn't altered it much.

(C) Since the line is displaced toward lower activation energies these data say that the desensitizers have actually <u>speeded</u> the chemical step and therefore must desensitize via the mechanical step. As discussed in more detail in Section 4.1.1., one can picture an impact initiation as consisting of two steps--a mechanical step followed by a chemical one:

$$\text{Impact} \xrightarrow{\text{Mechanical}} \text{Hot-Spot} \xrightarrow[\text{Growth}]{\text{Chemical Reaction}} \text{Explosion}$$

One could, in principle, desensitize a material by interfering with either step. Since the thermal sensitivity test (presumably) looks at only the chemical step, a thermal sensitivity study of a desensitized material versus the same material undesensitized should give insight into which step has been affected. In practice, the situation is far from easy to unravel without a much more extensive study.

Thickener-Desensitizer

(C) HPVA is a typical thickener-desensitizer for liquids and can desensitize FA-BDN up to nearly an order of magnitude. In the thermal sensitivity test, it reduces the activation energy by 5 kcal/mole, which should accelerate the decomposition; but it also reduces the frequency factor by one power of ten, which should retard it. These two opposing factors give a net increase in thermal decomposition rate at all temperatures examined.

Sample	E_{50}	$k_{540} \times 10^3$	k_{640}	k_{740}
FA-BDN	0.6	8.68	3.35	258
FA-BDN + 11% HPVA	3.2	92.5	17.2	781

Thus, HPVA appears actually to accelerate the chemical step, and its desensitizing action must be due to interference with energy concentration into a hot-spot in the mechanical step. This presumably has something to do with the increased viscosity, perhaps through increased resistance to shear or to bubble compression.

(C) The case is similar with FA-PETRIN/HPVA. HPVA again reduces both the activation energy and the frequency factor; and the decomposition rate is increased in the experimental temperature range.

Sample	E_{50}	E_a, kcal/mol	Z, sec.$^{-1}$	$k_{540} \times 10^3$	k_{640}	k_{740}
FA-PETRIN	3	43.7	7.58×10^{15}	15	8.77	915
FA-PETRIN + 10% HPVA	6	34.5	1.02×10^{13}	111	16.9	(661)
FA-PETRIN + 20% HPVA	9	25.4	1.98×10^{9}	104	(4.25)	(62.5)

Thickener-Sensitizer

(C) Finely divided silica (Cabot Corporation's Cab-O-Sil HS-5; 8 micron particle size; 300 - 350 M^2/g) will gel FA-BDN in concentrations of approximately 10 wt.%. The gels are somewhat more impact sensitive than pure FA-BDN, and they are considerably more friction sensitive. Concentrations of 1% and 2% remain suspended but do not gel the FA-BDN. The mixtures are sensitized to friction and are not appreciably changed in impact.

(C) Thermal sensitivity data on 1% and 2% suspensions show that both the activation energy and the frequency factor are lowered and that the rates are increased.

Sample	E_{50}	E_a, kcal/mol	Z, sec.$^{-1}$	$k_{540} \times 10^3$	k_{640}	k_{740}
FA-BDN	0.6	40.9	3.09×10^{14}	8.68	3.35	258
FA-BDN + 1% Silica	<0.6	33.0	9.87×10^{11}	43.6	5.33	(178)
FA-BDN + 2% Silica	<0.6	29.2	3.83×10^{11}	58.4	4.10	(91.2)

In this case, an obvious mechanical sensitizing mechanism exists: the addition of friction-producing grit. FA-BDN has been shown to explode reliably when rubbed with much softer grits than silica.

(U) Parenthetically, this experiment shows very clearly that thermal sensitivity data are not affected appreciably by random variations in the surface roughness of the sample capsule or by the presence of adventitous dirt. One per cent silica represents a 200-fold increase in surface area over the smooth capsule wall, yet the reaction rate is increased only by a factor of 5. A 400-fold surface area increase gives only a rate increase of 6.7.

Nonthickener-Desensitizer

(C) Tributyrin is typical of a group of soluble additives which were found to desensitize FA-BDN towards impact without having obvious effect on the viscosity. Sensitivity data are given below; the activation energy and frequency factor are reduced by the addition of desensitizer, as in all these cases, and the reaction rate is increased in the experimental temperature range.

Sample	E_a, kg-cm	E_a, kcal/mol	Z, sec.$^{-1}$	$k_{540} \times 10^3$	k_{640}	k_{740}
FA-BDN	0.6	40.9	3.09×10^{14}	8.68	3.25	258
FA-BDN + 20% TBN	3	27.4	6.61×10^{9}	53.9	(2.91)	(53.6)

Again, the desensitization appears to be mechanical. The reaction rate is <u>increased</u> at the temperature believed to be most meaningful (540°K); yet the solution is <u>less</u> impact sensitive than the pure FA-BDN.

5.2.2. More Sophisticated Data Treatment Is Needed

(U) It is clear that simple inspection of a few rate numbers is not sufficient to interpret small changes in sensitivity, except in the simplest of cases--and all these changes <u>are</u> small. Insufficient work has yet been done to know what magnitude of change is really significant, and it may well be that a more sophisticated treatment is needed anyway. For example, critical hot-spot size or temperature may be a much more meaningful

parameter than reaction rate; and this is the direction which is recommended for any future research based on these scouting investigations.

(C) One conclusion does emerge: the desensitizers appear to function via the mechanical step, where the possible effect is limited. This would seem to imply that there is little prospect of finding desensitizers which will improve impact sensitivity by the two or more orders of magnitude which are desired.

APPENDIX 1

DATA TABLES -- SENSITIVITIES OF NF COMPOUNDS

The following pages tabulate the structures, energetics, and sensitivities of the NF and NO_2 compounds used in the Sensitivity Survey, Section 3.1. The symbols and abbreviations used are explained below:

X = NF_2

ΔH_f = Estimated heat of formation in Kcal/mole taken from Esso Research and Engineering Company QPR-64-2 "Research on Advanced Solid Propellants (U)" 11 March-10 June 1964, Contract DA-30-069-ORD-2487; or estimated by the conventions described therein.

Q = Calculated approximate heat of detonation in cal/gram. Calculated by assuming reaction to HF, CF_4, CO, H_2O, CO_2, in that order. All materials in their standard state; no allowance made for heat of vaporization, dissociation, etc.

E_{50}, P.A. = Picatinny Arsenal Impact Sensitivity, 50% fire probability by Bruceton up-and-down method.

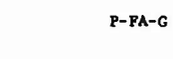
E_{50}, Bruc. = Bruceton-type impact sensitivity, 50% fire probability by Bruceton up-and-down method. Type 12 tools for solids and Type 13 tools for liquids.

Friction = Grit hardness for explosion in Esso friction test. See Esso Report ED-4, AFRPL-TR-65-156, June 1965, AD-366083 for discussion of test and its significance.

TRISDIFLUORAMINOMETHOXY (OCX_3) COMPOUNDS

Code	Structure	State	ΔH_f	Q	E_{50}, P.A.	E_{50}, Bruc.	Friction	Plotted?	Remarks
A-DET	$CH(COOEt)OCX_2NFH$ $CH(COOEt)OCX_2NFH$	Solid			16		0	No	No Q data
BPBTC	$CH_2OCONHCX_3$ CX_2 $CH_2OCONHCX_3$	Solid	-231.1	1362	28			+	
BTBU	$NHCONHCX_3$ $NHCONHCX_3$	Solid	-106.5	1469	20			+	
BTU	$X_3CNHCONHCX_3$	Solid	-68.0	1618	12	8	4	+	
FA-AD	$C(NO_2)_2CH_2OCX_3$ CH_2OCX_3	Liquid	-87.5	1790	5			+	
FA-BD	$CH_2CH_2OCX_3$ $CH_2CH_2OCX_3$	Liquid	-86	1600	6			+	
FA-BDG	$CH(OH)CH_2OCX_3$ $CH(OH)CH_2OCX_3$	Solid	-181.3	1455	6.5				
FA-BDE	$X_3COCH_2CH\overset{O}{\diagdown\diagup}CHCH_2OCX_3$	Liquid	-87.6	1624	3.5	0.4	0	+	
P-FA-BDE	$X_3COCH_2CH\overset{O}{\diagdown\diagup}CHCH_2OCX_3$ (polymeric, $[\ ]_n$)	Solid	-112.7	1566	10	2.6	4	+	
FA-BDN	$X_3COCH_2CHONO_2$ $X_3COCH_2CHONO_2$	Liquid	-119.7	1749	5	0.6	0	+	
FA-BDX	$X_3COCH_2-CH(O\diagdown\diagup CH_2\diagdown O)-CH-CH_2OCX_3$	Liquid	-150	1484			5.5	No	No PA Data

TRISDIFLUORAMINOMETHOXY (OCX_3) COMPOUNDS (Continued)

Code	Structure	State	ΔH_f	Q	E_{50}, P.A.	E_{50}, Bruc.	Friction	Plotted?	Remarks
FA-DHAMP	$(X_3COCH_2)_2CHNH_2 \cdot HClO_4$	Solid	-113	1651	18		5.5	No	Fine Fluff
FA-FDE	$(O_2N)_2CFCH_2OCX_3$	Liquid	-88.4	1500	9		6	+	
FA-G		Liquid	-50	1668	<1	<0.5	3	+	
P-FA-G		Liquid	-78	1550	2.5	2	4	+	
FA-GD	$X_3COCH_2CX_2CH_2OCX_3$	Liquid	-87	1732	2.5			+	
FA-GDN	$CH_2(ONO_2)CH(ONO_2)CH_2OCX_3$	Liquid	-110	1052	4	1		+	
FA-HADD	$CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCX_3$ $CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCX_3$	Solid	-120.8	1177		10	4	No	PA Data Indeterminate
FA-NG	$O_2NC(CH_2OCX_3)_3$	Solid	-131.7	1675	5			+	
FA-OD	$X_3CO-(CH_2)_8-OCX_3$	Liquid	-114	1625	4.5			+	
FA-PE	$C(CH_2OCX_3)_4$	Solid	-172	1659	<1			+	
FA-PEDIN	$(O_2NOCH_2)_2C(CH_2OCX_3)_2$	Liquid	-147	1582	5.0	2.3	4	+	
FA-PEMON	$O_2NOCH_2C(CH_2OCX_3)_3$	Liquid	-158	1599	5.1	2.9	4	+	

TRISDIFLUORAMINOMETHOXY (OCX_3) COMPOUNDS (Continued)

Code	Structure	State	ΔH_f	Q	E_{50}, P.A.	E_{50}, Bruc.	Friction	Plotted?	Remarks
FA-PETRIN	$(O_2NOCH_2)_3CCH_2OCX_3$	Liquid	-136	1535	5.6	2.1	4	+	
FA-PO	$(X_3COCH_2)_3PO$	Solid	-186	1578	2.5			+	
FA-TA	$CH(COOH)OCX_3$ $CH(COOH)OCX_3$	Solid			9.2	10.9	4	No	No Q data
FA-TNE	$X_3COCH\ C(NO_2)_3$	Liquid	-48.4	1407	7.5		5.5	+	
FA-TNEEG	$(O_2N)_3CCH_2CH(OCX_3)CH_2OCX_3$		-93	1440	10	1.9	4	+	
FA-TNEND	$(NO_2)_3CCH_2N(NO_2)CH(CH_2OCX_3)_2$	Solid	-93	1910	13	5.5	4	No	Fine Fluff
FA-TNENE	$(NO_2)_3CCH_2N(NO_2)CH_2CH_2OCX_3$	Solid	-55	1689	2.3	1.4	4	+	
FA-TNH	$CH_2C(NO_2)_2CH_2OCX_3$ $CH_2C(NO_2)_2CH_2OCX_3$	Solid	-129.6	1266	8.5			+	
FA-TNPD	$C(NO_2)_2CH_2OCX_3$ CH_2 $C(NO_2)_2CH_2OCX_3$	Solid	-112	1711	25		5.5	No	Fine Fluff
INFO-635	$X_3COCH_2CH_2NH_2 \cdot HClO_4$	Solid	-89.3	1548	13	20	5.5	+	

CONFIDENTIAL

NF_2 COMPOUNDS

Code	Compound	State	ΔH_f	Q	E_{50}, P.A.	E_{50}, Bruc.	Friction	Plotted?	Remarks
AAPC	$XCH_2CHXCH_2NH \cdot HClO_4$	Solid	-87.0	1267	25			+	
BDE	XCH_2CH_2X	Liquid	-36.8	1685	28			+	Very early data
BDM	$XCH_2N(NO_2)CH_2N(NO_2)CH_2X$	Solid	-31.0	1374	19		4	+	Cast button
BDP	XCH_2CHXCH_3	Liquid	-40.1	1501	35			+	Very early data
DCBDE	XCHClCHXCl	Liquid			46			No	No Q data
DNBP	$O_2NOCH_2CX_2CH_2ONO_2$	Liquid	-74	1744	2.5			+	
HPE	$XCH_2CHXCHXOCHXCHXCH_2X$	Liquid	-128.7	1560	5	6	5.5	+	
PBA	$-(CH_2CHXCHXCH_2)_n-$	Solid			18			No	No Q data
PEFA	$-(CH_2CH(OCHXCHX))_n-$				15			No	No Q data
PVA-DEI	$-(CH_2CH(OCONHCHXCH_2X))_n-$	Solid			61			No	No Q data
PVFA	$-(CH_2CH(OCOCXCHXCHXCHX))_n-$	Solid			43			No	No Q data
TAA	$XCH_2CHXCHCHXCH_2X$ with $OCOCH=CH_2$	Liquid	-146	1299	4			+	
P-TAA	$XCH_2CHXCHCHXCH_2X$ with $OCO-CH-CH_2$	Solid	-155	1203	48			+	

N_2 COMPOUNDS (Continued)

Code	Compound	State	ΔH_f	Q	E_{50}, P.A.	E_{50}, Bruc.	Friction	Plotted?	Remarks
TAMA	$XCH_2CHXCHCHXCH_2X$ $OCOC(CH_3)=CH_2$	Liquid			6			No	No Q data
P-TAMA	$XCH_2CHXCHCHXCH_2X$ $(OCOC(CH_3)=CH_2)_n$	Solid	-162	1137	36			+	
TBA	$XCH_2CHXCHXCH_2X$	Liquid	-57.5	1685	10			+	
TDE	X_2CHCH_2X	Liquid	-41.5	1739	2			+	
TDMF		Liquid			2.5			No	No Q data
TDP	XCH_2CHXCH_2X	Liquid	-45.6	1693	8			+	
THFA		Liquid	-73.5	1567	10			+	
TVOPA	$CH_2OCHXCH_2X$ $CHOCHXCH_2X$ $CH_2OCHXCH_2X$	Liquid	-206	1415	6.5	10	5.5	+	

CONFIDENTIAL

NO_2 COMPOUNDS

Code	Compound	State	ΔH_f	Q	E_{50}, P.A.	E_{50}, Bruc.	Friction	Plotted?	Remarks
NG	Nitroglycerin	Liquid	-400	1486	10	10	>9	+	
HMX	$\overline{(CH_2N(NO_2))}_4$	Solid	-60.5	1201	46			+	
HNF	$N_2H_5^{\oplus}C(NO_2)_3^{\ominus}$	Solid	-17.2	1212	36	38	9	+	
RDX	$\overline{(CH_2N(NO_2))}_3$	Solid	-96	1237	41			+	
PETN	$C(CH_2ONO_2)_4$	Solid	-383	1411	30		>9	+	

APPENDIX 2

PROPELLANT FORMULATIONS EXAMINED

D-A-1	4% HPVA/PAPI; 3.5% Boron; 36.0% FA-PEDIN; 56.5% FA-TNENE.
D-A-2	6% HPVA/PAPI; 3.5% Boron; 36.5% poly-FA-BDE; 54.0% FA-PEDIN.
306-125-3-2	3.6% HPVA/PAPI; 3.5% Boron; 60.5% poly-FA-BDE; 32.4% FA-PEDIN.
306-117-2	6% HPVA/PAPI; 2.5% Boron; 54.0% FA-PEMON; 37.5% FA-TNENE.
306-135-1	6.6% HPVA/PAPI; 3.5% Boron; 59.40% FA-PEDIN; 30.50% FA-TNENE.
306-135-2	6.6% HPVA/PAPI; 3.5% Boron; 30.50% poly-FA-BDE; 59.40% FA-PEDIN
306-136-1	3.6% HPVA/PAPI; 3.5% Boron; 32.40% FA-PEDIN; 60.50% FA-TNENE.
10-29-1	5.0% HPVA/PAPI; 3.0% Boron; 1% AP; 45% FA-BDX; 46.0% FA-TNENE.
5-25-1	3.7% HPVA/PAPI; 2.5% Boron; 33.3% FA-PETRIN; 60.5% FA-TNENE.
65-3-8-1	3.8% HPVA/PAPI; 1.5% Boron; 1.0% Zr° Staple; 34.4% FA-PETRIN; 59.3% FA-TNENE.
65-3-8-2	3.6% HPVA/PAPI; 3.5% Boron; 1.0% Zr° Staple; 32.4% TVOPA; 59.5% FA-TNENE.

APPENDIX 3

(U) SAMPLE THERMAL SENSITIVITY CALCULATION

Nitroglycerin

Zinn-Mader Model

(U) The Zinn-Mader treatment expresses the explosion delay time as a function of activation energy, surface temperature, minimum temperature for explosion and the physical properties of the sample.

$$t_{exp} = \frac{\rho C a^2}{\lambda} f\left(\frac{E}{T_m} - \frac{E}{T_1}\right)$$

Where: ρ = Density

C = Specific heat

λ = Thermal conductivity

a = Sample half-thickness

T_m = Minimum temperature for explosion

T_1 = Surface temperature

t_{exp} = Time to explosion

E = Activation energy

Z = Collision number

f = Geometry factor (0.88 for slab)

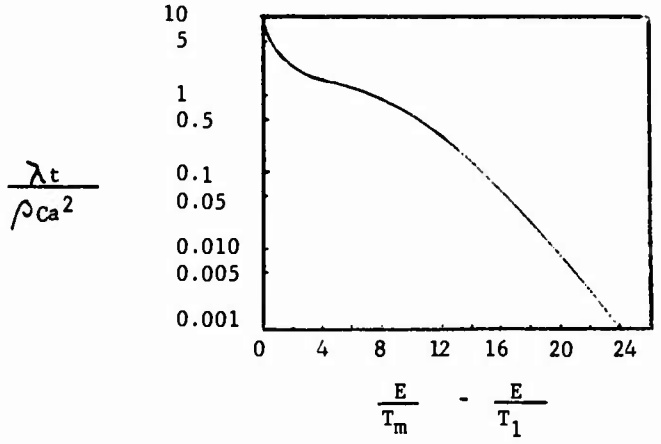
Q = Heat of reaction, cal/gram

From equation (1):

$$f\left(\frac{E}{T_m} - \frac{E}{T_1}\right) = \frac{\lambda t_{exp}}{\rho C a^2}$$

(U) The value for $\left(\frac{E}{T_m} - \frac{E}{T_1}\right)$ is obtained from $\left(\frac{E}{T_m} - \frac{E}{T_1}\right)$

by means of a graphical solution.



(U) If Y is set equal to $\left(\frac{E}{T_m} - \frac{E}{T_1}\right)$ and $\frac{E}{T_m}$ is assumed to be

constant, the data can be fitted, least squares, to $Y = a_1 X + a_o$.

Where: $X = 1/T_1$

$a_1 = E$

$a_o = E/T_m$

$T_m = E/a_o$

(U) The collision number, Z, is obtained by substitution of the above results in the Frank-Kammetskii equation.

$$T_m = \frac{E}{2.303\ R \log\left(\rho a^2 QZE / \lambda RT_m^2 \delta\right)}$$

or

$$Z = \frac{1}{K} \log^{-1}\left(E/2.303\ RT_m\right)$$

Where $K = \frac{\rho a^2 QE}{\lambda RT_m^2 \delta}$

(U) Sample Run (Nitroglycerin)

Input

Run number 104 — 17 shots

Density 1.591 — specific heat 0.356

Thermal conductivity 0.00046 — heat of reaction 1485.0 cal/gram

delta 0.88

Temperature, °C	Time, secs.	Sample wt., grams
292.0	0.454	0.0310
319.0	.323	0.0310
327.0	.103	0.0310
261.0	.855	0.0310
285.0	.713	0.0310
279.0	.859	0.0310
260.0	.997	0.0310
269.0	.736	0.0310
282.0	.688	0.0310
299.0	.565	0.0310
330.0	.109	0.0310
332.0	.106	0.0310
316.0	.312	0.0310
321.0	.344	0.0310
243.0	2.828	0.0310
247.0	.967	0.0310
237.0	1.446	0.0310

Output

Halfthickness, cm.	X	Y
0.025	1.769	9.83
0.025	1.689	11.33
0.025	1.666	14.13
0.025	1.872	6.28
0.025	1.792	7.37
0.025	1.811	6.25
0.025	1.876	5.33
0.025	1.845	7.19
0.025	1.801	7.56
0.025	1.748	8.68
0.025	1.658	13.98
0.025	1.652	14.05
0.025	1.697	11.40
0.025	1.683	11.21
0.025	1.937	0.57
0.025	1.923	5.52
0.025	1.960	2.71

(U)	Sigma X	30.387	Sigma Y	143.471
	Sigma X^2	54.488	Sigma Y^2	1458.031
	Sigma XY	250.253	Root mean square halfthickness 0.025 cm.	

Activation energy (E)	36.480 kcal/mole
E per T_m	73.648 kcal/mole/degree
T_m	495.3 degrees Kelvin
Collison number	4.777×10^{13}
Standard error	1.10792

APPENDIX 4

BIBLIOGRAPHY OF FOREGOING QUARTERLY PROGRESS REPORTS

The following table lists all the foregoing reports of this contract, with their DDC AD-numbers and an identification of their contents. Readers making an in-depth review are advised to acquire ED-4 through ED-7 for their detailed data. ED-1, ED-2 and ED-3 are recapitulated in sufficient depth in ED-4. Those desiring only an overview need only ED-8.

Report No.	Period	DDC AD-Number	Description
ED-1	July-Sept. 1964	354 417	1st QPR. Introductory studies of poly-FA-BDE, FA-BDN.
ED-2	Oct.-Dec. 1964	356 643	2nd QPR. Esso friction tester, empirical desensitization studies.
ED-3	Jan.-Mar. 1965	359 751	3rd QPR. Friction tester, empirical desensitization studies.
ED-4	July 64-June 65	366 083	Annual Report AFRPL-TR-65-156. Summary of all desensitization studies. Literature survey on desensitization. Final report on Esso friction tester.
ED-5	July-Sept. 1965	366 974	QPR. Approach to thermal sensitivity test. Empirical desensitization studies on oxidizers.
ED-6	Oct.-Dec. 1965	369 797	QPR. Thermal sensitivity test. Desensitization of NF oxidizers. Sensitivity of NF propellants.
ED-7	Jan.-Mar. 1966	371 756	QPR. Thermal sensitivity test. Thermal sensitivity studies. Sensitivity of NF propellants.

APPENDIX 5

GLOSSARY OF ABBREVIATIONS

(C)	BDM	$NF_2CH_2N(NO_2)CH_2N(NO_2)CH_2NF_2$
(C)	BPBTC	$(NF_2)_3CNHCOCH_2C(NF_2)_2CH_2OCNHC(NF_2)_3$ (O above NH and above O)
(C)	BTBU	$(NF_2)_3CNHCNHNHCNHC(NF_2)_3$ (O above each NH)
(C)	BTU	$(NF_2)_3CHNCNHC(NF_2)_3$ (O above N)
(U)	DEGDN	$O_2NOCH_2CH_2OCH_2CH_2ONO_2$
(C)	DELTA	$C(NF_2)_4$
(U)	DMP	Dimethylphthalate
(U)	EDNA	$O_2NNHCH_2CH_2NHNO_2$
(C)	FA-BDE	$(F_2N)_3COCH_2CH\text{-}CH\text{-}CH_2OC(NF_2)_3$ (O bridging CH–CH)
(C)	FA-BDG	$(F_2N)_3COCH_2CH(OH)\text{-}CH(OH)CH_2OC(NF_2)_3$
(C)	FA-BDN	$(F_2N)_3COCH_2CH(ONO_2)\text{-}CH(ONO_2)CH_2OC(NF_2)_3$
(C)	FA-G	$(F_2N)_3COCH_2CHCH_2$ (O bridging CH–CH$_2$)
(C)	FA-GDN	$(F_2N)_3COCH_2CH(ONO_2)CH_2ONO_2$

APPENDIX 5 (Continued)

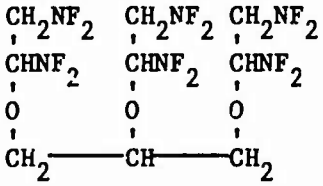
(C)	FA-HADE	$(F_2N)_3COCH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2OC(NF_2)_3$
(C)	FA-PE	$C[CH_2OC(NF_2)_3]_4$
(C)	FA-PEDIN	$[(F_2N)_3COCH_2]_2\ C[CH_2ONO_2]_2$
(C)	FA-PEMON	$[(F_2N)_3COCH_2]_3CCH_2ONO_2$
(C)	FA-PETRIN	$(F_2N)_3COCH_2C[CH_2ONO_2]_3$
(C)	FA-PO	$[(F_2N)_3COCH_2]_3P\rightarrow O$
(C)	FA-TNE	$(F_2N)_3COCH_2C(NO_2)_3$
(C)	FA-TNENE	$(F_2N)_3COCH_2CH_2N(NO_2)CH_2C(NO_2)_3$
(C)	FA-TNH	$(F_2N)_3COCH_2C(NO_2)_2CH_2CH_2C(NO_2)_2CH_2OC(NF_2)_3$
(U)	HMPA	Hexamethylphosphoramide
(C)	HPE	$H_2C(NF_2)-CH(NF_2)-CH(NF_2)-O-CH(NF_2)-CH(NF_2)-CH_2(NF_2)$
(U)	HPVA	Partially hydrolyzed polyvinyl acetate
(C)	IBA	$CH_3CH(NF_2)CH_2NF_2$
(C)	INFO-635	$(F_2N)_3COCH_2CH_2NH_2\cdot HClO_4$
(C)	OCX_3	$-OC(NF_2)_3$
(U)	PAPI	Poly aryl poly isocyanate, urethane crosslinking agent

APPENDIX 5 (Continued)

(U)	PEG	Poly ethylene glycol
(U)	PETN	Pentaerythritol tetranitrate
(C)	PFG	Perfluorogaunidine
(C)	Poly-FA-BDE	$(F_2N)_3COCH_2$ $\{CH\text{-}CH\text{-}O\}_n$ $CH_2OC(NF_2)_3$
(U)	PVA	Polyvinyl acetate
(C)	R	$(F_2N)_3CF$
(U)	RDX	Cyclotrimethylene trinitramine
(C)	TAA	$F_2NCH_2CH(NF_2)CHCH(NF_2)CH_2NF_2$ $OCOCH=CH_2$
(C)	TAMA	$F_2NCH_2CH(NF_2)CHCH(NF_2)CH_2NF_2$ $OCOC=CH_2$ CH_3
(U)	TBN	Tributyrin
(U)	TEGDN	$O_2NOCH_2CH_2OCH_2CH_2OCH_2CH_2ONO_2$
(U)	Tetryl	Trinitrophenyl methyl nitramine
(U)	TNT	Trinitrotoluene

APPENDIX 5 (Continued)

(C) TVOPA



(C) X $-NF_2$

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13. ABSTRACT

(U) A literature survey covering 54 NF and PFG compounds, an extensive empirical desensitization program on selected model PFG compounds, and a limited fundamental investigation of explosion phenomena have indicated that high-energy NF compounds are inherently ultra-sensitive and cannot be made insensitive except at an unacceptable sacrifice of energy. It appears to be futile to search for insensitive high-energy structures or dramatically effective desensitization techniques. Improvements can be made by both these approaches, but they are an order of magnitude smaller than what is needed.

(U) Nevertheless, it appears that high-impulse propellants based on PFG compounds can be made with no greater impact sensitivity than conventional double-base composites. There is, however, no reason to expect that card-gap sensitivity can be similarly improved.

(U) An improved thermal sensitivity test has been developed which yields activation energies and frequency factors from actual exploding condensed phase samples. The experimental procedure is an improvement of the Picatinny Arsenal Autoignition Test, and the data are unfolded by the treatments of Zinn and Mader and Frank-Kamenetskii. Calculated values for minimum explosion temperature are in good agreement with measured ones, calculated $T_{250\,\mu\,sec.}$ values agree with those determined by the Wenograd test, and activation energies for PETN and nitroglycerin agree well with those given in the literature.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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